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Review

Analysis of crystallographic and structural data of polymeric iron-alkaline metal complexes

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Abstract

The present review covers almost 100 polymeric MFe (M=Li, Na, K, Rb, and Cs) compounds. The metal atoms of group 1 as partners with iron atom build up complex polymeric chains. The iron atoms are found in the oxidation states 0, +2, and +3, of which the oxidation state +3 prevails. The coordination number of the iron atom ranges from 2 to 10 (sandwiched). The coordination sphere about the main group 1 metals varies, ranging from tetrahedral to mostly trigonal bipyramid. There are also higher coordination numbers involved, namely, from 6 to 10. The most common ligand atoms are oxygen and nitrogen. There are three compounds displaying distortion isomerism. Several relationships between structural parameters are found and discussed.

Keywords: classification; FeM; M=alkaline metal; polymeric; structure.

Abbreviations

m, monoclinic; NMe4, tetramethylammonium; or, orthorhombic; hmta, hexamethylenetetramine; [9]aneS3, 1,4,7-trithiacyclononane; 3,5-But_2cat,3,5-di-*tert*-butylcatecholborane;3,5-Cl_2tsa,3,5-dichlorosalicylthiosemicarbazonate; 4-cl-2-Phdta, 4-chloro-1,2-phenylenediamine-*N*,*N*,*N*′,*N*′-tetraacetate; acaeen, acetylacetoniminate; aer, anhydrocrythritole; ala, alaninate; bcdtttf, bis(ethylenedithio)-tetrathiafulvalene; bct, bicapped bis[tris(2-aminomethylamine)-*N*,*N*′,*N*″-tetraacetate]; bctpt, bicapped [tris(*N*,*N*′-dipropyl-2,3-dihydroxyterephtalamide)diamine]; bpy, 1,10-bipyridine; c, cubic; $C_4H_2O_6$, tartrate; $C_4H_8O_2$, 1,4-dioxane; $C_5H_4CH_2N(CH_2COO)_2$, phenylmethyleneaminodiacetate; cat, cathecholate; chp, 6-chloro-2-pyridinate; cp, cyclopentadienyl; crypt, cryptate; dbm, dibenzoylmethane; dcta, 1,2-diaminecyclohexane-*N*,*N*′-tetraacetate; dhpta, 1,3-diamino-2-hydroxypropane-*N*,*N*,*N*′,*N*′-tetraacetate; dota, 1,4,7,10-tetrakis(carboxymethyl)-1,4,7,10-tetraazacyclodecane; dtox, dithiooxalate; dtpa, diethylenetriaminepentaacetate; eddda, ethylenediamine-*N*,*N*′-diacetato-*N*,*N*′-di-3-propionate; edta, ethylenediaminetetraacetate; ehpg, *N*,*N*′-ethylene-bis(*o*-hydroxyphenylglycinate); ens, ethylnitrosolate; Et, ethyl; eta, *N*,*N*′-diethylterephtalamidate; hbcd, *N*,*N*′-bis(2-hydroxybenzyl)-ethylenediamine-*N*,*N*′-diacetate; hpdt, [(2-hydroxy-1,3-propanediyl)-diimino]tetraacetate; hx, hexagonal; ida, iminodiacetate; inma, isonitrosomalonamide; ino, inositolate; mal, malonate; Me, methyl; Me4en, *N*,*N*,*N*′,*N*′-tetramethylethylenediamine; nta, nitrilotriacetate; ox, oxalate; Ph, phenyl; phdta, *o*-phenylenediamine-*N*,*N*,*N*′,*N*′-tetraacetate; pr, propionate; py, pyridine; tdta, trimethylenediaminetetraacetate; tg, tetragonal; thf, tetrahydrofurane; tipcma, tris(*N*-isopropylcarbamoylmethyl)amine; tmbcma, tris(methylbenzylcarbamoylmethyl)amine; tpp, tetraphenylporphinate; tr, triclinic; trdta, trimethylenediaminetetraacetate; trencam, bis[tris(2-aminomethylamine)-*N*,*N*′,*N*″-tris(μ-catecholamide]; trg, trigonal; tsa, thiosemicarbazonate

Introduction

The last 50 years have seen many studies on the reaction of various metal salts. In many cases, heterometal compounds have been synthesized, for which also crystallographic and structural data could have been obtained. Structural properties of 850 heterobinuclear iron compounds have been reviewed recently (Melnik et al., 2006), as well as over 350 heterotrinuclear (Melnik et al., 2007), almost 300 heterotetranuclear (Melnik et al., 2008), 180 heteropentanuclear (Melnik et al., 2010), 160 heterohexa-a heteroheptanuclear (Melnik and Holloway, 2011), and 130 hetero-octa- and heterooligonuclear (Melnik et al., 2009) clusters. In this review, polymeric FeM (M=Li, Na, K, Rb, and Cs) compounds are classified and analyzed.

Polymeric MFe complexes

There are almost 100 polymeric MFe complexes (M=Li, Na, K, Rb, and Cs), for which crystallographic and structural parameters are available.

Polymeric FeLi compounds

There are 11 polymeric compounds, of which nine are FeLi and two are FeLiM′ compounds. Their crystallographic and structural data are listed in Table 1.

The cationic part of the crystalline dark yellow FeLi compound reported by Witzel et al. (1988) consists of an array $(NMe_4)^+$ cations and a $[Fe(\mu\text{-}\eta^2\text{-}CN)_6Li(H_2O)_2]^{2+}$ cation. The structure is elpasolite related by its face-centered pseudo-cubic arrangement of iron atoms within almost undistorted $[Fe(CN)_6]^{3-}$ octahedra. In the anions, the mean Fe–C bond length is 1.947(2) Å [range of 1.932(2)–1.959(2) Å] and the mean Fe–C–N angle is 178.4(2)°. Six of these pseudo-octahedra form strongly distorted the octahedral N6 cavities occupied by dihydrated lithium cations. The coordination polyhedron around Li is a distorted tetrahedron $[LiN_2O_2$, where the Li–N bond length is 2.086(4) Å and the respective Li–O(aq) bond length is 1.933(4) Å]. The remaining four nitrogen atoms of the N6 cavity are hydrogen bonded to the two-coordinated water molecules; O–H···N=2.83 and 2.95 Å.

The structure of yellow $Fe(CN)_6Li_3(htma)_2(H_2O)_5$ (Pickardt et al., 1984) can be regarded as a packing of $[Fe(CN)_6]^{3-}$ octahedra and Li^+ cations. The Li^+ cations form coordinate bonds with nitrogen atoms of the anions and nitrogen atoms of hexamethylenetetramine as well as with two water molecules (Table 1).

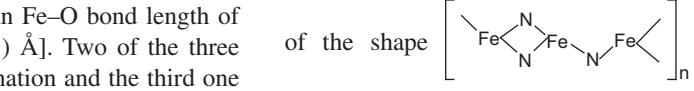
The structure of pale yellow $Fe(CN)_6Li_4(htma)_2(H_2O)_5$ (Meyer and Pickardt, 1988) consists of body-centered arrangement of $[Fe(CN)_6]^{4-}$ octahedral, htma molecules occupying tetrahedral interstices, and $[Li_4(H_2O)_5]^{4+}$ units occupying octahedral interstices. The Li(I) cations are connected also by Li–N contacts to the htma molecules and hexacyanidoferrate anions.

Merely crystallographic data are available for the white $(OC)_4Fe[B(3,5\text{-}But_2cat)Li]$ compound (He and Hartwig, 1996). In the green $Fe(ox)_3Li_3(H_2O)_5$ (Declerq et al., 1995) compound, the coordination polyhedron about the Fe(III) cation is distorted octahedron composed of oxygen atoms of three oxalate anions with the mean Fe–O bond length of 2.015(1) Å [range, 1.994(1)–2.035(1) Å]. Two of the three Li(I) cations show octahedral coordination and the third one tetrahedral coordination. There are infinite chains along the crystallographic *b* axis, with alternation of Fe(III) and Li(I) cations separated by oxalate anions.

In another green compound, $[Fe(ox_3)Li_4(H_2O)_3]Cl{\cdot}6H_2O$ (Declerq et al., 1993), the Fe^{3+}, Li^+, and Cl^- ions are on three different threefold axes at (⅓,⅔,z), (0,0,z), and (⅔,⅓,z), respectively. The cohesion inside the sheets is principally secured by the oxalate anions. For each oxalate ion, two oxygen atoms belonging to two different carboxylate groups are bound to the Fe(III) cation, and the two remaining ones are bound to the Li(I) cation. These create a hexagonal tile in which the vertices are alternatively occupied by iron and lithium cations and the edges by the oxalate anions. A hexahydrated chlorine atom lies at the center of the hexagon, arranged in such a way as a two-dimensional sheet. View of the atoms belonging to one sheet is shown in Figure 1. The space between two adjacent sheets (5.3 Å) is occupied by a Li(2) atom lying on a twofold axis (*x*,-*x*,0). Then O(2) atom of the oxalate, O(5) of a water molecule around the Cl atom, and two symmetry-related oxygen atoms create a distorted tetrahedron(LiO_4) about the Li(2) atom. The remaining Li(3) atom is located in a gap corresponding to the space between the sheets (8.0 Å) lying on a mirror plane at *z*=¼. Its tetrahedral coordination sphere (LiO_4) is formed by two symmetry-related oxygen atoms O(6) belonging to the hydration sphere of the chlorine atoms in two different sheets and two additional water molecules O(7) and O(8) in a mirror plane.

In the amber-colored $Fe(edta)Li(H_2O)_3$ compound (Lind et al., 1964), each Fe(III) cation is seven coordinated. A distorted pentagonal bipyramid is formed by a hexadentate edta ligand and an oxygen of a water molecule. The approximate pentagonal plane contains two oxygen atoms and two nitrogen atoms of the edta ligand as well as one oxygen atom of a water molecule. The mean Fe–O and Fe–N bond lengths are 2.115(3) and 2.325(3) Å, respectively. Two remaining oxygen atoms of the edta ligand occupy the apical positions [mean Fe–O=1.969(3) Å]. Interestingly, although in the orthorhombic $Fe(edta)Li(H_2O)_3$ (Lind et al., 1964), each Fe(III) cation is seven coordinated, as discussed previously; in the monoclinic form (Novozholiva et al., 1973), the Fe(III) cation is six coordinated, with the mean Fe–O and Fe–N bond lengths of 1.93(4) and 2.16(6) Å, respectively.

Single-crystal X-ray analysis of the yellow polymeric $Fe(trdta)Li(H_2O)_3$ shows (Yamamoto et al., 1988) that each Fe(III) cation is six coordinated by all of the six ligand atoms of $trdta^{4-}$, displaying an FeN_2O_4 coordination polyhedron. The mean Fe–N and Fe–O bond lengths are 2.194(3) and 1.989(3) Å, respectively. It must be noted that in the original paper (Yamamoto et al., 1988), data and discussion concerning the Li(I) cation were omitted.

There are two black polymeric compounds, $[Fe_2N_3LiM]_n$ (M=Sr or Ba) (Höhn et al., 1991), that are isostructural. Each Fe(II) cation has a trigonal planar coordination sphere (FeN_3) with the mean Fe–N bond length 1.901(4) Å (M=Sr) and 1.892(8) Å (M=Ba). The polymeric $\{(FeN_{3/2}))_2\}^{5-}$ anion of the shape  contains a central planar Fe_2N_2 fragment with the Fe···Fe distance of 2.408(2) Å and the mean Fe–N–Fe angle of 78.0(9)°. The distance and the angle are significantly different from those found in the singly N-bridged Fe–N–Fe fragment, where the respective values are 2.616(2) Å and 88.8(9)°. Each Li(I) cation is found between two sheets of the respective shapes by two nitrogen atoms of Fe_2N_2 fragment. The Li(I) cation is two coordinated with two equivalent Li–N bond lengths of 1.996(7) Å. The N–Li–N angle is 149.5(9)°. Each M (M=Sr or Ba) is five coordinated (Table 1).

Inspection of the data in Table 1 reveals that the compounds are mostly yellow (x6), but also, other colors are found, such as green (x2), black (x2), or even white (x1). There are four types of crystal classes involved, monoclinic (x4), orthorhombic (x3), hexagonal (x1), and triclinic (x1). All of the nine FeLi compounds contain iron in oxidation state +3 with the following chromophores: FeO_6, FeC_6, FeN_4O_2, and FeN_2O_5. There are mono-, bi-, and hexadentate ligands with the mean Fe–L bond lengths, which increase in the following order: 1.936 Å (μ-CN)<1.950 Å (CN)<2.018 Å (bi-OL) in the hexacoordinated compounds. In the series of the hexadentate N_2O_4 donor ligands, the mean values in FeN_2O_4 are somewhat

Table 1 Crystallographic and structural data of polymeric Li–Fe compounds[a].

Compound (color)	Crys.cl Sp.Grp Z	a (Å) b (Å) c (Å)	α (°) β (°) γ (°)	Chromophore	M–L (Å)	L–M–L (°)	References
$(NMe_4)_2[(NC)_4Fe{\cdot}(\mu\text{-}\eta^2\text{-}CN)_2Li(H_2O)_2]$ (dark yellow)	m c2/C 4	17·128(3) 8·760(1) 16·264(2)	 119·32(1) 	$Fe^{III}C_6$ $Li^iO_2N_2$	NC[b] 1·942(2,10) μNC 1·959(2,0) H_2O 1·933(4,0) μNC 2·086(4,0)	C,C[b] 90·0(1,1·7) O,O 92·7(2) N,N 110·6(2) O,N 118·3(1,1·5)	Witzel et al., 1988
$[(NC)_2Fe(\mu\text{-}\eta^2\text{-}CN)_4{\cdot}Li_3(hmta)_2(H_2O)_5]$ (yellow)	or 12 mm 2	9·094(5) 10·461(5) 14·558(5)	 	$Fe^{III}C_6$ Li^iO_3N $Li^iO_2N_2$	NC 1·968(5,0) μNC 1·927(4,10) H_2O 1·961(9,12) μNC 1·989(10) H_2O 1·961(9,12) μCN 2·075(12) LN 2·175(8)	C,C 90·0(2,1·0) 176·1(1,1·3) O,O 106·2(5,5·8) O,N 109·295,4·1) O,O 119·3(5) N,N 103·0(6) O,N 108·2(5,2·7)	Pickardt et al., 1984
$[Fe(\mu\text{-}\eta^2\text{-}CN)_6Li_4{\cdot}(hmta)_2(H_2O)_5]$ (pale yellow)	or Inm2 2	14·849(2) 10·393(5) 9·098(3)	 	$Fe^{III}C_6$ Li^iO_3N $Li^iO_2N_2$	μNC 1·928(8,7) μH_2O 1·979(2) 2·044(8,0) μNC 1·969(8) μH_2O 1·993(6,0) μCN 2·002(6) LN 2·187(8)	C,C 90·0(5,3·1) O,O 111·6(4) O,N 110·5(6,5·5) O,O 117·6(4) N,N 105·8(5) O,N 108·1(5,3·2)	Meyer and Pickardt, 1988
$[(OC)_4Fe_2.B(3,5\text{-}But_2cat)Li]$ (white) (at 153 K)	m $P2_1/m$ 4	8·217(2) 14·956(3) 20·17(1)	 91·63(3) 				He and Hartwig, 1996
$[Fe(\mu\text{-}\eta^2\text{:}\eta^2\text{-}ox)_3{\cdot}Li_3(H_2O)_5]$ (green)	tr_ P1 2	7·892(1) 9·272(1) 11·942(1)	104·75(1) 101·69(2) 107·92(1)	$Fe^{III}O_6$ Li^iO_6 (x2)	η^2O 1·985(3) 2·678(3) H_2O 2·072(3,6) η^2O 2·081(3) H_2O 1·943(4,16)	O,O 78·4(1,1·7)[c] 93·9(1,21·6) 160·4(2,13·4) O,O 109·5(2,13·4)	Declerq et al., 1995
$[Fe(\mu\text{-}\eta^2\text{:}\eta^2\text{-}ox)_3{\cdot}Li_4(H_2O)_3]Cl{\cdot}6H_2O$ (green)	hx_ P6c2 4	9·465(6) 26·72(2)	 	$Fe^{III}O_6$ Li^iO_4 (x2) Li^iO_4 (x2)	η^2O 2·020(2,0) 2·023(2,0) η^2O 2·160(5,33) η^2O 1·968(6,26) H_2O 1·895(10) 1·942(10,6)	O,O 80·4(1,0)[c] 93·6(1,3·4) 168·3(1) O,O 78·5(3)[c] 94·3(1,2·7) 167·1(1) O,O 106·6(1,9·4) 130·7(1,3·8)	Declerq et al., 1993

Table 1 (Continued)

Compound (color)	Crys.cl Sp.Grp *Z*	a (Å) b (Å) c (Å)	α (°) β (°) γ (°)	Chromophore	M–L (Å)	L–M–L (°)	References
$[(H_2O)Fe(\mu\text{-}\eta^6{:}\eta^2\text{-edta})\cdot Li(H_2O)_2]$ (amber)	or Pbca 8	9·68(1) 18·90(2) 17·64(2)		$Fe^{III}O_5N_2$	η^6O 1·969(3,31) 2·119(4,9) η^6N 2·325(3,21) H_2O 2·107(3)	O,O 72·5(1,1·4)[c] 94·6(1,3·6) 144·8(3); 165·6(3) N,N 73·7(1)[c] O,N 71·3(1,9)[c]	Lind et al., 1964
				$Li^{I}O_4$	η^2O 1·963(1,43) H_2O 1·935(1,24)	84·3(1,2·0) O,O 109·591,9·1)	
$[Fe(\mu\text{-}\eta^6{:}\eta^2\text{-edta})\cdot Li(H_2O)_3]$ (yellow)	m $P2_1/b$ 4	8·82(2) 17·80(3) 9·75(2)	110(1)	$Fe^{III}O_4N_2$ $Li^{I}O_x$	η^6O 1·93(4,11) η^6N 2·16(6,2) O not given	Not given Not given	Novozholiva et al., 1973
$[Fe(\mu\text{-}\eta^6{:}\eta^2\text{-trdta})\cdot Li(H_2O)_3]$ (yellow)	m $P2_1/n$ 4	14·775(3) 10·261(1) 8·883(2)	95·86(4)	$Fe^{III}O_4N_2$	η^6O 1·989(3,14) η^6N 2·194(3,16)	O,O 91·3(1,5·6) 112·5(1); 175·4(1) N,N 94·3(1)[c] O,N 79·0(1,1·3) 97·3(1,1·2);	Yamamoto et al., 1988
				$Li^{I}O_x$	O not given	153·4(1,2) Not given	
$[Fe_2(\mu_3\text{-}N)_3LiSr_2]$ (black)	m C2/c 4	6·559(1) 11·414(2) 6·593(1)	93·28(5)	$Fe^{II}N_3$	μ_3N 1·901(4,29) Fe 2·407(7) 2·616(7)	N,N 105·7(9,3·7) 148·5(9)	Höhn et al., 1991
				$Li^{I}N_2$ $Sr^{II}N_5$	μ_3N 1·996(7,0) μ_3N 2·578(1)– 2·776(1)	N,N 149·3(9) Not given	
$[Fe_2(\mu_3\text{-}N)_3LiBa_2]$ (black)	m C2/c 4	6·875(2) 11·781(4) 6·809(2)	92·35(2)	$Fe^{II}N_3$ $Li^{I}N_2$ $Ba^{II}N_5$	μ_3N 1·892(8,31) Fe not given μ_3N not given m_3N not given	Not given Not given Not given	Höhn et al., 1991

[a]Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis is the e.s.d., and the second is the maximum deviation from the mean.

