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Review

Structural characterization of heteropolymeric iron and main group metal complexes

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Abstract

This review summarizes almost 40 structures of polymeric Fe(M), where M=Mg, Ca, Sr, Ba, In, Te, Ge, Sn, Bi, Zn, Cd and Hg complexes. The complexes crystallized in the monoclinic, tetragonal, orthorhombic and triclinic classes, from which the monoclinic by far prevails (~50%). The most common ligands are with O, N and C donor atoms. The iron atoms are found in the oxidation states 0, +2 and +3, with +3 being the most common. In most complexes the iron(0) is 5-, iron(II) and iron(III) are 6-coordinated, but there are examples of 3-, 5- and even 7-coordinated complexes. The inner coordination spheres about the M atoms range from 3 to 11. The structures are discussed in terms of the coordination about the metal atoms, and correlations are outlined between donor atoms, bond lengths and interbond angles.

Keywords: classification; FeM (M=main group metal); polymeric; structure.

Introduction

Iron is widely distributed in the combined state. It is one of the most abundant elements of the Earth's crust, and it is one of the trace elements essential to life. The coordination compounds of iron have been extensively studied from a structural point of view. The past 50 years have seen many studies on the reaction of various metal salts. In many cases, heterometal compounds have been prepared for which crystallographic and structural data have been obtained. The structural chemistry of 800 heterodimer iron compounds has been reviewed (Melnik et al., 2006), as well as over 350 heterotrimers (Melnik et al., 2007), almost 300 heterotetramers (Melnik et al., 2008), 180 heteropentamers (Melnik et al., 2010), 160 heterohexa and heteroheptamers (Melnik and Holloway, 2011), and 130 heteroocta and heterooligomer clusters (Mirskij, 2009). The structural chemistry of polymeric heterometal iron compounds, in which alkali metals are partners to the iron, has been reviewed recently (Melník et al., in press).

In this review, polymeric FeM (M=Mg, Ca, Sr, Be, In, Tl, Sn, Bi, Zn, Cd and Hg) compounds are analyzed and classified.

Polymeric FeM complexes

Crystallographic and structural data for 40 polymeric FeM (M=Mg, Ca, Sr, Ba, In, Tl, Ge, Sn, Bi, Zn, Cd, Hg) complexes are presented in Table 1. The structure of the red orange monoclinic FeMg complex (Johnson et al., 1991) contains $(NC)_5Fe(1\text{-Meim})^{2-}$ units linked in extended chains through bridging CN groups (*cis* to 1-Meim), which are coordinated to the oxygen atoms (Figure 1). Two $N(NC^-)$ and two $O(OH_2)$, and two N(1-Meim), coordinated to Mg(II) atom (MgN_4C_2). The chains are bent about the N atom of the bridging CN groups at angles of 156.3(2) and 152.3(2)°. Each Fe(III) atom is 6-coordinated (FeC_5N) with a mean Fe-L bond distance, elongated in the order: 1.929(2) Å [L=μ-CN (×3)]<1.944(3) Å [CN (×2)]<1.950(2) Å (N, 1-Meim). The mean Mg-L bond distance elongated in the order: 2.074(3) Å ($L=OH_2$)<2.149(2) Å (μ-NC)<2.196(2) Å (N1-Meim). This is the only example of polymeric FeMg complexes.

There are three polymeric FeCa examples (Cohen and Hoard, 1966; Pavelčík and Kettmann, 1983; Mayer and Pichard, 1988). In colorless $Fe(CN)_6Ca_2(hmta)(H_2O)$ (Mayer and Pichard, 1988), each Fe(III) atom is hexa-coordinated (FeC_6) with the mean Fe-C (μ-CN) bond distance of 1.924(4) Å. Also, each Ca(II) atom is hexa-coordinated (CaN_4O_2), the mean Ca-L bond distances are elongated in the order: 2.452(3) Å ($l=\mu\text{-}OH_2$)<2:533(3) Å (μ-NC)<2.601(3) Å (μ-N, hmta).

In yellow monoclinic FeCa derivative (Pavelčík and Kettmann, 1983), each Fe(III) atom is hexa-coordinated by four oxygen atoms of the carbonyl groups, and two nitrogen atoms of the hexadentate edds ligand. Each Ca(II) atom is 7-coordinated (CaO_7). A capped-trigonal prism occupied about Ca(II) atom is created by three water molecules, W1, W3, W4, and O8 atom of carboxylate group. This occupied a square base, and atoms O(7) and O(18) form the edge of the prism and molecule (W2) sitting on the cap. The crystal structure is stabilized by bonds of the Ca(II) atom with O(7) and O(8) atoms, connecting the $[Fe(1)(edds)]^-$ anions in an infinite chain in the structure, in which the $[Fe(2)(edds)]^-$ anions are coordinated by a further Ca-O(18) bond.

