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Analysis of crystallographic and structural data of polymeric FeM (M = transition metals, lanthanides) complexes

Review Article

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Abstract: This review covers crystallographic and structural data for almost fifty polymeric FeM complexes (M = transition Cu, Ag, Au, Mo, W, Mn, Co, Ni and Pt and lanthanide elements Sm, Er and Yb) where iron is involved in polymeric chains. The complexes are for the most part yellow or black, but there are complexes of brown, orange, red, purple, blue and green colour. The complexes crystallized in the monoclinic (by far prevails), triclinic, tetragonal, orthorhombic, trigonal, hexagonal and rhombohedral crystal classes. The iron atoms are found in oxidation states 0, +2 and +3, of which +3 by far prevails. The inner coordination spheres about the Fe(0) atom are tetrahedral (FeC_4) or sandwiched (FeC_{10}), Fe(II) atoms are six-coordinated, and Fe(III) are six or even seven-coordinated. The inner coordination about M atoms range from four- through six- to eight-coordinated. The shortest Fe-Fe, Fe-M (transition) and Fe-M (lanthanide) and M-M separations are: 8.08 Å, 3.033 Å for Fe-Cu, 3.010 Å for Fe-Yb and 2.505 Å for Mo-Mo.

Keywords: *Structure • Analysis • Polymers • Fe-M (M = transition) • Lanthanide*

1. Introduction

A characteristic feature of the d-group transition metals is their ability to form clusters with a variety of transition, non-transition, and lanthanide elements, and iron is no exception. Very diverse types of cluster exist. Many iron clusters are of considerable structural interest, as well as having industrial importance in catalytic and other reactions. Many structural studies of heterometallic iron clusters have been carried out. To date there have been comprehensive overviews of structural data of heterodimeric [1], heterotrimeric [2], heterotetrameric [3], heteropentameric [4], heterohexa- and heteroheptameric [5], heterocta- and heteroligomeric clusters [6]. Recently structural data of polymeric heterometallic iron complexes (FeM), M = non-transition metals were summarised [7,8].

Polymeric heterometallic iron complexes in which transition metals or lanthanides are coupled with iron atoms have not been reviewed to date. The aims of this review are to compare and analyse crystallographic and structural data of these polymeric heterometallic iron compounds.

2. Polymeric FeM (M = transition metals) complexes

Crystallographic and structural data for forty seven coloured polymeric FeM complexes are gathered in Table 1.

The structure of dark green monoclinic $Fe(CN)_6\{Cu(dien)\}_2 \cdot 6H_2O$ [9] consists of a polymer of $[Fe(CN)_6]^{4-}$ and $[Cu(dien)]^{2+}$ ions linked together through cyanide bridges. Of the six (CN)- groups around each iron(II), two are not bonded to Cu(II) atoms, but only interact through hydrogen bonds with the water molecules. Two $(CN)^-$ groups are bonded to Cu(II) atoms of adjacent $[Cu(dien)]^{2+}$ units giving rise to linear Fe-C≡N-Cu linkages which are coordinated in the equatorial plane of the square-pyramidal configuration, and the remaining two $(CN)^-$ coordinate to Cu(II) atoms of adjacent $[Cu(dien)]^{2+}$ units in the apical position of the pyramid, leading to non-linear Fe-C≡N-Cu chains. The mean Cu-N bond distance increased in the order: 1.97(1) Å (μ-NC_{eq}) < 2.03(1) Å (ter-dien) < 2.21(1) Å (μ-NC_{ap}). Another two FeCu complexes [10,11] have polymeric structures similar to [9].

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Table 1. Crystallographic and structural data for polymeric FeM (M = transition and lanthanide elements) complexes[a]

COMPOUND (colour)	Crys.cl Sp.Gr. Z	a [Å] b [Å] c [Å]	α [°] ß [°] γ [°]	Chromo-phore	M - L [Å]	L – M - L [°]	Ref.
$[(NC)_2Fe(\mu\text{-}\eta^2\text{-}CN)_4\cdot\{Cu(\eta^3\text{-dien})\}_2]\cdot 6H_2O$ (dark green)	m C2/c 8	27.438(3) 7.778(1) 14.869(2)	 100.9(1) 	$Fe^{III}C_6$ $Cu^{II}N_5$	NC[b]1.90(1,1) μNC 1.91(1,0) η^3N 2.03(1,0) μCN 1.99(1,2)	C,C[b] 87.9(5,2.8) N,N 83.5(5,4)[c] 96.6(5,1.9)	9
$[\{(NC)_2Fe(\{\mu\text{-}\eta^2\text{-}CN)_4\}_2\{Cu(\eta^3\text{-dien})\}_3(H_2O)_6]$ (dark green)	m $P2_1/c$ 4	20.332(6) 14.162(5) 14.932(5)	 96.29(3) 	$Fe^{II}C_6$ $Cu^{II}N_5$ (x 2) $Cu^{II}N_4O$	NC 1.95(2,2) μNC 1.95(2,4) η^3N 2.01(2,2) μCN 1.98(2,3) 2.31(2,1) η^3N 2.01(2,2) μCN 1.99(1) H_2O 2.41(1)	C,C 90.0(7,4.4) 177.4(8,2.5) N,N 83.5(6,6)[c] 89.0(6,14.8) 162.9(6,8.0) N,N 84.2(7,1.4)[c] 93.0(7,5.9) 178.3(7) N,O 94.0(6,9.4)	10
$[\{(NC)_2Fe(\mu\text{-}\eta^2\text{-}CN_4\}_2\cdot\{Cu(\eta^3\text{-dien})\}_3(H_2O)_3]$ (dark blue)	m $P2_1/a$ 4	14.896(3) 14.128(5) 20.267(6)	 96.31(3) 	$Fe^{II}C_6$ $Cu^{II}N_5$ (x 2) $Cu^{II}N_4O$	NC 1.92(1,2) μNC 1.93(1,4) η^3N 2.03(2,1) μCN 2.14(1,15) η^3N 2.03(1,2) μCN 1.96(1) H_2O 2.43(1)	C,C not given N,N not given N,N not given	11
$\{[Fe(CN)_6][H_2Fe(CN)_6]_{0.5}\cdot[Cu(\eta^4\text{-tmppor})(H_2O)]\}\cdot 1.5H_2O$ (blue)	m C2/c 4	20.756(3) 21.311(3) 30.109(4)	 102.79(2) 	$Fe^{II}C_6$ $Cu^{II}N_4O$	NC 1.926(15,22) η^4N 2.000(9,5) H_2O 2.538(8)	C,C 90.0(6,3.9) 178.2(6,4.0) N,N 90.0(4,8) 176.4(3,3.1)	12
$[(\eta^4\text{-acac})Fe\{Cu\cdot(\mu\text{-Mesalen})\}_3](PF_6)_2$ (dark)	hx $P6_122$ 6	14.471(2) 50.372(2)	 	$Fe^{II}O_6$ $Cu^{II}O_3N_2$	η^4O 1.967(2,0) LμO 2.023(7,10) μO 1.932(8,8) 2.397(8) LN 1.94(1,1)	O,O 75.4(3)[c] 92.4(3,5.0) 172.7(3) O,O 80.3(3) 101.1(4,7.4) N,N 88.5(4)[c] O,N 95.8(4,4.4)[d] 158.2(4,5.4)	13
$[\{Fe(\mu\text{-edta})\}_2Cu\cdot(\eta^2\text{-en})_2(H_2O)_2(\mu\text{-O})]$ (blue)	m C2/c 8	16.662(2) 15.254(3) 18.751(3)	 102.58(1) 	$Fe^{III}O_4N_2$ $Cu^{II}N_4O_2$	μO 1.773(1) LO 2.024(2,15) LN 2.236(2,10) η^2N 2.006(3,7) LO 2.678(3) H_2O 2.652(3)	O,O 96.8(1,6.5) N,N 80.2(1)[c] O,N 78.1(1,1.6)[c] 92.1(1,8.8) 164.7(1,9.9) N,N 84.8(1,1.6)[c] 86.2(1,3.3) 102.5(1)	14
$[Fe(\mu\text{-acac})_3Ag\cdot(OClO_3)(H_2O)]$ (dark red)	m $P2_1/c$ 4	12.274(5) 11.761(5) 17.235(5)	 120.64 (12)	$Fe^{III}O_6$ $Ag^{I}O_2C$	LO 2.00(1,3) H_2O 2.25(2) O_3ClO 2.50(2) LC 2.29(2)	O,O 88.0(4,1.6)[d] 90.5(4,3.2) 176.7(4,3.1) O,O 100.5(4) O,C 86.0(4)	15
$[(H_2O)Fe(\mu\text{-edta})\cdot Ag(H_2O)_2]$ (yellow brown)	m Cc 4	8.928(4) 11.871(1) 15.116(2)	 99.85(2) 	$Fe^{III}O_5N_2$ $Ag^{I}O_6$	LO 1.957(7) 2.052(7,49) LμO 2.079(6) LN 2.340(8,2) H_2O 2.109(7) LO 2.351(7) 2.558(7,56) LμO 2.673(6) H_2O 2.334(7)	not given not given 	16
$[Fe(\mu\text{-}cpS_2CNEt_2)_2Ag]\cdot ClO_4\cdot CH_2Cl_2$ (yellow) (at 173 K)	m C2/c 4	20.066(5) 9.859(3) 18.463(5)	 113.02(3) 	FeC_{10} $Ag^{I}C_4S_2$	cpC not given cpμC 2.972(8) 3.027(8) S 2.286(3,0)	not given not given 	17
$[\{CH_2(Ph_2PS)_2Ag\}_2\cdot(\mu\text{-dptdf})_2](ClO_4)_2\cdot CH_2Cl_2$ (orange) (at 173 K)	m C2/c 4	26.933(4) 11.209(2) 31.404(3)	 105.74(1) 	FeC_{10} $Ag^{I}S_4$	cpC not given S 2.524(2,2) μS 2.530(2) 2.801(2)	not given S,S 99.3(1,5.7) 125.0(1,4.8)	18

