

Crystallographic and Structural Analysis of Heterometallic FeCu Complexes

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ABSTRACT

Over 100 heterometallic FeCu complexes, from heterodi- to heteropolymeric have been included in this review. The complexes contain the FeCu, Fe₂Cu, FeCu₂, FeCuMo; Fe₃Cu, Fe₂Cu₂, Fe₂CuM (M=Hg or Co); Fe₄Cu, Fe₃CuTe; Fe₄Cu₂, Fe₃Cu₃; FeCu₆, FeCu₂Ru₄; Fe₄Cu₄, Fe₄Cu₅; Fe₆Cu₅ and {FeCu}_n metallic cores. The mean M-M bond distance elongated in the order: 2.520Å (Fe-Cu) < 2.638Å (Cu-Cu) < 2.663Å (Fe-Fe). The most common ligands for the iron atoms are C donors, and for copper atoms are O and N donors. There are several relationships between the M-L, M-L-M and L-M-L data, which are discussed and compared with those found in FeAu complexes.

Keywords: Structure; heterometallic; iron/copper; review.

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ABBREVIATIONS

<i>(fse)₂en</i>	<i>N,N'</i> -bis(2-hydroxy-3-carboxybenzylidene)-1,2-diaminoethane
<i>ac</i>	acetate
<i>acac</i>	acetylacetonate
<i>bnpy</i>	<i>N,N'</i> -bis(2-(2-pyridylethyl))benzylamine
<i>bpbp</i>	2,6-bis((bis(2-pyridylmethyl)amine)methyl-4-tert-butylphenolate
<i>bpm</i>	bipyrimidine
<i>bpmp</i>	2,6-bis((bis(2-pyridylmethyl)amine)methyl-4-methylphenolate
<i>C₅H₄P(Ph₂)S</i>	sulfodiphenylphosphinocyclopentadienyl
<i>cp</i>	cyclopentadienyl
<i>cp*</i>	pentamethylcyclopentadiene
<i>cy</i>	cyclohexyl
<i>dchpe</i>	<i>Cy₂PCH₂CH₂Pcy₂</i>
<i>dien</i>	diethylenetriamine
<i>dmpph</i>	(<i>C₅H₄CHNN(Me)₂P(S)(Ph)</i>)
<i>dcpc</i>	4,5-dichloro-1,2-bis(pyridine-2-carboxamido)benzene
<i>dppm</i>	bis(diphenylphosphino)methane
<i>ema</i>	ethylenebis((cyclopentadienylmethyl)amine)
<i>Et</i>	ethyl
<i>hfa</i>	hexafluoroacetylacetonate
<i>Him</i>	imidazole
<i>m</i>	monoclinic
<i>mac</i>	macrocyclic adduk tof 2,6-diacetylpyridine and hydrazine
<i>mao</i>	methylazoximate
<i>Me</i>	methyl
<i>Me₅dien</i>	1,1,4,7,7-pentamethyldiethylenetriamine
<i>Me₆tren</i>	2,2',2''-tris(dimethylaminoethyl)amine
<i>mnt</i>	1,2-dicyano-1,2-ethylenedithiolate
<i>mpyc</i>	tetramethyl-5-(2-pyridyl)cyclopentadienyl
<i>nprh</i>	meso- $\alpha,\alpha, \alpha,\alpha$ -tetra(o-nicotinamidophenyl)porphinate
<i>oep</i>	2,3,7,8,12,13,17,18-octaethylporphyrinate
<i>or</i>	orthorhombic
<i>otf</i>	trifluoromethanesulfonate
<i>P(NMe₂)₂(OMe)</i>	methoxydi(dimethylamino)phosphine
<i>Pcy₃</i>	tricyclohexylphosphine
<i>PEtPh₂</i>	ethylidiphenylphosphine
<i>Ph</i>	phenyl
<i>Ph₂Ppy</i>	2-(diphenylphosphino) pyridine
<i>PPh₃</i>	triphenylphosphine
<i>ppn</i>	bis(triphenylphosphine)iminium
<i>PrⁱS</i>	iso-propylsulfide
<i>prpn</i>	o-hydroxypropiophenone
<i>py</i>	pyridine
<i>Si(OMe)₂(NMe₂)</i>	dimethylaminodimethoxysilane
<i>Si(OMe)₃</i>	trimethylcyclosilicene
<i>tac</i>	1,4,8,11-tetra-azacyclotetradecane
<i>thf</i>	tetrahydrofuran
<i>tim</i>	2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetra-deca-1,3,8,10-tetraene
<i>tn</i>	1,3-diaminopropane
<i>tp</i>	hydrotris(pyrazolyl)borate
<i>tpa</i>	tris(2-pyridylmethyl)amine
<i>tpp</i>	5,1,15,20-tetraphenylporphinate
<i>tr</i>	triclinic

1. INTRODUCTION

Compounds containing metal-metal bonds are called cluster compounds. Clusters of more than three metal atoms generally consist of polyhedral arrangements of the metal atoms and thus are part of the fascinating and rapidly growing branch of chemistry which we can call „polyhedral cluster chemistry“. The formation and reactivity of metal-metal bonds are important aspects of metal cluster chemistry [1]. Basic as well as application oriented reactions of clusters may originate from metal-metal bond opening and closing. The chemistry of heterometallic iron in the presence of a transition metal/s covers a wide range of compounds, many of which are important in the field of catalysis and biochemistry. Many structural studies of the heterometallic compounds have been carried out. There are over hundred heterometallic FeCu compounds for which crystallographic and structural data are available and are summarised in this review. Variations and trends in bond lengths and angles were found and their importance is discussed in this review. The factors relevant to the stereochemical interactions around these metals are discussed and where appropriate comparisons are made with heterometallic FeCu complexes, which were classified and analyzed by us [2].

2. HETERODIMERIC COMPLEXES

There are four examples of FeCu double salts and thirty three heterodimeric FeCu complexes. Their structural parameters are gathered in (Table 1). Two derivatives of double salts [3] contain $[\text{FeCl}_4]^-$ anion and $[\text{Cu}(\text{PPh}_3)_2]^+$ cation. One is monoclinic and the other is triclinic. The mean Fe(III)-Cl and Cu(I)-P bond distances (monoclinic vs triclinic) are 2.154 and 2.295 Å vs 2.178 and 2.304 Å. Each iron (III) atom is tetrahedrally coordinated and copper (I) atom is trigonally coordinated (Y shape). The deviation of the Cl-Fe-Cl and P-Cu-P bond angles, from the ideal values 109.5 and 120.0° (monoclinic vs triclinic) is 4.3 and 3.8° vs 2.8 and 3.4°. This indicates that the monoclinic complex is somewhat more distorted than the triclinic. Black double salt [4] contains $[\text{Fe}(\text{cp}^*)_2]_2$ and $[\text{Cu}(\eta^2\text{-mnt})_2]$ units. While the iron atoms are sandwiched (FeC_{10}), the copper (II) has a square-planar arrangement (CuS_4) with the mean Cu-S bond distance of 2.271 Å and the mean cis S-Cu-S bond angle of 90.67(5)°. Dark double salt [5] contains well separated $[\text{Fe}(\eta^4\text{-$

$\text{tpp})(\text{Him})_2]$, $[\text{Cu}(\eta^2\text{-mnt})_2]$ units and tetrahydrofurane molecules. Each metal atom is in oxidation state +3. The iron atom is six- FeN_6 , (tetragonal bipyramidal), and the copper atom is four- CuS_4 , (tetrahedral) coordinated.