Table 1 Crystallographic and structural data for polymeric FeM (M=non-transition metals)[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
$[(\eta^1\text{-Meim})(NC)_3Fe.(\mu\text{-}\eta^2\text{-CN})_2Mg(H_2O)_2.(\eta^1\text{-1-Meim})_2]\cdot H_2O$ (red orange)	m $P2_1$ 2	8.471(2) 15.678(9) 9.722(2)	119.05(4)	$Fe^{III}C_5N$	NC[b]1.944(3,7) μNC 1.929(2,7) η^1N 1.950(2)	C,C[b] 89.2(1,5.4) 176.1(1,2.0) C,N 91.6(1,7) 173.9(1)	Johnson et al., 1991
				$Mg^{II}N_4O_2$	η^1N 2.196(3,6) μCN 2.149(2,5) H_2O 2.074(3,34)	N,N 89.9(1,1.6) 177.6(1,4) O,O 176.1(1) N,O 89.7(1,2.9)	
$Fe(\mu\text{-}\eta^2\text{-CN})_6Ca_2.(\mu\text{-}\eta^2\text{-hmta})(\mu\text{-}OH_2)_6$ (colorless)	m B2/b 4	11.302(4) 13.735(4) 13.550(4)	97.17(1)	$Fe^{III}C_6$	μNC 1.934(4,14)	C,C 90.0(2,3.3)	Mayer and Pichard, 1988
				$Ca_2N_4O_2$	μCN 2.533(3,34) $\mu\eta^2$N 2.601(3) μH_2O 2.450(3,1)	Not given	
$[\{Fe(\mu\text{-}\eta^6\text{:}\eta^2\text{-edds})\}_2\cdot Ca(H_2O)_4]\cdot 4H_2O$ (yellow)	m Pc 2	10.284(4) 8.402(4) 21.273(12)	116.04(4)	$Fe^{III}O_4N_2$	η^6O 1.93–2.07(2) N 2.13(2,0)	O,O 102.6(2,3.0) 170.8(2,1.8) N,N 81.4(2)[c] O,N 77.2(2,8) 88.9(2,1.5)	Pavelčík and Kettmann, 1983
				$Ca^{II}O_7$	η^7O not given H_2O not given	O,O 71(-,2) 169	
$[(H_2O)Fe(\mu\text{-}\eta^6\text{:}\eta^1\text{-dcta})\cdot Ca(H_2O)_8]$ (red)	m C2/c 4	34.34(20) 8.844(1) 13.527(9)	91.02(5)	$Fe^{III}O_5N_2$	η^6O 2.017(4) 2.094(4) N 2.290(4) H_2O 2.009(3)	O,O 87.3(3,15.5) 148.9(7),173.8(8) N,N 76.5(2)[c] O,N 73.6(3,2.1)[c] 100.0(3,9)	Cohen and Hoard, 1966
				$Ca^{II}O_7$	η^1O 2.417(5,0) H_2O 2.403(7,24)	O,O 77.6(3,7.0) 94.9(3),161.9(8,1.2)	
$[Fe_4(\mu\text{-}\eta^4\text{-ara})_4\cdot(\mu\text{-}OH)_2Sr_4(H_2O)_x]\cdot CO_3$ (yellow)	m C2/c 4	17.990(5) 12.7265(6) 27.74(6)	110.15(2)	$Fe^{III}O_6$	η^4μO 1.952(7,10) η^4μO 2.052(7,60) μHO 1.969(7,13)	O,O not given	Burger and Klüfers, 1966a
				$Sr^{II}O_9$ $Sr^{II}O_{10}$	LO 2.673(7,34) μO 2.593(7,4) 2.816(7,109) H_2O 2.646(7,104)	O,O not given	
$\{Fe(\mu\text{-}\eta^2\text{-CN})_6\}_2Sr_3\cdot(\mu\text{-}\eta^2\text{-hmta})_3\cdot 18\ H_2O$ (red)	tg $P4_2/$ nmc 4	19.318(4) 15.799(4)		$Fe^{III}C$	μNC 1.928(1,10)	C,C 90.0(6,4.0) 177.4(4,4)	Meyer and Pickerdt, 1989
				$Sr^{II}O_3N_2$	H_2O 2.579(2,26) μCN 2.691(2,0) η^2N 3.183(2)	Not given	
				$Sr^{II}O_8$	H_2O 2.588(2,151)	Not given	
$(ON)Fe(\mu\text{-}\eta^2\text{-CN})_5.Sr(H_2O)_4$ (red)	m C2/m 4	20.08(3) 7.51(4) 8.42(2)	98.4(2)	$Fe^{II}CN$	μNC 1.93(2,0) 1.97(2) ON 1.64(2)	C,C 89.1(2,7) C,N 94.6(2,5) 178.2(2)	Castellano et al., 1977
				$Sr^{II}N_4O_2$	μCN 2.69(2,5) H_2O 2.59(3,6)	N,N 79.6(5) 126.2(5) O,O 123.1(6) N,O 72.9(6,7.1) 150.8(5)	
$Fe_2(\mu_3\text{-N})_3LiSr_2$ (black)	m C2/c 4	6.559(1) 11.414(2) 6.593(1)	93.28(5)	$Fe^{III}N_3$	μ_3N 1.901(4,29)	N,N 105.7(9,3.7) 148.5(9)	Höhn et al., 1991
				$Li^{I}N$	μ_3N 1.996(7,0)	N,N 149.5(9)	
				$Sr^{II}N_5$	μ_3N 2.571(5) 2.776(5)	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)	$Fe^{II}N_3$	μ_3N 1.892(8,31)	N,N not given	Höhn et al., 1991
				$Li^{I}N_2$	μ_3N not given	N,N not given	
				$Ba^{II}N_5$	μ_3N not given	N,N not given	

(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
$Fe(\mu\text{-mal})_3Na.$	m	11.113(2)		$Fe^{III}O_6$	malO 1.971(3,14)	O,O 90.0(7,4.8)	Burger and
$Ba(H_2O)_3$	$P2_1/m$	13.512(2)	90.8(1)	Na^IO_6	malO 2.498(4,138)	O,O 64.8(1)	Klüfers,
(green)	4	10.276(2)			H_2O 2.340(4,7)		1966b
				$Ba^{II}O_8$	malO 2.693(4,27)	O,O 80.1(1,5)	
					2.905(4,35)		
					H_2O 2.862(4,50)	136.1(1)	
$Fe_2(\mu\text{-OH})_2(\mu\text{-aca})_4.$	m	11.032(2)		$Fe^{III}O_6$	µHO 2.082(1,10)	O,O not given	Calogero et
$Ba_2(H_2O)_{12}$	$P2_1/n$	11.844(2)	103.13(2)		acaO 1.965(1,5)		al., 1977
(brown)	2	13.791(3)			2.014(1,5)		
				$Ba^{II}O_8$	acaO 2.701(2,95)	O,O not given	
					H_2O 2.773(2)		
					2.862(2,5)		
$Fe_2(\mu\text{-man})_2$	m	9.610(5)		$Fe^{III}O_6$	manO 1.979(6)	O,O not given	Burger and
$Ba_2(H_2O)_{12}$	$P2_1/c$	9.643(3)	96.19(4)		µO 1.998(6,26)		Klüfers,
(yellow)	2	14.666(7)		$Ba^{II}O_8$	manµO 2.815(7,110)	O,O not given	1966a
					H_2O 2.849(7,147)		
$(H_2O)_2Fe(\mu\text{-tri})_2.$	m	21.069(4)		$Fe^{III}O_6$	HO 2.003(4,18)	O,O not given	Burger and
$Ba_2(H_2O)_{12.5}$	C2	9.626(2)	110.15(2)		trieµO 1.970(4,19)		Klüfers,
(yellow)	4	13.882(6)			2.037(4,44)		1966a
					2.238(4)		
					H_2O 1.959(4,2)		
				$Ba^{II}O_8$	triµO 2.734(4,31)	O,O not given	
					H_2O 2.862(4,148)		
$\{Fe(\mu\text{-}\eta^2\text{-CN})_6\}_2Ba_3.$	m	11.480(4)		$Fe^{III}C_6$	µNC 1.94(1,2)	C,C 90.0(6,3.9)	Meyer and
$(\mu\text{-}\eta^2\text{-hmta})_2(H_2O)_{11}$	$P2_1/n$	13.697(4)				176.5(6,8)	Pickerdt,
(red)	2	15.845(4)	93.7(3)	$Ba^{II}O_3N_3$	H_2O 2.77(1,8)		1989
					µCN 2.87(1,4)	Not given	
				$Ba^{II}O_5N_2$	hmtaN 3.09(1)		
					H_2O 2.88(2,6)		
					3.36(5)	Not given	
					µCN 3.18(1,9)		
$(ON)Fe(\mu\text{-}\eta^2\text{-CN})_5.$	or	16.039(6)		$Fe^{III}C_5N$	µNC 1.949(7,0)	C,N 94.3(3,13)	Klüfers and
$Ba(H_2O)_{6.5}$	$Cmc2_1$	11.539(6)			ON 1.665(6)		Haussül,
(red brown)	8	16.696(6)		$Ba^{II}C_5N_4$		179.0(3)	1985
				$Ba^{II}O_8N_2$			
$[(ON)Fe(\mu\text{-}\eta^2\text{-CN})_5.$	or	7.620(7)		$Fe^{III}C_5N$	µNC 1.931(2,2)	C,C 89.5(1,2.8)	Navaza et
$Ba(H_2O)_3$	Pbcm	19.394(17)			ON 1.665(1)	169.6(1)	al., 1990
(orange red)	4	8.631(8)		$Ba^{II}N_5O_4$	µCN 2.857(3,32)	Not given	
(by neutron diffraction)					H_2O 2.84(1,7)		
					3.021(6,35)		
$[\{(H_2O)Fe(\mu\text{-edta})\}_2.$	m	30.407(7)		$Fe^{III}O_5N_2$	edtaO 1.97(2,2)	O,O 74.6(8,1.3)	Solans et al.,
$Ba(H_2O)_4]$	C2/c	7.659(3)	108.53(6)		edtaµO 2.08(2,1)	86.0(9,2.9)	1984b
(black)	4	14.487(5)			edtaN 2.27(3,8)	100.3(8,4.2)	
					H_2O 2.08(2)	N,N 73.7(9)[c]	
						O,N 75.8(8,5.7)[c]	
						87.0(8)	
				$Ba^{II}O_{11}$	edtaO 2.84(2,5)	O,O not given	
					edtaµO 3.06(2,1)		
					H_2O 2.78(2)		
[Fe(µ-Hdpa)Ba.	m	15.160(3)		$Fe^{III}O_4N_3$	LO 1.948(4,17)	O,O 73.2(2)	Chuklianova
$(H_2O)_4]$ ClO_4	$P2_1/c$	10.873(2)	98.47(1)		LµO 2.103(4,64)	93.5(2,6.5)	et al., 1981
(red brown)	4	15.707(4)			LN 2.309(4,10)	170.0(2)	
					2.460(4)	N,N 74.7(2,1.2)[c]	
						O,N 74.0(2,4.4)[c]	
						92.2(2,6.3)	
				Ba_2O_9	LO 2.713(4,28)	O,O not given	
					LµO 3.035(4,6)		
					H_2O 2.809(4.62)		