[b]The chemical identity of the coordinated atom or ligand is specified in these columns.

[c]The five-membered metallocyclic ring.

[d]The six-membered metallocyclic ring.

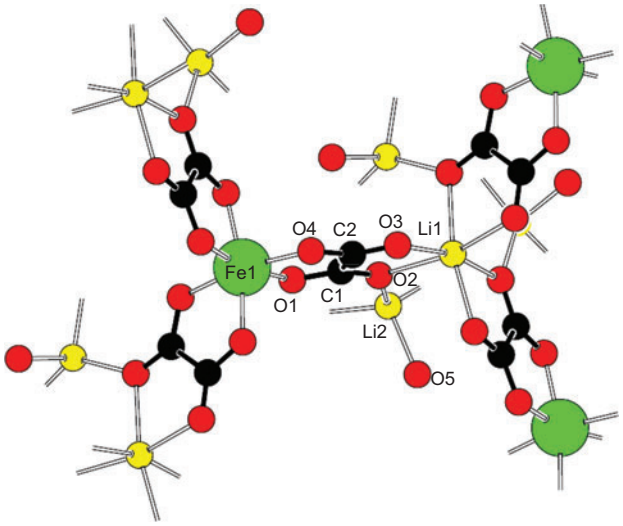


Figure 1 View of the atoms belonging to one sheet of $[Fe(ox_3)Li_4(H_2O)_3]Cl{\cdot}6H_2O$ (Declerq et al., 1993).

shorter than those found for the FeN_2O_5 compounds. The mean Fe–O and Fe–N bond lengths in the six- vs. seven-coordinated compounds are 1.989 and 2.194 Å vs. 2.44 and 2.325 Å, respectively.

The effect of electronic and steric factors of the coordinated atoms can be seen in the opening of the L–Fe–L bond angles of the respective metallocycles. The mean L–Fe–L bond angle opens in the following order: 79.0° ($-OC_2N-$)<80.6° ($-OC_2O-$)<94.3° ($-NC_3N-$) in FeO_6 and FeN_2O_4; 71.3° ($-OC_2N-$)<72.5° ($-OC_2O-$)<73.7° ($-NC_2N-$) in FeN_2O_5.

In two black FeLiM (M=Sr or Ba) compounds, each iron has the oxidation state +2 displaying trigonal-planar (FeN_3) coordination sphere with the mean Fe-μ_3N bond length of 1.90 Å (M=Sr). The Fe(II)-Fe(II) distances are 2.408(2) and 2.616(2) Å. There are different coordination spheres around the Li(I) cation, namely, LiN_2, LiO_4, $LiNO_3$, and LiO_6. The mean Li–L bond length in the four-coordinated species increase in the following order: 1.935 Å (OH_2)<2.005 Å (μ-OH_2)<2.012 Å (bi-OL)<2.035 Å (μ-NC)<2.180 Å (bi-NL). In LiO_6, the values are as follows: 2.072 Å (OH_2)<2.173 Å (bi-OL), which are longer than those in four-coordinated species.

Polymeric FeNa compounds

There are, in total, 36 polymeric FeNa and six FeNaM derivatives. Their crystallographic and structural parameters are gathered in Table 2. Usually, their structures are very complex.

In the orange $(NMe_4)[Fe(CN)_5(NO)Na(H_2O)_{2.5}]$ compound (Longridge et al., 1997), five CN and one NO group form a distorted octahedron about the Fe(III) atom (FeC_5N). The Fe–N bond distance is 1.654(4) Å, and the mean Fe–C distance is 1.935 Å. The Na(I) cation has an approximate trigonal bipyramidal sphere around it. The distance from the cation to the three oxygen atoms of water molecules ranges from 2.302(4) to 2.574(4) Å, and the distance to the two nitrogen atoms of cyanide anions are 2.406(4) and 2.474 Å. One of the water molecules bridges two symmetry-related Na(I) cations. The N atoms of the two CN groups take up axial and equatorial position about the Na(I) cation and are themselves trans with respect to one another within the NO groups. This combination of interactions leads to layers composed by NO groups and solvated Na(I) atoms interspersed with layers of $(NMe_4)^+$ cations.

In the yellow $(NMe_4)[Fe(CN)_6Na(H_2O)]$ (Witzel and Babel, 1984), each Fe(III) atom is hexacoordinated with the mean Fe–C bond lengths of 1.981 Å (CN) and 1.948 Å (μ-CN). The distorted octahedral N_6 cavities formed by six $[Fe(CN)_6]^{3-}$ units are occupied by $Na(H_2O)^+$ moieties [Na–O 2.218(3) Å]. The main distortion of the polyhedron around Na is due to its approach to one of the octahedral faces of the N_6 cavity. This in turn creates a distorted tetrahedron around the Na(I) cation of the form NaN_3O: Na-N=2×2.380(3) and 2.413(3) Å.

In the orthorhombic yellow $Fe(CN)_6Na_3(htma)_2(H_2O)_5$ (Meyer and Pickardt, 1988), each Fe(III) cation is six coordinated, whereas the Na(I) cation is five coordinated (NaN_2O_3). In other five $(FeNa)_n$ derivatives, $Fe(CO)_4Na(cryptate)_2$ (Teller et al., 1977), $Fe(CO)_4Na_2(C_4H_8O_2)_{1.5}$ (Chin and Bau, 1976), $Fe_2(CO)_8[Na(py)_4]_2$ (Deng and Shore, 1992), $[Fe(CO)_2cp]_2Na(thf)_4$ (Minghai et al., 1989), and $[Fe(CO)_2cp]$-$Na(Me_4en)$ (Minghai et al., 1989), carbonyl groups serve as bridges between iron and sodium cations. In three of them (Chin and Bau, 1976; Teller et al., 1977; Deng and Shore, 1992), each iron atom has a tetrahedral coordination sphere (FeC_6), and in the remaining two compounds (Minghai et al., 1989), coordination spheres are FeC_8 and FeC_7. In two of the derivatives (Minghai et al., 1989; Deng and Shore, 1992), there is an Fe–Fe bond with the respective distances of 2.815(1) Å (Deng and Shore, 1992) and 2.534(3) Å (FeC_8) (Minghai et al., 1989). The coordination spheres around a Na(I) cations are NaN_2O_6C (Teller et al., 1977), NaC_2O_2 and NaO_6 (Chin and Bau, 1976), NaN_4O_2 (Deng and Shore, 1992), NaN_2O_2, and NaO_6 (Minghai et al., 1989).

Two red compounds, $[Fe(\mu\text{-chp})_6Na_3(MeOH)_6].1.2Et_2O$ (Blake et al., 1995) (Figure 2) and $Fe(\mu\text{-chp})_6Na_3(MeOH)_6(thf)_2$ (Blake et al., 1996), crystallize in the trigonal crystal class. Both have similar structures. Each chp ligand acts as a bridge between the iron and sodium atoms. Moreover, both metal atoms are hexacoordinated (FeO_6, NaO_6). The Fe···Na and Na···Na distances are 3.017(2) and 3.047(2) Å, respectively. In two other derivatives, in cubic $\{Na[Fe(bpy)_3][Fe(ox)_3]\}$ (Decurtins et al., 1994) and in monoclinic $[Na_3(H_2O)_5Fe(ox)_3]$ (Zheng et al., 1994), the oxalate ligands serve as a bridge, creating a three-dimensional network. Each metal cation is hexacoordinated (FeO_6 and NaO_6). The mean Fe–O and Na–O bond lengths are 1.994(2) and 2.319(3) Å, respectively. The mean O–Fe–O and O–Na–O chelate angles are 82.0° and 75.0°, respectively. In the $[Fe(bpy)_3]^{2+}$ cation, the iron atom is hexacoordinated (FeN_6) with the mean bond length of 1.977(2) Å and the mean N–Fe–N chelate angle of 81.8(1)°. In the monoclinic derivative (Zheng et al., 1994), the Fe(III) cation displays an FeO_6 chromophore with the mean Fe–O bond length of 2.011(2) Å and the O–Fe–O bond angle of 80.4(9)°. The sodium atoms are hexacoordinated (NaO_6).

Table 2 Crystallographic and structural data of polymeric Na–Fe compounds[a].

Compound (color)	Crys.cl Sp.Grp *Z*	a (Å) b (Å) c (Å)	α (°) β (°) γ (°)	Chromophore	M–L (Å)	L–M–L (°)	References
$(NMe_4)_2[(NC)_3(ON)Fe$ $(\mu\text{-}\eta^2\text{-}CN)_2Na(H_2O)_{8.5}]$ (dark yellow)	m C2/c 4	21·454(4) 9·102(2) 17·364(3)	93·57(3)	$Fe^{III}C_5N$	NC[b] 1·9325,3) μNC 1·942(5,6) ON 1·654(4)	C,C[b] 87·7(3,3·0) 170·6(2) C,N 94·8(2,2·2) 173·7(2,3·6)	Longridge et al., 1997
				$Na^IO_3O_3$	H_2O 2·323(5,21) μH_2O 2·574(4) μCN 2·440(4,34)	O,O 83·8(2,11·9) N,N 98·1(2) O,N 85·0(2) 101·7(2,1·1) 160·8(2,5·7)	
$(NMe_4)_2[(NC)_3Fe\cdot$ $(\mu\text{-}\eta^2\text{-}CN)_2Na(H_2O)]$ (yellow)	or Pnma 4	18·639(2) 8·617(1) 13·172(2)		$Fe^{III}C_6$ Na^IN_3O	NC 1·931(3,5) μNC 1·948(3,4) μCN 2·391(3,22) H_2O 2·218(3)	C,C 90·0(1,4·4) 177·091,7) N,N 109·3(2,5·7) N,O 109·0(1,9·1)	Witzel and Babel, 1984
$[(NC)_3Fe(\mu\text{-}\eta^2\text{-}CN)\cdot$ $Na_3(hmta)_2(H_2O)_5]$ (yellow)	or $Pca2_1$ 4	14·122(4) 14·380(4) 14·381(4)		$Fe^{III}C_6$ $Na^IO_3N_2$	NC 1·938(5,18) μNC 1·940(5,19) H_2O 2·37(-,8) μCN 2·378(5,15) 2·526(5) LN2·639(3,62)	Not given	Meyer and Pickardt, 1988
$[(OC)_2Fe(\mu\text{-}CO)_2\cdot$ $\{Na(\eta^8\text{-cryptate})\}_2]$ (colorless)	or $P2_12_12_1$ 4	16·360(3) 12·592(2) 28·058(6)		Fe^0C_4 $Na^IO_6N_2C$	OC 1·76(2,5) η^8O 2·53(3,9) η^8N 2·80(2,8) OC 3·050(2)	C,C 109·5(9,2·7) O,O 65·4(5,2·3) 165·8(5,7·6) N,N 176·8(6,6) O,N 65·6(5,2·6)	Teller et al., 1977
$[Fe(\mu\text{-}\eta^2\text{-}CO)_4Na_2\cdot$ $(C_4H_8O_2)_{1.5}]$ (pale yellow)	tg P4/m 4	10·690(5) 12·283(6)		Fe^0C_4 Na^IO_6	OC 1·942(6,4) μCO 2·321(5,3) LO 2·339(6) 2·988(6)	C,C 105·1(2,9) 129·7(2) O,O 90·0(2,12·2) 170·8(2,6·0)	Chin and Bau, 1976
$[(OC)_4Fe_2(\mu\text{-}\eta^2\text{-}CO)_4\cdot$ $\{Na(Py)_4\}_2]$ (red) (at 213 K)	or Pbca 4	15·796(4) 17·203(6) 18·428(4)		Fe^0C_4 $Na^IN_4O_2$	OC 1·780(5,1) μOC 1·758(5,22) Fe 2·815(1) pyN 2·464(4,17) μCO 2·586(3,1)	C,C 96·7(2,1·8) 118·792,1·2) C,Fe 83·3(1,3·4 175·7(1) N,N 90·0(1,4·7)\ 174·4(1,1) O,O 178·8(1) N,O 90·0(1,5·4)	Deng and Shore, 1992
$[(cp)(OC)Fe(\mu\text{-}\eta^2\text{-}CO)_2\cdot$ $Na(thf)_4]$ (dark red)	m $P2_1/n$ 4	10·155(5) 17·121(4) 18·667(6)	97·61(3)	Fe^0C_{10}	cpC 2·15(2,25) OC 1·76(2,2) μOC 1·91(2,2) Fe 2·534(3)	C,C 92·7(7,8·8)	Minghai et al., 1989

Table 2 (Continued)

Compound (color)	Crys.cl Sp.Grp *Z*	a (Å) b (Å) c (Å)	α (°) β (°) γ (°)	Chromophore	M–L (Å)	L–M–L (°)	References
				$Na^{I}O_6$	thfO 2·34(2,4) μCO 2·45(1,1)	O,O 174·6(4)	
[(cp)Fe(μ-η²-CO)$_2$· Na(Meen)]	or $R2_12_12_1$	6·001(4) 10·644(6)		$Fe^{0}C_7$	cpC 2·102(7,18) μOC 1·716(1,12)	C,C 90·2(3)	Minghai et al., 1989
(yellow)	4	24·214(11)		$Na^{I}O_2N_2$	μCO 2·376(5,12) LN 2·464(6) 2·632(6)	O,O 81·5(2) N,N 72·1(3)[c] O,N 86·0(2,1·4) 133·4(2,10·8)	
[Fe(μ-chp)$_6$Na$_3$· (μ-MeOH)$_6$]·1·2Et$_2$O	trg P-3	11·742(2)		$Fe^{III}O_6$ $Na^{I}O_6$	μchpO 2·000(9,0) μchpO 2·343(9,0)	O,O 90·0(4,5·7) O,O 90·0(4,6·8)	Blake et al., 1995
(red)	1	12·153(4)			μMeHO 2·380(9,1)	150·3(4)	
{[Fe(μ-chp)$_6$Na$_3$· (μ-MeOH)$_6$]·2thf}$_2$	trg P-3	11·601(1)		$Fe^{III}O_6$	μchpO 1·999(2,0) Na 3·017(1)	O,O 95·6(1) O,O 70·0–	Blake et al., 1996
(red) (at 150 K)	1	12·129(1)		$Na^{I}O_6$	μchpO 2·342(2,0) μMeHO 2·376(2,7) Na 3·047(2)	143·6(1)	
[Fe^{II}(η²-bpy)$_3$][Fe^{III}(μ- η²:η²-OC)$_3$Na]	c $P2_13$	15·507(3)		$Fe^{II}N_6$	η²N 1·977(2,0)	N,N 81·8(1,0)[c] 92·8(1,2·2) 174·0(1,0)	Decurtins et al., 1994
(red)	4			$Fe^{III}O_6$	oxO 1·994(2,8)	O,O 82·0(1,0)[c] 92·9(1,3·2) 170·2(1,0)	
				$Na^{I}O_6$	oxO 2·319(3,2)	O,O 75·0(1,0)[c] 95·0(1,8·0)	
[Fe(μ-η²:η²- ox)$_3$·Na$_3$(H$_2$O)$_5$]	m C2/c	17·380(1) 12·693(5)	100·47(2)	$Fe^{III}O_6$ $Na^{I}O_6$	oxO 2·011(2,19) oxO 2·498(3,209)	O,O 80·4(9,3)[c] O,O not given	Zheng et al., 1994
(red)	8	15·196(6)			H$_2$O 2·397(3,171)		
[(H$_2$O)Fe(μ- edta)·Na(H$_2$O)$_2$]	m Cc	8·896(1) 11·931(2)	100·15(2)	$Fe^{III}O_5N_2$	edtaO 1·975(4,8) 2·096(4)	Not given	Solans et al., 1984
(yellow-brown)	4	15·065(2)			edtaμO 2·102(5) edtaN 2·316(5,0) H$_2$O 2·128(5)		
				$Na^{I}O_6$	edtaO 2·320(5) 2·447(5,16) edtaμO 2·507(5) H$_2$O 2·324(5)	Not given	
[(H$_2$O)Fe(μ-edta)· Na(H$_2$O)$_2$]	m Cc	8·895(1) 11·241(2)	100·06(1)	$Fe^{III}O_5N_2$	edtaO 1·975(2,3) 2·096(2)	O,O 73·7(1,5) 94·1(1,12·1)	Lopez-Alcala et al., 1984
(yellow-brown)	4	15·043(2)			edtaμO 2·096(2)	N,N 73·4(1)[c]	

Table 2 (Continued)

Compound (color)	Crys.cl Sp.Grp *Z*	a (Å) b (Å) c (Å)	α (°) β (°) γ (°)	Chromophore	M–L (Å)	L–M–L (°)	References
						O,N 75·4(1,3·7)[c]	
					edtaN 2·318(2,1) H_2O 2·122(1)		
				Na^IO_6	O not given	not given	
$[(H_2O)Fe(\mu\text{-edta})\cdot Na(H_2O)_2]$ (yellow)	m Bb 4	8·82(3) 14·83(3) 12·04(3)	112·0(5)	$Fe^{III}O_5N_2$	edtaO 1·96(1,10) edtaμO 2·11(2) edtaN 2·26(2,4) H_2O 2·11(1)	O,O 73·8(6,7) 92·7(6,16·4) 153·8(6,10·7) N,N 74·2 (6)[c] O,N 75·4(6,7·0)[c] 87·7(6,1·4) 142·2(6,3·0)	Novozhilova et al., 1975
				Na^IO_6	edtaO 2·30(2,19) edtaμO 2·43(2) H_2O 2·39(2)	Not given	
$[\{Fe(\mu\text{-edta})\}_2(\mu\text{-O})\cdot Na_4(H_2O)_3]$ (deep red)	m $P2_1/n$ 4	16·08(1) 10·776(4) 18·367(8)	106·44(4)	$Fe^{III}O_4N_2$	μO 1·778(5,6) edtaO 2·03695,40) edtaN 2·335(6,19)	O,O 97·0(2,8·5) 161·7(2,8) N,N 80·6(2,4)[c] O,N 78·3(2,1·4)[c] 91·5(2,9·4) 166·0(2,13·5)	Ozarowski et al., 1995
				Na^IO_5 (x3) Na^IO_4 (x1)	edtaμO 2·291(2) edtaO 2·679(5) H_2O 2·389(6)– 2·517(7)	Not given Not given	
$[Fe(\mu\text{-tdta})Na(H_2O)_3]$ (yellow)	or $P2_12_12_1$ 4	11·486(4) 16·664(7) 8·867(3)		$Fe^{III}O_4N_2$	tdtaO 1·973(2,14) tdtaN 2·175(2,2)	O,O 95·6(1,10·2) 169·9(1) N,N 92·1(1)[d] O,N 81·0(1,1·7)[c] 92·4(1,2) 169·2(1,1·5)	Okamoto et al., 1990
				Na^IO_6	tdtaO 2·343(3)– H_2O 2·515(3)	Not given	
$[(H_2O)Fe(\mu\text{-4-Cl-2-Phdta})Na(H_2O)_{1.5}]$ (yellow)	m C2/c 8	10·693(3) 13·931(3) 24·686(6)	94·21(2)	$Fe^{III}O_5N_2$	LO 1·982(3,2) 2·046(3,23) LN 2·331(3,10) H_2O 2·080(3)	O,O 73·7(1,1·3)[c] 93·6(2,8·1) 153·6(1,12·2) N,N 73·6(1)[c] O,N 73·7(1,3·7)[c] 91·4(1,2·5) 141·7(1,2·8)	Sanchez et al., 1997