Crystal structure of red orange $[(\text{PEtPh}_2)\text{Fe}(\mu\text{-H})_3\text{Cu}(\text{PEtPh}_2)]$ [6] consists of a facial P_3FeH_3 moiety, bridged by three hydrides to a CuP fragment with an Fe-Cu bond distance of 2.319(2) Å. This is the shortest Fe-Cu bond distance found in heterodimeric FeCu complexes. The phosphines coordinated to iron adopt a face stereochemistry with the P-Fe-P angles of 100.8, 107.6 and 106.4°. In yellow FeCu dimer [7] two units, $\text{Fe}(\text{CO})\{\text{Si}(\text{OMe})_3\}$ and $\text{Cu}(\text{AsPh}_3)$ are triple bridged by two carbonyl groups and one dppm-P,P' ligand. The Fe-Cu bond distance is 2.497(2) Å. The inner coordination spheres about the metal atoms are: FeC_3PSiCu and CuC_2PAsFe .

There are two FeCu dimers [8] which are isostructural. In both the $\text{Fe}(\text{CO})_2$ and CuL (L=ac or H_2O) fragments are connected by carbonyl group and by two Ph_2Ppy ligands, which bound to the iron atom through P atom and the copper atom through the N atom. The Fe-Cu bond distances are 2.501(2) Å (L=ac) and 2.512(2) Å (L= H_2O). The Fe-C-Cu bridge angles are 74.4(4) and 74.3(3)°, respectively. The inner coordination spheres about the metal centres are: $\text{FeC}_3\text{P}_2\text{Cu}$ and CuN_2OCFe .

In yellow FeCu dimer [9] the $\{\text{Si}(\text{OMe})_2(\text{NMe}_2)\}$ ligand serve as bridge between the $\text{Fe}(\text{CO})_3\{\text{P}(\text{NMe}_2)_2(\text{OMe})\}$ and $\text{Cu}(\text{PPh}_3)$ units, by Si atom to iron and by N atom to copper atom. The Fe-Cu bond distance is 2.530(2) Å. While the iron atom is six- FeC_3PSiCu the copper atom is three- CuNPFe (distorted Y shape) coordinated. In another FeCu dimer [10] an $\text{Fe}(\text{CO})_3\{\text{Si}(\text{OMe})_3\}$ fragment and $\text{Cu}(\text{PPh}_3)$ fragment are connected by a bidentate dppm-P,P' ligand. The Fe-Cu bond distance is 2.540(2) Å. Also in this dimer the iron atom is six- FeC_3PSiCu and copper atom is three- CuP_2Fe (distorted Y shape) coordinated.

In another three FeCu dimers [11,12], two oxygen ligands serve as bridges between the respective fragments (Table 1). The mean Fe-O-Cu bridge angle is 98.7°. In brown FeCu dimer [13] two metal atoms are bridged by a chlorine and by an octadentate nprh- $\text{N}_4\text{N}'_4$ ligand. The Fe(II) atom is six- FeN_4OCl and Cu(II) atom is five- CuN_4Cl , (square pyramidal) coordinated. In

triclinic FeCu dimer [14] three methylazoximate ligands serve as bridges between the iron(II) atom and Cu(PPh₃) fragment (Fig. 1). Each of the ligand is terdentate – N, N', O. While the iron(II) atom is six- FeN₆ the copper(I) is four- CuO₃P, (tetrahedral) coordinated. The Fe...Cu separation is 3.394(1) Å.

There are two dark brown FeCu dimers [15] in which a fluorine atom serve as bridge between Fe(ocp) and Cu(bnpy)(L)Cl (L=OCIO₃ or MeCN) fragments. The Fe...Cu separations and Fe-F-Cu bridge angles are 3.956(1) Å and 171.9(1)° (L=OCIO₃) and 4.047(3) Å and 166.2(5)° (L=MeCN), respectively. Each metal centers are five coordinated: FeN₄F and CuN₃FO (square pyramidal) in the former and MN₄F (M=Fe or Cu) in the latter.

There are another two violet, orthorhombic and monoclinic [(oep)Fe(μ-O)Cu. (Me₆tren)]ClO₄.S (S=thf or MeOH), which are isostructural [16]. In each two fragments, Fe(oep) and Cu(Me₆tren), are connected by oxygen atom. The monoclinic dimer contains two crystallographically

independent molecules. Each metal atom (Fe(III) and Cu(II)) has a square-pyramidal arrangement (MN₄O). The Fe...Cu separations and Fe-O-Cu bridge angles are 3.575(1) Å and 178.2(3)° (or), 2.570(1) Å and 175.2(3)° (m, molecule 1), and 3.572(1) and 176.6(3)° (m, molecule 2). For purple monoclinic [(mac)Fe(μ-bpm)Cu(acac)₂](ClO₄)₂ [17] only dimensions of elementary cell are available.

There are seven coloured FeCu dimers [18,19] in which CN groups serve as bridge between the metal atoms, in the manner Fe-CN-Cu, with the Fe...Cu separation from 4.90 to 5.11 Å (Table 1). In another two FeCu dimers [20] a carboxylate group (acetate or formate) in a syn-syn arrangement serve as a bridge between the respective fragments of the metal (Fe(III) and Cu(II)) atoms. In the former the iron atom is five- FeN₄O (square pyramidal) and copper atom is four- CuN₃O (square planar), coordinated, and in the latter both metal centres are five- FeN₄O and CuN₃O₂, coordinated. The Fe...Cu separations are 4.430 and 5.860 Å, respectively.