(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
[In{$Fe_2(\mu\text{-}\eta^2\text{-}CO)_8)_2$· K(thf)]	tg P4/n	11.850(2)		Fe^0C_4In	μOC 1.783(9,34) In 2.627(1)	C,C 95.5(4,10.0) 168.5(4)	Che-Chieh et al., 1993
(dark red)	2	10.696(2)			Fe′ 2.900(2)	In,Fe 56.5(1)	
				In^IFe_4	Fe 2.627(1)	Fe,Fe 67,0(1) 134.1(1)	
				K^IO_9	μCO 2.767(6,0) 2.949(8,0) thfO 2.739(15)	O,O 63.1-159.6(2)	
$(NMe_4)[Fe(\mu\text{-}\eta^2\text{-}CN)_6Tl]$	m	15.114(17)		$Fe^{III}C_6$	μNC 1.93(1,3)	C,C 90(1,5)	Swartner et al., 1997
(yellow)	C2/c 4	8.848(8) 15.259(16)	110.0(1)	Tl^IN_6	μCN 3.11(3,4)	N,N 90(1,4)	
$[(H_2O)Fe(\mu\text{-edta}).TlH_2O]$	tr_ P1	13.825(2) 8.591(1)	87.79(1) 97.75(1)	$Fe^{III}O_5N_2$	edtaO 1.959(7,28) 2.115(6) edtaμO 2.105(7) edtaN 2.321(7,13) H_2O 2.109(6)	Not given	Solans et al., 1984a
(yellow brown)	2	6.807(1)	104.34(1)				
				Tl^IO_7	edtaO 2.805(7) edtaμO 2.744(8)-3.115(7)	Not given	
$[(\eta^5\text{-cp})Fe(\mu\text{-}\eta^5\text{:}\eta^3\text{-}C_5H_4Bpz_3)Tl$	m $P2_1/m$	10.006(1) 10.072(1)	93.50(1)	FeC_{10} Tl^IN_3	cpC not given η^3N 2.657(5,19)	Not given N,N 70.9(2)	Yukle et al., 1996
(orange)	4	19.928(2)			2.780(5)	87.3(1,4.6)	
$(NMe_4)_2[Fe(\mu\text{-}S)_{10}Ge_4]$	tg I-4	9.439(3)		$Fe^{II}S_4$	μS 2.39(1,0)	S,S 106.9(9,0) 114.6(9,0)	Achak et al., 1996
(not given)	2	14.1637(7)		$Ge^{IV}S_4$	μS 2.19(1,5)	S,S 109.5(9,9.7)	
$(NMe_4)_2[Fe(\mu\text{-}S)_{10}Ge_4]$	tg I-4	9.429(4)		$Fe^{II}S_4$			Akari et al., 1998
(red brown)	2	14.206(6)		$Ge^{IV}S_4$			
$(NMe_4)_2[Fe(\mu\text{-}S)_{10}Ge_4]$	tg I-4	9.696(5)		$Fe^{II}S_4$			Akari et al., 1998
(red brown)	2	14.705(8)		$Ge^{IV}S_4$			
$(NMe_4)_2[Fe(\mu\text{-}S)_{10}Ge_4]$	tg I-4	9.374(3)		$Fe^{II}S_4$	μS 2.348(7,0)	S,S 103.4 122.4	Bowers et al., 1996
(red brown)	2	14.174(4)		$Ge^{IV}S_4$	μS not given	S,S not given	
$Cs_2[Fe(\mu\text{-}S)_{10}Ge_4]$ $H_2O_{0.42}$	tg I-4	8.413(2)		$Fe^{II}S_4$	μS 2.325(11,0)	S,S 106.3 116.0	Bowers et al., 1996
(red brown)	2	14.75(2)		Cs^IS_x	μS not given	S,S not given	
				$Ge^{IV}S_4$	μS not given	S,S not given	
$[Fe(\mu\text{-}\eta^2\text{-}CN)_6.(SnMe_3)_4(H_2O)_4]$	or Cmca	17.064(2) 18.534(2)		$Fe^{II}C_6$ $Sn^{IV}C_3ON$	μNC 1.886(6,0) MeC 2.116(9,11)	C,C not given C,C 118.2(2)	Behrens et al., 1991
(colorless)	4	11.586(1)			H_2O 2.350(7) μCN 2.281(7)	C,O 87.1(2,5) C,N 92.6(3,1.3) O,N 178.9(3)	
				$Fe^{III}C_3$ $Sn^{IV}C_3N_2$	μNC 1.898(4,0) MeC 2.116(11,19) μCN 2.320(4,0)	C,C not given C,C 89.1(2,4);119.4(2) N,N 178.7(3) C,N 90.0(2,1.6)	
$[Fe(\mu\text{-}\eta^2\text{-}CN)_6(SnMe_3)_4.(H_2O)_2C_4H_8O_2]$	m $P2_1/n$	13.242(2) 11.396(2)	101.37(1)	$Fe^{II}C_6$ $Sn^{IV}C_3N_2$	μNC 1.920(10,3) MeC not given	C,C not given C,N 89.5	Adam et al., 1990
(colorless)	2	13.322(3)			μCN 2.329(9,45)		
				$Fe^{II}C_6$ $Sn^{IV}C_3N_2O$	μNC 1.891(10,0) MeC not given μCN 2.160(9) H_2O 2.451(8)	C,C not given C,N 94.2	