Table 2 (Continued)

Compound (color)	Crys.cl Sp.Grp *Z*	a (Å) b (Å) c (Å)	α (°) β (°) γ (°)	Chromophore	M–L (Å)	L–M–L (°)	References
				$Na^{I}O_6$	LO 2·377(4) H_2O 2·758(3)	Not given	
$[(H_2O)Fe(\mu\text{-dcta})\cdot Na(H_2O)_5]$ (yellow-brown)	or Pbca 8	13·517(5) 13·862(5) 22·893(5)		$Fe^{III}O_5N_2$	dctaO 2·063(5,43) dctaμO 2·883(6) dctaN 2·290(6,2) H_2O 2·005(6)	O,O 78·1(2,4·6) 95·5(2,10·5) 162·6(2,11·80 N,N 75·4(2)[c] O,N 74·1(2,2·1)[c] 102·9(2,4·2)	Seibig and van Eldik, 1998
				$Na^{I}O_6$	dctaO 2·409(7,122) dctaμO 2·883(6) H_2O 2·362(7,11) 2·85(3)	138·2(2,10·0) O,O 47·9(2)– 166·2(5)	
$[Fe(\mu\text{-dtpa})Na(H_2O)_2]$ (amber)	tr P1 2	7·080(3) 10·118(5) 14·549(3)	104·26(3) 93·17(2) 89·77(3)	$Fe^{III}O_4N_3$	dtpaO 1·959(3,2) 2·112(2,35) dtpaN 2·317(3) 2·352(3,11)	O,O 80·0(1,7·9) 98·1(1,1·7) N,N 74·4(1,1)[c] 144·90(8) O,N 74·7(1,4·2)[c] 90·7(1,4·8) 142·7(1,1·4) 164·16(9)	Finnen et al., 1991
				$Na^{I}O_x$	Not given	Not given	
$[Fe(\mu\text{-eddda})Na(H_2O)_3]$ (yellow)	m $P2_1/n$ 4	6·894(2) 20·710(6) 13·966(5)	101·44(2)	$Fe^{III}O_4N_2$	edddaO 1·939(4,10) 2·002(4,3) edddaN 2·202(4,3)	O,O 95·1(2,6·7) 168·2(2) N,N 81·9(2)[c] O,N 79·7(2,1)[c] 90·0(2,1)[d] 91·5(2,7) 165·9(2,4)	Yamamoto et al., 1988
				$Na^{I}O_x$	Not given	Not given	
$[\{Fe(\mu\text{-iada})_2\}_2\cdot Na(H_2O)_3]$ (red)	m $P2_1/c$ 3	15·648(1) 16·787(1) 10·347(2)	90·79(1)	$Fe^{III}O_4N_2$ $Na^{I}O_x$			Jun et al., 1997
$Fe_6(\mu_3\text{-}O)_2(\mu\text{-}OH)_6\cdot(\mu\text{-ida})_6Na_4(H_2O)_{14\cdot5}$ (red)	tr_ P1 2	11·381(4) 14·897(6) 18·788(8)	96·30(3) 90·48(3) 108·79(3)	$Fe^{III}O_5N$ $Na^{I}O_x$			Harding et al., 1993
$[Fe(\mu\text{-nta})_2Na_3(H_2O)_{1\cdot5}]$ (yellow)	m $P2_1/n$	10·102(1) 10·859(1)	102·78(1)	$Fe^{III}O_5N_2$	ntaO 2·025(5,15) 2·066(2,13)	O,O 75·0(1)– 166·4(1)	Clegg et al., 1984

Table 2 (Continued)

Compound (color)	Crys.cl Sp.Grp *Z*	a (Å) b (Å) c (Å)	α (°) β (°) γ (°)	Chromophore	M–L (Å)	L–M–L (°)	References
	4	20·441(2)			ntaN 2·303(3,12)	N,N 146·2(1) O,N 75·9(1,3·8)[c]	
				$Na^{I}O_6$	ntaO 2·310(3)– H_2O 2·993(4)	129·3(1,12·2) O,O 64·0	
$Fe(\mu\text{-}C_4H_2O_6)_2\cdot$ $Na_5(H_2O)_{14}$	tr_ P1	10·909(5) 10·222(5)	102·95(5) 100·64(5)	$Fe^{III}O_6$	LO 1·980(3,3) LμO 2·149(3)	O,O 80·7(1,3·2)[c] 86·8(1)[d]	Ivanov and Kosoy, 1975
(yellow)	1	6·998(5)	111·10(5)	$Na^{I}O_6$	LO 2·298(4)– H_2O 2·711(4)	O,O 71·9(1)– 103·1(1)	
$[Fe(\mu\text{-}mal)_3\cdot Na_3(H_2O)_8]$	tr_	14·497(2)	91·0(1)	$Fe^{III}O_6$	malO 1·982(8,14)	O,O 90·0(3,4·4)[d]	Calogero et al., 1997
(green)	P1	14·758(2)	105·4(1)		2·017(6,28)		
	2	9·148(1)	67·6(1)	$Na^{I}O_6$	malO 2·388(9)– 2·727(9) H_2O 2·286(9)– 2·638(9)	O,O 73·8(3)– 119·6(3) O,O 86·5(1)	
				$Na^{I}O_5$	malO 2·339(9,44) H_2O 2·440(9,25)		
$[Fe(\mu\text{-}mal)_3Na_3(H_2O)_8\cdot$	tr_	11·395(1)	101·2(1)	$Fe^{III}O_6$	malO 1·989(3,10)	O,O 90·0(2,7·2)[d]	Calogero et al., 1997
$(sol)_{0\cdot5})]$	P1	11·970(1)	90·8(1)		2·010(3,3)		
(green)	1	9·995(1)	62·5(1)	$Na^{I}O_6$	malO 2·360(3)– 2·581(3) H_2O 2·338(4)– 2·565(4) solO 2·669(5,15)	O,O 51·8(2)– 107·9(2) 170·2(2,2·0)	
$[Fe(\mu\text{-}ehpg)(Na(H_2O)_4]$	or	37·66(2)		$Fe^{III}O_4N_2$	ehpgO 1·907(3,15)	O,O 92·2(3,3·20)	Bailey et al., 1981
(red)	Pbcn	7·12(1)			2·011(8)	112·6; 172·1(3)	
	12	24·44(1)			ehpgμO 2·037(8)	N,N 79·2(3)[c]	
					ehpgN 2·148(9,9)	O,N 77·8(3,2)[c] 86·9(3,60[d] 96·1; 154·6(3)	
				$Fe^{III}O_4N_2$	ehpgO 1·904(8,0)	O,O 92·3(3,1·4)	
					ehpgμO 2·029(8,0)	107·2; 172·1(3)	
					ehpgN 2·151(9,0)	N,N 80·6(3)[c]	
						O,N 78·0(3)[c]	
						87·3(3)[d]	
						95·9; 172·1(3)	
				$Na^{I}O_6$	ehpgO 2·186(43)– 3·080(28) H_2O 2·117(63)– 3·139(33)	Not given	

Table 2 (Continued)

Compound (color)	Crys.cl Sp.Grp *Z*	a (Å) b (Å) c (Å)	α (°) β (°) γ (°)	Chromophore	M–L (Å)	L–M–L (°)	References
[Fe(μ-dota)·Na(H_2O)$_3$] (red)	or Pna2$_1$ 4	8·764(2) 18·618(4) 14·382(2)		$Fe^{III}N_4O_3$	dotaN 2·207(7) 2·270(7,1) 2·353(7) dotaO 2·050(7,9)	N,N 77·2(2,3·9)[c] 124·0(3,2) N,O 76·7(3,2·8)[c] 92·9(3) 122·6(3,2) 150·4(3,2·4)	Chang et al., 1993
				Na^IO_x	O Not given	Not given	
Fe{μ-$C_5H_4CH_2N(CH_2$- $COO)_2$}$_2Na_4(H_2O)_2$·EtOH (yellow)	tr_ P1 1	6·068(1) 11·888(2) 14·854(3)	76·23(3) 86·68(3) 77·38(3)	FeC_{10} Na^IO_4N	LC not given LO 2·24–2·29 LN 2·25	Not given Not given	Plenio et al., 1993
Fe_4(μ-O)$_2$(μ-η^2-$O_2CO)_2$· (μ-hpdt)$_2Na_6(H_2O)_{20}$ (brown-green)	tr_ P1 1	11·712(4) 12·914(3) 10·987(3)	94·03(2) 116·00(2) 77·70(2)	$Fe^{III}O_5N$	μO 1·829(4,10 μOCO_2 1·993(4,4) μLO 2·057(5,37) μLN 2·200(5,2)	O,O 93·7(2,13·0) 163·5(2,10·9) O,N 78·592,3·5)[c] 94·2(2,6) 172·2(2,1·10	Jameson et al., 1987
				Na^IO_6	μO 2·22(2)– H_2O 3·00(2)	O,O Not given	
Fe(μ-OH) (μ-η^3-aer)$_2$·$Na_{2.5}$(η^2- $O_2NO)_{0.5}$·3·5H_2O (colorless)	m P2$_1$ 4	6·136(1) 15·046(3) 17·760(5)	92·13(2)	$Fe^{III}O_6$ Na^IO_6	μHO 1·906(6,3) aerO 1·957(5,23) Not given	O,O Not given Not given	Burger and Klüfers, 1996
{Fe_3(μ$_3$-OMe)(μ-η^3- aer)$_6$·Na_4}·2·5$NaNO_3$ (yellow-green)	hx P6$_3$/m 4	11·709(4) 33·153(6)		$Fe^{III}O_6$ Na^IO_6	μ$_3$MeO 2·146(3) aerμO 2·048(4,40) aerO 1·948(4,29) aerO 2·258(4,3) 2·39194,32) O_2NO 2·841(4)	O,O not given Not given	Burger and Klüfers, 1996
Fe_4(μ-Ala)$_2$(μ-O)(μ-OH)· (μ-dhpta)$_2$Na(H_2O)$_6$ (pale yellow)	m P2$_1$ 2	11·762(1) 15·924(2) 12·948(2)	109·46(1)	$Fe^{III}O_5N$ Na^IO_6	μO 1·857(4,6) LμO 2·018(5,3) LO 2·023(5,13) LN 2·182(4,3) alaO 2·086(6,11) LO 2·378(6)– H_2O 2·629(7)	μO,μO 92·5(2) O,O 78·5(2)– 91·3(3)	Yano et al., 1996
Fe(μ-trencam)Na_3·17·5H_2O (red)	hx P6$_3$/m 2	13·785(3) 16·244(5)		$Fe^{III}O_6$ Na^IO_x	LO 2·012(2,0) Not given	O,O 77·75(10[c] 84·78(8) 134·18(4) Not given	McMurry et al., 1987

Table 2 (Continued)

Compound (color)	Crys.cl Sp.Grp Z	a (Å) b (Å) c (Å)	α (°) β (°) γ (°)	Chromophore	M–L (Å)	L–M–L (°)	References
(η^3-[9]aneS_3)Fe· (μ-[9]	tr_ P1	10·145970 12·323(6)	82·91(4) 86·09(4)	$Fe^{II}S_6$	η^3S 2·255(1,5) LOS 2·205(1)	S,S 90·0(1,3)[c] 180·0(1)	Küppers et al., 1987
aneS_3(O))·Na_2=$(ClO_4)_4(H_2O)$[e] (green)	4	12·465960	83·16(4)	$Fe^{II}S_6$ $Na^{I}O_6$	η^3S 2·260(1,3) LOS 2·209(1) LOS 2·407(7) 2·575(9) O_3ClO 2·280(6)– 2·555(6)	S,S 90·0(1,30[c] 180·0(1) O,O Not given	
				$Na^{I}O_6$	O_3ClO 2·331(6)– H_2O 2·674(4)	O,O Not given	
Fe(μ-η^2:n^2-ox)$_3$·$K_{2·5}Na_{0·5}$ (green)	c P_432 8	13·536(3)		$Fe^{III}O_6$ $M^{I}O_6$	oxO Not given oxO Not given	O,O Not given O,O Not given	Henneicke and Wartchow, 1997
[{Na(thf)$_2$}$_2$Hg·{Fe(μ-η^2- CO)$_4$}$_2$] (deep yellow)	m C2/m 2	12·39(3) 8·54(1) 16·01(1)	105·5(2)	$Fe^{0}C_4$	μOC 1·75(2,4) Hg 2·522(5)	C,C 98·2(8,4) 117·5(7,1·4) C,Hg 81·5(6,1·2) 179·0(6)	Sosinsky et al., 1983
				HgC_2Fe_2 $Na^{I}O_5$	μOC 2·84(2,4) μCO 2·29(2,3) thfO 2·28(1,2)	C,C not given O,O 89·0(6,4·4) 116·4(6,10·7) 170·4(5)	
[{Na(thf)$_2$}$_2$·Zn{Fe(μ-η^2- CO)$_4$}$_2$] (lightb pink)	m I2/m 2	10·654(3) 9·848(3) 15·333(3)	100·79(2)	$Fe^{0}C_4$ ZnC_4Fe_2 $Na^{I}O_6$	μOC 1·756 Zn 2·317 μOC 1·724 2·502 μCO 2·308(4,0) 2·584(7) thfμO 2·514(6,58) thfO 2·315(6)	C,Zn 74·8(2) 162·3(2) C,C not given O,O not given	Pierpont et al., 1982
[$Fe_{0·5}Cr_{0·5}Mo_3$(μ-O)·(μ$_3$- O)$_3$(μ-η^2-pr)$_5$·(μ-pr)$_3$Na]$_2$ (black)	tr_ P1 1	12·981(5) 14·021(4) 12·356(6)	109·81(4) 117·51(5) 90·36(4)	$Fe^{III}/Cr^{III}O_6$ $Mo^{IV}O_6$ $Na^{I}O_5$	μ_3O 1·980(9,4) μO 1·99(1,2) μ_3O 1·937(9,28) μO 1·997(9,10) prO 2·08(8,8) Mo 2·519(2,14) prO 2·31(2,8)	O,O 89·594,7) 177·0(4,1·2) O,O 90·0(4,10·8) 171·0(1,7·3) Mo,Mo 60·0(1,5) O,O 82·1(4,1·5) 111·6(4,9·3) 151·2(5,4·5)	Huang et al., 1996

Table 2 (Continued)

Compound (color)	Crys.cl Sp.Grp Z	a (Å) b (Å) c (Å)	α (°) β (°) γ (°)	Chromophore	M–L (Å)	L–M–L (°)	References
$[Fe_2\{Mo_3(\mu\text{-}O)(\mu_3\text{-}O)_3\cdot(\mu\text{-}\eta^2\text{-}pr)_5(\mu\text{-}pr)_3\}_2Na_2]$ (black)	tr_ P1 1	12·988(6) 14·021(7) 12·378(9)	109·79(5) 117·50(4) 90·52(5)	$Fe^{III}O_6$	μO 1·992(8,19) prO 1·993(9,18)	O,O 90·0(3,3·8) 176·4(3,1)	Li et al., 1997
				$Mo^{III}O_6$	μ_3O 1·946(7,29) 2·027(7,28) μO 1·916(7,2) prO 2·084(7,93) Mo 2·517(1,12)	O,O not given	
				$Na^{I}O_5$	prO 2·30(2,10)	O,O not given	
$[Fe_2\{W_3(\mu\text{-}O)(\mu_3\text{-}O)_3\cdot(\mu\text{-}\eta^2\text{-}pr)_5(\mu\text{-}pr)_3\}_2Na_2]$ (black)	tr_ P1 1	12·984(6) 14·072(7) 12·436(9)	109·91(5) 117·54(4) 90·50(5)	$Fe^{III}O_6$	μ_3O 1·98(2,2) prO 2·02(2,3)	O,O 90·0(4,4·6) 176·0(4,4)	Li et al., 1997
				$W^{IV}O_6$	μ_3O 1·98(1,1) 2·04(1,2) μO 1·92(2,0) prO 2·06(1,25) W 2·535(9,17)	O,O not given	
				$Na^{I}O_5$	prO 2·26(2,15)	O,O not given	

[a]Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis is the e.s.d., and the second is the maximum deviation from the mean.

[b]The chemical identity of the coordinated atom or ligand is specified in these columns.

[c]The five-membered metallocyclic ring.

[d]The six-membered metallocyclic ring.

[e]There are two crystallographically independent molecules.

There are two monoclinic $(FeNa)_n$ species, namely, $[Na(H_2O)_3Fe(edta)]$ (Novazhilova et al., 1975; Lopez-Alcala et al., 1984; Solans et al., 1984) and $[Na_4(H_2O)_2Fe(edta)(\mu\text{-}O)Fe(edta)]$ (Ozarowski et al., 1995), where edta bridges the metal cations. The former compound has been studied by three different groups. The Fe(III) cations are coordinated by four oxygen atoms and two nitrogen atoms of the edta ligand. The seventh coordination site of an approximate pentagonal bipyramid is occupied by a water molecule. The Na(I) cations are six coordinated (NaO_6). The anions form layers along a crystallographic plane. Single layers are loosely linked by the Na(I) cation into electrically neutral double layers. Cohesion between double layers depends largely on van der Waals interactions supplemented by weak hydrogen bonds formed by water molecules with carboxylate O atoms (Solans et al., 1984). In the other monoclinic compound (Ozarowski et al., 1995), there are binuclear $[Fe(edta)(\mu\text{-}O)Fe(edta)]^{4-}$ units with an oxygen bridge having an angle of 163.2(3)°. The bridging oxygen atom lies trans to one of the nitrogen atoms of edta, with a slight deviation from linearity [174.9(2)° and 179.5(2)°]. Three of the four acetate groups are coordinated, whereas the fourth one is turned away from the central iron atom. The mean Fe–O(acetate) bond length of 2.036(5) Å is considerably longer than the mean Fe–O(bridge) bond length [1.778(5) Å]. Three Na(I) cations are five and one four coordinated (NaO_5 x3 and NaO_4).

In the yellow polymeric $Na(H_2O)_3Fe(tdta)$ (Okamoto et al., 1990), the nonadentate tdta ligand serves as a bridge between the metal atoms, resulting in polymeric sheets. The Fe(III) cation is octahedrally coordinated (FeN_2O_4) with the mean Fe–O and Fe–N bond lengths of 1.973(2) and 2.175(2) Å, respectively. The chromophore NaO_6 consists of three oxygen atoms of water molecules and other three oxygen atoms of the tdta ligand. There is a hydrogen bonding network between the water molecules and the oxygen atoms of the tdta ligand.