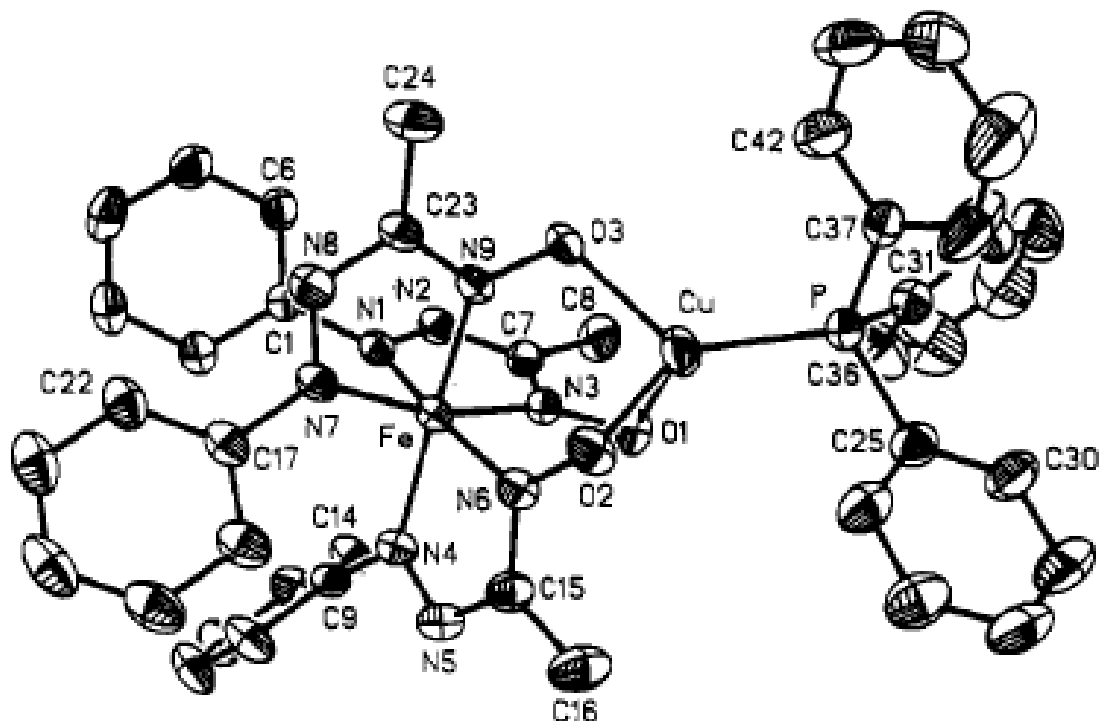


Fig. 1. Structure of [Fe(mao)₃Cu(PPh₃)] [14]

In yellow FeCu dimer [21] two fragments, $\text{Fe}(\text{CO})_3$ and $\text{Cu}(\text{PPh}_3)_2$, are connected by a B_5H_8 ligand in the fashion $\mu\text{-B}_5\text{H}(\text{Fe})\text{:B}_2\text{H}(\text{Cu})$. In dark monoclinic FeCu dimer [22] an EtO group together with macrocyclic hbp ligand in the fashion $\mu\text{-N}_3\text{O}(\text{Fe})\text{:N}_3\text{O}(\text{Cu})$ bridged two metal (Fe(III) and Cu(II)) atoms, which are six- (MO_3N_3) coordinated. The Fe...Cu separation is 3.149(2) Å and Fe-O-Cu bridge angle is 118.0(2)°.

In another three (orthorhombic [23], triclinic [23], monoclinic [24]) FeCu dimers, a macrocyclic bpmp ligand (or, tr) or pbpp (m) in the fashion $\mu\text{-}\eta^4\text{:}\eta^4$ with propionate (or) or acetate (tr, m) in a syn-syn arrangement serve as a bridges between the metal (Fe(III) and Cu(II)) atoms. The Fe...Cu separations are 3.401(4)Å (or), 3.641(1)Å (tr) and 3.149(2)Å (m).

In two red (triclinic and orthorhombic) FeCu dimers [25] the metal atoms are bridged by two mpyc ligands in the fashion $\mu\text{-C}_5(\text{Fe})\text{:N}(\text{Cu})$. The iron atoms are sandwiched (FeC_{10}) and copper(I) are two- CuN_2 , coordinated, with the N-Cu-N bond angles of 178.28(11)° (tr) and 171.4(6)° (or). The Fe...Cu separations are 3.231 and 3.292Å, respectively.

In yellow orthorhombic FeCu dimer [26] two $\text{C}_5\text{H}_4\text{P}(\text{Ph}_2)\text{S}$ ligands in the fashion $\mu\text{-C}_5(\text{Fe})\text{:S}(\text{Cu})$ serve as a bridges between the metal atoms. The iron is sandwiched (FeC_{10}) and copper(I) atom is almost linearly coordinated, S-Cu-S, 171.5(2)°.

Inspection of the data in (Table 1) reveals that the iron atoms have the following inner coordination spheres (chromophores): FeN_5 , FeN_4X (X=F or C), FeX_6 (X=O or N), FeO_5Cl , FeN_5Cl , FeO_3N_3 , FeH_{23}Cu , $\text{FeC}_3\text{P}_2\text{Cu}$, FeC_3PSiCu , $\text{FeC}_3\text{B}_3\text{H}$ and FeC_{10} . The copper atoms have the following chromophores: CuX_2 (X=N or S), CuP_2Fe , CuNPF_e , CuO_3P , CuN_3X (X=O or C), CuO_2N_2 , CuN_3Fe , CuN_5 , CuO_4N , CuN_4X (X=F, O or Cl), CuO_3N_2 , CuN_3O_2 , CuH_3PFe , $\text{CuB}_2\text{P}_2\text{H}$, CuN_2OCFe , CuC_2PAsFe and CuO_3N_3 .

The ligands which created the respective inner coordination spheres about the central metal atoms can be divided into three groups, one which are bound only iron atoms, the other which are bound only copper atoms and the third one which serve as bridge/s between the heterometals. The mean Fe-L bond distance elongated in the sequence: 1.75Å (CO) < 1.98Å (OL) < 2.07Å (NL) < 2.12Å (Cl) < 2.17Å (tetra-NL) < 2.19Å (PL) <

2.275Å (SiL). The mean Cu-L bond distance elongated in the sequence: 2.01Å (NL) < 2.06Å (ter-NL) < 2.22Å (bi-SL) < 2.24Å (OL, PL) < 2.355Å (AsL). The third type of the ligands which serve as bridge/s between the heterometals is reached with the mean Fe-L vs Cu-L bond distances: 1.52 vs 1.70Å ($\mu = \text{H}$), 1.76 vs 1.83Å ($\mu - \text{O}$), 1.76 vs 2.385Å ($\mu - \text{CO}$), 1.86 vs 2.16Å ($\mu - \text{F}$), 1.97 vs 1.93Å ($\mu - \text{OL}$), 2.55 vs 2.44Å ($\mu - \text{Cl}$). The mean values of Fe-L vs Cu-L bond distances for bi- and higher dentate ligands are: $\mu\text{-}\eta^1\text{:}\eta^1\text{-CN}$, 1.91Å (C) vs 1.98Å (N); $\mu\text{-}\eta^1\text{:}\eta^1\text{-O}_2\text{L}$ 2.04 vs 1.99 Å; $\mu\text{-}\eta^1\text{:}\eta^1\text{-P}_2\text{L}$ 2.225 vs 2.27Å; $\mu\text{-}\eta^1\text{:}\eta^1\text{-PNL}$, 2.21Å (P) vs 2.05Å (N); $\mu\text{-}\eta^1\text{:}\eta^1\text{-SiNL}$, 2.27Å (Si) vs 2.15Å (N); $\mu\text{-}\eta^2\text{:}\eta^1\text{-N}_2\text{O}$ 1.93Å (N_2) vs 2.10 Å (O); $\mu\text{-}\eta^5\text{:}\eta^1\text{-C}_5\text{NL}$, 2.07Å (C_5) vs 1.89Å (N); $\mu\text{-}\eta^5\text{:}\eta^1\text{-C}_5\text{SL}$, not given vs 2.14Å (S); $\mu\text{-}\eta^3\eta^1\text{:}\eta^2\eta^1\text{-B}_{53}\text{H}_8$, 2.115Å (B_3), 1.56Å (H) vs 2.22Å (B_2), 1.96Å (H); $\mu\text{-}\eta^4\text{:}\eta^4\text{-O}_4\text{N}_4\text{L}$, 2.01Å (O_4) vs 2.16Å (N_4).