(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
(NBu_4^n) [Fe(μ-η²-CN)$_6$.	or $P2_12_12_1$ 4	13.514(5) 26.353(10) 10.962(5)		$Fe^{II}C_6$	μNC 1.876(13)-1.932(14)	C,C 90.0(6,8) 176.3(6,2.4)	Schwarz et al., 1996
($SnMe_3$)$_{3.5}$(H_2O)] (colorless)				$Sn^{IV}C_3N_2$	MeC not given μCN 2.286(14,31)	Not given	
				$Sn^{IV}C_3NO$	μMeC not given μCN 2.187(16) H_2O 2.664(13)	Not given	
[Fe(μ-η² -CN)$_6$($CnPh_3$)$_3$. (H_2O)]. 2MeCN (at 223 K)	or Pbca 8	16.253(4) 21.746(7) 34.389(3)		$Fe^{II}C_6$	μNC 1.93(2,3) PhC not given	C,C not given Not given	Yian et al., 1996
				$Sn^{IV}C_3N_2$	μCN 2.34(1,7) PhC not given	Not given	
				$Sn^{IV}C_3NO$	μCN 2.30(1) H_2O 2.34(1)		
(η⁵-cp)Fe(μ-η⁵:η²-C_5H_4. COO)Sn(η¹-CH=CH_2)$_3$ (red orange)	m $P2_1/a$ 4	15.105(5) 10.030(4) 11.402(4)	104.06(4)	FeC_{10} $Sn^{IV}C_3O_2$	η⁵C 2.02(1,2) LC 2.12(2,4) η²O 2.27(1,15)	C,C not given Not given	Graziani et al., 1980
[(η⁵-cp)$_2$FeBiCl_4] (black)	m $P2_1/c$ 4	10.998(5) 17.449(4) 7.569(4)	98.46(5)	FeC_{10} $BiCl_6$	η⁵C 2.07(1,4) Cl 2.511(3,11) μCl 2.725(3,24) 3.025(3,76)	C,C not given Cl,Cl 90.0(1,9.7) 172.1(1,6.1)	Mammano et al., 1977
[$PhCH_2NMe_3$]. [(OC)$_6$(μ-H)Fe_2. Bi_2(μ-Cl)$_2$] (red brown)	m P2/n 4	7.864(2) 22.465(4) 13.797(3)	105.96(3)	FeC_3HBi_2	OC not given μH 1.68(9,9) Bi 2.654(2,13) Fe′ 2.759(2)	Bi,Bi 81.44(4,25) Bi,Fe 58.68(4,36)	Enland et al., 1997
				$BiCl_2Fe_2$	μCl 2.865(3,47) Fe′ 2.759(2)	Cl,Cl 165.82(8.6) Fe,Fe 62.65(5,10) Cl,Fe 96.4(7,5.6)	
[Zn{Fe(CO)$_4$}$_2$. {Na(thf)$_2$}$_2$] (light pink)	m I2/m 2	10.654(3) 9.848(3) 15.333(3)	100.79(2)	FeC_4Zn ZnC_4Fe_2 NaO_5	μOC 1.956 μOC 1.729; 2.502 μCO 2.308(4,0) 2.584(7) thfμO 2.514(6,58) thf 2.315(6)	C,Zn 74.8(2); 62.3(2) Not given O,O not given	Pierpont et al., 1982
[(ON)Fe(μ-η²-CN)$_5$. Cd(H_2O)]·2H_2O	m $P2_1/n$ 4	7.405(2) 14.963(2) 10.848(3)	91.64(2)	$Fe^{III}C_5N$	μNC 1.942(3,9)	C,C 87.6(2,3.1) 191.1(1,9) C,N 94.5(1,1.8) 171.9(1)	Mulliza et al., 1990
				$Cd^{II}N_5O$	μCN 2.214(3,35) H_2O 2.335(2)	N,N 91.1(1,5.7) 175.4(1,1.2) N,O 88.6(1,5.8) 170.5(1)	
[Hg{Fe(μ-η²-CO)$_4$). {Na(thf)$_2$)$_2$]	m C2/m 2	12.39(3) 8.54(1) 16.01(1)	105.5(2)	FeC_4Hg	μOC 1.75(2,1) 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)	Sosinski et al., 1983
				HgC_2Fe_2	μOC 2.84(2,4) Fe 2.522(5)	C,C not given	
				NaO_5	μCO 2.29(2,3) thfO 2.28(1,2)	O,O 89.0(6,4.4) 116.4(6,10.2); 170.4(5)	

(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
[(η^1-dmtq)(H_2O)$_{1.5}$. Fe(μ-η^2-NCS)$_4$Hg] (yellow)	tr_ P1 2	16.318(10) 18.389(14) 10.088(4)	105.15(4) 101.24(6) 83.31(9)	$Fe^{II}N_5O$	η^1N 2.213(13,2) μSCN 2.111(14.1) 2.150(14) H_2O 2.148(9)	N,N 90.9(5,4.9) 176.2(5,2) N,O 88.1(5,2.2) 175.5(8)	Cingi et al., 1985
				$Fe^{II}N_4O_2$	η^1N 2.197(12,11) μSCN 2.122(15,13) H_2O 2.167(11,30)	N,N 91.8(5,9.0) 176.2(5) O,O 87.3(2) N,O 88.9(5,5.4) 172.6(5,2.6)	
				$Hg^{II}S_4$	μNCS 2.533(5,62)	S,S 109.5(3,8.3)	
[(η^1-dmtp)$_2$(H_2O)Fe. (μ-η^2-NCS)$_3$Hg(SCN] (yellow)	m $P2_1/n$ 4	11.599(7) 16.541(5) 14.766(10)	98.47(5)	$Fe^{II}N_5O$	η^1N 2.167(12,2) μSCN 2.137(14,10) H_2O 2.130(10)	N,N 90.7(5,4.6) 174.6(1.1) N,O 88.7(5,2.6) 177.8(4)	Cingi et al., 1985
				$Hg^{II}S_4$	NCS 2.602(5) μNCS 2.440(5) 2.555(6,12)	S,S 109.5(2,16.0)	
[(η^1-dmtp)(H_2O)$_2$Fe. (μ-η^2-NCS)$_3$Hg(SCN)]. Me_2CO (yellow)	m $P2_1/n$ 2	12.285(7) 13.689(6) 7.562(5)		$Fe^{II}N_4O_2$	η^1N 2.246(17) μSCN 2.093(20) 2.148(18,7) H_2O 2.530(17,10)	N,N 91.2(7,2.9) 174.6(7) O,O 90.2(6) N,O 89.0(7,5.3) 177.0(7,5)	Cingi et al., 1985
				$Hg^{II}S_4$	NCS 2.574(6) μNCS 2.515(6,56)	S,S 109.5(6,8.0)	