In $Na(H_2O)_{1.5}Fe(H_2O)$(4-Cl-2Phdta) (Sanchez et al., 1997), the 4-Cl-2Phdta ligand acts as a bridge between the metal atoms forming a polymeric structure. The Fe(III) cation is seven coordinated (FeN_2O_5). Two oxygen atoms and two nitrogen atoms of the ligand together with one oxygen atom of a water molecule form a pseudo-pentagonal plane. Two additional oxygen atoms of the ligand occupy the apical positions. The mean $Fe–O_{eq}$, $Fe–N_{eq}$, and $Fe–O_{ap}$ bond lengths are 2.031(3), 2.331(3), and 1.982(3) Å, respectively. Each Na(I) cation is six coordinated (NaO_6) with the mean Na–O distance of 2.518(4) Å with the range of 2.377(4)–2.758(3) Å. One oxygen atom of a water molecule bridges two Na(I) cations.

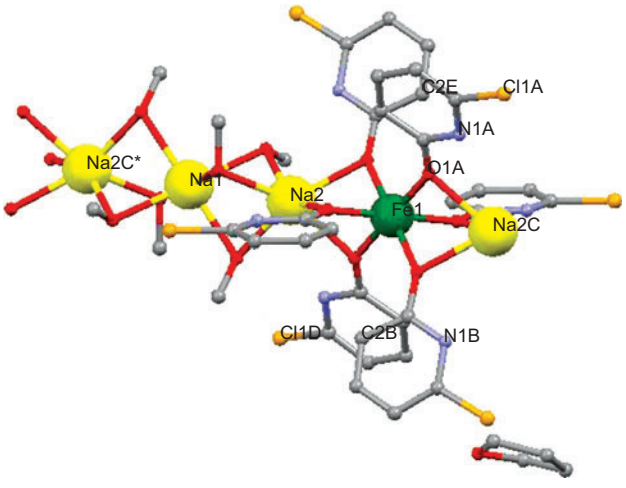


Figure 2 A segment of the polymer $[Fe(chp)_6Na_3(MeOH)_6]$ (Blake et al., 1995). Hydrogen atoms have been omitted for clarity.

X-ray analysis of orthorhombic brownish yellow $Na(H_2O)_5Fe(H_2O)$(dcta) (Seibig and van Eldik, 1998) shows that the iron(III) cation is seven coordinated surrounded by a monocapped twisted trigonal prism. The polyhedron is formed by four oxygen atoms and two N atoms of the dcta ligand, whereas the oxygen atom of a water molecule occupies the cap position. The Na(I) cation is six coordinated by water molecules and carboxylate oxygen atoms (Figure 3).

The amber-colored $Na_2(H_2O)_2Fe(dtpa)$ (Finnen et al., 1991) crystallizes in triclinic system, forming a polymeric structure. The dtpa ligand creates about the Fe(III) cation a distorted pentagonal bipyramid (FeN_3O_4). Two axial positions are occupied by oxygen atoms. In the equatorial plane, two oxygen atoms occupy adjacent coordination sites. The mean $Fe–O_{ax}$ bond length of 1.958(3) Å is shorter than the mean $Fe–O_{eq}$ value, 2.112(2) Å. The Fe–N bond length has the mean value of 2.347(2) Å.

The structure of $Na(H_2O)_3Fe(eddda)$ (Yamamoto et al., 1988) is similar to its Li(I) analog (Yamamoto et al., 1988). Merely crystallographic data are available for the red $Na(H_2O)_3[Fe(ida)_2]_2$ (Jun et al., 1997). Instead, full structural analysis was carried out for another red complex, $Na_4Fe_6(\mu_3\text{-}O)_2(\mu\text{-}OH)_6(\mu\text{-}ida)_6\cdot 14.5(H_2O)$ (Harding et al., 1993). There is a distorted octahedron around the Fe(III) cation ($FeNO_5$). The tridentate ida ligand is facially coordinated. The other coordination sites are occupied by one μ_3-O atom and two μ-OH groups. The core of $[Fe_6(\mu_3\text{-}O)_2(\mu\text{-}OH)_6]^{8+}$ consists of two μ_3-O bridged Fe_3 triangles, defined by Fe(1), Fe(2), Fe(3),O(3), and Fe(1a),Fe(2a),Fe(3a),O(3a) atoms. These triangles are in two parallel planes. The apical iron atom Fe(1) is connected to the base iron atoms Fe(2a) and Fe(3a) of the adjacent triangle by two intertrimer μ-OH bridges. Two remaining μ-OH groups form intratrimer bridges across the base of two triangles between Fe(2), Fe(3), and Fe(2a),Fe(3a). The angles Fe(2)–O–Fe(3) and Fe(2)–O(3)–Fe(3) are 95.7(5)° and 97.8(5)°, respectively. Consequently, the iron atoms Fe(2) and Fe(3) are only 2.934 Å apart, whereas the Fe(1)–Fe(2) and Fe(1)–Fe(3) distances are 3.470 and 3.459 Å, respectively. Unfortunately, for the NaO_x, data are not available.

In the yellow $Na_3(H_2O)_{1.5}Fe(nta)_2$ (Clegg et al., 1984), the Fe(III) cation displays a distorted pentagonal bipyramidal coordination polyhedron (FeN_2O_5) with two axial oxygen atoms [Fe–O=2.025(2) Å, av.], three equatorial oxygen atoms [Fe–O=2.066(2) Å, av.], and two equatorial nitrogen atoms [Fe–N=2.303(3) Å, av.]. One nta ligand is tetradentately (NO_3) and the other tridentately (NO_2) coordinated. Each Na(I) cation is coordinated by six oxygen atoms. In the first polyhedron, two water molecules and four oxygen atoms of the uncoordinated carboxylate groups are involved, whereas

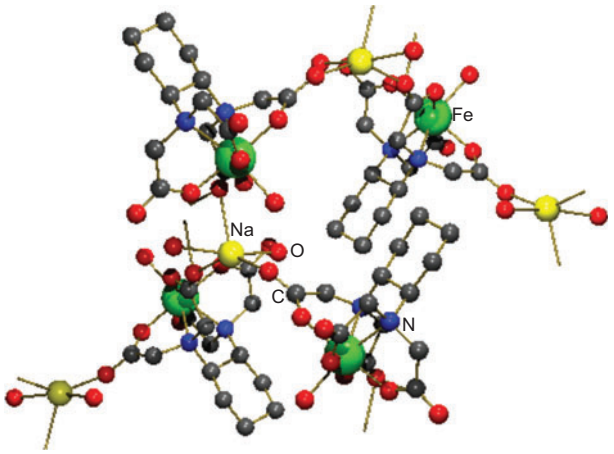


Figure 3 View of the part of $Fe(H_2O)(dcta)Na(H_2O)_5$ (Seibig and van Eldik, 1998).

in the second polyhedron, the respective numbers are three and three. The two coordination polyhedra are quite irregular with the ranges for Na–O and for O–Na–O 2.310(3)–2.993(4) Å and 64.6(2)–176.0(1)°, respectively.

In another yellow polymeric complex, $Na_5(H_2O)_{14}Fe(C_4H_2O_6)_2$ (Ivanov and Kosoy, 1975), both metal cations are six coordinated (chromophores FeO_6 and NaO_6). Three oxygen atoms of two tartrates are connected to one Fe(III) cations, four (out of six) oxygen atoms belong to two hydroxyl groups of each tartrate with the mean Fe–O bond length of 1.980(3) Å, whereas two opposite octahedral summits (distorted toward a tetragonal bipyramid) are each occupied by an oxygen atom of one of the carboxyl groups [$Fe–O_{ax}$=2.149(3) Å (x2)]. The mean Na(1)–O bond length is 1.99 Å [$Na(1)O_6$ and $Na(3)O_6$] and 2.45 Å for the $Na(2)O_6$ unit.

There are two green triclinic complexes, $Na_3(H_2O)_8[Fe(mal)_3]$ and $Na_3(H_2O)_8[Fe(mal)_3](sol)_{0.5}$ (Calogero et al., 1997). The former one contains two distinct octahedral Fe(III) sites with six surrounding oxygen atoms from the malonate anions. Moreover, there are totally seven crystallographically independent sodium sites surrounded by oxygen atoms of either malonate anions or water molecules. Because the site occupancy for Na(I) and Na(2) is 0.5, the unit cell contains six sodium ions, each of them normally six coordinated (NaO_6). The exception is Na(7), which is pentacoordinated. The latter compound contains one Fe(III) coordination site (FeO_6) and four octahedral sodium sites (NaO_6). The Na(1) cation is bound to three oxygen atoms from a malonate anion, one oxygen of another malonate anion, and two oxygen atoms of water molecules. The Na(2) cation has a different surrounding consisting of four oxygen atoms of water molecules and two oxygen atoms of two malonate anions. The third Na(I) cation is also bound to four oxygen atoms of water molecules, one oxygen atom of a malonate, and one oxygen atom of the solvent molecule. The coordination sphere of the fourth Na(I) cation consists of two oxygen atoms of water molecules, two oxygen atoms of malonates, and two oxygen atoms of the solvent molecule.

The asymmetric unit of the polymeric red $Na(H_2O)_4Fe(ehpg)$ (Bailey et al., 1981) contains one [Fe(*meso*-ehpg)] ion. The central Fe(III) cation is six coordinated (FeN_2O_4). The crystal lattice contains hydrophilic channels with disordered water molecules and Na(I) cations. Each Na(I) cation is surrounded by six oxygen atoms (NaO_6).

In $Na(H_2O)Fe(dopa)$ (Chang et al., 1993), the heptadentate dopa ligand creates a pentagonal-bipyramidal arrangement about each Fe(III) cation (FeN_4O_3). Each sodium atom is connected to two oxygen atoms of the respective ligand and water molecules.

In the yellow $Na_4(H_2O)_7Fe[C_5H_4CH_2N(CH_2COO)_2]_2·EtOH$ (Plenio et al., 1993), the ligand serves as a bridge between the metal atoms and creates a three-dimensional structure. The iron atom is sandwiched (FeC_{10}) and the sodium atom is five coordinated ($NaNO_4$).

The structure of the brown-green $Na_6[H_2O)_{20}Fe_4(hpdt)_2(CO_3)_2(O)_2$ (Jameson et al., 1987) consists of centrosymmetric tetranuclear units. Two binuclear $Fe_2[hpdt)(CO_3)(O)$ units are linked by an extensive network involving Na(I) cations and water molecules. Each Fe(III) cation is six coordinated ($FeNO_5$). The sodium atom is bonded to water molecules and to the carboxylate and carbonate oxygen atoms not coordinated to iron [O(2), O(4), O(7), O(9)]. Each sodium atom is six coordinated (NaO_6). The Na(1) atom joins the tetranuclear units via strictly linear O(2)–Na(1)–O(2′) bonds to form an infinite Na–(Fe_4)–Na chain along [110].

In the colorless polymeric $Na_{3.5}Fe(aer)_2(OH)(NO_3)_{0.5}·3.5H_2O$ (Burger and Klüfers, 1996), each Fe(III) cation has a square-pyramidal arrangement (FeO_5) created by two coordinated aer ligands with the OH group occupying the apical position [$Fe–O_{eq}$=1.957(5) Å (av.) and $Fe–O_{ap}$=1.906(6) Å]. The hydroxyl group and the aer ligand form bridges between the metal atoms. Unfortunately, the coordination around the Na(I) cation is not discussed in the original paper.

The yellow-green polymeric $Na_{6.5}[Fe_3(aer)_6(OMe)](NO_3)_{2.5}$ reported also by Burger and Klüfers (1996) contains a trinuclear $[Fe(\mu\text{-aer})_6(\mu_3\text{-OMe})]^{4-}$ anion possessing a C_3 rotation axis. The iron atoms are six coordinated (FeO_6). The mean Fe–O bond length increases in the following order: 1.948(4) Å (O)<2.048(4) Å (μ-O)<2.146(3) Å (μ_3-O). The distance between the iron atoms is 3.292(1) Å, and the mean Fe–O–Fe angle is 106.9(1)°. Each sodium atom is also six coordinated (NaO_6). The coordination sphere is built up by five oxygen atoms of the aer ligands and nitrate anion.

In the pale yellow $NaFe_4(ala)(dhpta)_2(O)(OH)·6H_2O$ (Yano et al., 1996), the Fe(III) cation displays a distorted octahedral polyhedron, where the O donor atoms are supplied by two nonbridging acetate anions, a bridging oxide, a bridging alkoxide, and a bridging bidentate L-alanine moiety. The structure can be viewed as a dimer of dimers. The resulting tetramer has a twofold rotation axis. In each dimer unit, the $dhpta^{5-}$ ligand binds two Fe(III) cations bridged by the alkoxy oxygen. The two dimers are linked by the $(O_2H)^{3-}$ fragment and L-alanine behaving as zwitterion. The long Fe(1)···Fe(2) and Fe(1)···Fe(4) distances of 3.473(12) and 3.676(15) Å rule out the existence of a direct

chemical bond. The NaO_6 unit involves four oxygen atoms of water molecules and two oxygen atoms of the carboxylate group of the dhpta anion.

In the red polymeric $Na_3Fe(trencam)\cdot 17.5H_2O$ (McMurry et al., 1987), the Fe(III) cation is surrounded by a trigonal prism involving six oxygen atoms of trencam ligand. The six equal Fe–O bond lengths have the value 2.012(2) Å. The site symmetry around the Fe(III) cation is C_{3h}. The surroundings of the Na(I) cation were not dealt with in the original paper.

The green $Na_2Fe([9]aneS_3)([9]anesS_3(O))ClO_4\cdot H_2O$ (Küppers et al., 1987) crystallizes in a triclinic space group. The structure contains two crystallographically independent $[Fe([9]aneS_3)([9]aneS_3(O))]^{2+}$ cations. The FeS_6 chromophore is created by two terdentate ligands. The mean Fe–S ($[9]aneS_3$) and Fe–S ($[9]aneS_3(O)$) bond lengths are 2.255(1) and 2.2205 Å in cation 1 and 2.260(1) and 2.009(1) Å in cation 2. The arrangement around the Na(I) cations forms two independent strands. The Na(1) has a distorted octahedral polyhedron around, consisting of one oxygen atom of one perchlorate anion and three oxygen atoms of another perchlorate anion, and one oxygen atom of a water molecule. The first perchlorate is coordinated in a bidentate fashion to Na(1), as is also Na(2) cation. The latter has also one oxygen atom serving as bridge to Na(1′). The second sodium atom is coordinated to the sulfoxide oxygen atoms, and the two locations Na(2) and Na(3), each with the occupancy of 0.5 [O(1)–Na(3)=2.575(9) Å and O(3)–Na(2)=2.417(7) Å]. The two positions are quite close to each other [Na(2)···Na(3)=0.836(7) Å]. Four oxygen atoms of the $(Cl(4)O)^{4-}$ anion are flipping between two distinct positions with the occupancy number of 0.5. Both Na(2) and Na(3) are six coordinated (NaO_6).

There are six NaFeM′ polymers reported, for which the crystallographic and structural parameters are gathered in Table 2. In the green $Na_{0.5}K_{2.5}Fe(ox)_3$ (Henneicke and Wartchow, 1997), the oxalate anion acts as a bridge between the metal atoms in polymeric chains. Each metal atom is six coordinated.

The molecular structure in a monoclinic deep yellow crystal of $Hg[Fe(CO)_4Na(thf)_2]_2$ (Sosinsky et al., 1983) contains a mercury atom at a special position (2/*m*) between two $Fe(CO)_4$ units [Fe···Hg=2.522(5) Å]. Moreover, there are two carbonyl groups attached to the mercury atom [Hg–C=2.84(2) Å av.]. The Na(I) cation is five coordinated (NaO_5). The bonds between carbonyl oxygen atoms of the $\{Hg[Fe(CO)_4]\}^-$ anion and $[Na(thf)_2]^+$ cations result in an extended polymeric structure.

In the light pink polymeric $Zn\{[Na(thf)_2]_2[Fe(CO)_4]_2\}$ (Pierpont et al., 1982), the Zn(II) cation is located at a 2/*m* site with the Fe atom and two carbonyl groups lying on the mirror plane. This results in C_{2v} site symmetry for Zn. Each Fe atom is five coordinated (FeC_4Zn) with the Fe–C and Fe–Zn bond lengths of 1.756 and 2.317 Å, respectively. The Zn atom shows six coordination $(ZnCeFe_2)^-$. The Zn–C bond lengths have the values of 1.729 (x2) and 2.502 (x2). There is a strong interaction between the dimeric $[Na_2(\mu\text{-thf})_2(thf)_2]^{2+}$ cations and the carbonyl oxygen atoms. Each Na(I) cation is six coordinated (NaO_6). The inner coordination sphere consists of three μ-η^2-CO groups, two μ-thf, and one terminal thf molecule. The mean Na–O bond lengths increase in the following order: 2.315(6) Å (thf)<2.400(6) Å (μ-OC)<2.516(6) Å (μ-thf).

The structure in the black triclinic $Na_2[Fe_{0.5}Cr_{0.5}Mo_3(O)_4(pr)_8]_2$ (Huang et al., 1996) consists of a centrosymmetric cluster anion, where two $[Mo_3O_4(pr)_8]^{4-}$ units are joined by two M atoms (M=0.5 Fe+0.5 Cr, disordered) *via* four bridging oxygen atoms and eight bridging propionate groups (Figure 4). Each M atom is coordinated by six oxygen atoms: two of the μ_3-O atoms and four oxygen atoms of the propionate bridges. Each Mo atom is also six coordinated, displaying a distorted octahedral coordination polyhedron (MoO_6). The atoms M(1), O(2), Mo(1), and O(3) form a nearly planar $Mo_2M_2O_4$ eight-membered ring about a center of symmetry. The average M–Mo distance of 3.64(9) Å is too long to represent a chemical bond. The mean Mo–Mo bond length is 2.517(1) Å. Each Na(1) atom is five coordinated, displaying a trigonal bipyramidal coordination sphere (NaO_5). The anions are connected by Na(I) cation, forming Na_2O_2 four-membered rings about the origin. There are also two other black triclinic compounds, $[Fe_2\{Mo_3O_4(pr)_8\}_2Na_2]$ (M=Mo or W) (Li et al., 1997), which are isostructural with the complex discussed previously (Huang et al., 1996).

Inspection of the data in Table 2 reveals that there are 36 examples of NaFe and six examples of NaFeM′ polymeric compounds. These complexes show a wide variety of colors: yellow (x14), red (x8), green (x6), brown (x3), black (x3), orange (x2), and colorless (x2). The compounds crystallize in different crystal classes: monoclinic (x16), triclinic (13), orthorhombic (x8), cubic (x2), hexagonal (x2), tetragonal (x1), and trigonal (x1).