The mean Fe-Cu bond distance is 2.483Å (range 2.319(2) – 2.540(2)Å) and the mean Fe...Cu separation of 4.182Å (range 3.122- 5.860Å) ruled out a direct bond. The mean Fe-X-Cu bridge angle opens in the order: 74.3° (X=CO) < 92.8Å (H) < 105.4° (OL) < 169.0° (F) < 176.5° (O). The effect of both electronic and steric factors of the coordinated atoms can be seen in the opening of the L-M-L bond angles of the respective metallocycles. The mean L-Fe-L bond angle opens in the order: 78.8° (- NC_2N -) < 86.0° (- OC_3O -) < 88.8° (- NC_3N -); and L-Cu-L: 84.0° (- NC_2N -) < 87.4° (- NC_3N -) < 92.6° (- SC_3S -) < 96.4° (- OC_3N -) < 96.5° (- NC_4N -).

There are two examples which exist in two isomeric forms, monoclinic and triclinic $[\text{FeCl}_4][\text{Cu}(\text{PPh}_3)_3]$ [3] and orthorhombic and monoclinic $[(\text{oep})\text{Fe}(\mu\text{-O})\text{Cu}(\text{Me}_6\text{tren})]\text{ClO}_4$ [16]. The monoclinic $[(\eta^4\text{-oep})\text{Fe}(\mu\text{-O})\text{Cu}(\eta^4\text{-Me}_6\text{tren})]\text{ClO}_4$. MeCN [16] and triclinic $[(\text{oep})(\text{py})\text{Fe}(\mu\text{-}\eta^2\text{-CN})\text{Cu}(\text{Me}_6\text{tren})]$ (SbF_6) $_2\text{Me}_2\text{Co}$ [19] contain two crystallographically independent molecules within the same crystal. All of these complexes are examples of distortion isomerism [27].

The complexes crystallized in three crystal classes, triclinic (19 examples) > monoclinic (14 examples) > orthorhombic (4 examples). The complexes cover wide range of colour: violet, yellow, red (each x6), brown, black (each x2), orange and blue (each x1).

3. HETEROTRIMERIC COMPLEXES

There are twenty four heterotrimeric complexes $\{\text{Fe}_2\text{Cu}$ (18 examples), FeCu_2 (5 examples),

FeCuMo (1 example)} for which structural parameters are available and are summarized in (Table 2).

Structural data for eighteen coloured Fe₂Cu complexes are gathered in (Table 2). Their structures are very complex. The basic skeleton of red Fe₂Cu complex [28] consists of a Fe₂Cu triangle. In this complex serve as bridges carbonyl group and a phosphido group and brings the iron atoms within at (2.627(1)Å). The Fe-Cu bond distances are 2.481(1) and 2.509(1)Å. The Fe-Cu-Fe bond angle of 63.5(1)° is about 5.3° more open than the Fe-Fe-Cu bond angle as, 57.7(1) and 58.7(1)°.

Crystal structure of another red Fe₂Cu complex [29] consists of well separated complex $[(OC)_4Fe_2Cu(Pcy_3)]^-$ anions, PPh₄⁺ cations and disordered thf molecules of solvation. The anion contains a Fe₂(CO)₈ unit bridged by a Cu(Pcy₃) fragment. The bridging of the Cu(Pcy₃) group to the Fe-Fe bond (2.900(2)Å) distorts the D_{3d} symmetry of the Fe₂(CO)₈ unit. The Fe-Cu bond distances are 2.487(2) and 2.503(2)Å. In [28,29] the Cu(I) atoms are three coordinated (CuPF₂) with the mean P-Cu-Fe bond angles of 146.4° and the mean Fe-Cu-Fe bond angles of 67.3°. A dark $[(pab)_3Fe(\mu-pab)_3]_2Cu \cdot 2CH_2Cl_2$ complex [30] is centrosymmetric with Cu(II) atom lying at a crystallographic inversion centre (0, 0, 0). The Fe...Cu...Fe fragment is thus exactly linear with the Fe...Cu separation of 3.480(1)Å. All metal atoms are six- coordinated FeN₆ (x 2) and CuO₆. In Fe₂Cu complex [31] the $\{Cu(dmg)_3\}^{4-}$ anion bridges the two iron(III) atoms through its deprotonated oxime oxygens with a Cu...Fe separation of 3.58Å. Two facially coordinated terdentate amine ligands complete the trigonally distorted octahedral coordination sphere of the two Fe(III) centres. The coordination around Cu(II) atom is strongly distorted (CuN₆).

In black Fe₂Cu complex [18] two iron(III) atoms and the Cu(II) atom are bridged by CN groups in the manner Fe-CN-Cu-NC-Fe. Two tetradentate oep and two pyridine ligands complete a pseudo-octahedral coordination sphere of the two Fe(III) centres (FeN₅C). The tetradentate cyclam ligand completes a tetragonal-bipyramidal coordination about the Cu(II) atom (CuN₆). The Cu...Fe separation is 5.15Å.

Structure of orange Fe₂Cu complex [32] which contains three crystallographically independent complex $[(cp)Fe(\mu-\eta^5:\eta^2-C_{12}H_{18}NS_2)_2Cu]^+$ cations is shown in (Fig. 2). The Cu(I) atom possesses a distorted tetrahedral geometry (CuS₄). The three independent copper(I) environments are very similar, this similarity extends to the ring conformation. The Cu...Fe separations vary between 5.781(4) and 7.802(5)Å, but these probably represents extremes of the possible range. Each iron atom is sandwiched (FeC₁₀).

There are three yellow-brown Fe₂Cu complexes of the composition $[(cp)Fe(\mu-\eta^5:\eta^2-C_5H_4CO_2)Cu(L)_2]$ (L=pyridine or imidazole) [33], which are isostructural. Each iron atom is sandwiched (FeC₁₀). Each Cu(II) atom has a highly trigonal-bipyramidal arrangement (CuO₃N₂). The pyridine complex was studied at two different temperatures, at ambient temperature and at 163 K. While at the former temperature the complex is triclinic, and at 163 K is monoclinic (Table 2).