Continued **Table 1.** Crystallographic and structural data for polymeric FeM (M = transition and lanthanide elements) complexes[a]

COMPOUND (colour)	Crys.cl Sp.Gr. Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromo-phore	M - L [Å]	L – M - L [°]	Ref.
$[ClAu(\mu\text{-dppf})] \cdot 0.4CH_2Cl_2$ (yellow)	or F2dd 16	11.096(4) 31.507(10) 39.71(3)		FeC_{10} Au^IP_2Cl	cpC not given LP 2.303(6,6) Cl 2.624(9)	not given P,P 143.0(2) P,Cl 108.4(2,4.4)	19
$[ClAu(\mu\text{-dppf})] \cdot 2.85CHCl_3$ (yellow)	m $P2_1c$ 4	12.917(6) 18.321(6) 16.242(4)	110.1(1)	FeC_{10} Au^IP_2Cl	cpC not given LP 2.315(2,0) Cl 2.580(3)	not given P,P 136.5(1) P,Cl 111.7(1,1.0)	19
$[ClAu(\mu\text{-dppf})] \cdot CH_2Cl_2$ (yellow)	m $P2_1/c$ 4	11.059(7) 24.154(9) 13.122(4)	128.94(4)	FeC_{10} Au^IP_2Cl	cpC 2.046(6,3) LP 2.308(2,15) Cl 2.709(2)	C,C not given P,P 155.2(1) P,Cl 102.4(1,11.2)	20
$[Fe_{0.5}Cr_{0.5}Mo_3(\mu\text{-O}) \cdot (\mu_3\text{-O})_3(\mu\text{-}\eta^2\text{-pr})_5 \cdot (\mu\text{-pr})_3Na]_2$ (black)	tr P-1 1	12.981(5) 14.021(4) 12.356(4)	109.81(4) 117.5(3) 90.36(4)	$Fe^{III}/Cr^{III}O_6$ $Mo^{IV}O_6$ Na^IO_5	μ_3O 1.980(9,4) prO 1.99(1,2) μ_3O 1.937(9,27) μO 1.997(9,10) prO 2.08(2,8) Mo 2.519(2,14) prO 2.31(2,8)	O,O 89.5(4,7) 177.0(7,1.2) O,O 90.0(4,10.8) 171.0(4,7.3) Mo,Mo 60.0(1,5) O,O 81.2-155.7(5)	21
$[Fe_2\{Mo_3(\mu\text{-O})(\mu_3\text{-O})_3 \cdot (\mu\text{-}\eta^2\text{-pr})_5(\mu\text{-pr})_3\}_2Na_2]$ (black)	tr P-1 1	12.988(6) 14.021(3) 12.378(9)	109.79(5) 117.50(4) 90.52(5)	$Fe^{III}O_6$ $Mo^{IV}O_6$ Na^IO_5	μ_3O 1.992(8,19) prO 1.993(8,18) μ_3O 1.946(7,29) 2.027(7,28) μO 1.916(7,3) prO 2.084(7,93) Mo 2.517(1,12) prO 2.30(2,10)	O,O 90.0(3,3.8) 176.4(3,1) O,O not given O,O not given	22
$[Fe_2\{W_3(\mu\text{-O})(\mu_3\text{-O})_3 \cdot (\mu\text{-}\eta^2\text{-pr})_5(\mu\text{-pr})_3\}_2Na_2]$ (black)	tr P-1 1	12.984(6) 14.072(7) 12.436(9)	109.91(5) 117.54(4) 90.52(5)	$Fe^{III}O_6$ $W^{IV}O_6$ Na^IO_5	μ_3O 1.98(2,2) prO 2.02(2,3) μ_3O 1.98(1,1) 2.04(1,2) μO 1.92(2,0) prO 2.092(2,75) W 2.535(9,17) prO 2.26(2,15)	O,O 90.0(4,4.6) 176.0(4,4) O,O not given O,O not given	22
$(NMe_4)_2(NH_4)_2 \cdot [Fe_2Mo_{12}O_{30}(H_2PO_4)_6 \cdot (HPO_4)_2] \cdot 11H_2O$ (orange)	rh R-3m 1	14.274(3)	51.64(1)	$Fe^{III}O_6$ Mo^VO_6	μ_3O 2.13(2,0) O 1.91(2,0) O 1.63(2) 2.02(2,8) 2.27(1) Mo 2.589(1)	O,O not given O,O not given	23
$(NMe_4)_2Na_4 \cdot Fe_3Mo_{12}O_{30}(HPO_4)_8 \cdot 16H_2O$ (orange)	tr P-1 2	12.719(5) 13.844(7) 18.701(6)	109.34(4) 119.22(7) 83.42(3)	$Fe^{III}O_6$ Mo^VO_6	μ_3O 2.16(2,6) O 1.66(2,2) 2.02(2,10) 2.28(2,3) Mo 2.591(3,4)	O,O not given	23
$[(ON)Fe(\mu\text{-}\eta^2\text{-CN})_5 \cdot Mn(H_2O] \cdot 2H_2O$ (brown)	m $P2_1/n$ 4	7.302(4) 14.782(6) 10.751(1)	91.47(2)	$Fe^{III}C_5N$ $Mn^{II}N_5O$	μNC 1.935(2,8) ON 1.659(2) μCN 2.226(2,35) H_2O 2.218(2)	C,C 87.6(1,3.6) 171.1(1,7) C,N 74.4(1,1.7) 176.80(7) N,N 90.3(1,6.9) 170.0(1,1.3) N,O 88.2(1,6.1) 171.46(6)	24
$(NMe_4)[(NC)_4Fe \cdot (\mu\text{-}\eta^2\text{-CN})_2Mn \cdot (H_2O)_4] \cdot 4H_2O$ (brown)	tg P4/n 2	10.670(2) 10.568(2)		$Fe^{III}C_6$ $Mn^{II}O_4N_2$	NC 1.939(2,0) μNC 1.938(4,4) H_2O 2.188(2,0) μCN 2.202(4,16)	C,C 91.5(4) O,N 92.2(1)	25
$[(NC)_4Fe(\mu\text{-}\eta^2\text{-CN})_2 \cdot Mn(\eta^4\text{-acacen})]$ (brown)	or Pnma 4	17.415(5) 19.79(1) 14.471(4)		$Fe^{III}C_6$ $Mn^{III}N_4O_2$	NC 1.960(5,5) μNC 1.953(4,0) μCN 2.316(4,0) η^4N 1.973(5,7) η^4O 1.909(4,3)	C,C not given N,N 172.0(2)	26
$[(NC)_2Fe(\mu\text{-}\eta^2\text{-CN})_4 \cdot \{Mn(\mu\text{-}\eta^4\text{-salmen})\}_4] \cdot ClO_4 \cdot H_2O$ (dark brown)	tg I4/m 4	18.756(3) 28.279(3)		$Fe^{III}C_6$ $Mn^{III}N_4O_2$	NC 1.97(1,4) μNC 1.94(1,0) μCN 2.19(1) η^4N 1,96(1,2) η^4O 1.885(9,9) $\eta^4\mu$O 2.847(9)	C,C 90.0(5,1.6) N,N 94.8(4,4.8) N,O 95.5(4,6)	27

Continued **Table 1.** Crystallographic and structural data for polymeric FeM (M = transition and lanthanide elements) complexes[a]