[a]Where more than chemically equivalent distance or angle is present, the mean value is tabulated, the first number in parentheses is e.s.d., and the second is maximum deviation from the mean.
[b]The chemical identity of coordinated atom or ligand is specified in these columns.
[c]The 5-member metallocyclic ring.
[d]The 6-member metallocyclic ring.
aer, anhydroerythritolate; ara, arabitolate; Cp, cyclopentadienyl; dcta, 1,2-diaminecyclohexane-N,N-tetraacetate; edds, ethylendiamine-N,N′-disuccinate; edta, ethylenediamine-N,N-tetraacetate; hdtpa, diethylenetriaminetetraacetate; hmta, hexamethylenetetramine; m, monoclinic; mal, malonate; man, mannofuranose; 1-Meim, 1-methyleneimidazole; NBu_4^n, n-tetrabutylammonium; NMe_4, tetramethylammonium; or, orthorhombic; Ph, phenyl; tg, tetragonal; thf, tetrahydrofuran; tr, triclinic; tri, threitolate.

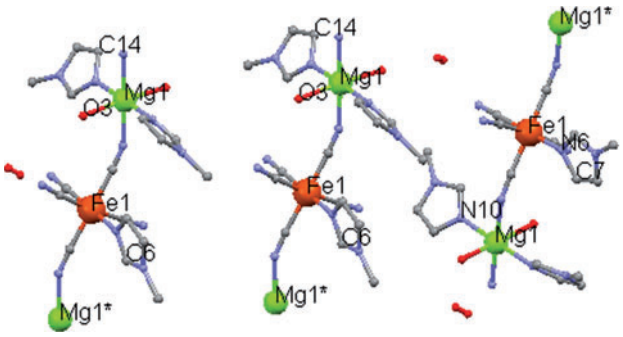

Figure 1 View of the structure of (1-Meim)$(NC)_3$Fe(μ-CN)$_2$Mg(H_2O)$_2$(1-Meim) (Johnson et al., 1991).

In red monoclinic [(H_2O)(Fe(dcta)Ca(H_2O)$_8$] (Cohen and Hoard, 1966), each metal atom is 7-coordinated (FeO_5 N_2, CaO_7). The Fe(III) atom has a pentagonal bipyramidal arrangement, the pentagonal plane is created by two O and two N atoms of the dcta ligand and water molecule, and another two O atoms of hexa-dentate dcta occupy apical positions. The hexadentate ligand forms about each Fe(III) atom 5-membered metallocycles (one -NS_2N- and four -OC_2N-) with the N-Fe-N and O-Fe-N (av) interligand angles of 76.5(2) and 73.6(3)°, respectively. Each Ca(II) atom has a cape trigonal prism arrangement, created by two O atoms of dcta ligand and five O atoms of water molecules.

There are three examples of FeSr (Burger and Klüfers, 1966b; Castellano et al., 1977; Meyer and Pickerdt, 1989) and one FeSrLi (Höhn et al., 1991) derivative (Table 1). In yellow $[Fe_4(ara)_4(OH)_2Sr_4(H_2O)_x]CO_3$ (Burger and Klüfers, 1966b), the tetranuclear plane is built up from four edge-sharing FeO_6 octahedra by four tetradentate ara ligands and by the OH group. Each Fe(III) atom is hexa-coordinated (FeO_6). The Sr(II) atoms are 9- (SrO_9) and 10- (SrO_{10}) coordinated.

In red tetragonal $\{Fe(CN)_6\}_2Sr_3(hmta)_3(H_2O)_{18}$ (Meyer and Pickerdt, 1989), each Fe(III) atom is hexa-coordinated (FeC_6) with a mean Fe-C bond distance of 1.928(1) Å. The CN groups serve as bridges between Fe(III) and Sr(II) atoms and between Sr(II) atoms in addition to hmta ligands and created three-dimensional chains. The Sr(II) atoms are with the inner coordination spheres of SrO_3N_2 and SrO_8, respectively (Table 1).

In another red monoclinic $(ON)Fe(CN)_5Sr(H_2O)_4$ (Castellano et al., 1977), each Fe(III) is 6-coordinated (FeC_5N) with the Fe-N (NO) bond distance of 1.64(2) Å and Fe-C (CN) bond distance *trans* to the NO group of 1.97(2) Å. The remaining four Fe-C bond distances are equal: 1.93(2) Å. In the structure, the Sr(II) atoms are one N atom of a CN group of each of five nitropruside anions, completing the octahedron with the O atom of a water molecule (SrN_4O_2).

In each monoclinic $Fe_2(\mu_3\text{-}N)_3LiSr_2$ (Höhn et al., 1991), the nitrido serves as a bridge between the metal atoms and form polymeric chains. Each Fe(III) atom has a trigonal planar coordination with the mean Fe-N bond distances of 1.901(4) Å, whereas the Li(I) atom is 2-coordinated (LiN_2) with the mean Li-N of 1.996(7) Å and N-Li-N angle of 149.5(9)°. However, each Sr(II) atom has a trigonal bipyramidal arrangement (SrN_5) with the Sr-N bond distances from 2.571(5) to 2.776(1) Å.

There are 10 examples (one FeLiBa, FeNaBa and eight FeBa) which are the richest in the series of FeM polymeric complexes (Table 1). The structure of black $Fe_2(\mu_3\text{-}N)_3LiBa_2$ (Höhn et al., 1991) is similar to that of strontium analogous (Höhn et al., 1991). In green monoclinic $Fe(mal)_3NaBa(H_2O)_3$ (Burger and Klüfers, 1966a), a slightly distorted octahedral coordination around Fe(III) atom is formed by six oxygen atoms from the malonate moieties. The Na(I) site is formed by the oxygen atoms O(4), O(5) and O(11) from the different malonate rings together with the oxygen atoms O(1W) (NaO_6). The tricapped trigonal prism around the Ba(II) atoms is achieved by six carbonyl oxygens from the three malonate moieties and by three oxygens from water (BaO_8). All the oxygen atoms of the malonate rings are involved in bonds, the non-carbonylic ones around the iron(III) center, and the carbonylic ones around Na(I) and Ba(II) atoms. These with the hydrogen bonds form polymeric chains.

In brown monoclinic FeBa complex (Calogero et al., 1977), two $Fe(aer)_2$ moieties are held together by two OH groups [$Fe(OH)_2Fe$] with the mean Fe-O-Fe bridge angle of 102.55(7)° and Fe···Fe separation of 3.247(1) Å which ruled out a direct bond. Each Fe(III) atom is 6-coordinated (FeO_6). The anhydroerythritol ligands also connected Ba(II) atoms and with the four water molecules created an eight coordination about each Ba(II) atom (BaO_8) in polymeric chains.