In another two Fe₂Cu complexes [34,35] of the composition $[(cp)Fe(\mu-\eta^5:\eta^2-L)_2Cu]$ (L=C₁₀H₁₅NO [34], C₁₂H₁₄NO [35]) each copper atom is bonded to the two O and two N atoms of L ligands in a very distorted tetrahedral arrangement with and O-Cu-O and N-Cu-N bond angles of 66.4(1) and 163.1(2)° [34] and 137.0(2) and 138.3(2)° [35], respectively. Each iron atom is sandwiched (FeC₁₀).

In green and gold brown Fe₂Cu complexes [36] are isostructural. Each copper(II) atom is in a square-planar arrangement consisting of two imidazole nitrogen atoms and a carboxylate oxygen atom from each ferrocenylcarboxylate ligand (CuO₂N₂). In yellow $[Fe_2(\mu-C_5H_4PPh_2)_2\{\mu-C_5H_4P(Ph_2)O\}_2Cu]BF_4$ [37] the cyclopentadienyl rings are all planar. Pairs of the rings (A and C, B and D) which have sandwiched iron atoms are practically parallel, mean planes through A and C making an angle of 3.0(5)° and planes B and D 0.5(6)°. Rings A and C are staggered being rotated with respect to each other by ca. 36°, while rings B and D are „half-staggered“ with an angle of ca. 15°.

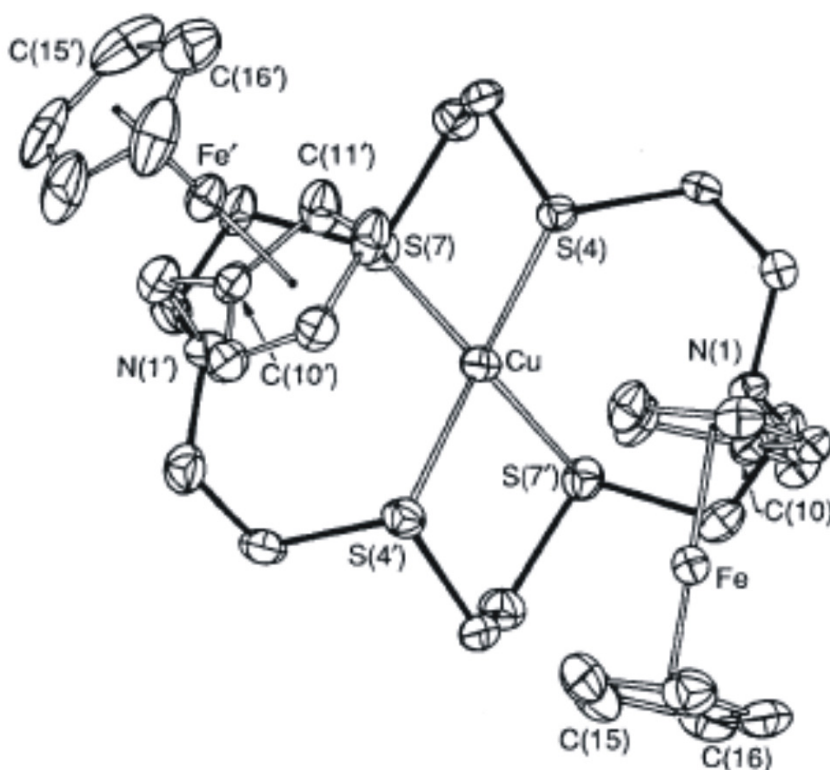


Fig. 2. Structure of $[(cp)Fe(C_{12}H_{18}NS_2)]_2Cu^+$ [32]

In two orange Fe_2Cu complexes [38,39] the two ferrocenophane ligands form a distorted tetrahedral arrangement around the Cu(I) atom (CuS_4). Each ferrocenophane acts as a chelate ligand in the manner $\mu-\eta^5(C):\eta^1(S)L$. In the remaining two Fe_2Cu complexes [40] the four O atoms of two 1,1'-bis(oxodiphenylphosphoranyl)ferrocene ligands are directly bonded to the copper(I) center with Cu-O bond distances from 1.92 to 2.076 Å.

There are five mostly violet $FeCu_2$ complexes (Table 2). Structure of yellow $FeCu_2$ complex [41] consists of two $Cu(PPh_3)_2$ groups bridging opposite edges of a flattened $Fe(CO)_4$ tetrahedron, resulting in a nearly linear Cu-Fe-Cu angle, 168.7(2)°. The mean Fe-Cu bond distances are 2.511(4) Å. In dark violet $FeCu_2$ complex [19] two CN groups serve as bridges between two satellites $Cu(Me_6tren)$ and a central $Fe(ocp)$ unit in the manner Cu-NC-Fe-CN-Cu with the Fe...Cu separation of 4.99 Å. The Fe(III) atom is six- (FeN_4C_2) and each Cu(II) atom is five- (CuN_5) trigonal bipyramidal coordinated.

In another violet $FeCu_2$ complex [20] two OCHO groups serve as bridges between the two

satellites (Me_6tren)Cu and a central $Fe(ocp)$ unit in the manner Cu-OC(H(O-Fe-OC(H)O)-Cu with the Fe...Cu separation of 5.422 Å. The Fe(III) atom is six- (FeN_4O_2) and each Cu(II) atom is five- (CuN_4O) trigonal bipyramidal coordinated. Structure of $[(tpp)Fe(\mu-schb)_2Cu_2]$ [42] is shown in (Fig. 3). The figure also shows the overlapping Cu(schb) ligands of adjacent cations. The essentially square-planar CuN_3O act as axial ligands to the Fe(III)(η^4 -tpp) cation via imidazole bridges. The intramolecular Fe...Cu separation is 6.0 Å. There is a slipped face-to-face relationship between adjacent copper chelate giving a linear chain of Cu-Fe-Cu units throughout the lattice. The interchelate mean plane spacing is 3.37 Å, and the intermolecular Cu...Cu separation is 4.33 Å.

In red $FeCu_2$ complex [43] the 1,1'-bis(2-pyridyl) octamethylferrocene is bound via N donor atoms to Cu(I) atom (CuN_2). In addition the $CuCl_2$ anion makes a remarkably short ligand unsupported Cu(I)-Cu(I) contact of 2.810(2) Å. Both Cu(I) atoms are in an almost linear dicoordinate environment with N-Cu-N and Cl-Cu-Cl bond angles of 171.4(6) and 176.1(3)°.