COMPOUND (colour)	Crys.cl Sp.Gr. Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromo-phore	M - L [Å]	L – M - L [°]	Ref.
$[(NC)_2Fe(\mu\text{-}\eta^2\text{-}CN)_2 \cdot \{Mn(\mu\text{-}3\text{-salmen}\}_2K] \cdot 2dmf$ (dark brown)	m $P2_1/c$ 4	13.750(4) 12.456(2) 15.646(2)	 102.91(1)	$Fe^{III}C_6$ $Mn^{III}N_4O_2$ K^IO_8	NC 1.941(7,0) μNC 1.937(6,6) μCN 2.290(5) 2.415(5) LN 1.969(5,16) LμO 1.873(4,5) LμO 2.755(4,3.4) 3.160(4,51)	C,C 90.0(2,3.6) N,N 90.0(3,5.6) 173.8(2) O,O 51.0(1,5) 60.6(1,2.2)	27
$(NBu^n_4) \cdot [Fe(\mu\text{-}\eta^2\text{:}\eta^2\text{-}ox)_3Mn]$ (yellow) (by neutron diff.)	hx $P6_3$ 2	9.482(2) 17.827(8)		$Fe^{III}O_6$ $Mn^{II}O_6$	η^2O 2.056(6,0) 2.082(6,0) η^2O 2.110(6,0) 2.138(6,0)	O,O 79.5(2,0)[c] 94.1(2,4.0) 167.8(2,0) O,O 78.2(2,0)[c] 94.2(2,2.5) 168.3(2,0)	28
$\{N(n\text{-}C_5H_{11})_4\} \cdot [Fe(\mu\text{-}\eta^2\text{:}\eta^2\text{-}ox)_3Mn]$ (yellow) (at 120 K)	or $C222_1$ 4	9.707(3) 16.140(2) 19.883(7)		$Fe^{III}O_6$ $Mn^{II}O_6$	η^2O 2.102(6,0) 2.103(6,0) 2.129(6,0) η^2O 2.085(6,3) 2.108(6,0)	O,O 77.7(2,1.1)[c] 95.2(3,5.8) 166.2(4,3.0) O,O 79.3(3,5)[c] 94.8(2,6.0) 167.2(2,2.8)	29
$[Fe(cp^*)_2] \cdot [Fe(\mu\text{-}\eta^2\text{:}\eta^2\text{-}ox)_3Mn]$ (yellow)	m $P2_1/m$ 2	9.0645(8) 17.143(3) 9.215(4)	 93.66(8)	FeC_{10} FeO_6 MnO_6			30
$[\{Fe(\mu\text{–dfed})Co\} \cdot (\mu\text{-}\eta^2\text{-}NCS)]ClO_4$ (red)	m $P2_1/n$ 4	14.373(1) 12.438(2) 15.814(1)	 93.28(1)	$Fe^{II}N_4O_2$ $Co^{II}O_2N_2S$	LμO 2.229(3,27) LμN 2.142(3,8) 2.376(4) μSCN 2.087(3) LμO 1.899(3,2) LμN 1.867(3,0) μNCS 2.575(1)	N,N 75.5(1.2)[c] 86.8–124.4(1) O,O 69.7(9) N,O 79.5(1,9)[d] 84.3;140.9(1,8.4) O,O 83.4(1) N,N 85.5(1)[c] O,N 95.0(1,9)[d] 171.6(1,2.5) O,S 92.3(1,2.9) N,S 96.0(1,6)	31
$(PPh_4)[(NC)_4Fe(\mu\text{-}\eta^2\text{-}CN)_2 Ni(\eta^2\text{-}1,2\text{-}pn)_2] \cdot 2H_2O$ (yellow)	m $P2_1/c$ 2	12.958(3) 8.437(3) 17.250(2)	 99.96(1)	$Fe^{III}C_6$ $Ni^{II}N_6$	NC 1.957(9,2) μNC 1.978(7,0) η^2N not given μCN not given	C,C not given N,N not given	32
$(H_2O)_2Fe(\mu\text{-}\eta^2\text{-}NC)_4Ni] \cdot 2C_4H_8O_2$ (grey yellow)	m $P2_1/n$ 1	7.222(1) 7.470(1)	 94.11(1)	$Fe^{II}N_4O_2$ $Ni^{II}C_4$			33
$[(H_3N)_2Fe(\mu\text{-}\eta^2\text{-}NC)_4Ni] \cdot 2C_6H_6$ (grey-yellow)	tg ? ?	7.34 8.31		$Fe^{II}N_6$ $Ni^{II}C_4$			34
$[(H_3N)_2Fe(\mu\text{-}\eta^2\text{-}NC)_4Ni] \cdot 2$ aniline (grey-yellow)	tg ? ?	7.30 9.18		$Fe^{II}N_6$ $Ni^{II}C_4$			34
$[(H_3N)_2Fe(\mu\text{-}\eta^2\text{-}NC)_4Ni] \cdot 2C_6H_6$ (grey-yellow)	tg P4/mmm 1	7.353(2) 8.316(2)		$Fe^{II}N_6$ $Ni^{II}C_4$	H_3N 2.20(1,0) μCN 2.183(8,0) μNC not given	N,N not given C,C not given	35
$[(py)_2Fe(\mu\text{-}\eta^2\text{-}NC)_4Ni]$ (yellow)	m C2/m 2	15.426(3) 7.392(2) 7.067(2)	 101.26(2)	$Fe^{II}N_6$ $Ni^{II}C_4$	pyN 2.208(7,0) μCN 2.155(5,0) μNC not given	N,N not given C,C not given	35
$[(NC)_2Fe(\mu\text{-}\eta^2\text{-}CN)_4 \cdot \{Ni(\eta^2\text{-}Me_2en)_2\}_2] (CF_3SO_3) \cdot 2H_2O$ (black)	m $P2_1/n$ 2	10.300(6) 20.632(4) 10.352(7)	 109.45(4)	$Fe^{III}C_6$ $Ni^{II}N_6$	NC 1.97(2,0) μNC 1.96(2,4) η^2N 2.12(2,8) μCN 2.11(1,0)	C,C 90.0(6,2.6) N,N 81.6(9,2.6)[c] 92.2(7,9.8) 177(1,3)	36

Continued **Table 1.** Crystallographic and structural data for polymeric FeM (M = transition and lanthanide elements) complexes[a]