The structure of two polymeric yellow monoclinic FeBa complexes (Burger and Klüfers, 1966b) is similar to that of the Sr analogous (Burger and Klüfers, 1966b). Each Fe(III) atom is 6-coordinated and Ba(II) atoms are 8-coordinated (Table 1). The structure of $\{Fe(CN)_6\}_2Ba_3(hmta)_2(H_2O)_{11}$ (Meyer and Pickerdt, 1989) is similar to that of Sr(II) analogous (Meyer and Pickerdt, 1989). Each Fe(III) atom is 6-coordinated and the Ba(II) atoms are 6- (BaO_3N_3) and 7- (BaO_5N_2) coordinated. The CN group and hmta ligands which serve as a bridge form a polymeric chain.

The red brown orthorhombic $(ON)Fe(CN)_5Ba(H_2O)_{6.5}$ complex (Klüfers and Haussül, 1985) has 6-coordinated Fe(III) atoms (FeC_5N). The Fe-N (NO) and Fe-N (NC) *trans* to NO bond distances are 1.665(6) and 1.961(6) Å with the N-Fe-N angle of 179°. The mean Fe-N (NC) bond distance is approximately 0.015 Å shorter (1.946 Å). The eight Ba atoms per unit cell occupy two different quartets of type (o, y, z) with symmetry m. The Ba(1) is coordinated by five H_2O and four CN (BaO_5N_4), Ba(2) by eight H_2O and two CN (BaO_8N_2). In the crystal structure, the $Fe(NO)(CN)_5$ ions are staggered in form columns along [010].

The structure of orange-red orthorhombic $(ON)Fe(CN)_5Ba(H_2O)_3$ (Navaza et al., 1990) also contains the 6-coordinated Fe(III) atom (FeC_5N) with Fe-N (NO), Fe-N (*trans* to NO) and the mean Fe-N (NC) bond distances of 1.665(1), 1.931(4) and 1.931(2), respectively. Each Ba(II) atom is 9-coordinated (triply capped trigonal prism) (BaN_5O_4).

In blue monoclinic $\{(H_2O)Fe(edta)\}_2Ba(H_2O)_4$ (Solans et al., 1984b), the edta ligands serve as bridges between the metal atoms. Each Fe(III) atom has pentagonal bipyramidal arrangement created by four O and two N atoms of edta ligand and O atom of water molecule completed the geometry (FeO_5N_2). The edta ligand about Fe(III) atom form 5-membered metallocycles with the N-Fe-N and N-Fe-O intraligand bond angles of 73.7(9) and 75.8(8)° (av.). Each Ba atom is coordinated by 11 O atoms (O atoms of carboxylate groups of edta and O atoms of water molecules) forming polymeric chains.

Also in red brown $[Fe(Hdpa)Ba(H_2O)_4]ClO_4$ (Chuklianova et al., 1981), the Fe(III) atom is 7-coordinated (FeO_4N_3). The pentagonal-bipyramidal geometry is created by the hepta-dentate Hdpa ligand. There are six 5-membered metallocycles, with mean N-Fe-N and N-Fe-O interligand bond angles of 74.7(2) and 74.0(2)°, respectively. Each Ba atom is 9-coordinated by five O atoms of Hdpa and four O atoms of water molecules (Table 1). The polymeric chains contain $Fe(Hdpa)^-$ and Ba^{2+} ions.

The structure of dark red tetragonal $In\{Fe_2(CO)_8\}_2K(thf)$ (Che-Chieh et al., 1993) is composed of an indium atom coordinated to four $Fe_2(CO)_8$ moieties. The complex lies on a crystallographic 4-fold inversion axis bisect the two Fe-Fe bonds: 2.900(2) Å, with the indium(I) residing on the inversion center. The Fe(0)-In bond distance is 2.627(1) Å ($InFe_4$). The coordination about the K(1) atom is created by a thf and two carbonyl oxygen atoms [one from each iron of an $Fe_2(CO)_8$ moiety] from each of four anions to give a total coordination number of nine (square antiprism) (KO_9). The K(1) atom is located on a crystallographic 4-fold axis, as is the thf.

In yellow triclinic $(NH_4)_2[Fe(CN)_6Tl]$ (Swartner et al., 1997), six CN^- groups built up an octahedral arrangement about each metal atom [Fe(III)C_6 and Tl(I)N_6] with mean Fe-C and Tl-N bond distances of 1.93(1) and 3.11(3) Å, respectively, and form polymeric chains.

The inner coordination sphere about each Fe(III) atom in $Fe(H_2O)(edta)Tl(H_2O)$ (Solans et al., 1984a) is similar to that in Solans et al., (1984b). A pentagonal bipyramid (FeO_5N_2) is built up by hexadentate (O_4N_2) edta ligand and water molecule. Each Tl(I) atom is also 7-coordinated (TlO_7) (Table 1).

The structure of orange monoclinic $(cp)Fe(C_5H_4Bpz_3)Tl$ (Yukle et al., 1996) is shown in Figure 2. The tris-1-pyrazolylborate moiety coordinates to two different thalium atoms, thereby generating a polymeric structure. The Tl-N distances are 2.638(5), 2.676(5) and 2.780(5) Å. The Fe(III) atoms are sandwiched (FeC_{10}).

The red tetragonal $(NMe_4)Fe(S)_{10}Ge_4$ was studied by three groups (Achak et al., 1996; Bowers et al., 1996; Akari et al., 1998), the crystallographic and structural data are in good agreement. The sulfur atoms bridged to metal atoms and are tetrahedrally coordinated [Fe(II)S_4, Ge(IV)S_4] with mean M-S bond distances of 2.37 Å (M=Fe) and 2.19 Å (M=Ge). For red brown $(NMe_4)_2Fe(S)_{10}Ge_4$ (Akari et al., 1998), only crystallographic data are available. In another red brown tetragonal $Cs_2Fe(S)_{10}Ge$ (Bowers et al., 1996), the sulfur atoms serve as bridges between metal atoms and form a polymeric structure. Each metal atom is tetrahedrally coordinated (MS_4).

There are five FeSn derivatives (Mammano et al., 1977; Graziani et al., 1980; Adam et al., 1990; Behrens et al., 1991; Schwarz et al., 1996; Yian et al., 1996; Enland et al., 1997) (Table 1). The structure of colorless orthorhombic $Fe(CN)_6(SnMe_3)_4(H_2O)$ (Behrens et al., 1991) is built up of non-linear $(\text{-Fe-C}\equiv\text{N-Sn-N}\equiv\text{C-})_n$ and $(H_2O\cdots H_2O\text{-Sn-N}\equiv\text{C-Fe-C}\equiv\text{N-Sn-}OH_2\cdots OH_2)$ chains [O···O 2.628(1) Å] are interlinked by the coordinated and 'zeolitic' water molecules, respectively. Each Fe(II) atom is 6-coordinated (FeC_6). The Sn(IV) atoms are 5-coordinated (SnC_3N_2 and SnC_3ON). Structures of another three FeSn derivatives (Adam et al., 1990; Schwarz et al., 1996; Yian et al., 1996) are very similar to that in Behrens et al., (1991).