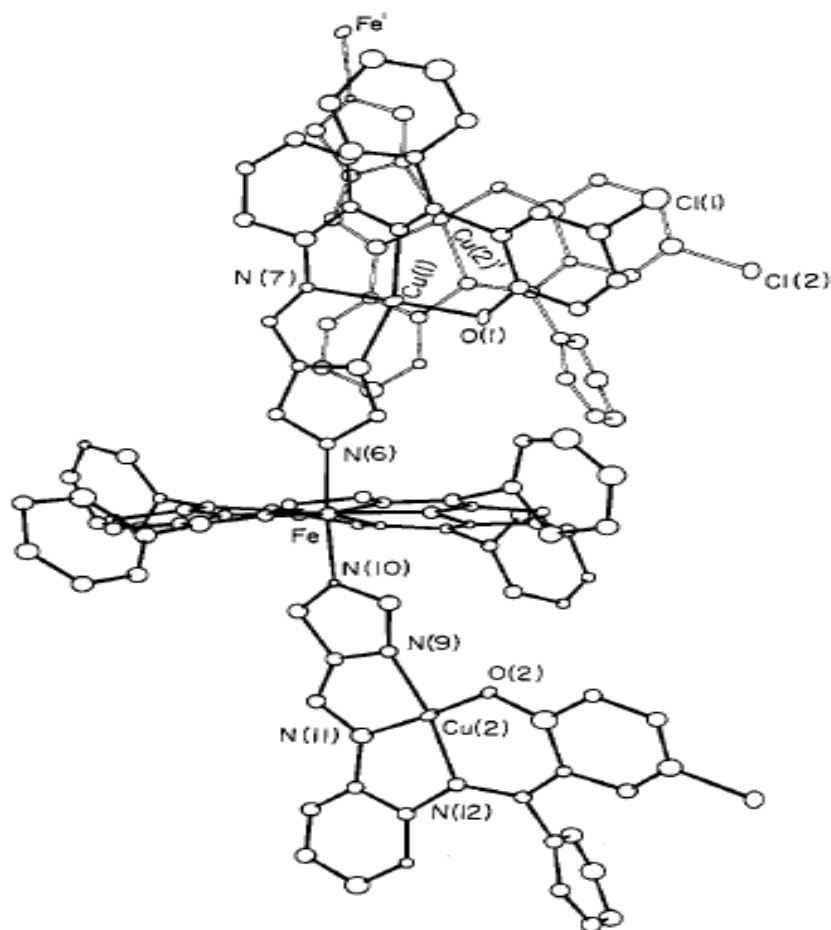


Fig. 3. Structure of [(tpp)Fe(schb)₂Cu₂] [42]

A red FeCuMo complex [44] is the only example, in which all the metal centers are differ. A pairs of S²⁻ atoms serve as a bridges in the manner Cl₂Fe(S)₂Mo(S)₂Cu(PPh₃)₂. The Fe-Mo and Mo-Cu bond distances are 2.769(2) and 2.785(2)Å, respectively. The mean Fe-S-Mo and Mo-S-Cu bridge angles are 75.9 and 76.4°, respectively. Each metal is tetrahedrally (FeCl₂S₂, MoS₄, CuS₂P₂) coordinated (Table 2).

Inspection of the data in (Table 2) reveals that there are twenty four (Fe₂Cu (18 examples), FeCu₂ (5 examples), FeCuMo (1 example)) complexes. The inner coordination sphere about iron atoms are: FeCl₂S₂, FeN₆, FeN₄O₂, FeN₅C, FeO₃N₃, FeC₄Cu₂, FeC₄CuFe, FeC₄PCuFe and FeC₁₀ (sandwich). The inner coordination spheres about copper atoms are: CuX₂Cu (X=N or Cl), CuP₂Fe, CuPFe₂, CuX₄ (X=O or S), CuN₃O, CuO₂X₂ (X=N or P), CuS₂P₂, CuX₅ (X=O or N), CuN₄O, CuX₆ (X=O or N), and CuO₃N₂.

There is a wide range of the ligands with N, C and P donor sites which by far prevails. The mean Fe-L bond distance elongated in the order: 1.77Å (CO) < 1.97Å (NL) < 2.005Å (tetra – NL) < 2.21Å (Cl) < 2.215Å (ter – NL). The mean Cu-L bond distance elongate in the order: 1.96Å (ter – NL) < 1.965 (NL) < 2.02Å (OL) < 2.025Å (tetra – NL) < 2.26Å (PL). The more variable are ligands which serve as bridge/s between the heterometals (Fe : Cu) with the donor sites: μ-S; μ-η¹: η¹-CN; μ-η¹(N) : η¹(O); μ-η²(N) : η²(N); μ-η¹(O) : η¹(O); μ-η¹(N) : η³(N₂O₁); μ-η⁵(C) : η¹(O); μ-η⁵(C) : η¹(N); μ-η⁵(C) : η¹(P); μ-η⁵(C) : η²(O); μ-η⁵(C) : η¹(O) η¹N; and μ-η⁵(C) : η²(S). The mean M-M bond distance elongated in the order: 2.495Å (Fe-Cu) < 2.660Å (Cu-Cu) < 2.764Å (Fe-Fe). The mean Fe...Cu separation is 5.535Å.

4. HETEROTETRAMERIC COMPLEXES

There are ten heterotetrameric (Fe₃Cu (x3), Fe₂Cu₂ (x5), Fe₂CuM (M=Hg or Co)) complexes

and their crystallographic and structural parameters are gathered in (Table 3). There are three Fe_3Cu complexes [45-47]. Structure of black complex [45] consists of a Fe_3Cu core in a „butterfly“ conformation (interplanar angle 133.3°) with the copper(I) atom occupying a „wing-tip“ site. The $\mu_3\text{-CMe}$ ligand acts as a triple bridge between the iron atoms at the tips of a triangle. On the opposite site of the triangle a carbonyl ligands bridges one of the basal iron atom and the iron atom at the „wing-tip“ site. The mean Fe-Cu bond distance of 2.529\AA ($2.494(1)$ and $2.564(1)\text{\AA}$) is 0.039\AA shorter than the mean Fe-Fe bond distance (2.568\AA). The structure of the dark brown Fe_3Cu complex [46] reveals also a four-metal „butterfly“ conformation with a $\mu_4\text{-CCO}$ bridging system. The copper(I) atom is again found at a „wing-tip“ site. The mean Fe...Cu bond distance of 2.556\AA as well as the mean Fe-Fe bond distance of 2.583\AA are somewhat longer than those values found for the black analogue described before [45]. The dianionic complex $[\text{Fe}_3\text{Cu}(\mu\text{-SPr})_6\text{Cl}_3]^{2-}$ [47] contains an Fe_3Cu trigonal pyramidal displaying C_{3v} symmetry (Fig. 4). The three iron atoms define vertices of a basal triangular plane with Fe...Fe separations of 3.852\AA . The apex of the pyramid is occupied by the copper atom (Fe-Cu distance of 3.205\AA). This metal core is held together by six thiolate groups. The Fe-S and Cu-S bond distances are 2.345 and 2.241\AA , respectively.