COMPOUND (colour)	Crys.cl Sp.Gr. Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromo-phore	M - L [Å]	L – M - L [°]	Ref.
$[(NC)_2Fe(\mu\text{-}\eta^2\text{-}CN)_4 \cdot \{Ni(\eta^2\text{-}Me_2en)_2\}_2] \cdot bzO.0.6H_2O$ (black)	tr P-1 2	10.413(6) 22.060(6) 10.377(3)	101.78(2) 95.71(4) 77.29(3)	$Fe^{III}C_6$ $Ni^{II}N_6$	NC 1.963(9,4) μNC 1.953(7,14) η^2N 2.113(7,25) μCN 2.121(6,28)	C,C 90.0(3,1.4) 178.7(4,7) N,N 83.3(3,2.1)[c] 90.3(3,4.3) 178.4(3,6)	36
$[(NC)_2Fe(\mu\text{-}\eta^2\text{-}CN)_4 \cdot \{Ni(\eta^2\text{-}Me_2en)_2\}_2] N_3 \cdot 4H_2O$ (black)	tr P-1 2	10.314(1) 10.347(1) 10.223(1)	93.23(1) 106.15(1) 86.37(1)	$Fe^{III}C_6$ $Ni^{II}N_6$	NC 1.937(7,8) μNC 1.948(6,6) η^2N 2.104(3,2) μCN 2.100(5,12)	C,C 90.0(2,1.3) N,N 81.5(2,1)[c] 91.7(2,6.8)	36
$[Fe(\mu\text{-}\eta^2\text{-}CN)_6 \cdot \{Ni(\eta^2\text{-}en)_2\}_3](PF_6)_2$ (purple)	tg R-3 3	13.743(1) 17.802(2)		$Fe^{II}C_6$ $Ni^{II}N_6$	μNC 1.913(4,0) η^2N not given μCN 2.104(3,0)	C,C not given N,N not given	37
$[Fe(\mu\text{-}\eta^2\text{-}CN)_6 \cdot \{Ni(\eta^2\text{-}en)_2\}_3](PF_6)_2$ (purple)	tg R-3 3	14.588(1) 17.050(2)		$Fe^{II}C_6$ $Ni^{II}N_6$	μNC 1.936(2,0) η^2N not given μCN 2.160(2,0)	C,C not given N,N not given	37
$[Fe(\mu\text{-}\eta^2\text{-}CN)_6 \cdot \{Ni(\eta^2\text{-}en)_2\}_3](ClO_4)_2$ (purple)	tg R-3 3	14.337(2) 17.294(4)		$Fe^{II}C_6$ $Ni^{II}N_6$	μNC 1.930(2,0) η^2N not given μCN 2.164(3,0)	C,C not given N,N not given	37
$[Fe(cp^*)_2Ni\{S_2C_2 \cdot (CN)_2\}_2]$ (black)	m $P2_1/c$ 4	9.959(1) 12.338(2) 25.086(6)	99.54(1)	FeC_{10} $Ni^{II}S_4$	cp*C 2.07 S 2.141	C,C not given S,S not given	38
$[Fe(cp^*)_2Ni\{S_2C_2 \cdot (CF_3)_2\}_2]$ (black) (at 203 K)	m C2/c 4	14.417(4) 12.659(2) 18.454(6)	95.17(2)	FeC_{10} $Ni^{II}S_4$	cp*C 2.087 S 2.135	C,C not given S,S not given	38
$\alpha\text{-}[Fe(cp^*)_2Pt \cdot \{S_2C_2(CN)_2\}_2]$ (black)	m C2/m 6	16.802(3) 21.035(3) 12.342(4)	94.52(4)	FeC_{10} $Pt^{II}S_4$	cp*C 2.098 S 2.265	C,C not given S,S not given	38
$\beta\text{-}[Fe(cp^*)_2Pt \cdot \{S_2C_2(CN)_2\}_2]$ (black)	tr P-1 3	10.106(2) 14.152(5) 14.394(5)	108.94(3) 96.27(2) 90.51(2)	FeC_{10} $Pt^{II}S_4$	cp*C 2.085 S 2.265	C,C not given S,S not given	38
$[Fe(\mu\text{-}\eta^2\text{-}CN)_6 \cdot Sm(H_2O)_4]$ (red)	m $P2_1/m$ 2	7.431(1) 13.724(3) 7.429(1)	119.95(1)	$Fe^{III}C_6$ $Sm^{III}N_6O_2$	μNC 1.93(3) μCN 2.505(15) H_2O 2.401(1)		39
$[Fe(\mu\text{-}\eta^2\text{-}CN)_6Er \cdot (H_2O)_4]$ (red)	or Cmcm 4	7.3212(6) 12.7576(8) 12.5636(9)		$Fe^{III}C_6$ $Er^{III}N_6O_2$	μNC 1.925(2,0) 1.944(4,0) μCN 2.420(5,15) H_2O 2.317(4,6)	C,C 90.0(2,1.2) 180.0(2) N,N 75.4(1,1.7) 115.5(2,2.6) 142.4(1) O,O 109.9(2)	40
$[(OC)_2Fe(\mu\text{-}\eta^2\text{-}CO)_2 \cdot Yb(NCMe)_3]_2 \cdot MeCN$ (orange) (at 213 K)	m $P2_1/c$ 4	21.515(8) 7.838(2) 19.866(6)	105.47(2)	FeC_4 $Yb^{II}N_3O_2$	OC 1.762(8,8) μOC 1.722(7,7) Yb 3.011(1,1) LN 2.509(7,22) μCO 2.377(5,3)	C,C 109.1(3,9.6) C,Yb 76.4(2,4.3) 175.7(3) N,N 83.0(2,4.3) O,O 81.3(2) N,O 86.7(2,7.9) 161.1(2,3.7)	41 42
$(OC)Fe(\mu\text{-}\eta^2\text{-}CO)_3 Yb(NCMe)_3$ (orange) (at 113 K)	m $P2_1/m$ 4	8.364(3) 9.605(5) 17.240(6)	92.22(3)	FeC_4 $Yb^{II}O_3N_3$	OC 1.75(1) μOC 1.73(1,1) Yb 3.046(1) μCO 2.452(8,8) 2.541(6) LN 2.559(9,12)	C,C 109.0(6,11.3) C,Yb 76.7(4,9) 174.8(3) O,O 79.2(3,1.4) 140.0(2) N,N 74.9(3) 138.2(3,1.1) O,N 75.1(3,10.6) 141.0(3,1.2)	42

Footnotes: [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 - member metallocyclic ring. [d]The six - member metallocyclic ring.

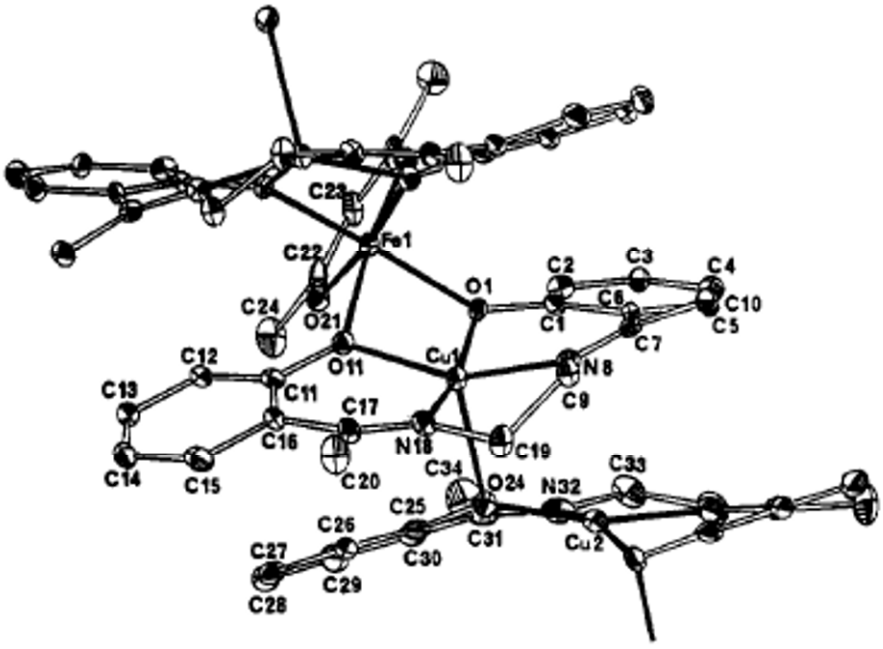

Figure 1. Structure of $[\eta^4\text{-acacFe}\{Cu(\mu\text{-Mesalen})\}_3]^{2+}$ [13]

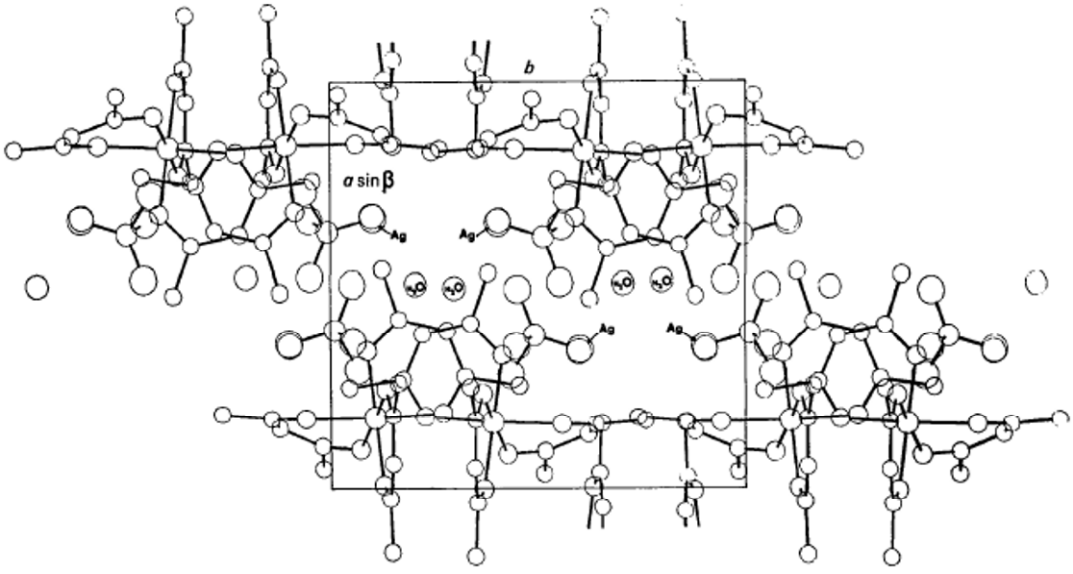

Figure 2. Structure of $Fe(acac)_3Ag(OClO_3)(H_2O)$ [15]

In blue monoclinic FeCu complex [12] the Cu(II) has a square-pyramidal geometry (CuN_4O), with four N atoms of porphyrin ligand in the square plane and water in an axial position. The porphyrins are stacked in a regular sandwich array, with interporphyrin distance of 3.85 Å and Cu...Cu separation of 5.95 Å. There are two types of ferrocyanide ions in the structure. The first type (one per porphyrin) is in the water rich regions and appears to form a dimer (Fe...Fe = 8.68 Å) held together by hydrogen bonding to water sitting at the intersection of the CN vectors. The second type of $Fe(CN)_6^{4-}$ (0.5 per porphyrin, situated on an inversion center) is embedded in the hydrophobic region of the structure. The two types of ferrocyanide units are linked *via* hydrogen bonded waters. The crystal lattice also contains a very large amount of lattice water, with hydrogen bonds as well as van der Waals interactions involved in the connections between the complex units.