The structure of $(cp)Fe(C_5H_4COO)Sn(CH{=}CH_2)_3$ (Graziani et al., 1980) is shown in Figure 3. Each Sn(IV) atom has a tetragonal-bipyramidal geometry, with vinyl groups in equatorial and two apical oxygen atoms from bridging carboxylate groups. The resulting structure is a linear polymer.

In the black monoclinic $(cp)_2FeBiCl_4$ (Mammano et al., 1977), the Bi(III) atom is coordinated by six chloride atoms in an irregular octahedral array, two pairs of Cl^- anions form bridges with neighboring Bi atoms resulting in an infinite chain of edge-sharing octahedra. The mean Bi-Cl (no-bridging) bond distance of 2.51(1) Å is much shorter than the remaining four Fe-Cl (bridging), with a mean of 2.875 Å [range: 2.70–3.10(1) Å]. The ferrocenium cations stack between the polymer chains with cp ring in the eclipsed conformation Fe-C, 2.07(1) Å.

The red brown monoclinic $(PhCH_2NMe_3)[(OC)_6(\mu\text{-H})Fe_2Bi_2(\mu\text{-Cl})_2]$ (Enland et al., 1997) has a tetrahedral Fe_2Bi_2 core edge-bridged across the iron centers by a hydrogen and across the bismuth centers by a chlorine atom. Two $[(OC)_6(\mu\text{-H})Fe_2Bi_2(\mu\text{-Cl})]$ units are connected by a chlorine atom and the molecules joined into infinite polymeric chains. The mean Fe-Bi and Fe-Fe bond distances are 2.654(2) and 2.759(2) Å, respectively. The Bi···Bi separations of 3.452(1) Å ruled out a direct bond. Each iron atom is hexa-coordinated (FeC_3HBi_2) and Bi atom is tetrahedrally coordinated ($BiCl_2Fe_2$).

In light pink monoclinic $[Zn\{Fe(CO)_4\}_2\{Na(thf)_2\}_2]$ (Pierpont et al., 1982), the zinc atom is located at a site of 2/m symmetry with the iron atom and two carbonyl groups of the independent $Fe(CO)_4$ fragment lying on a crystallographic minor plane. The Fe-Zn bond distance is 2.371(1) Å. There is strong ion pairing between dimeric $[Na_2(thf)_4]^{2+}$ cations and the carbonyl oxygen of the $[Zn\{Fe(CO)_4\}_2]^{2-}$ anions. Each Na(I) atom is coordinated by two bridging thf molecules, one terminal thf, and the carbonyl oxygens of three different complex molecules.

In the CdFe complex (Mulliza et al., 1990), both iron(II) and cadmium(II) centers have distorted octahedral symmetries. The cyanide groups serve as bridges between the metal atoms in the manner····Fe-C≡N-Cd···. The nitrosyl group

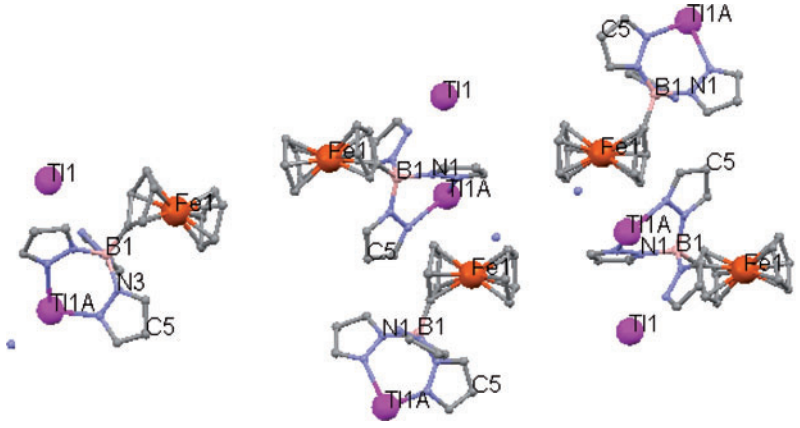

Figure 2 View of the structure of $(cp)Fe(C_5H_4Bpz_3)Tl$ (Yukle et al., 1996).

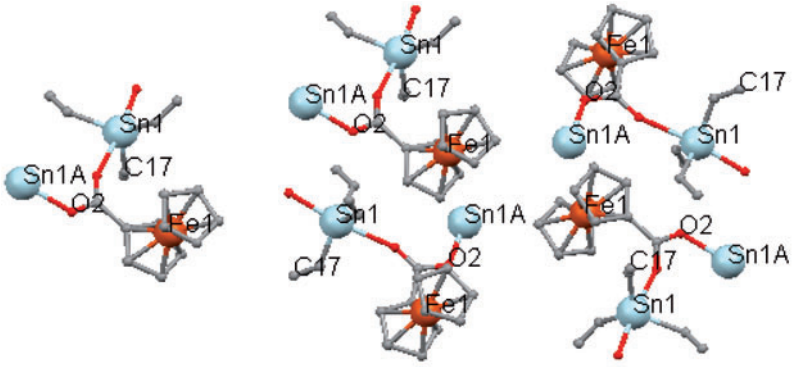

Figure 3 Scheme of the polymeric (cp)Fe(C_5H_4COO)Sn($CH{=}CH_2$)$_3$ (Graziani et al., 1980).

completed an octahedral coordination about each Fe(III) atom (FeC_5N) and a water molecule about each Cd(II) atom (CdN_5O). The two uncoordinated water molecules are hydrogen bonded to the coordinated water, and occupy channels in the crystal lattice. The coordinated water molecules bonded NO groups and are geometrically arranged so that extensive tunnel-like formations permeate the crystal lattice.

There are four yellow HgFe complexes, for which X-ray data are available and are given in Table 1. In monoclinic [Hg{Fe(μ-η^2-CO)$_4$}$_2${Na(thf)$_2$}$_2$] (Sosinski et al., 1983), the mercury atom is located at a site of 2/m symmetry with the iron atom and two carbonyl ligands of the independent $Fe(CO)_4$ moiety located on a crystallographic mirror plane (HgC_2Fe_2). The two remaining carbonyls are symmetrically related across the mirror plane. Coordination about iron approximates a trigonal bipyramid (FeC_4Hg) with the mercury atom at an axial site Fe-Hg=2.522(5) Å. Each sodium(I) atom is 5-coordinated (NaO_5).