The iron atoms have the oxidation states 0, +2, or +3, of which +3 prevails by far. The Fe(0) atoms are bonded to carbon, displaying four coordination (Chin and Bau, 1976; Teller et al., 1977; Deng and Shore, 1992), five coordination (Pierpont et al., 1982; Sosinsky et al., 1983), eight coordination (Minghai et al., 1989), or 10 coordination (double sandwiched) (Plenio et al., 1993). The mean Fe(0)–C distances are 1.76 Å (CO)<1.81 Å (μ-η^2-CO)<2.15 Å (η^5-cp). In some examples, there is a metal-metal bond: Fe–Fe=2.815(1) Å (Deng and Shore, 1992), Fe–Fe=2.534(2) Å (Blake et al., 1996), Fe–Hg=2.522 Å (Sosinsky et al., 1983), and Fe–Zn=2.217 Å (Pierpont et al., 1982). There are only two

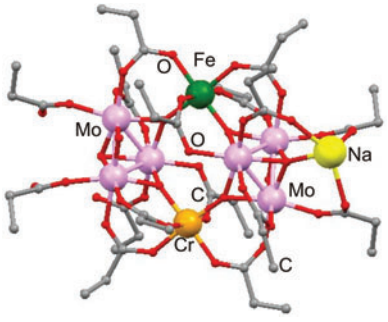


Figure 4 View of the $[MMo_3O_4(pr)_8]_2^{2-}$ anion (M=Fe or Cr) (Huang et al., 1996).

examples where iron has the oxidation state +2 (Küppers et al., 1987). In each case, there is an FeS_6 chromophore with the mean L_3S vs. $L_3S(O)$ bond lengths of 2.258 and 2.207 Å, respectively. The mean S–Fe–S angle in the five-membered rings is 90.0°. All remaining compounds contain an Fe(III) cation with a wide variety of chromophores: FeC_5N (Longridge et al., 1997), FeC_6 (Witzel and Babel, 1984; Meyer and Pickardt, 1988), FeO_6 (Ivanov and Kosoy, 1975; McMurry et al., 1987; Decurtins et al., 1994; Blake et al., 1995, 1996; Burger and Klüfers, 1996; Huang et al., 1996; Calogero et al., 1997; Li et al., 1997), FeN_2O_5 (Novozhilova et al., 1975; Clegg et al., 1984; Lopez-Alcala et al., 1984; Solans et al., 1984; Finnen et al., 1991; Sanchez et al., 1997; Seibig and van Eldik, 1998), FeN_2O_4 (Bailey et al., 1981; Yamamoto et al., 1988; Okamoto et al., 1990; Ozarowski et al., 1995; Jun et al., 1997), FeN_3O_4 (Finnen et al., 1991), $FeNO_5$ (Jameson et al., 1987; Harding et al., 1993; Yano et al., 1996), and FeO_5 (Burger and Klüfers, 1996).

The 'hard' behavior of the Fe(III) and Na(I) cations is evident from the nature of the ligands most commonly found in the complexes and, in particular, from the nature of the bonding. There are examples ranging from mono- to heptadentate coordination. The mean Fe(III)–L bond length in five-coordinated polyhedra (FeO_5) increases in the following order: 1.906 Å (μ-OH)<1.957 Å (ter-OL). For the six-coordinated complexes, the order is as follows: 1.65 Å (NO)<1.93 Å (CN)<1.94 Å (μ-η^2-CN)<1.95 Å (ter-OL)<1.99 Å (μ_3-O, μ-OL)<2.00 Å (OL, bi-OL)<2.01 Å (hexa-OL)<2.15 Å (μ_3-OL). For the pentadenated ligands (N_2O_3), the values are as follows: 2.02 Å (O)<2.04 Å (μ-O)<2.19 Å (N). For the hexadentate ligands (N_2O_4), the values are as follows: 1.99 Å (O)<2.09 Å (μ-O)<2.19 Å (N). In the series of the seven-coordinated complexes, the Fe(III)–L bond length increases in the following order: 2.045 Å (O)<2.30 Å (N) for LNO_3, 2.03 Å (O)<2.10 Å (μ-O)<2.30 Å (N) for LN_2O_4, and 2.09 Å (H_2O).

The effect of both electronic and steric factors of the coordinated atoms can be seen in the opening of the L–Fe(III)–L bond angles of their respective metallocycles. In the five-membered ring, the mean L–Fe(III)–L intraligand angles (six vs. seven coordination) open in the following order: 78.5° vs. 74.9° ($-OC_2N-$)<80.3° vs. 73.7° ($-OC_2O-$)<80.5° vs. 74.1° ($-NC_2N-$). In the six-membered ring (only in the six-coordinated species), the angle opens in the following order: 88.0° ($-OC_3N-$)<88.5° ($-OC_3O-$)<92.9° ($-NC_3N-$). There is one example (Harding et al., 1993) where the Fe(III)··Fe(III) distance is <3.0 Å, namely, 2.934 Å.

The number of the atoms in the inner coordination sphere around Na(I) cation varies. The number ranges from four (NaN_3O [Witzel and Babel, 1984), $NaNO_3$ (Meyer and Pickardt, 1988)] to five [NaN_2O_3 (Longridge et al., 1997), NaO_5 (Sosinsky et al., 1983; Huang et al., 1996; Li et al., 1997)], six [NaO_6 (Ivanov and Kosoy, 1975; Novozhilova et al., 1975; Bailey et al., 1981; Pierpont et al., 1982; Clegg et al., 1984; Lopez-Alcala et al., 1984; Solans et al., 1984; Jameson et al., 1987; Küppers et al., 1987; McMurry et al., 1987; Yamamoto et al., 1988; Minghai et al., 1989; Okamoto et al., 1990; Finnen et al., 1991; Chang et al., 1993; Harding et al., 1993; Decurtins et al., 1994; Zheng et al., 1994; Blake et al., 1995, 1996; Burger and Klüfers, 1996; Yano et al., 1996; Jun et al., 1997; Sanchez et al., 1997; Seibig and van Eldik, 1998)], and even nine [NaN_2CO_6 (Teller et al., 1977)]. There are also examples where there are different surroundings about the Na(I) cations in a same compound: NaC_2O_2+NaO_6 (Chin and Bau, 1976), NaO_4+NaO_5 (Ozarowski et al., 1995), and NaO_5+NaO_6 (Calogero et al., 1997). The mean Na–L bond length for four-coordinated moieties increases in the following order: 2.22 Å (OH_2)<2.35 Å (μ-η^2-OC)<2.36 Å (bi-OL)<2.53 Å (μ-η^2-NC)<2.64 Å (bi-NL)<2.95 Å (μ-OC). In the series of the five-coordinated moieties, the order is as follows: 2.25 Å (NL)<2.27 Å (*tert*-OL)<2.30 Å (OL)<2.32 Å (μ-OH_2)<2.44 Å (μ-η^2-NC); in the six-coordinated species, the order is as follows: 2.38 Å (μ-η^2-OC)<2.42 Å (tetra-OL)<2.45 Å (OL)<2.46 Å (NL)<2.48 Å (μ-OL)<2.51 Å (hexa-OL)<2.52 Å (*tert*-OL)<2.65 Å (bi-OL). The shortest Na···Na distance is 3.047(2) Å (Blake et al., 1996).

Polymeric $(KFe)_n$ compounds

There are 26 example (24 KFe and 2 KFeM′) compounds in this series. Their crystallographic and structural data are summarized in Table 3. There are two compounds in the series where the oxidation state of iron is 0, namely, in the black $K_4Fe_2(dtox)_4(NO)_2(H_2O)_2$ (Lingqian et al., 1990) and in the deep red KFe(μ-η^2-$CO)_2$(η^5-cp) (Hey-Hawkins and von Schnering, 1991) (Figure 5). In the former compound, each Fe(0) atom shows a distorted tetragonal pyramidal coordination ($FeNS_4$). The average Fe–S bond length in the basal plane is 2.27 Å, with the average S–Fe–S angle of 88.7°. The apical position is occupied by the NO molecule. The Fe–N bond length is 1.690(2) Å. No discussion of the surroundings of the K(I) cation is presented in the original paper (Lingqian et al., 1990). In the latter compound, the Fe(O) is surrounded by seven carbon atoms. Five of these belong to cyclopentadienyl anion and two to CO ligands. The K(I) cation is bonded to two CO molecules with the K–O bond lengths of 2.773(2) and 2.915(2) Å. There is a one-dimensional helical chain in the crystal structure. The chains exhibit a simple rod-packing orientation parallel to [010]. The K(I) cations interact with three anions of neighboring helices with two short K–C distances to each cyclopentadienyl anion. Accordingly, a three-dimensional network is formed. There are two Fe···K distances of 3.472(1) and 3.589(1) Å.

In the gold-yellow monoclinic K[Fe(cp)(CO)(μ-η^2-CN)] (Darensbourg et al., 1977), the [Fe(cp)(CO)(μ-η^2-CN)] anion is a typical three-legged piano stool with substantially linear Fe–CN and Fe–CO legs, oriented at angles of approximately 90° to each other. The K(I) cation interacts with six CN anions displaying a distorted octahedral polyhedron (KN_6).

There are five derivatives containing Fe(II) and K(I) cations (Raston et al., 1977; Ray et al., 1996; Hammes et al., 1997; Nieuwenhuyzen et al., 1998). In the yellow K[Fe(tipcma)]dmf (Ray et al., 1996), there is a trigonal monopyramidal coordination about the Fe(II) cation. Three of the sites are occupied by N atoms of the ticpma ligand with the average Fe–N bond length of 2.020(3) Å. The average N–Fe–N angle is 118.7(1)°. The bond length from the Fe(II) cation to the apical nitrogen

Table 3 Crystallographic and structural data of polymeric K – Fe compounds[a].

Compound (color)	Crys.cl Sp.Grp *Z*	a (Å) b (Å) c (Å)	α. (°) β (°) γ (°)	Chromophore	M–L (Å)	L–M–L (°)	References
$[(ON)_2Fe_2(\mu\text{-dtox})_4\cdot K_4(H_2O)_2]$ (black)	m C2/c 4	18·416(6) 15·800(6) 7·843(4)	 111·26(3)	$Fe^{O}S_4N$	LS[b] 2·271(1,16) ON 1·690(2)	S,S[b] 88·7(1,2)[c] 85·7(1,4) 154·5(1,1·1) S,N 102·7(1,3·9)	Lingqian et al., 1990
				$K^{I}O_x$	O not given	O,O not given	
$[Fe(\mu\text{-}CO)_2(\mu\text{-}\eta^2\text{-}CO)_2\cdot K_2]$ (light gold)	or Fddd 8	23·072(6) 11·557(2) 5·543(1)		$Fe^{0}C_4$	μOC 1·746(4,0)	C,C 104·0(2,3·1) 121·8(2)	Teller et al., 1977
				$K^{I}O_4C_4$	μCO 2·793(4,84) μOC 3·280(3,0)	O,O 89·2(1,9) 178·0(1)	
$[(\eta^5\text{-cp*})Fe(\mu\text{-}\eta^2\text{-}CO)_2K]$ (deep red)	m $P2_1/a$ 4	10·953(4) 10·159(3) 7·347(2)	 107·89(2)	$Fe^{0}C_7$	cp*C 2·105(3,19) μOC 1·712(3,6)	C,C 39·2(1,4)[d] 65·7(1,4)[e] 92·0–158·2(1)	Hey-Hawkins and von Schnering, 1991
				$K^{I}O_2C_4$	μOC 2·793(2) 2·915(2) μOC 3·282(4,10) cp*μC 3·183(3,11)	Not given	
$[(\eta^5\text{cp})(OC)Fe\cdot(\mu\text{-}\eta^2\text{-}CN)_2K]$ (gold brown)	m $P2_1/c$ 4	13·442(3) 7·852(2) 8·731(2)	 99·60(5)	$Fe^{I}C_8$	cpC 2·11 OC 1·73(2) μNC 1·906(9,7)	C,C 93·1(4,3·0)	Darensbourg et al., 1977
				$K^{I}N_6$	μCN 3·0	N,N not given	
[Fe(μ-tipcma)K(dmf)] (yellow) (at 173 K)	tr P1 2	8·6150(7) 10·3589(8) 14·289(1)	69·800(1) 83·897(1) 84·599(1)	$Fe^{II}N_4$	LN 2·020(3,6) 2·098(3)	N,N 83·4(1)[c] 118·7(1,2·7)	Ray et al., 1996
				$K^{I}O_x$	O not given	O,O not given	
$[(OC)Fe(\mu\text{-tipcma})\cdot K(dmf)(H_2O)]$ (d $K^{I}O_x$ deep blue)	tr_ P1 2	9·4318(1) 10·904(3) 12·840(3)	82·938(1) 87·196(1) 83·674(1)	$Fe^{II}N_4$	LN1·997(3,6) OC 1·749(2))	N,N117·9(1,2·1)[c]	Ray et al., 1996
				$K^{I}O_x$	O not given	O,O not given	
[(ON)Fe(μ-tipcma)·K(dmf)(H_2O)] (not given) (at 173K)	m $P2_1$ 2	11·4342(6) 35·790(2) 16·759(1)	 101·39(2)	$Fe^{II}N_5$	ON 1·745(5) LN 2·020(3,0)	N,N 79·5(1)[c] 116·3(1)	Hammes et al., 1997
				$Fe^{II}N_5$	ON 1·745(5) LN 2·039(3,0)	N,N 77·8(1)[c] 115·7(1)	
				$Fe^{II}N_5$	ON 1·737(5) LN 2·040(3,0)	N,N 77·3(1)[c] 115·3(1)	
				$Fe^{II}N_5$	ON 1·737(1) LN 2·048(3,0)	N,N 77·8(1)[c] 115·6(1)	
				$K^{I}O_x$	O not given	O,O not given	
$[Fe(\mu\text{-inma})_3\cdot K(H_2O)_2]$ (deep blue)	m C2/c 8	29·89(1) 9·780(2) 13·980(3)	 106·68(2)	$Fe^{III}O_3N_2$	LO 1·972(2,4) LN 1·882(2,9)	O,O 89·2(1,5) N,N 96·2(1,9) O,N 82·5(1,1)[c] 92·1(1,3) 171·6(1,6)	Raston et al., 1977

Table 3 (Continued)

Compound (color)	Crys.cl Sp.Grp *Z*	a (Å) b (Å) c (Å)	α. (°) β (°) γ (°)	Chromophore	M–L (Å)	L–M–L (°)	References
				$K^{I}O_8$	LO 2·701(2,2) 2·385(2,35) H_2O 2·788(3)	O,O 58·9(1)–154·3(1)	
$[(\eta^2\text{-bpy})Fe(\mu\text{-}\eta^2\text{-}CN)_4\cdot K_2(H_2O)_{2.5}]$[g] (red)	m $P2_1/c$ 8	17·756(1) 26·708(2) 7·615(1)	99·46(1)	$Fe^{II}C_4N_2$	μNC 1·916(5,20) η^2N 1·990(4,4)	C,C not given	Nieuwenhuyzen et al., 1998
				$K^{I}N_6$	μNC 2·873(4)–3·117(4)	N,N not given	
				$K^{I}ON_3$	H_2O 2·833(4,8) 3·188(4,46) μCN 3·030(4,92)	O,O not given	
				$Fe^{II}C_4N_2$	μNC 1·914(5,18) η^2N 1·998(4,5)	C,C not given	
				$K^{I}N_6$	μCN 2·846(4)–3·104(4)	N,N not given	
				$K^{I}ON_3$	μCN 2·765(4)–3·156(4) H_2O 2·727(4,55)	N,N not given	
$[Fe(\mu\text{-}\eta^2\text{-cat})_3\cdot K_3(H_2O)_{1.5}]$ (dark red-brown)	m C2/c 8	20·612(7) 15·873(5) 12·307(4)	91·76(1)	$Fe^{III}O_6$	catμO 2·015(6,20)	O,O 81·2(2,1)[c] 93·4(2,7·8) 167·392,6)	Raymond et al., 1976
				$K^{I}O_4$	catμO 2·628(6) 2·810(6,6) H_2O 2·706(5)	O,O not given	
				$K^{I}O_5$ (x2)	catμO 2·627(6)–3·008(7) H_2O 2·672(8) 3·013(12)	O,O not given	
$(bcdt\text{-}thf)_4\cdot[Fe(\mu\text{-}\eta^2\text{-}ox)_3\cdot K(PhCN)]$ [at 120(2) K]	or Pbcn 4	10·33(2) 19·53(3) 35·94(2)		$Fe^{III}O_6$	oxO 1·998(4,0) 2·018(4,1)	O,O 81·3(2,0)[c] 93·1(2,3·3) 170·3(2)	Kurmoo et al., 1995
				$K^{I}O_6N$	oxO 2·852(6,27) PhCN 2·952	O,O not given	
$[Fe_3(\eta^2\text{-dbm})_3(OMe)_3(\mu\text{-}OMe)_3(\mu_3\text{-}OMe)\cdot K(MeOH)_3]$ MeOH (yellow-red) (at 192 K)	tr_ P1 2	13·044(1) 14·174(1) 18·657(2)	97·94(1) 104·13(1) 114·12(1)	$Fe^{III}O_6$	μ_3MeO 2·144(2,11) μMeO 2·00592,16) MeO 1·886(3,11) dbmO 2·027(3,19)	O,O 84·9(1,2)[h] 76·5–96·7(1) 168·8(1,5·6) Fe,Fe 60·0(1,1)	Caneschi et al., 1995
				$K^{I}O_6$	O 2·607(4)–2·974(2)	O,O 59·2–161·9(1) Fe,Fe 50·76(1,39)	

Table 3 (Continued)

Compound (color)	Crys.cl Sp.Grp *Z*	a (Å) b (Å) c (Å)	α. (°) β (°) γ (°)	Chromophore	M–L (Å)	L–M–L (°)	References
$Fe(\mu_3\text{-}O)(\mu\text{-}ino)_6\cdot K(H_2O)_{11\cdot5}$ (pale yellow)	tr_ P1 2	12·730(3) 13·850(3) 19·742(4)	90·65(3) 93·29(3) 112·34(3)	$Fe^{III}O_5$ $Fe^{III}O_6$	μ_3O 1·924 LμO 2·066 LO 1·929	O,O not given	Hegetschweiler et al., 1995
				K^IO_x	O not given	O,O not given	
$Fe(\mu\text{-}eta)_3K_3\cdot(Me_2CO)_3(EtOH)_2$ (red) (at 180 K)	rh R3c 6	14·529930 52·021(12)		$Fe^{III}O_6$ K^IO_x	etaO 2·03 O not given	O,O 79·1[c] O,O not given	Karpishin et al., 1993
$Fe(\mu\text{-}bct)_3K_3\cdot(dmf)_6(H_2O)$ (red) (at 160 K)	m $P2_1/c$ 4	17·039(6) 16·374(6) 24·138(4)	 102·00(3)	$Fe^{III}O_6$ K^IO_x	bctO 1·99 O not given	O,O 78·7[c] O,O not given	Karpishin et al., 1993
$Fe(\mu\text{-}bctpt)K\cdot(dmf)_4(H_2O)_{0\cdot5}$ (red) (at 176 K)	m $P2_1/n$ 4	12·018(2) 22·187(7) 24·887(6)	 92·96(2)	$Fe^{III}O_6$ K^IO_x	bctptO 2·01 O not given	O,O 79·6[c] O,O not given	Karpishin et al., 1993
$Fe(\mu\text{-}bct)K_3\cdot(MeOH)(H_2O)$ (red) (at 175 K)	c $P2_13$ 4	15·962(3)		$Fe^{III}O_6$ K^IO_x	bctO 1·990(6) 2·028(7) O not given	O,O 79·5(3)[c] O,O not given	Stack et al., 1992
$Fe_2(\mu\text{-}O)(\mu\text{-}\eta^2\text{-}O_2CO)\cdot(\mu\text{-}nta)_2K_4(MeOH)_2\cdot(H_2O)$ (dark green)	m C2/c 4	15·628(2) 12·915(2) 14·533(2)	 102·90(1)	$Fe^{III}O_5N$	μO 1·830(2) μOCO_2 2·005(3) ntaO 2·023(3,3) 2·082(3) ntaN 2·246(4)	O,O 94·3(1,9·5) 159·7(1,5·8) O,N 77·1(1,7)[c] 82·8(1,2·7) 175·4(1)	Fujita et al., 1994
				K^IO_x	O not given	O,O not given	
$[Fe(\mu\text{-}hbcd)\cdot K(MeOH)]CHCl_3$ (red)	m $P2_1/a$ 4	12·589(2) 17·414(2) 12·727(2)	 102·54(1)	$Fe^{III}O_4N_2$	hbcdO 2·042(7,11) hbcdμO 1·887(6,0) hbcdN 2·215(6,3)	O,O 95·4(3,3·3) 101·3(2) 163·0(2) N,N 81·6(2)[c] O,N 83·4(3,6·0)[c] 88·3(2,6) 167·2(3,6)	Larsen et al., 1990
				K^IO_6	hbcdμO 2·344(5,42) MeOH 2·378(7)	O,O 87·3(2,2·1) 102·5(2)	
				K^IO_6	hbcdμO 3·23 MeHO 2·98(2)	O,O not given	
$[Fe_2(\mu\text{-}O)(\mu_3\text{-}ida)_4\cdot K_4(H_2O)_{10}]$ (red)	m $P2_1/c$ 2	11·124(2) 17·165(4) 9·560(2)	 105·89(1)	$Fe^{III}O_4N_2$	μO 1·798(1) idaO 2·046(3,42) idaN 2·236(3,50)	O,O 96·49(1,9·7) 160·4(1) O,N 76·9(1,6)[c] 91·1(1,6·9) 165·3(1,6·0)	Yong-Ge et al., 1997
				K^IO_7	idaO 2·807(3,136) H_2O 2·761(4,119)	O,O not given	