There are five Fe_2Cu_2 complexes [29,48,49]. Two of them [29,48] contain a Fe_2Cu_2 butterfly metal core with Fe-Fe bond ($2.863(1)\text{\AA}$) in [29] and $2.850(1)\text{\AA}$ in [48], double bridges mediated by CuPcy_3 [29] or CuPBu_3 [48] fragments, with the mean Fe-Cu bond distances of 2.535\AA in the former and 2.565\AA in the latter.

The remaining three Fe_2Cu_2 complexes [49] contain two linked $\text{Fe}(\mu\text{-}\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{. PPh}_2)_2\text{Cu}$ moieties. In the first one the bridging takes place by an oxygen atom of a nitrate anions, while in the second one there are two iodine atoms forming the bridges. The third one contains a centrosymmetric copper(I) dimer with a formatted anion acting in a bidentate end-to-end bridging mode and the bulkier $\text{Fe}(\text{C}_5\text{H}_4\text{PPh}_2)_2$ serving as chelating agent. As the result of this arrangement, the complex can be described as eight-membered ring

$\{\text{CuOCO}\}_2$ sandwiched between two ferrocenyl rings.

In an orange Fe_2CuHg complex [50] a Fe-Hg-Fe unit is linked to a copper atom by $\mu\text{-}\eta^2\text{-dppm-P,P'}$ ligands. The Fe-Hg bond distance is $2.613(2)\text{\AA}$ which is somewhat shorter than the value of Hg-Cu bond distance, $2.689(2)\text{\AA}$. The linearity of the Fe-Hg-Fe chain ($176.62(4)^\circ$) and the value for the Fe-Hg-Cu ($91.96(2)^\circ$) is consistent with a T-shaped conformation.

In a Fe_2CoCu complex [51] the Fe_2Co triangular plane is capped from one side by a CuPPh_3 unit and from the other side by a $\mu\text{-S}$ atom, thus displaying a trigonal bipyramid polyhedron. The mean Fe-Co bond distance of 2.595\AA is somewhat longer than that for the Fe-Cu bond distance (av. 2.582\AA), but shorter than the Fe-Fe bond distance of $2.624(2)\text{\AA}$.

Inspection of the data in (Table 3) that the heterotetramers crystallized in the three crystal classes: monoclinic (x3), triclinic (x4), and orthorhombic (x1). The complexes are colored yellow (x4), brown and orange (each x2) and even black (x1). The iron atoms have the following inner coordination spheres: FeS_3Cl , FeC_4Fe , FeC_3PSiHg , FeC_5Fe_2 , $\text{FeC}_4\text{Cu}_2\text{Fe}$, $\text{FeC}_4\text{CuFe}_2$, $\text{FeC}_3\text{ICuCoFe}$, $\text{FeC}_5\text{CuFe}_2$, and FeC_{10} (sandwich). The copper atoms CuS_3 , CuPFe_2 , CuP_2Hg , CuP_2X_2 (X=O, S or I), CuClFe_2 , CuPFe_3 and CuPCoFe_2 . The mercury has HgFe_2Cu and cobalt, $\text{CoC}_2\text{SPCuFe}_2$. The ligands can be divided into three groups, one which coordinated only iron atoms with the most common C donor; another one which bound to copper atoms (prevails PL) and the third one which serve as bridge/s between the heterometals. The mean Fe-L bond distance elongate in the order: 1.78\AA (CO) < 1.965\AA ($\mu_3\text{-CL}$) < 2.01\AA ($\mu\text{-CO}$) < 2.315\AA (Cl) < 2.33\AA (SiL). The mean Cu-L bond distance elongate in the order: 2.16\AA ($\mu\text{-OL}$) < 2.24\AA (PL) < 2.438\AA (I) < 2.736\AA ($\mu\text{-I}$). The mean values for the ligands which serve as bridge/s between the heterometals (Fe-L vs Cu-L) are: 2.26 vs 2.23\AA ($\eta^1\text{P}$: $\eta^1\text{PL}$); 2.345 vs 2.34\AA ($\mu\text{-S}$); 2.025 vs 2.36\AA ($\mu\text{-}\eta^2\text{(C)}$: $\eta^1\text{(P)L}$); and 1.99 vs 2.01\AA ($\mu_4\text{-CCO}$). The mean M-M bond distance elongate in the sequence: 2.521\AA (Cu-Co) < 2.552\AA (Fe-Cu) < 2.595\AA (Fe-Co) < 2.613\AA (Fe-Hg) < 2.655\AA (Fe-Fe) < 2.689\AA (Cu-Hg).

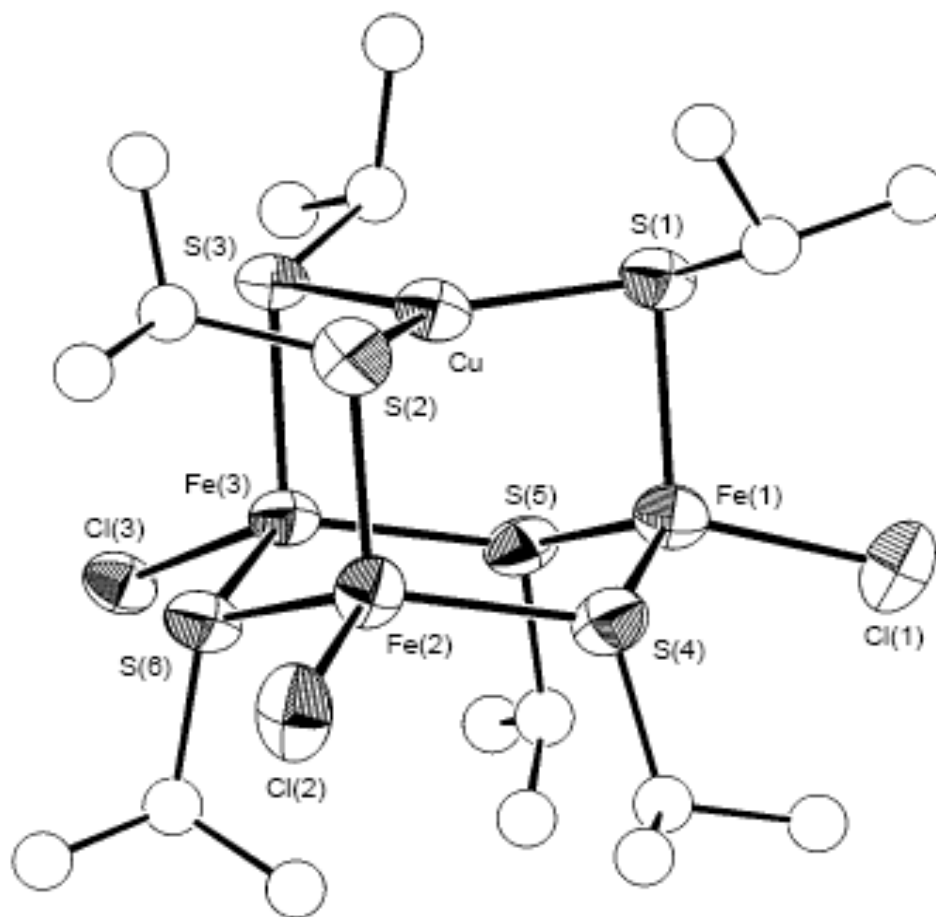


Fig. 4. Structure of $[\text{Fe}_3\text{Cu}(\text{SPr})_6\text{Cl}_3]^{2-}$ [47]