Crystal structure of triclinic (dmtp)$_2$(H_2O)$_{1.5}$Fe(μ-η^2-NCS)$_4$Hg (Cingi et al., 1985) consists of two different octahedral iron complexes [Fe(NCS)$_4$(dmtp)$_2$(H_2O)] **(a)** and [Fe(NCS)$_2$(dmtp)$_2$(H_2O] **(b)** and tetrahedral [Hg(SCN)$_4$] units. The coordination of the iron(II) atom in complex **(a)** involves two N atoms from dmtp ligands in *trans* positions, an O atom from a water and three atoms from bridging NCS^- ligands (FeN_5O). Complex **(b)** differs from **(a)** in a second water molecule replacing a NCS group in the mutual orientations of the dmtp molecules (FeN_4O_2). Each Hg(I) is tetrahedrally coordinated (HgS_4).

In monoclinic (dmtp)$_2$(H_2O)Fe(μ-η^2-NCS)$_2$Hg(SCN) (Cingi et al., 1985), the (dmtp)$_2$(H_2O)Fe and Hg(SCN) moieties are triply bridges by thiocyanate groups in the manner -Fe-NCS-Hg- and form a polymeric chain. Each Fe(III) atom is 6-coordinated (FeN_5O) and each Hg(II) atom, tetrahedrally (HgS_4). The structure of another monoclinic (dmtp) (H_2O)$_2$Fe(μ-η^2-NCS)$_3$ Hg(SCN) Me_2CO (Cingi et al., 1985) is similar to the upper. Each Fe(III) atom is a distorted octahedral (FeN_4O_2) and Hg(II) tetrahedral (HgS_4) coordinated.

Conclusions

The data presented in this review cover almost 40 polymeric FeM (M=Mg, Ca, Zn, Ca, Sr, Ba, In, Tl, Ge, Sn, Bi, Zn, Cd and Hg) complexes for which the structural data are available. The crystal class of monoclinic (×26) in the series of complexes by far prevails, with some examples of tetragonal, orthorhombic each (×5) and triclinic (×3). The complexes are colored: red, red orange, red brown and yellow each (×8), colorless and black (×3), blue and green each (×1).

There are examples of ligands from unidentate to nonadentate, with most common O, N and C donor atoms. The iron atoms exist in the oxidation states 0, +2 and +3, from which +3 by far prevails. The inner coordination sphere about iron atoms are Fe(0): FeC_4M [M=In (Che-Chieh et al., 1993), Zn (Achak et al., 1996), Hg (Sosinski et al., 1983), FeC_{10} (Mammano et al., 1977; Graziani et al., 1980; Yukle et al., 1996), FeC_3HBr_2 (Enland et al., 1997)]; Fe(II): [FeN_3 (Höhn et al., 1991), FeS_4 (Achak et al., 1996; Bowers et al., 1996; Akari et al., 1998), FeC_6 (Adam et al., 1990; Behrens et al., 1991; Schwarz et al., 1996; Yian et al., 1996), FeN_5O and FeN_4O_2 (Cingi et al., 1985)]; Fe(III): [FeC_5N (Castellano et al., 1977, Klüfers and Haussül, 1985; Mulliza et al., 1990; Navaza et al., 1990; Johnson et al., 1991), FeC_6 (Mayer and Pichard, 1988; Meyer and Pickerdt, 1989; Swartner et al., 1997), FeO_4N_2 (Pavelčík and Kettmann, 1983), FeO_6 (Burger and Klüfers, 1966a,b; Calogero et al., 1977), FeO_5N_2 (Cohen and Hoard, 1966; Solans et al., 1984a,b), and FeO_4N_3 (Chuklianova et al., 1981)]. The mean Fe(0)-L bond distance elongated in the order: 1.69 Å (μ-H)<1.78 Å (μ-CO)<2.045 Å (C, cp)<2.317 Å (Zn)<2.522 Å (Hg)<2.627 Å (In)<2.641 Å (Bi). The Fe(0)-Fe(0) bond distance of 2.759(2) Å (Enland et al., 1997) is the shortest. The mean Fe(II)-L bond distance elongated in the order: 1.89 Å (μ_3-N)<1.905 Å (μ-CN)<2.13 Å (μ-NCS)<2.15 Å (OH_2)<2.21 Å (NL)<2.35 Å (μ-S). The mean Fe(III)-L bond distance elongated in the order: 1.67 Å (NO)<1.93 Å (μ-CN)<1.94 Å (CN)<1.95 Å (NL)<1.96 Å (OH_2)<1.98 Å (μ-OL)<1.99 Å (tetra-OL)<2.025 Å (μ-OH_2, μ-OH). There are heterodentate (O_4N_3) ligands, the Fe-O bond distances

are shorter than Fe-N bond distances with mean values of 2.045 and 2.337 Å, respectively.

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 of the respective metallocycles. In 5-member rings mean L-Fe-L intraligand angle opening in the sequence 75.4° (-OC_2N-)<79.0° (-NC_2N-).

The inner coordination sphere about the M atoms are: MgN_4O_2 (Johnson et al., 1991), CaN_4O_2 (Mayer and Pichard, 1988) and CaO_7 (Cohen and Hoard, 1966; Pavelčík and Kettmann, 1983); SrO_9+SrO_{10} (Burger and Klüfers, 1966b), SrO_3N_2+SrO_8 (Meyer and Pickerdt, 1989), Sr_4O_2 (Castellano et al., 1977) and SrN_5 (Höhn et al., 1991); BaO_8 (Burger and Klüfers, 1966a,b; Calogero et al., 1977), BaO_3N_3+BaO_5N_2 (Meyer and Pickerdt, 1989), BaN_5 (Höhn et al., 1991), BaO_5N_4+BaO_2N_2 (Klüfers and Haussül, 1985), BaN_5O_4 (Navaza et al., 1990), BaO_{11} (Solans et al., 1984b) and BaO_9 (Chuklianova et al., 1981); $InFe_4$ (Che-Chieh et al., 1993), TlN_6 (Swartner et al., 1997), TlO_7 (Solans et al., 1984a) and TlN_3 (Yukle et al., 1996); GeS_4 (Achak et al., 1996; Bowers et al., 1996; Akari et al., 1998), $GeSe_4$ (Akari et al., 1998); SnC_3ON+SnC_3N_2 (Adam et al., 1990; Behrens et al., 1991; Schwarz et al., 1996; Yian et al., 1996), SnC_3O_2 (Graziani et al., 1980); $BiCl_6$ (Mammano et al., 1977), $BiCl_2Fe_2$ (Enland et al., 1997), ZnC_4Fe_2 (Pierpont et al., 1982), CdN_5O (Mulliza et al., 1990), HgC_2Fe_2 (Sosinski et al., 1983) and HgS_4 (Cingi et al., 1985).

This review together with a review by Melník et al. (in press), which classified around 100 polymeric FeM (M=Li, Na, K, Rb and Cs) structures, shows the wide range of stereochemistry around iron as well as M atoms of the alkaline metals.

During the collection and organization of the data it became clear, despite the increasing availability of data retrieval systems, that tracing of relevant material is not always a straight forward 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 limitation in information retrieval, we believe that it is necessary to make a systematic overall review and that such a review serves the useful purpose of delineating areas of both interest and weakness.

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