Table 3 (Continued)

Compound (color)	Crys.cl Sp.Grp *Z*	a (Å) b (Å) c (Å)	α. (°) β (°) γ (°)	Chromophore	M–L (Å)	L–M–L (°)	References
				$K^{I}O_{10}$	idaO 3·00(-,23) H_2O 2·817(8,106)	O,O not given	
$[(\eta^4\text{-tpp})Fe(\mu\text{-}\eta^2\text{-}CN)_2 \cdot K(Me_2CO)_2]$ (not given)	m $P2_1/n$ 2	9·604(2) 11·439(2) 20·283(3)	100·78(1)	$Fe^{III}N_4C_2$	tpnN 2·000(2,5) μC 1·97592,0)	N,N 90·07(7,0)[h] C,C 180 N,C 89·50(7,2·7)	Scheidt et al., 1980
				$K^{I}O_3N_2$	Me_2CO 2·722(3,16) μCN 2·748(3,2)	O,N 87·2(1,3)	
$(NC)_2Fe(\mu\text{-acacen}) \cdot K(H_2O)_2$ (deep green)	tg $P3_1$ 6	11·873(3) 23·001(1)		$Fe^{III}O_2N_2C_2$	LO 1·927(7,12) LN 1·918(8,3) NC 1·997(11,14)	O,O 87·4(3,1·4) N,N 85·1(3,3)[c] C,C 178·4(1,5) O,N 95·3(3,8)[h] 178·4(3,9) O,C 95·3(3,2·6) N,C 90·5(3,2·2)	Wang et al., 1992
				$K^{I}O_4$	LO 2·392(6,235) H_2O 3·012(6)	O,O not given	
				$K^{I}O_5$	LO 2·867(6,61) H_2O 2·781(6,107)	O,O not given	
$[Fe(\mu\text{-}3,5\text{-}Cl_2tsa)_2 \cdot K(H_2O)_{1\cdot5}]$[g] (green)	m $P2_1/a$ 4	20·221(8) 27·210(9) 8·916(5)	98·08(8)	$Fe^{III}O_2N_2S_2$	tsaO 1·937(12,5) tsaN 1·995912,16) tsaS 2·344(6,26)	O,O 88·5(4) N,N 173·7(5) S,S 91·4(2) O,N 92·2(5,2·8) O,S 90·5(4,2·3) 172·2(4,2·4) N,S 81·2(2,1)[e] 94·5(4,1·0)	Rjabova et al., 1982
				$Fe^{III}O_2N_2S_2$	tsaO 1·944(11,2) tsaN 2·049(15,6) tsaS 2·416(5,12)	O,O 88·1(4) N,N 174·4(5) S,S 89·8(2) O,N 91·9(5,5·7) O,S 92·8(4,5) 165·6(4,5) N,S 79·2(4,2)[e] 97·1(4,1·8)	
				$K^{I}X_n$	X not given	X,X not given	
$[Fe(\mu\text{-}3,5\text{-}Cl_2tsa)_2 \cdot K(H_2O)_{1\cdot5}]$[g] (green) (at 103 K)	m $P2_1/a$ 4	20·090(7) 26·996(10) 8·695(4)	98·37(9)	$Fe^{III}O_2N_2S_2$	tsaO 1·928(14,24) tsaN 1·882(17,29) tsaS 2·254(7,23)	O,O 86·6(6) N,N 176·1(8) S,S 90·3(2)	Rjabova et al., 1982

Table 3 (Continued)

Compound (color)	Crys.cl Sp.Grp *Z*	a (Å) b (Å) c (Å)	α. (°) β (°) γ (°)	Chromophore	M–L (Å)	L–M–L (°)	References
						O,N 91·3(7,3·3) O,S 91·5(7,3) 170·8(4,1·6) N,S 84·4(6,50[e] 93·2(4,1·8)	
				$Fe^{III}O_2N_2S_2$	tsaO 1·931(13,20) tsan 1·919917,12) tsaS 2·295(6,21)	O,O 87·4(6) N,N 178·3(6) S,S 88·092)	
						O,N 90·6(6,3) O,S 92·8(4,4) 174·1(1,1) N,S 83·6(5,1)[e] 95·2(5,30	
				K^IX_n	X not given	X,X not given	
Fe(μ-edta)K(H_2O)$_2$ (brown)	m $P2_1/n$ 4	11·361(2) 13·396(2) 10·484(1)	106·00(2)	$Fe^{III}O_5N_2$	edtaO 1·77592,8) 2·110(2) edtaμO 2·126(2) edtaN 2·329(2,17) H_2O 2·111(2)	O,O not given	Solans et al., 1984
				K^IO_7	edtaO 2·753(3,4) 2·2·918(3) edtaμO 2·730(7,19) 3·025(3,61)	O,O not given	
(H_2O)Fe(μ-phdta)·k(H_2O)$_2$ (yellow-brown)	m $P2_1/c$ 2	8·638(1) 13·099(1) 8·184(1)	96·43(1)	$Fe^{III}O_5N_2$	phdtaO 1·990(3,0) 2·087(3,0) phdtaN 2·344(3,0) H_2O 2·057(4)	O,O 73·62(8) 94·3(1,6·8) 147·2; 163·5(1) N,N 73·08(15)[c] O,N 73·9(1,2·6)[c] 142·1(1,1·4)	Mizuno et al., 1991
				K^IO_x	O not given	O,O not given	
(NC)Fe(μ-η^2-CN)$_5$·K_3(η^2-hmta)$_2$(H_2O)$_4$ (not given)	tr_ P1 4	14·125(4) 17·808(4) 14·116(4)	114·14(5) 94·91(4) 108·36(5)	$Fe^{III}C_6$ $K^IN_9O_4$ $K^IN_8O_4$	NC 1·940(5,24) μNC 1·943(5,19) μNC 2·869(5,115) LN 2·939(5,53) H_2O 2·04–3·23	C,C not given not given	Meyer and Pickardt, 1988
[Fe(μ-η^2-CN)$_6$$KCs_2$] (red-brown) [at 295(2) K]	m $P2_1/n$ 2	11·145(4) 8·131(4) 7·664(2)	90·16(3)	$Fe^{III}C_6$ K^IN_6 Cs^IN_6	μNC 1·913(4,0) 1·936(2,1) μNC 2·790(3,7) μCN 3·197(2,12)	C,C 90·1(1,1) N,N not given N,N not given	Figgis et al., 1990

Table 3 (Continued)

Compound (color)	Crys.cl Sp.Grp *Z*	a (Å) b (Å) c (Å)	α. (°) β (°) γ (°)	Chromophore	M–L (Å)	L–M–L (°)	References
[at 85(2) K]				$Fe^{III}C_6$	μNC 1·930(3,3)	C,C 90·2(1,0)	Figgis et al., 1990
				$K^{I}N_6$	μCN 2·767(4,10)	N,N not given	
				$Cs^{I}N_6$	μCN 3·255(4,60)	N,N not given	
(at 4K) by neutron diffr·				$Fe^{III}C_6$	μNC 1·931(2,3)	C,C 90·0(1,2)	Figgis et al., 1987
				$K^{I}N_6$	μCN 2·812(3,10)	N,N not given	
				$Cs^{I}N_6$	μCN 3·326(3,37)	N,N not given	
$[In\{Fe_2(\mu\text{-}\eta^2\text{-}CO)_8\}_2 \cdot K(thf)]$ (dark red)	tg P4/m 2	11·850(2) 10·696(2)		$Fe^{0}C_4In$	μOC 1·783(9,34) In 2·627(1) Fe‘ 2·900(2)	C,C 95·5(4,10·0) 168·5(4) In,Fe‘ 56·5(1)	
				$K^{I}O_9$	μCO 2·767(6,0) 2·949(8,0)	O,O 68·1– 159·6(2)	
				$InFe_4$	Fe 2·627(1)	Fe,Fe 67·0(1) 134·1(1)	

[a]Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis is the e.s.d., and the second is the maximum deviation from the mean.
[b]The chemical identity of the coordinated atom or ligand is specified in these columns.
[c]The five-membered metallocyclic ring.
[d]The three-membered metallocyclic ring.
[e]The four-membered metallocyclic ring.
[f]There are four crystallographically independent molecules.
[g]There are two crystallographically independent molecules.
[h]The six-membered metallocyclic ring.

is 2.098(3) Å. No information of the surroundings of the K(I) is given in the original paper (Ray et al., 1996). In the blue triclinic K[Fe(CO)(tipcma)]dmf·H_2O (Ray et al., 1996), the Fe(II) cation shows five coordination ($FeCN_4$). The mean Fe–N bond length is 1.997(3) Å, and the mean N–Fe–N angle is 117.9(1)°. The Fe–C bond length is 1.749(3) Å.

In the unit cell of monoclinic K[Fe(NO)(tmbcma)]dmf·Et_2O (Hammes et al., 1997), there are four crystallographically independent molecules. Each Fe(II) cation shows trigonal bipyramidal coordination. The basal coordination plane includes three amidate nitrogen atoms, whereas the axial sites are occupied by amine nitrogen atom and a nitro group. The K(I) cations are not dealt with in the study of Hammes et al. (1997).

The structure of the deep blue monoclinic K[Fe(inma)$_3$]·$2H_2O$ (Raston et al., 1977) comprises infinite zigzag chains of K(I) cations and [Fe(inma)$_3$]$^-$ anions, running parallel to the crystallographic *c* axis. The inma ligands are coordinated to the iron atoms *via* one oxygen atom of the amide groups and one nitrogen atom of the nitroso group forming a *fac* coordination mode. The coordination sphere around a K(I) cation consists of eight oxygen atoms. Two of them belong to water molecules. The rest of the oxygen atoms come from nitroso oxygen atoms of two adjacent ligands. The mean Fe–O and Fe–N bond lengths are 1.972(2) and 1.882(2) Å, respectively. Whereas two K(I) cations about an iron atom are almost linearly disposed [K···Fe···K, 178.2(1)°], the disposition of the atoms about each potassium cation is angular [Fe···K···Fe, 136.2(3)°]. The shortest Fe···K distance is 3.488(1) Å.

The monoclinic red K_2[Fe(bpy)$(CN)_4$]·$2.5H_2O$ (Nieuwenhuyzen et al., 1998) contains two crystallographically independent molecules. There is an extensive three-dimensional hydrogen bonding network in the crystal structure. The water molecules and the K(I) cations occupy three different channels created by the [Fe(bpy)$(CN)_4$]$^-$ complex units. Each Fe(III) cation is six coordinated (FeN_6). The K(I) cations are either six coordinated with two different surroundings (KN_6 and KN_4O_2) or seven coordinated (KN_3O_4).

All the remaining compounds with $(FeK)_n$ moieties (Raymond et al., 1976; Scheidt et al., 1980; Rjabova et al., 1982; Solans et al., 1984; Larsen et al., 1990; Mizuno et al., 1991; Stack et al., 1992; Wang et al., 1992; Karpishin et al., 1993; Fujita et al., 1994; Caneschi et al., 1995; Hegetschweiler et al., 1995; Kurmoo et al., 1995; Yong-Ge et al., 1997) contain an Fe(III) cation and a K(I) cation.

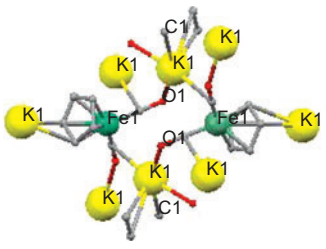


Figure 5 View of the (cp)Fe(CO_2)K (Hey-Hawkins and von Schnering, 1991).

In the red K_3[Fe(cat)$_3$]·$4.5H_2O$ (Raymond et al., 1976), three catecholate anions result in an octahedral coordination sphere around the central Fe(III) cation, displaying approximate D_3 site symmetry. The mean Fe–O bond length is 2.015(6) Å. One of the K(I) cations is surrounded by four oxygen atoms, whereas the other two have five oxygen atoms around. In the former case, there are three oxygen atoms of catecholate anions and one water molecule involved, and in the latter case, the cat anions are involved by four oxygen atoms. The fifth site is occupied by an oxygen atom of a water molecule.

In the orthorhombic [bcdt-ttf]$_4$[KFe(ox)$_3$]·PhCN (Kurmoo et al., 1995), the anion layers display a clear honeycomb network with alternate Fe(III) and K(I) cations forming an approximate hexagonal structure. The Fe(III) cations are octahedrally coordinated by three bidentate oxalate anions. The mean Fe–O bond length is 2.011 Å. The noncoordinated oxygen atoms of the oxalate anions form cavities occupied by K(I) cations. The K(I) cations are surrounded by six oxygen atoms and by one nitrogen atom of a PhCN molecule. The K···N distance is 2.952 Å, and the mean K···O distance is 2.852(6) Å.

The structure of K[Fe_3(dbm)$_3$(OMe)$_7$]·3MeOH (Caneschi et al., 1995) is shown in Figure 6. The structure consists of Fe(III) atoms connected by a triply bridging methoxide anion and three μ-methoxide ligands. The oxygen donor atoms of a monodentate methoxide and chelating dbm complete the coordination sphere of each metal cation (FeO_6, KO_6). The mean Fe–O bond length increases in the following order: 1.886(3) Å (OMe)<2.005(2) Å (μ-OMe)<2.027 Å (O,dbm)<2.144(2) Å (μ_3-OMe). The Fe···Fe distance of 3.242(1) Å excludes direct bond. The mean Fe–μ_3–O–Fe angle of 98.2° is narrower than that of the Fe–O–Fe angle of 108.3°. The mean Fe···K separation is 3.802 Å.

In the pale yellow triclinic K_3[Fe_6(O)(ino)$_6$]·$14.5H_2O$ (Hegetschweiler et al., 1995), the Fe(III) cations display five (FeO_5) and six coordination (FeO_6). In the former coordination sphere, the mean Fe–O bond length is 1.97 Å, and in the latter one, 2.02 Å. The mean Fe–O bond length increases in the following order: 1.924 Å (μ_3-O)<1.929 Å (O_t, ino)<2.066 Å (O_{br}, ino). The surroundings of K(I) cations were not considered in the study of Stack et al. (1992).

There are three red compounds, K_3[Fe(bct)]·6dmf·H_2O, K[Fe(bctpt)]·4dmf·$0.5H_2O$, and K_3[Fe(eta)$_3$]·3MeCO·2EtOH, displaying hexacoordinated Fe(III) cations (FeO_6) (Karpishin et al., 1993). The crystals of the first two belong to the monoclinic and the third one to the orthorhombic crystal classes. In the first two compounds, the coordination polyhedra are distorted trigonal prisms with the mean Fe–O bond lengths of 1.94 and 2.01 Å, respectively. The respective O–Fe–O bond angles are 78.7° and 79.6° in the FeO_6 polyhedra formed by hexadentate ligands. A similar coordination is found also in the orthorhombic compound, although now, the polyhedron is formed by three chelating eta ligands. The mean Fe–O bond length is 2.03 Å, and the mean O–Fe–O angle is 79.1°. In the red cubic K_3[Febct]·MeOH·H_2O (Stack et al., 1992), each Fe(III) cation displays a similar coordination than in the monoclinic K_3[Febct]·6dmf·H_2O (Karpishin et al., 1993) with

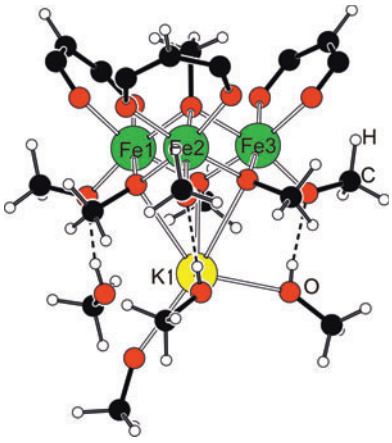


Figure 6 View of the $Fe(dbm)_3(OMe)_7K(MeOH)_3$ (Caneschi et al., 1995). The phenyl rings of the dbm ligands have been omitted.

the mean Fe–O bond length of 1.99 Å and an O–Fe–O angle of 79.5°. Unfortunately, no discussion is given about the surroundings of the K(I) cations (Stack et al., 1992; Karpishin et al., 1993).

In the dark green monoclinic KFe derivative (Fujita et al., 1994), two [Fe(η^4-nta)] complex units are bridged by μ-O and μ-η^2-O_2CO fragments in a syn-syn arrangement. Each Fe(III) atom is hexacoordinated ($FeNO_5$). The long Fe···Fe distance of 3.188(1) Å rules out a direct bond. The Fe–O–Fe bridge angle is 121.1(2)°. The nta ligand with NO_3 donors creates about each Fe(III) cation three five-membered metallocyclic rings with the mean O–Fe–N intraligand angle of 77.1(1)°. The potassium cations were not mentioned.

Structural analysis of the red monoclinic K[Fe(hbed)]·MeOH·$CHCl_3$ (Larsen et al., 1990) revealed a pseudo-octahedral environment about the Fe(III) cation (FeN_2O_4) with hbed acting as the hexadentate ligand. The mean Fe–L bond length increases in the following order: 1.887(6) Å (μ-OL)<2.042(7) Å (OL)<2.215(6) Å (NL). Also, the K(I) cations display octahedral coordination (KO_6). The K(1) cation located at the inversion center [½,0,0] is coordinated by four carboxylate oxygen atoms of the hbed ligands (the average Fe–O=2.344 Å) and oxygen atoms coordinated to iron (Fe–O=2.378 Å). The K(2) cation situated at [0,0,0] is coordinated by phenolate (Fe–O=3.23 Å) and methanol oxygen atoms (Fe–O=2.83 Å).