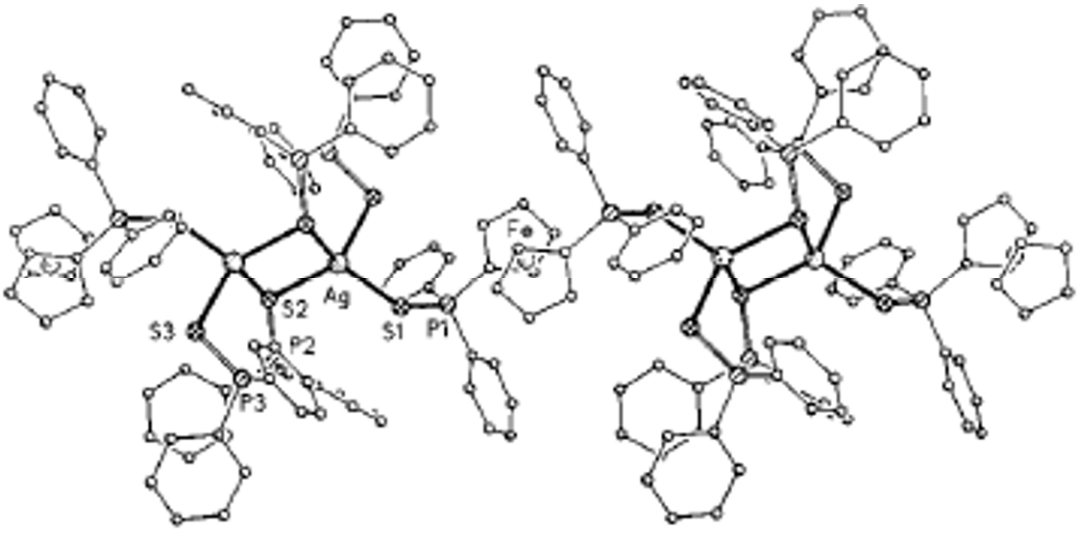

Figure 3. Structure of $[\{CH_2(Ph_2PS)_2Ag\}_2(\mu\text{-dptdf})]^{2+}$ [18]

The cation $[\{Cu(Mesalen)\}_3Fe(acac)]^{2+}$ of the (3 CuFe) system has a polymeric structure [13]. The asymmetric unit is formed by a trinuclear $\{Cu(Mesalen)\}_2Fe(acac)\}$ unit plus a Cu(Mesalen) unit. The asymmetric units are related one to another by binary axes passing respectively through the Fe(1) or the Cu(2) atoms (Fig. 1). The Fe(II) atom is six coordinated (FeO_6). Each Cu(II) atom is five coordinated (CuO_3N_2). The Fe-Cu and Cu-Cu distances are 3.033(2) and 3.654(2) Å respectively.

Monoclinic $[Cu(en)_2(H_2O)_2\{Fe(edta)\}_2(\mu\text{-O})]$ [14] is a three-dimensional polymer consisting of a μ-oxo Fe(edta) dimers connected with two different $Cu(en)_2$ moieties [Cu(1) and Cu(2)] sitting on non equivalent inversion centres. In one case the ligand edta provides a carboxylate group that coordinates axially to the Cu(2) atom. In the other, a water molecule axially coordinated to Cu(1) forms a hydrogen bond with a carboxylate coordinated to the Fe(III) atom. Each Cu(1) atom is connected with four Fe(III) atoms through hydrogen bonds. The Cu(2) is linked to an iron atom through a covalent iminoacetate group ($-N-CH_2COO^-$). This connection is reproduced by symmetry, and an ordered bimetallic chain of the type [...Cu(2)…Fe...Fe…Cu(2)... Fe...Fe...] is formed. Some relevant intermetallic distances are Fe...Fe 3.533(1), Fe…Cu(1) 5.734(1), Fe'…Cu(1) 5.986(1) and Fe…Cu(1) 6.681(1) Å.

There are four polymeric FeAg complexes [15-18] (Table 1). In dark red monoclinic $Fe(acac)_3Ag(OClO_3)(H_2O)$ [15] the $Fe(acac)_3$ moieties are arranged in a staggered array along z to form a bulky sheet-like structure parallel to the bc plane (Fig. 2). These sheets create "cylindrical holes" in a direction parallel to y. These "holes" are filled with Ag(I) and perchlorate ions. The Fe(III) atom is six coordinated (FeO_6), built up by three bidentate chelating acac ligands. Each Ag(I) atom is surrounded by a perchlorate oxygen, the hydrate oxygen and the central carbon atom of one acac ring (AgO_2C). The bulky sheet like structure is created by covalent Ag-C (centre carbon atom of acac ring) bonds, (2.29 Å).

In yellow brown monoclinic $Fe(edta)Ag(H_2O)_3$ [16] the Fe(III) atom is surrounded by four O atoms and two N atoms of an edta ligand, which acts in hexadentate fashion, and by a water molecule (FeO_5N_2). The coordination polyhedron is of roughly pentagonal bipyramidal shape. Each Ag(I) atom is six coordinated (AgO_6). The anions form layers along a crystallographic plane. Single layers are loosely linked by the cations into neutral double layers. Cohesion between double layers is realized by hydrogen bonds formed between water molecules and carboxylate O atoms as well as by van der Waals interaction.

In linear one dimensional polymeric $[Fe(C_5H_4S_2CNEt_2)_2Ag]ClO_4 \cdot CH_2Cl_2$ [17] the Ag(I) centres are bonded to two sulphur atoms of different ferrocene moieties, and also to the cyclopentadienyl ring in an η^2 fashion. The silver atom lies on an inversion centre and the iron atom on the twofold axis.

In the structure of orange $[\{CH_2(Ph_2PS)_2Ag\}_2(\mu\text{-dptdf})](ClO_4)_2 \cdot CH_2Cl_2$ [18] the complex cationic units are repeated to form a polymeric chain (Fig. 3). The single Ag(I) atom displays a distorted tetrahedral geometry, and is coordinated to a chelating $(SPPh_2)_2CH_2$ ligand (atoms S2 and S3) where one sulphur atom (S2) also forms a bridge to an adjacent silver atom, leading to four-membered Ag_2S_2 rings with inversion symmetry.

The Ag…Ag separation of 3.554(1) Å ruled out a direct bond. The mean Ag-S-Ag bond angle is 83.43(6)°. There are three yellow $[Fe(C_5H_4PPh_2)AuCl]•S$ ($S = 0.4CH_2Cl_2$) [19], $0.48CHCl_3$ [19] and CH_2Cl_2 [20] which are isostructural. All three compounds comprise polymeric chain structures involving bridging ferrocenylphosphine units linking trigonal (P_2AuCl) groups. The Fe…Au, Fe…Fe and Au…Au separations of 4.2, 11.2 and 8.4 Å, ruled out a bond.

The structure of the triclinic black $Na_2Fe_{0.5}Cr_{0.5}Mo_3$ cluster [21] consists of a centrosymmetric cluster anion $[(pr)_8Mo_3O_4FeCrO_4Mo_3(pr)_8]^{2-}$, in which two $[Mo_3O_4(pr)_8]^{4-}$ units are joined by two M (M = Cr, Fe) atoms through four μ_3-O (from μ–O atoms in both the Mo_3 units) and eight bridging propionate groups as shown in Fig 4. The anions are connected by Na(1) cations to form a one dimensional infinite chain structure. Each Na(1) atom is coordinated to five O atoms to form a trigonal bipyramid, consisting of one capping O, three O atoms from one anion and one O atom from another. Each Fe(III) and Cr(III) atom is coordinated by six O atoms, two from μ_3–O atoms and four from propionate bridges. Also each Mo(III) atom is bonded to six O atoms, three bridging O atoms (one μ–O and two μ_3-O atoms for Mo(2) and Mo(3), three μ_3–O atoms for Mo(1)), one O_t (terminal pr) and two O_{br} (bridging pr) atoms, forming a distorted octahedron. The mean value of the Mo–Mo bond distance is 2.519(2) Å (Table 1).

The structure of $[Fe_2\{M_3(\mu\text{-}O)(\mu_3\text{-}O)_3(\mu\text{-}\eta^2\text{-}pr)_5(\mu\text{-}pr)_3\}_2Na_2]$ (M = Mo or W) [22] is similar to that of the analogous $FeCrMo_3Na_2$ [21]. The mean values of Mo-Mo and W-W bond distances are 2.517, and 2.535 Å, respectively.

There are two orange complexes, one $rhombohedral(NMe_4)_2(NH_4)_2[Fe_2Mo_{12}O_{30}(H_2PO_4)_6(HPO_4)_2]•11H_2O$ [23] and the other triclinic $(NMe_4)_4[Fe_3Mo_{12}O_{30}(H_xPO_4)_8]•16H_2O$ [23]. Both structures are based on $Fe[Mo_6O_{15}(H_xPO_4)]_2$ moieties which are connected *via* their phosphate groups to additional Fe(III) atoms to give three-dimensional frameworks whose pores are filled with a mixture of water solvate and the templating cations (Fig. 5). This cluster consists of three metal–metal bonded, oxo-bridged Mo dimers connected together by additional oxo groups into a ring containing six Mo atoms and four phosphate groups. Three of the four phosphate groups are located on the periphery of the Mo_6 ring and bridge the three non-bonded Mo-Mo contacts, and each has two terminal P-OH groups. Each metal atom is pseudo-octahedrally coordinated (MO_6). The mean Mo-Mo bond distances are 2.589 and 2.591 Å respectively (Table 1).

Structural data for eight FeMn complexes [24-30] are gathered in Table 1. In monoclinic brown $[(ON)Fe(\mu\text{-}\eta^2\text{-}CN)_5Mn(H_2O)]•2H_2O$ [24], both iron(III) and manganese(II) centres have distorted octahedral symmetry. The cyanide groups serve as bridges between the metal atoms in the manner Fe-C≡N-Mn. The nitrosyl group completes an octahedral coordination about Fe(III) atoms (FeC_5N) and water completes the Mn(II) octahedron (MnN_5O). The two uncoordinated water molecules are hydrogen bonded to the coordinated water, and occupy channels in the crystal lattice. The coordinated water and nitrosyl groups are geometrically arranged so that extensive tunnel-like formations permeate the crystal lattice.

The structure of tetragonal brown $(NH_4)[(NC)_4Fe(\mu\text{-}\eta^2\text{-}CN)_2Mn(H_2O)_4]•4H_2O$ [25] is built up from slightly distorted $Fe(CN)_6^{3-}$ octahedral anions and square planar $Mn(H_2O)_4^{2+}$ cations, stacked one upon the other in nearly eclipsed positions to form cyano bridged chains -Fe-C≡N-Mn-NC- along [001]. Tetramethylammonium cations and crystal water, forming H-bonded $(H_2O)_4$ rings, occupy positions in the centre of elpasolite-like sub-cells, which result from O-H ···N bridging between different chains. Both metal atoms are six-coordinated (FeC_6 and MnO_4N_2).

Brown orthorhombic $[(NC)_4Fe(\mu\text{-}\eta^2\text{-}CN)_2Mn(\eta^4\text{-}acac)]$ [26] assumes a one dimensional snaky chain structure consisting of $(\text{-Mn-NC-Fe-CN-})_n$ repeating units, in which the Fe(III) atom is positioned at the inversion centre, the [Mn(acac)] moiety lies on a mirror plane, and the adjacent one-dimensional chains wind along the b axis with the same phase. Each metal atom is six-coordinated ($Fe(III)C_6$ and $Mn(III)N_4O_2$).

In pentanuclear $[(NC)_2Fe(\mu\text{-}\eta^2\text{-}CN)_4\{Mn(\mu\text{-}\eta^4\text{-}salmen)\}_4]^+$ cation [27] the Fe(III) atom and two cyanide groups lie on a 4-fold rotation axis (0, 0, 2). The Fe(III) atom is coordinated octahedrally by six (CN)- groups $(FeC)_6$, with each of the four equatorial (CN)- ligands coordinated axially to Mn(III) from a Mn(salmen) moiety. This occurs in pairs via the sharing of oxygen from the salmen. The coordination geometry around the Mn(III) atoms is distorted square-bipyramidal (MnN_4O_2). The structure of the complex consists of a two-dimensional layer containing a cyclic dodecamer as the repeating unit. The layers stack along the c axis and ClO_4^- anions are positioned between the layers.

The structure of $[K\{Mn(\mu\text{-}3\text{-}salmen)\}_2Fe(CN)_6]$ [27] is shown in Fig 6. Iron(III) and potassium(I) occupy the special positions, (the inversion centers, Fe (1/2, 1, 1/2) and K(1/2, 0, 0)). The chains are made up by the $FeMn_2$ trimers bridged by K cations which are surrounded by the two O_4 sets from two adjacent trimers. The $[Fe(CN)_6]^{3-}$ building block provides both the intra- and interchain linkages. It contains three different pairs of (CN)- ligands, two terminal, two intrachain and two interchain bridging. The intrachain CN bridges are shorter than the

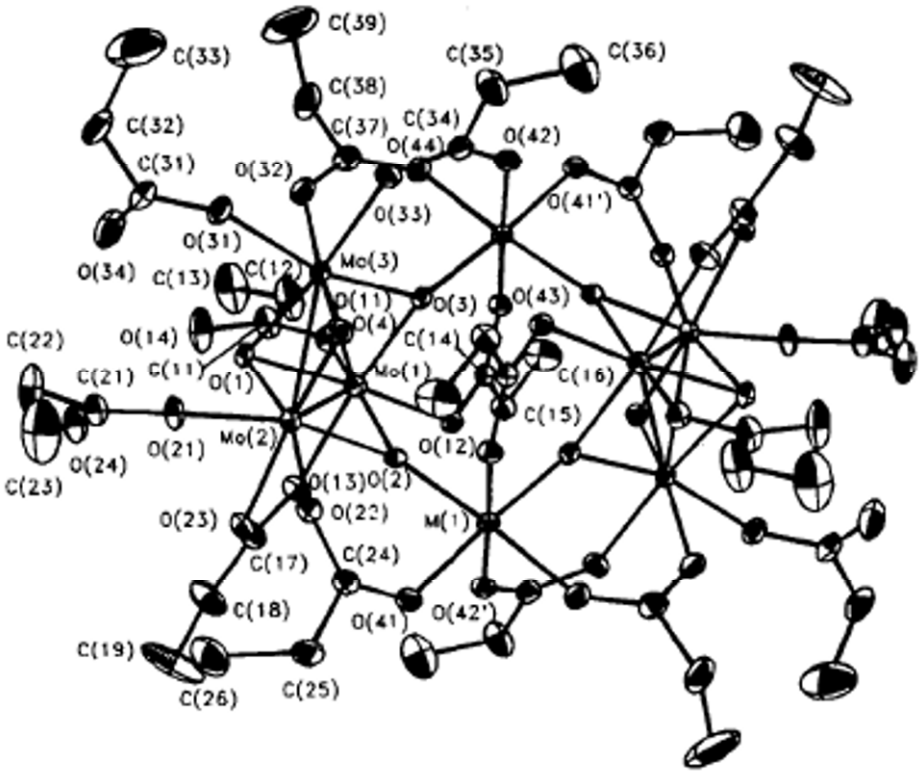

Figure 4. Structure of the $[MMo_3O_4(pr)_8]^{2-}$ anion, where M = 0.5Cr + 0.5Fe [21]

interchain CN bridges (Fe–CN–Mn). These Fe–CN–Mn interactions produce a two-dimensional network with a repeating cyclic octameric $[(-Mn-NC-Fe-CN-)]_4$ unit. The center of the octameric ring is occupied by a KO_8 sandwich.

The structures of yellow hexagonal $(NBu_4)[Fe(\mu\text{-}ox)_3Mn]$ [28], yellow orthorhombic $\{N(n\text{-}C_5H_{11})_4\}[Fe(\mu\text{-}ox)_3Mn]$ [29] and monoclinic $[Fe(cp^*)_2][Fe(\mu\text{-}ox)_3Mn]$ [30], consist of anionic, two-dimensional honeycomb networks formed by the oxalate-bridged metal atoms, interleaved with templating cations. Both metal atoms are hexacoordinated ($Fe(III)O_6$ and $Mn(II)O_6$).

In red monoclinic $[\{Fe(\mu\text{-dfed})Co\}(\mu\text{-}\eta^2\text{-NCS})]ClO_4$ [31], the heterodinucleating macrocycle (dfed) derived by the 2:1:1 condensation of 2,6-diformyl-4-methylphenol, ethylenediamine, and diethylenetriamine has two disimilar N_2O_2 and N_3O_2 metal binding sites sharing the phenolic oxygens. The Co(II) resides at the N_2O_2 site and the Fe(II) at the N_3O_2 site. The Co...Fe separation bridged by the two phenolic oxygens is 3.1717(8) Å and the mean Fe-O-Co bridge angle is 100.2(1)°. The SCN^- group coordinates to the Fe(II) atom through its nitrogen atom and to the Co(II) atom of the neighboring complex through its sulfur atom, forming a one-dimensional chain through Fe-NCS-Co linkages. The geometry about Co(II) is square-pyramidal with the thiocyanate sulfur at the apex (CoN_2O_2S), while that about Fe(II) is a distorted six-coordination (FeN_4O_2) (Table 1).

Crystal structure analysis of $(PPh_4)[(NC)_4Fe(\mu\text{-}\eta^2\text{-}CN)_2Ni(\eta^2\text{-}1,2\text{-}pn)_2]\bullet 2H_2O$ [32] reveals a one-dimensional zigzag chain structure extending through the Fe–CN–Ni–NC–Fe linkage Each metal atom is six-coordinated ($Fe(III)C_6$ and $Ni(II)N_6$). The intrachain Fe... Ni separation is 5.116(1) Å and the nearest interchain separations are 7.134(2) Å (Fe...Ni), 8.437(3) Å (Ni...Ni and Fe...Fe).