In a red monoclinic derivative (Yong-Ge et al., 1997), two equivalent [Fe$(ida)_2$] units are linked by a μ-oxo bridge at a center of symmetry forming a stick-like core (Fe_2O). The Fe atoms display distorted octahedral environment. One tridentate and one 'bidentate-like' (N,O) ida ligands complete the coordination sphere FeN_2O_4. The mean Fe–L bond length increases in the following order: 1.798(1) Å (μ-O)<2.046(3) Å (OL)<2.236(2) Å (NL). The ida ligand creates a five-membered metallocyclic ring around each Fe(III) cation [mean O–Fe–N=76.9(1)°]. The Fe···Fe separation of 3.596(1) Å rules out a direct bond. The K(I) cations are grouped into two sets. In the first set, the K(1) cation lies within the distance of 3.2 Å of seven oxygen atoms. Three of them belong to crystal water molecules (mean Fe–O=2.761 Å), and the remaining four are carboxylate group oxygen atoms from two ida ligands (mean Fe–O=2.807 Å). In the other set, the K(2) cation is surrounded by 10 oxygen atoms. Seven of them belong to crystal water molecules (mean Fe–O=2.817 Å), and the remaining three are oxygen atoms of carboxylate groups of three ida ligands (mean Fe–O=3.00 Å).

In the monoclinic K[Fe(tpp)(μ-η^2-$CN)_2$]·$2Me_2CO$ (Scheidt et al., 1980), each Fe(III) cation displays a compressed tetragonal bipyramidal coordination (Figure 7). The tetragonal FeN_4 plane is created by the tetradentate tpp ligand with the mean Fe–N bond length of 2.000(2) Å. The apical positions are occupied by cyanide groups with the mean Fe–C bond length of 1.975(2) Å. The CN anions act as bridges between the iron and potassium atoms forming thus a polymeric structure. Each K(I) cation is four coordinated (KN_2O_2) with the mean K–L bond lengths of 2.722(3) Å (Fe–$OCMe_2$) and 2.748 (3) Å (μ-NC) with oxygen and nitrogen, respectively.

The deep green tetragonal K[Fe(acacen)$(CN)_2$]·$2H_2O$ (Wang et al., 1992) has two anions in the asymmetric unit surrounding the Fe(III) cation, forming distorted octahedral environment around it. The nonplanar tetradentate acacen ligand is in the equatorial position, whereas the axial positions are occupied by cyanide anions ($FeC_2N_2O_2$). The acacen ligand displays a 'stepped' or a 'chair-like' conformation with one of the six-membered chelate rings pointing up and the opposite one pointing down. The mean Fe–L bond lengths increase in the following order: 1.918(7) Å (L=N)<1.927(7) Å (O)<1.997(11) Å (CN). The mean values of the intraligand N–Fe–N bond angle are 85.1(3)° (–NC_2N–) and that of the O–Fe–N angle are 95.3(3)° (–OC_3N–). The anions are packed in spiraling columns along the *c* axis of the unit cell. The tunnels at the centers of these columns contain the K(I) cations and water molecules. The ionic and hydrogen bonding networks between the anions, the K(I) cations, and the solvent molecules dominate the packing. The K(1) cation is bound to O(2) of the anion 1, O(3) and O(4) of the anion 2 (mean K–O=2.93 Å), as well as to O(1) of water molecule [K–O=3.012(6) Å]. The K(2) cation is five coordinated (FeO_5) by the oxygen atoms O(3) and O(4) of the anion 2 (K–O=2.867 Å) and by the oxygen atoms of water molecules (K–O=2.780).

The crystal structure of the green monoclinic K[Fe(3,5-Cl_2tsa)$_2$]·$1.5H_2O$ (Rjabova et al., 1982) contains two crystallographically independent molecules. Crystallographic data are available at ambient temperature and at 103 K. The Fe(III) cations are six coordinated ($FeN_2O_2S_2$). Two terdentate (O,N,S) 3,5-Cl_2tsa ligands creates a pseudo-octahedral coordination sphere about each iron atom. The unit cell dimensions as well as the Fe–L bond lengths are somewhat reduced with the decreasing temperature. The sum of all six bond lengths in the chromophore 1 and the chromophore 2 (at 298 vs. 103 K) are as follows: 12.55 and 12.82 Å vs. 12.13 and 12.29 Å. The K(I) cations are not mentioned in the study of Figgis et al. (1990).

Structure of the brown monoclinic K[Fe(edta)]·H_2O (Solans et al., 1984) is similar to that of the sodium analog (Solans et al., 1984). In the yellow-brown monoclinic K[Fe(phdta)]·$3H_2O$ (Mizuno et al., 1991), a distorted

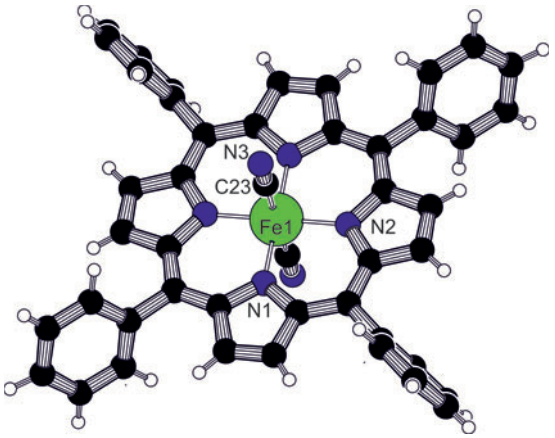


Figure 7 View of the (tpp)Fe$(CN)_2$K$(Me_2CO)_2$ (Scheidt et al., 1980). The K$(MeCO)_2$, which is bound through N3 atom of CN groups, is omitted.

pentagonal bipyramidal arrangement about each Fe(III) cation is formed by a hexadentate phdta ligand and one water molecule (FeN_2O_5). The complex unit has a twofold rotation axis passing through the central Fe(III) cation and coordinated oxygen atom of the water molecule. Two carboxylate oxygen atoms of the phdta ligand occupy the apical positions. The mean Fe–L bond lengths increase in the following order: 1.990(3) Å (O_{ap})<2.072(4) Å (O_{eq})<2.344(3) Å (N_{eq}). Once again, discussion of the stereochemistry about K(I) was neglected (Mizuno et al., 1991).

There are two compounds that apart from Fe and K contain also another metal atom, namely, Cs (Figgis et al., 1987, 1990) and In (Chu-Chieh et al., 1993). The structure of red-brown monoclinic $KCs_2[Fe(\mu\text{-}\eta^2\text{-}CN)_6]$ was studied by X-ray diffraction at 295(2) and 85(2) K (Figgis et al., 1990) and at 4 K by neutron diffraction techniques (Figgis et al., 1987). All metal atoms are six coordinated (FeC_6, KN_6, CsN_6).

In the dark red tetragonal In derivative (Chu-Chieh et al., 1993), two $[Fe_2(CO)_8]$ units are bound to indium atom in a pseudo-tetrahedral fashion [Fe-In=2.627(1) Å]. The K(I) cation is coordinated to one molecule of thf and totally eight carbonyl oxygen atoms to sum up to the total coordination number of 9 (KO_9). The coordination polyhedron can be described as capped square antiprism. The K–O distances for the two sets of symmetry-related carbonyl oxygen atoms are 2.767(6) and 2.949(8) Å, whereas the distance from the K(I) cation to the capping thf oxygen is 2.739(15) Å.

Inspection of the data given in Table 3 reveals that there are 27 (25 FeK and two FeKM) polymeric compounds. They belong to six crystal classes: monoclinic (x18)>triclinic (x4)>tetragonal (x2)>orthorhombic, rhombohedral, and cubic (each x1). The compounds have the following colors: red (x9)>red-brown(x5)>green, blue-yellow (each x3)>black (x2). The iron atom exists in the oxidation state 0, +2, and +3, of which +3 prevails by far. The inner coordination sphere about the iron atoms is built by a wide variety of ligands, ranging from mono- to hexadentate moieties. The Fe(0) are involved in the coordination polyhedra of the type $FeNS_4$ (Lingqian et al., 1990), FeC_4In (Chu-Chieh et al., 1993), and FeC_7 (Hey-Hawkins and von Schnering, 1991). The respective chromophores in the case of Fe(II) are FeC_8 (Darensbourg et al., 1977), FeN_4 (Ray et al., 1996), $FeCN_4$ (Ray et al., 1996), FeN_5 (Hammes et al., 1997), FeN_2O_3 (Raston et al., 1977), and FeC_4N_2 (Nieuwenhuyzen et al., 1998). The chromophores containing an Fe(III) cation are as follows: FeO_6 (Raymond et al., 1976; Stack et al., 1992; Karpishin et al., 1993; Caneschi et al., 1995; Kurmoo et al., 1995), $FeNO_5$ (Fujita et al., 1994), FeN_2O_4 (Larsen et al., 1990; Yong-Ge et al., 1997), FeC_2N_4 (Scheidt et al., 1980), $FeN_2O_2S_2$ (Wang et al., 1992), FeN_2O_5 (Rjabova et al., 1982), and FeC_4 (Figgis et al., 1987). There is one compound that contains two different coordination polyhedra in the unit cell, namely, FeO_5 and FeO_6 (Hegetschweiler et al., 1995).

In the compounds containing Fe(0) atoms, the mean Fe–L bond length increases in the following order: 1.69 Å (NO)<1.75 Å (μ-η²-CO)<2.11 Å (penta-C, cp)<2.27 Å (bi-SL)<2.627 Å (In). The order of the intraligand angles is as follows: 39.2° (–CC–)<65.7° (–CCC–)<88.7° (–SCS–).

In the case of the Fe(II) atoms, the Fe–L bond length order is as follows: 1.73 Å (CO)<1.74 Å (NO)<1.91 Å (μ-CN)≈1.915 Å (μ-η²-CN)<1.995 Å (bi-NL)<2.03 Å (tetra-NL)<2.11 Å (penta-C, cp). The order for the intraligand angles is as follows: 80.7° (–NC_2N–)<82.5° (–OC_2N–).

The mean Fe(III)_L bond lengths for six-coordinated moieties increase in the following order: 1.836 Å (μ-O)<1.93 Å (tetra-OL)<1.95 Å (μ-η²-CN)<1.96 Å (hexa-OL)<1.995 Å (μ_3-OMe)<2.00 Å (CN)=2.00 Å (tetra-NL)<2.005 Å (μ-OMe)<2.15 Å (μ_3-OMe)<2.18 Å (bi-OL) for the homoligands; and 1.918 Å (N)+1.927 Å (O) (tetra-N_2+O_2L)<1.935 Å (O)+1.96 Å (N)+2.33 Å (S) (ter-O+N+SL)<2.043 Å (O)+2.246 Å (N) (tetra-O_3+NL)<2.046 Å (O)+2.236 Å (N) (ter-O_2+NL). The mean intraligand L–Fe–L bond angles open in the following order: 77.0° (–OC_2N–)<80.0° (–OC_2O–)<82.1° (–NC_2S–)<83.4° (–NC_2N–)<84.9° (–OC_3O–)<90.0° (–NC_3N–)<95.3° (–OC_3N–). The mean Fe(III)–L bond lengths and intraligand L–Fe–L bond angles of hetero-Hexa-O_4N_2 ligands reflect the difference between six- and seven-coordinated species: 2.042 Å (O), 2.215 Å (N), 81.6° (–NC_2N–), 83.4° (–OC_2N–) vs. 2.037 Å, 2.344 Å, 73.1°, 73.9°, respectively.

There is a wide range of different chromophores including a K atom: KO_4 (Raymond et al., 1976; Wang et al., 1992), KN_2O_2 (Scheidt et al., 1980), KO_5 (Raymond et al., 1976; Wang et al., 1992), KO_6 (Larsen et al., 1990; Caneschi et al., 1995), KN_6 (Darensbourg et al., 1977; Figgis et al., 1987, 1990; Nieuwenhuyzen et al., 1998), KN_2O_2 (Nieuwenhuyzen et al., 1998), KO_7 (Yong-Ge et al., 1997; Rjabova et al., 1982), KNO_6 (Kurmoo et al., 1995), KO_8 (Raston et al., 1977), KO_9 (Greene and Bryan, 1970), and KO_{10} (Yong-Ge et al., 1997). However, it must be noted that in several papers (Rjabova et al., 1982; Lingqian et al., 1990; Mizuno et al., 1991; Stack et al., 1992; Karpishin et al., 1993; Fujita et al., 1994; Hegetschweiler et al., 1995; Ray et al., 1996; Hammes et al., 1997), the K atoms are not discussed at all. The mean K–L bond lengths increase in the following order: 2.76 Å (μ-OL)<2.785 Å (OL)<2.79

Å (hexa-OL)<2.81 Å (bi-OL)<2.82 Å (ter-OL)<2.95 Å (NL)<2.97 Å (μ-η^2-NC)<3.10 (μ-O).

Polymeric $(FeRb)_n$ and $(FeCs)_n$ compounds

There are three $(FeRb)_n$, eight $(FeCs)_n$, and one($FeCsGe)_n$ units reported. Their crystallographic and structural data are gathered in Table 4. In the colorless orthorhombic $Fe(\mu\text{-}F)_5Rb_2$ (Herdtweck et al., 1987, 1990), each Fe(III) atom is six coordinated (FeF_6) with the mean Fe–F bond length of 1.943(3) Å. The Rb(I) cations are 10 coordinated (RbF_{10}) with the mean Rb–F bond length of 2.966(3) Å.

In the yellow hexagonal $(NMe_4)_2[RbFe(\mu\text{-}\eta^2\text{-}CN)_6]$ (Schwarten et al., 1997), each Fe(III) cation is six coordinated (FeC_6) with the Fe–C bond length of 1.946(6) Å. Each Rb(I) cation is also six coordinated (RbN_6) with the Rb–N bond length of 3.196(8) Å.

The structure of the amber-colored monoclinic $[RbFe(edta)]\cdot 2H_2O$ (Lind et al., 1964) is similar to that of the Li analog (Lind et al., 1964). Each Fe(III) cation shows pentagonal bipyramidal coordination polyhedron (FeN_2O_5), whereas the Rb(I) cation is six coordinated (RbO_6) with the mean Rb–O bond length of 3.05 Å.

In the dark red triclinic $Cs_2[Fe(CO)_2(B_9C_2H_{11})]\cdot H_2O\cdot Me_2CO$ (Greene and Bryan, 1970), two complex anions are doubly bridged by CO molecules with the short Fe–Fe distance of 2.591(5) Å. The mean Fe–C–Fe angle is 83.9(5)°. There is a cisoid, almost totally eclipsed conformation with a close approach to C_2 symmetry. Each Fe atom is eight coordinated (FeB_3C_5). The mean Fe–L bond length increases in the following order: 1.692 Å (CO)<1.941 Å (μ-CO)<2.122 Å (CL)<2.179 Å (BL). The surroundings of the Cs(I) cations were not discussed in the study of Fleischer and Hoppe (1982).

In the deep blue monoclinic $Cs[Fe(inma)_3]\cdot 2H_2O$ (Raston et al., 1977), three heterobidentate inma ligands create a pseudo-octahedral coordination around the Fe(II) cation (FeN_3O_3). The Cs(I) cations are six (CsO_6) and nine coordinated (CsO_9).

Crystals of $Cs[Fe(ens)_3]\cdot H_2O$ (Gourezh et al., 1979) are monoclinic. There are two crystallographically independent units in the unit cell. Each ens ligand is bound to an Fe(II) cation *via* the N atom of the nitroso group and the O atom of the oxime group forming a five-membered ring. The complex unit displays facial coordination polyhedron (FeN_3O_3). The Fe–L bond lengths in the complex units 1 and 2 are 1.926 and 1.918 Å (Fe–O) and 1.857 and 1.874 Å (Fe–N), respectively. The Cs(I) cations, the water molecules, and the Fe(II) cations with their immediate surroundings are roughly related by a pseudo-translation of *a*/2 along the *a* axis.

The compound $CsFeF_4$ exists in three isomeric forms, one orthorhombic (Tressaud et al., 1970) and two tetragonal (Babel et al., 1974; Fleischer and Hoppe, 1982). The fluorine atoms serve as a bridge between the metal atoms and form polymeric chain. Each iron(III) atom is six coordinated (FeF_6), and cesium(I) atom is octa coordinated (CsF_8). In the cubic $(NMe_4)_2[CsFe(CN)_6]$ (Babel, 1982), the CN anions serve as bridges between Fe(III) and Cs(I) cations (Figure 8). The $[Fe(CN)_6]^{3-}$ octahedral are rotated by 7.4° around the *z* axis. The Fe–C bond lengths are mutually equal, 1.984(6) Å.

The structure of the orthorhombic $[CsFe(tsa)_2]$ (Rjabova et al., 1981) has been determined at two temperatures, namely, at 298 and 103 K. Each Fe(III) cation is coordinated by two heteroterdentate (O,N,S) tsa ligands ($FeN_2O_2S_2$). The mean Fe–L bond lengths increase in the following order (at 298 vs. 103 K): 1.961 Å (L=O)<2.125 Å (L=N)<2.443 Å (L=S) vs. 1.964<2.149>2.441 Å, respectively. Each Cs(I) cation is connected with N, O, and C atoms of the tsa ligands forming a polymeric structure. The Cs–L distances range from 3.06 to 3.82 Å.

In the tetragonal $Cs_2Fe(\mu\text{-}S)_{10}Ge_4\cdot 0.42(H_2O)$ (Bowes et al., 1996), the sulfur atoms act as bridges between the metal atoms forming a polymeric chain. Each Fe(III) cation is tetrahedrally coordinated with the Fe–S bond length of 2.325 Å. The stereochemistry concerning the Cs(I) and Ge(IV) cations was not dealt with (Bowes et al., 1996).

Conclusions

There are almost 100 polymeric FeM (M=Li, Na, K, Rb, or Cs) coordination compounds reviewed in this paper. The number of M examples increases in the following order: 3x (M=Rb)<10x (Cs)<11x (Li)<26x (K)<42x (Na). The most common colors in the compounds are yellow or red; there are also examples of brown, green, orange, blue, white, and even black moieties. The compounds belong to several crystal classes. Of them, monoclinic and triclinic are the most common ones with further examples belonging to the other crystal classes.

The iron atoms are found in the oxidation states 0, +2, and +3; the oxidation state +3 clearly prevails. The following inner coordination spheres are found:

Fe(0): C_4 (Chin and Bau, 1976; Teller et al., 1977; Pierpont et al., 1982; Sosinsky et al., 1983; Deng and Shore, 1992; Chu-Chieh et al., 1993), NS_4 (Lingqian et al., 1990), C_7 (Hey-Hawkins and von Schnering, 1991), C_8 (Minghai et al., 1989), B_3C_5 (Greene and Bryan, 1970), and C_{10} (Plenio et al., 1993).

Fe(II): N_3 (Höhn et al., 1991), N_4 (Ray et al., 1996), S_4 (Bowes et al., 1996), CN_4 (Ray et al., 1996), N_5 (Hammes et al., 1997), S_6 (Küppers et al., 1987), N_3O_3 (Raston et al., 1977; Gourezh et al., 1979), C_4N_2 (Nieuwenhuyzen et al., 1998), and C_8 (Darensbourg et al., 1977).