There are four grey-yellow FeNi complexes, monoclinic $[(H_2O)_2Fe(\mu\text{-}\eta^2\text{-}NC)_4Ni]\bullet 2C_4H_8O_2$ [33] and two tetragonal $[(NH_3)_2Fe(\mu\text{-}\eta^2\text{–}NC)_4Ni]\bullet 2S$ (S = aniline [34], and benzene [34,35]) and monoclinic $[(py)_2Fe(\mu\text{-}\eta^2\text{-}NC)_4Ni]$ [35] which are isostructural. The host layer comprises a close two dimensional network of $[FeNi(CN)_4]_n$, from which a pair of H_2O [33], NH_3 [34,35] or py [35] ligands protrude above and below the layer at Fe(II). The guest molecules, 1,4-dioxane [33], benzene and aniline [34], are accommodated in the interlayer space. The Fe(III) atoms are six-coordinated (FeN_4O_2 [33], FeN_6 [34]), and Ni(II) atoms are four-coordinated (NiC_4).

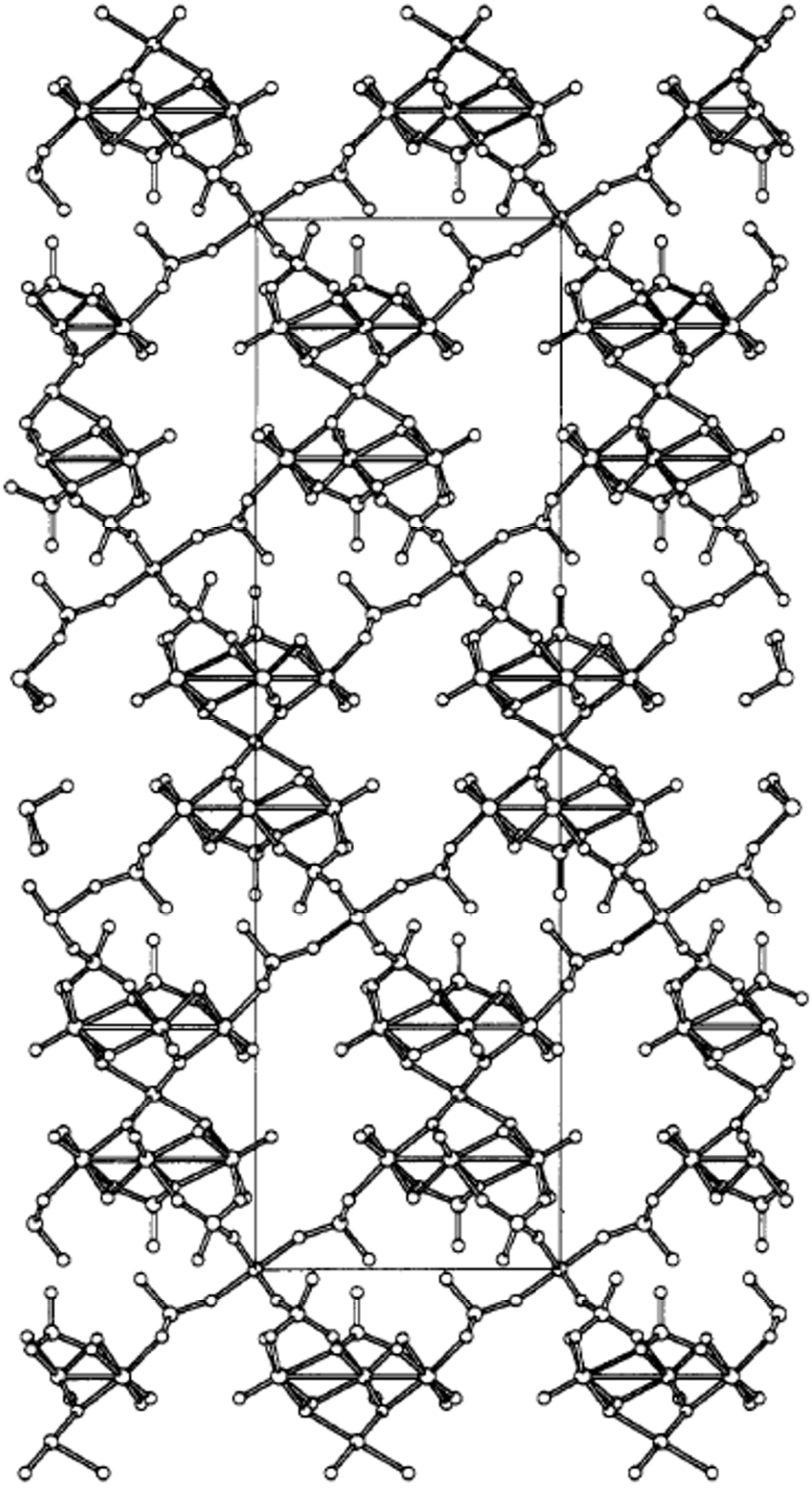

Figure 5. Structure of $[Fe_2Mo_{12}O_{30}(H_2PO_4)_6(HPO_4)_2]^{4-}$ [23]

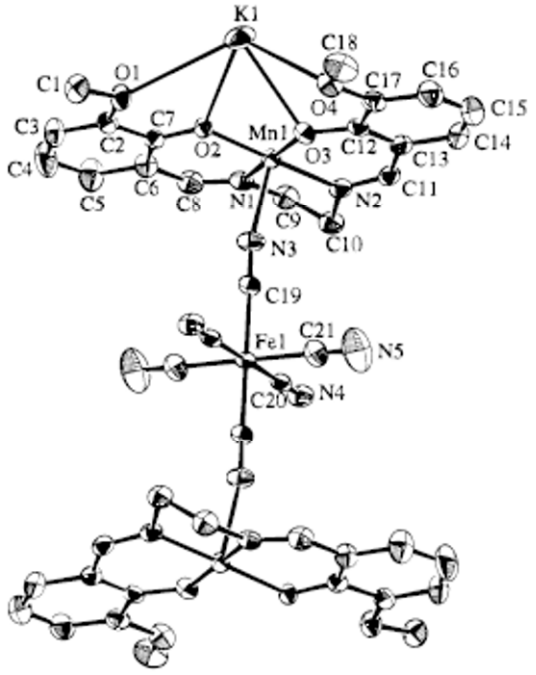

Figure 6. Structure of [K{Mn(μ-3- salmen)}$_2$Fe(CN)$_6$] [27]

There are another three black Fe(II)Ni complexes [36] of the composition [(NC)$_2$Fe(μ-η^2 -CN)$_4${Ni(η^2-Me$_2$en)$_2$}$_2$] X•nH$_2$O, where (X = CF_3SO_3 and n = 2; X = bzO and n = 6, and X = N_3 and n = 4), which are isostructural. In each complex [Fe(CN$_6$]$^{3-}$ anions coordinate to four [Ni(Me$_2$en)$_2$]$^{2+}$ cations through four cyano- nitrogens in a plane, providing a two-dimensional sheet of a square structure extended by Fe–CN–Ni linkages. The square with four Fe(III) atoms at the corners and four trans-Ni(II) on the edges shows a slight distortion to a rhombus. Each metal atom is six coordinated (FeC_6 and NiN_6). The mean values of Fe···Ni, Ni ···Ni and Fe···Fe separations are 5.157, 7.118 and 10.352 Å (X= CF_3SO_3); 5.195, 11.416 and 12.757 Å (X = bzO); and 5.142, 10.878 and 10.314 Å (X = N_3).

The purple trigonal FeNi complexes [37] of composition {Fe(μ-η^2-CN)$_6$[Ni(η^2-en)$_2$]$_3$}•2X, (X = PF_6 (×2) and ClO_4 (×2)) are isostructural and all the assemblies have an isotropic three-dimensional network structure extended through Fe-CN-Ni linkages. The network is based on a cube formed with 8 [Fe(CN)$_6$]$^{3-}$ anions in the corners and 12 [Ni(en)$_2$]$^{2+}$ cations at the edges. Two PF_6^- or ClO_4^- anions are located in the cavity of Fe_8Ni_{12} cube and align along a diagonal axis that coincides with c axis. Each metal cation is six-coordinated (FeC_6 and NiN_6). The Fe···Ni, Fe···Fe and Ni···Ni separations are 4.954, 9.908 and 8.388 Å.

Another two black monoclinic complexes, [Fe(cp*)$_2$Ni(S$_2$C$_2$R$_2$)$_2$], (R = CN or CF_3), are isostructural [38]. These complexes possess [Fe(cp*)$_2$]$^+$ (D) cations and [Ni(S$_2$C$_2$R$_2$)]$^-$ (A) anions. The unit cell is composed of isolated, centrosymmetric DAAD dimers with an essentially eclipsed (A2) anions (separated by 3.482 Å) and two D cations. The cations lie essentially on the NiS_2C_2 chelate ring. The intradimer Fe···Fe separation is 14.64 Å, whereas the interdimer Fe···Fe separations are 9.959, 9.971 and 12.66 Å. Black [Fe(cp*)$_2$Ni{S$_2$C$_2$(CN)$_2$}$_2$] [38] exists in two isomeric forms, α- monoclinic and β- triclinic. Both are centrosymmetric. The unit cell of α-isomer is complex with ···DAADAA··· chains also containing an essentially eclipsed (A2) anions separated by 3.537 Å and D (0.5 cation). Orthogonal to this chain is a layered motif comprised of alternating [D$^+$]$_2$ A$^-$ moieties such that the D's and A's form extended edge-to-edge chains. The adjacent and intrachain Fe···Fe separations are 8.401 and 10.548 Å, respectively. The unit cell of β-isomer possesses parallel –DADADA– chains with intra- and interchain Fe···Fe separations of 12.11 and 16.58 Å, respectively.

3. Polymeric FeM (M = lanthanide elements) complexes

Four FeM (M = Sm [39], Er [40], Yb [41,42]) compounds and their structural parameters are gathered in Table 1. In monoclinic Fe(μ-η^2-CN)$_6$Sm(H$_2$O)$_4$ [39] the samarium(II) atom is eight-coordinated and iron(III) is six-coordinated. The samarium atom is bonded to six cyano- nitrogen atoms and two water molecules in a square antiprism geometry (D_{4d}). The six cyano-carbon atoms form an octahedral coordination about the Fe(III) atom. Cyanide bridging links these groups to build an infinite polymeric array. The structure of red monoclinic Fe(μ-η^2-CN)$_6$Er(H$_2$O)$_4$ [40] is similar to the Sm analogue.

There are two orange monoclinic FeYb compounds [(OC)$_2$Fe(μ-η^2-CO)$_2$Yb(NCMe)$_3$]$_2$. MeCN [41,42] and [(OC)$_2$Fe(μ-η^2-CO)$_2$Yb(NCMe)$_3$] [42]. The structure of the former is shown in Fig. 7. This structure consists of "polymeric ladders" extending along the crystallographic b axis of the lattice. There are two crystallographically independent ladders. The geometries of the [Fe(CO)$_4$]$^{2-}$ units are intermediate between a tetrahedron and a trigonal bipyramid, while those of the Yb(II) atoms are distorted octahedrons. In addition to three MeCN ligands, each Yb(II) atom is coordinated by two carbonyl oxygens from two different [Fe(CO)$_4$] units, and each [Fe(CO)$_4$] unit is in turn connected to the two different Yb(II) atoms *via* isocarbonyl linkage, thus forming a zigzag ···Yb-O-C-Fe-C-O··· chain. Two such chains are coupled to form a ladder through Fe-Yb interactions (3.012(1) and 3.009(1) Å).

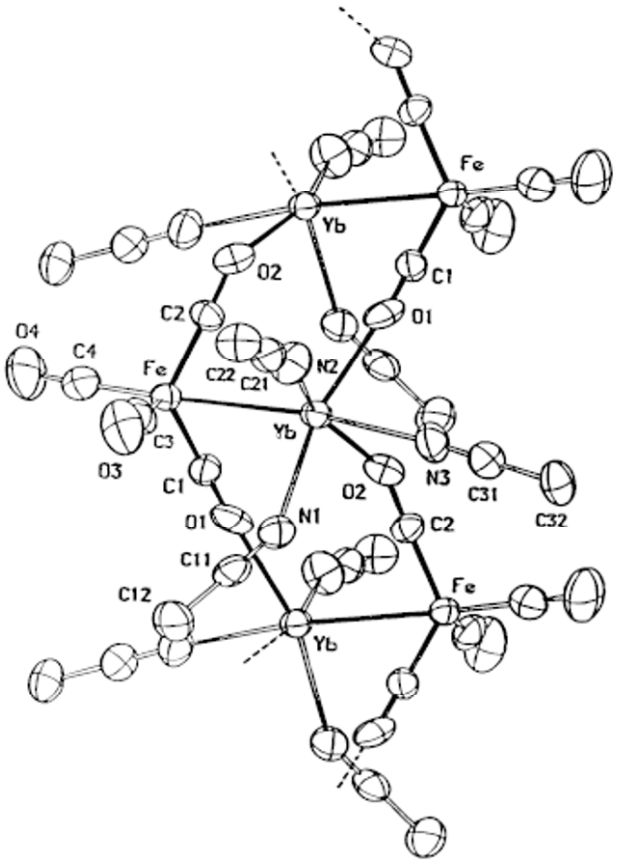

Figure 7. Structure of $[(OC)_2Fe(\mu\text{-}CO)_2Yb(NCMe)_3]$ [42]

The structure of $Fe(CO)_4Yb(NCMe)_3$ [42] consists of "polymeric sheets" stacked perpendicular to the crystallographic c axis. The structure of $[Fe(CO)_4Yb(NCMe)_3]$, is closely related to that of $\{[Fe(CO)_4Yb(NCMe)_3]_2MeCN\}$ in that the polymeric ladders are cross-linked through an extra Fe-C-O-Yb isocarbonyl linkage to form the sheet. The Fe-Yb distance of 3.0461Å is slightly longer than the corresponding distance in $\{[Fe(CO)_4Yb(NCMe)_3]_2MeCN\}$. Yb-O and Yb-N bond distances also follow this trend (Table 1).

4. Conclusion

There are almost fifty polymeric FeM (M = transition and lanthanide metals) complexes in this review. The complexes are for the most part yellow or black, but there are examples with brown, orange, red, purple, blue or green colour. The complexes crystallize in a wide range of crystal classes (monoclinic, triclinic, tetragonal, orthorhombic, trigonal, hexagonal and rhombohedral), but monoclinic structures are most prevalent by far (×25). The iron atoms are found in oxidation states 0, +2 and +3, with iron(III) complexes most numerous by far. The inner coordination sphere about the Fe(0) atom is tetrahedral (FeC_4 [42]) or sandwiched (FeC_{10} [17-20,30,38]). The Fe(II) atoms are six-coordinated with the chromophores: FeC_6 [1-12], FeO_6 [13], FeN_4O_2 [31,33,34] and FeN_6 [36]. The Fe(III) atoms are coordinated by six donor atoms with the chromophores: FeO_4N_2 [14], FeO_6 [15,22,23,28-30], FeC_6 [25-27,32,36,37,39-42], and FeC_5N [14] and even by seven donor atoms FeO_5N_2 [16].

The inner coordination sphere about the transition metal partners are: three – AgO_2C [15], and AuP_2Cl [19,20], four – AgS_4 [18], NiC_4 [33-35], NiS_4 [38], and PtS_4 [38]; five – CuN_5 [9-11], CuN_4O [10-12], CuO_3N_2 [13], CoO_2N_2S [31]; six – CuO_4N_2 [14], AgO_6 [16], AgC_4S_2 [17], MoO_6 [21,22], MnN_5O [24], MnO_4N_2 [25], MnN_4O_2 [26,27], MnO_6 [28-30] and NiN_6 [32,36,37] coordinated. Lanthanide partners show five- YbN_3O_2 [41,42], six- SmN_4O_2 [39], YbO_3N_3 [42] and eight- ErN_6O_2 [40] coordination. The shortest Fe–Fe, Fe-M (transition), Fe-M (lanthanide) and M–M separations are 8.08 Å [12], 3.033(2) Å for Fe-Cu [13], 3.010(1) Å for Fe-Yb [41] and 2.505(2) Å for Mo-Mo [22].

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Abbrevations

acac	acetylacetonate
bzO	benzoate
$C_4H_8O_2$	1,4-dioxane
cp	cyclopentadienyl
cp*	pentamethylcyclopentadienyl
dfcd	macrocycle derived by the 2:1:1 condensation of 2,6-diformyl-4-methylphenol, ethylenediamine and diethylenetriamine
dpdpf	1,1'-bis(diphenylthiophosphonyl)ferrocene
edta	ethylenediamine-N,N,N,N-tetraacetate
en	ethylenediamine
Et	ethyl
Et_2NCS_2	diethyldithiocarbamate
dien	diethylenediamine
dmtp	5,7-dimethyl[1.2.4]triazolo[1.5.a]pyrimidine
hx	hexagonal
m	monoclinic
Mesalen	1,2-bis(methylsalicydene)amino ethane
NBu_4	tetra(n-butyl)ammonium
$N(n\text{-}C_5H_{11})_4$	tetra(n-pentyl)ammonium
NMe_4	tetramethylammonium
ox	oxalate
1,2-pn	1,2-propanediamine
PPh_4	tetraphenylphosphonium
py	pyridine
pz	pyrazolate
rh	rhombohedral
salmen	N,N´-ethylene-bis(3-methoxysalicylideneiminate)
thf	tetrahydrofuran
tmppor	5,10,15,20-teterakis(N-methylpyridinium)porphyrinate
tg	tetragonal
tr	triclinic

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