Fe(III): O_5 (Hegetschweiler et al., 1995; Burger and Klüfers, 1996), C_6 (Babel, 1982; Pickardt et al., 1984; Witzel and Babel, 1984; Figgis et al., 1987, 1990; Meyer and Pickardt, 1988; Witzel et al., 1988), O_6 (Ivanov and Kosoy, 1975; Raymond et al., 1976; McMurry et al., 1987; Stack et al., 1992; Declerq et al., 1993, 1995; Karpishin et al., 1993; Decurtins et al., 1994; Blake et al., 1995, 1996; Caneschi et al., 1995; Hegetschweiler et al., 1995; Kurmoo et al., 1995; Burger and Klüfers, 1996; He and Hartwig, 1996; Huang et al., 1996; Calogero et al., 1997; Henneicke and Wartchow, 1997; Li et al., 1997), NO_5 (Jameson et al., 1987; Harding et al., 1993; Fujita et al., 1994; Yano et al., 1996; Longridge et al., 1997), C_5N (Longridge et al., 1997), C_2N_4 (Scheidt et al., 1980), N_2O_4 (Bailey et al., 1981; Yamamoto et al., 1988; Larsen et al., 1990; Okamoto et al., 1990; Ozarowski et al.,

Table 4 Crystallographic and structural data for polymeric Rb–Fe and Cs–Fe compounds[a].

Compound (color)	Crys.cl Sp.Grp *Z*	a (Å) b (Å) c (Å)	α (°) β (°) γ (°)	Chromophore	M–L (Å)	L–M–L (°)	References
$Fe(\mu\text{-}F)_5Rb_2$ (colorless)	or Pnma 4	7·565(1) 5·810(1) 12·001(1)		$Fe^{III}F_6$ $Rb^{I}F_{10}$	μF[b] 1·892(3,27) 2·04492,0) μF 2·914(2,85) 3·089(2,83)	F,F[b] 90·0(1,4·2) 175·5(1,4·7) F,F not given	Herdtweck et al., 1987, 1990
$(NMe_4)_2[Fe(\mu\text{-}\eta^2\text{-}CN)_6Rb]$ (yellow)	hx_ R3m 3	8·867(4) 21·499(10)		$Fe^{III}C_6$ $Rb^{I}N_6$	μNC 1·946(6,0) μCN 3·196(8,0)	C,C 90·6(2) N,N 90·3(2)	Schwarten et al., 1997
$[(H_2O)Fe(\mu\text{-edta})\cdot Rb(H_2O)]$ (amber)	m $P2_1/a$ 4	14·17(2) 7·73(1) 14·63(2)	90·4(1)	$Fe^{III}O_5N_2$ $Rb^{I}O_6$ $Fe^{O}C_5B_2$	edtaO 1·993(11,19) 2·078(12,9) edtaN 2·317(12,5) H_2O 2·106(11) edtaO 2·99(1,10) H_2O 3·18(1,3) OC 1·692(15)	O,O 72·8(3,7) 91·7(1,4·3) 139·2(1) 162·6(1) N,N 74·8(1)[c] O,N 73·6(1,4·10[c] 88·0(1,1·8) O,O not given C,C 90·4(6,4·7)	Lind et al., 1964
$\{(\eta^5\text{-}1,2\text{-}B_9C_2H_{11})(OC)\cdot Fe(\mu\text{-}\eta^2\text{-}CO)\}_2Cs_2\cdot(H_2O)(Me_2CO)$ (dark red)	tr_ P1 2	11·57(2) 15·19(3) 9·35(2)	88·48(5) 76·54(5) 112·18(5)		μOC 1·941(14,41) η^5C 2·122913,14) η^5B 2·171(16,32)		Greene and Bryan, 1970
$[Fe(\mu\text{-inma})_3\cdot Cs(H_2O)_2]$ (deep blue)	m Aa 4	33·312(6) 24·792(5) 13·323(2)	91·55(1)	$Cs^{I}O_x$ $Fe^{II}O_3N_3$ $Cs^{I}O_6$ $Cs^{I}O_9$	O not given	O,O not given	Raston et al., 1977
$[Fe(\mu\text{-ens})_3\cdot Cs(H_2O)]$[d] (not given)	m $P2_1/c$ 8	14·97(1) 14·07(1) 14·05(1)	94·31(4)	$Fe^{II}O_3N_3$ $Fe^{III}O_3N_3$ $Cs^{I}O_x$	ensO 1·926(12,17) ensN 1·857(11,4) ensO 1·918(11,8) ensN 1·874(11,16) O not given	O,N 80·8(5,1)[c] O,N 80·9(5,6)[c] O,O not given	Gourezh et al., 1979
α-$Fe(\mu\text{-}F)_4Cs$ (not given)	or C2c 4	7·84(2) 12·49(2) 5·96(2)		FeF_6 CsF_8			Tressaud et al., 1970
β-$Fe(\mu\text{-}F)_4Cs$ (not given)	tg I4c2 20	12·491(1) 13·272(10		$Fe^{III}F_6$ $Cs^{I}F_8$	μF 1·84(-,1) 1·959-,5) μF 3·11(-,22)	F,F not given F,F not given	Fleischer and Hoppe, 1982
γ-$Fe(\mu\text{-}F)_4Cs$				$Fe^{III}F_6$ $Cs^{I}F_8$	Not given Not given		Babel et al., 1974
$(NMe_4)_2[Fe(\mu\text{-}\eta^2\text{-}CN)_6Cs]$ (not given)	c Fd3c 32	25·274(6)		$Fe^{III}C_6$ $Cs^{I}N_6$	μNC 1·934(6,0) μCN not given	C,C 90·0(5,2) N,N not given	Babel, 1982

Table 4 (Continued)

Compound (color)	Crys.cl Sp.Grp Z	a (Å) b (Å) c (Å)	α (°) β (°) γ (°)	Chromophore	M–L (Å)	L–M–L (°)	References
$Fe(\mu\text{-tsa})_2Cs$ (not given) (at 298 K)	or $Pna2_1$= 4	15·285(3) 13·402(4) 9·449(8)		$Fe^{III}O_2N_2S_2$	tsaO 1·961(11,25) tsaN 2·125(12,1) tsaS 2·443(5,14)	O,O 84·3(5) N,N 159·9(5) S,S 100·3(2) O,N 86·2(5,6)[c] 108·9(5,9) O,S 90·2(4,8)[d] 161·3(4,1) N,S 78·7(4,3)[d] 88·6(4,1·4)	Rjabova et al., 1981
				$Cs^I(ONC)_x$	Not given	Not given	
$Fe(\mu\text{-tsa})_2Cs$ (not given) (at 103 K)	or $Pna2_1$ 4	15·161(3) 13·340(3) 9·394(7)		$Fe^{III}O_2N_2S_2$	tsaO 1·964(6,8) tsaN 2·149(8,6) tsaS 2·441(2,12)	O,O 82·9(3) N,N 158·4(3) S,S 101·8(1) O,N 86·5(3,4)[c] 109·9(3,1·1) O,S 90·3(2,1·0)[d] 160·3(2,1) N,S 78·4(2,0)[d] 88·1(2,1·6)	Rjabova et al., 1981
				$Cs^I(ONC)_x$	Not given	Not given	
$Cs_2Fe(\mu\text{-S})_{10}Ge_4\cdot(H_2O)_{0·42}$	tg_ I4 2	8·413(7) 14·75(2)		$Fe^{II}S_4$	μS 2·325(11,0)	S,S 106·3 116·0	Bowes et al., 1996
				Cs^IS_x	μS not given	S,S not given	
				GeS_x	μS not given	S,S not given	
$Fe(\mu\text{-}\eta^2\text{-CN})_6Cs_2Li$	tg Fm3m 4			$Fe^{III}C_6$ Cs^I Li^I	μNC 1·926(3) Not given Not given		Swanson and Ryan, 1973
$Fe(\mu\text{-}\eta^2\text{-CN})_6Cs_2Na$	m $P2_1/n$ 2			$Fe^{III}C_6$ Cs^I Li^I	μNC 1·927 Not given Not given		Fletcher and Gibb, 1977
$Fe(\mu\text{-}\eta^2\text{-CN})_6Cs_2K$	m $P2_1/n$ 2			$Fe^{III}C_6$ Cs^I Li^I	μNC 1·925 Not given Not given		Haegele et al., 1975

[a]Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis is the e.s.d., and the second is the maximum deviation from the mean.

[b]The chemical identity of the coordinated atom or ligand is specified in these columns.

[c]The five-membered metallocyclic ring.

[d]The six-membered metallocyclic ring.

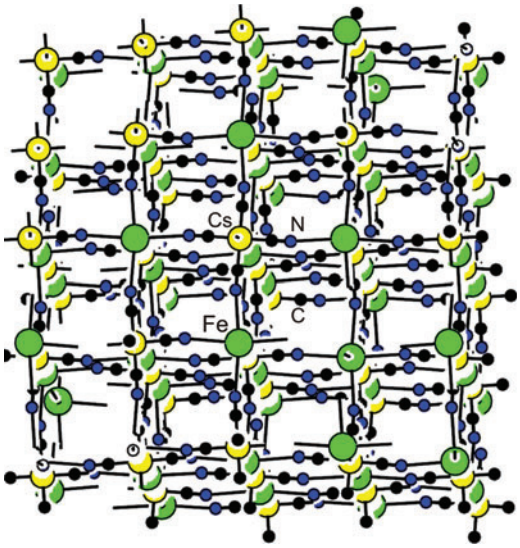


Figure 8 View of the $[NMe_4][Fe(CN)_6Cs]^{2-}$ (Babel, 1982).

1995; Jun et al., 1997; Yong-Ge et al., 1997), $C_2N_2O_2$ (Wang et al., 1992), $N_2O_2S_2$ (Rjabova et al., 1981; Wang et al., 1992), N_2O_5 (Novozhilova et al., 1975; Rjabova et al., 1982; Clegg et al., 1984; Lopez-Alcala et al., 1984; Solans et al., 1984; Mizuno et al., 1991; Sanchez et al., 1997; Seibig and van Eldik, 1998), N_3O_4 (Finnen et al., 1991), and N_4O_3 (Chang et al., 1993).

The inner coordination spheres about an M atom are as follows:

Li(I): N_2 (Höhn et al., 1991), O_4 (Lind et al., 1964; Novozholiva et al., 1973; Yamamoto et al., 1988; Declerq et al., 1993, 1995), NO_3 (Pickardth et al., 1984; Meyer and Pickardt, 1988), N_2O_2 (Pickardt et al., 1984; Meyer and Pickardt, 1988; Witzel et al., 1988), and O_6 (Novozholiva et al., 1973; Yamamoto et al., 1988; Declerq et al., 1993, 1995).

Na(I): O_4 (Ozarowski et al., 1995), N_3O (Witzel and Babel, 1984), NO_3 (Meyer and Pickardt, 1988), C_2O_2 (Chin and Bau, 1976), O_5 (Ozarowski et al., 1995; Calogero et al., 1997; Sosinsky et al., 1983; Huang et al., 1996; Li et al., 1997), NO_4 (Plenio et al., 1993), N_2O_3 (Longridge et al., 1997), O_6 (Ivanov and Kosoy, 1975; Novozhilova et al., 1975; Chin and Bau, 1976; Bailey et al., 1981; Pierpont et al., 1982; Clegg et al., 1984; Lopez-Alcala et al., 1984; Solans et al., 1984; Jameson et al., 1987; Küppers et al., 1987; McMurry et al., 1987; Yamamoto et al., 1988; Minghai et al., 1989; Okamoto et al., 1990; Finnen et al., 1991; Chang et al., 1993; Harding et al., 1993; Decurtins et al., 1994; Zheng et al., 1994; Blake et al., 1995, 1996; Burger and Klüfers, 1996; Yano et al., 1996; Calogero et al., 1997; Jun et al., 1997; Sanchez et al., 1997; Seibig and van Eldik, 1998), N_4O_2 (Deng and Shore, 1992), and CN_2O_6 (Teller et al., 1977).

K(I): O_4 (Raymond et al., 1976; Wang et al., 1992), N_2O_2 (Scheidt et al., 1980), O_5 (Raymond et al., 1976; Wang et al., 1992), O_6 (Larsen et al., 1990; Caneschi et al., 1995), N_6 (Darensbourg et al., 1977; Figgis et al., 1987; Figgis et al., 1990; Nieuwenhuyzen et al., 1998), N_4O_2 (Nieuwenhuyzen et al., 1998), O_7 (Yong-Ge et al., 1997; Rjabova et al., 1982), N_3O_4 (Nieuwenhuyzen et al., 1998), NO_6 (Kurmoo et al., 1995), O_8 (Raston et al., 1977), O_9 (Chu-Chieh et al., 1993), and O_{10} (Yong-Ge et al., 1997).

Rb(I): O_6 (Lind et al., 1964), N_6 (Schwarten et al., 1997), and F_{10} (Herdtweck et al., 1987, 1990).

Cs(I): O_6 (Raston et al., 1977), N_6 (Babel, 1982), $N_2O_2S_2$ (Rjabova et al., 1981), F_8 (Tressaud et al., 1970; Babel et al., 1974; Fleischer and Hoppe, 1982), and O_9 (Raston et al., 1977).

In the series of seven-coordinated iron(III) cations in the polymeric MFe complexes, there are two types: pentagonal bipyramids (most common) and a monocapped tetragonal prism. The pentagonal bipyramid is formed by hexadentate edta ligand (N_2O_4 donor sites) and one water molecule. This type of coordination polyhedron is 'sensitive' to an M atom. The mean values of $Fe–L_{eq}$ vs. $Fe–L_{ap}$ bond lengths are as follows: 2.199 vs. 1.969 Å (M=Li), 2.177 vs. 1.960 Å (Na), 2.192 vs. 1.975 Å (K), and 2.179 vs. 1.993 Å (Rb). These relatively large differences are in accordance with the idea that two apical (L_{ap}) sites are less sterically hindered than five equatorial sites (L_{eq}). An important shape indicator to describe pentagonal bipyramidal geometry is the ratio of bond distances

$$\tau = \frac{M\text{-}L_{ap}}{M\text{-}L_{eq}}$$

The τ parameter describes distortion about the Fe centers. The value for the FeN_2O_5 polyhedra decreases with increasing covalent radius of M atom (in parenthesis) in the following order: 0.915 (Rb, 2.16 Å)>0.905 (K, 20,251 Å)>0.900 (Na, 1.57 Å)>0.895 (Li, 1.225 Å). Another factor influencing the degree of distortion is the connectivity between the ligand and metal atom, as shown in the following order: 0.937 $[Fe(\eta^4\text{-nta})(\eta^3\text{-nta})]^{3-}$ (Clegg et al., 1984)<0.900 $[Fe(\eta^6\text{-edta})(H_2O)]^-$ (Lind et al., 1964; Novozhilova et al., 1975; Lopez-Alcala et al., 1984; Solans et al., 1984; Sanchez et al., 1997)<0.871 $[Fe(\eta^7\text{-dtpa})]^{2-}$ (Finnen et al., 1991).

It should be noted that in several papers, stereochemistry about M(I) atoms is not mentioned (Tables 1–4).

There is a wide variety of mono- and heteroatomic ligands coordinated to the metal cations. The coordination mode varies also, ranging from mono- to nonadentate coordination modes. The great majority of the ligands contain N and O donor atoms. The effect of both electronic and steric factors of the coordinated atoms can be seen in the opening of the L–Fe–L bond angles in the metallocycles. In the five-membered rings, the mean L–Fe–L intraligand angle opens in the following order: 77.5° ($–NC_2N–$)<77.8° ($–CN_2N–$)<79.6 ($–OC_2O–$)<82.1° ($–NC_2S–$)<90.0° ($–SC_2S–$). In the six-membered rings, the order is as follows: 87.5° ($–OC_3O–$)<90.0° ($–OC_3N–$)<90.4° ($–OC_3S–$)<92.4° ($–NC_3N–$). The shortest Fe–Fe bond lengths are as follows: Fe(0)–Fe(0)=2.534(3) Å (Minghai et al., 1989) and Fe(III)–Fe(III)=2.804(1) Å (Minghai et al., 1989; Hegetschweiler et al., 1995). The shortest Fe–M distance is 3.017 Å for Fe(III)–Na(I) (Blake et al., 1995), whereas the shortest M–M distance is 3.047(1) Å for Na(I)–Na(I) (Blake et al., 1996).

There are two polymeric $(FeK)_n$ derivatives that contain in their unit cell two crystallographically independent complex

units (Wang et al., 1992; Nieuwenhuyzen et al., 1998). In one case, there are even four of them (Hammes et al., 1997). The compound $(FeCs)_n$ exists in three isomeric forms (Tressaud et al., 1970; Babel et al., 1974; Fleischer and Hoppe, 1982). These complex units as well the three isomers differ from each other by the degree of distortion in metal-ligand distances and ligand-metal-ligand angles. They are typical examples of distortion isomerism (Melnik, 1982).

The properties of the complexes are very complex and variable. Mössbauer spectra have been recorded only for a few examples (Raston et al., 1977; Sosinsky et al., 1983; Pickardt et al., 1984; Jameson et al., 1987; Küppers et al., 1987; Figgis et al., 1990; Chang et al., 1993; Declerq et al., 1993, 1995; Zheng et al., 1994; Ray et al., 1996; Yano et al., 1996; Calogero et al., 1997). In most examples, the Mössbauer spectra consist of an asymmetric and strongly broadened absorption pattern, indicating the presence of both paramagnetic relaxation effects and quadrupolar interaction, which result from an iron(III) interionic distance of about 6.6 Å and from a noncubic iron environment, respectively. The magnetic properties are also available only for a few examples (Jameson et al., 1987; Lingqian et al., 1990; Deng and Shore, 1992; Wang et al., 1992; Chang et al., 1993; Harding et al., 1993; Decurtins et al., 1994; Zheng et al., 1994; Blake et al., 1995, 1996; Caneschi et al., 1995; Kurmoo et al., 1995; Ozarowski et al., 1995; Ray et al., 1996; Yong-Ge et al., 1997); there are low spin as well as high spin. The high-spin iron(III) atoms are antiferromagnetically coupled with an S=1/2 spin ground state.

Several other methods have been used for the study of the respective FeM complexes, but only very sporadically, for example, nuclear magnetic resonance (NMR) (Küppers et al., 1987; Mizuno et al., 1991; Deng and Shore, 1992), infrared (Raymond et al., 1976; Darensbourg et al., 1977), and ultraviolet-visible (Figgis et al., 1990; Lingqian et al., 1990; Finnen et al., 1991; Zheng et al., 1994; Caneschi et al., 1995; Kurmoo et al., 1995) spectroscopy. The structures of the complexes are very complex and therefore, from the very limited number of the respective examples, cannot be made a general conclusion.

In general, iron compounds have both chemical and biological importance. It is necessary to gain structural information to understand their role in both areas. The present paper is the first overview of structural data for polymeric FeM (M=Li, Na, K, Rb, Cs) complexes. Another related review is in preparation for polymeric FeM′ complexes (M′=Mg, Ca, Sr, Ba, In, Te, Ge, Sn, Pb).

During the collection of the present data, it became clear that in spite of the increasing availability of data retrieval systems, tracing of relevant material is not always a straightforward task. Some of the data are only available as supplementary material, and some are not mentioned at all. This can lead to overlooking of relevant structural features, which should be compared with other derivatives. In view of such limitations in data retrieval, we believe that it is necessary to make systematic reviews. These kinds of reviews serve the useful purpose of delineating area of both interest and weakness.

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