5. HETEROPENTA-, HETEROHEXA-, AND HETEROHEPTAMERIC COMPLEXES

There only three heteropentamers (Fe_4Cu (x2) and Fe_3CuTe (x1)) complexes and their structural parameters are gathered in (Table 4). Structure of black Fe_4Cu complex [52] contains well separated ppn cation and $[(\text{CO})_{13}\text{Fe}_4\text{Cu}(\text{PPh}_3)]$ anion. The complex anion has a tetrahedral iron core capped by CuPPh_3 unit. The mean Fe-Cu bond distance of 2.556\AA is about 0.050\AA shorter than that of Fe-Fe bond distance (av. 2.606\AA). Structure of yellow Fe_4Cu complex [53] consists of a centrosymmetric neutral $[(\text{cp})\text{Fe}_2(\mu\text{-ema})_2\text{Cu}(\text{NO}_3)_2]$ units (Fig. 5) and methanol crystallization molecules. The copper(II) atom exhibits a distorted octahedral environment (CuN_4O_2). The four equatorial positions are occupied by the nitrogen atoms of the bidentate (ema)Fe(cp) fragments, and nitrate anions. The Fe...Cu separations are $6.024(2)$ and $6.211(2)\text{\AA}$.

Structure of deep purple Fe_3CuTe complex [54] composites of an $\{\text{Fe}(\text{CO})_3\}_3$ triangle which is capped by a $\mu_3\text{-Te}^{2-}$ ion, with one edge bridged by a CuCl unit. The $\{\text{CuCl}\}$ fragment is approximately evenly placed across one iron-iron bond. The bridged Fe-Fe bond distance $2.738(3)\text{\AA}$ is noticeably longer compared to the unbridged Fe-Fe bond distances, av. 2.648\AA . The mean Fe-Cu bond distance is 2.485\AA .

There are five heterohexameric (Fe_4Cu_2 (3 examples), Fe_3Cu_3 (2 examples)) complexes (Table 4). In the structure of $[(\text{CO})_8\text{Fe}_2]_2\text{Cu}_2(\text{dchpe})^{2-}$ [29] the inversion center resides on the midpoint of the ethylene C-C bond in the diphos ligand, and only half of the dianion is in the asymmetric point. In the dianion two $\text{Fe}_2(\text{CO})_8$ units are connected by a $\text{Cu}(\text{dchpe})\text{Cu}$ fragment. The Fe-Fe bond distance is $2.8238(6)\text{\AA}$. The Fe-Cu bond distances are $2.4781(6)$ and $2.5310(5)\text{\AA}$.

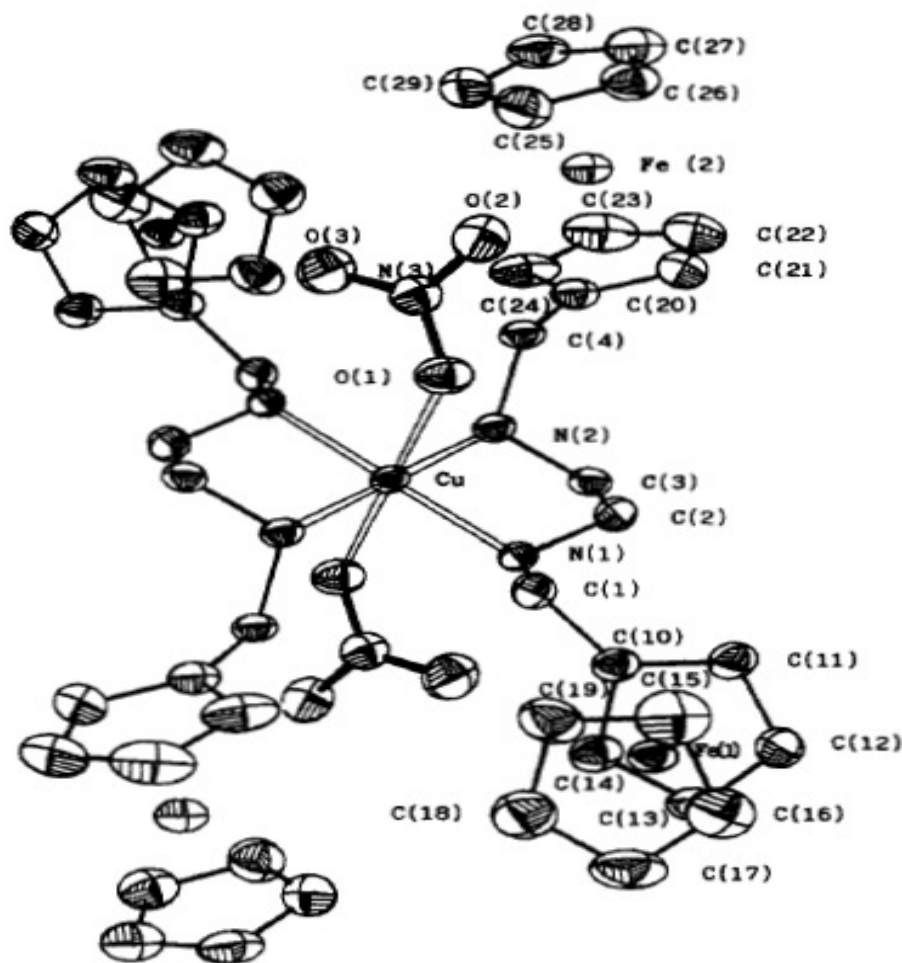


Fig. 5. Structure of $[(cp)Fe_2(ema)_2Cu(NO_3)_2]$ [53]

X-ray analysis of the dark green Fe_4Cu_2 complex [55] shows that the $[(cp)Fe_4(C_5H_4COO)_4Cu_2(thf)_2]$ molecule has a strict, crystallographically imposed, inversion center. Each copper(II) atom is linked to oxygen atoms from four distinct carboxylate groups and one thf molecule. The Cu-Cu bond distance is 2.605(1)Å. Each copper(II) atom has a square – pyramidal arrangement with the copper atoms displaced from the basal plane toward the apical thf ligand by 0.182(1)Å. Of the two crystallographically independent conformations that around Fe(1) is eclipsed while that around Fe(2) is staggered. Each iron atom is sandwiched (FeC_{10}). The dihedral angle between the $\eta^5-C_5H_4$ and $\eta^5-C_5H_5$ planes is 3.65° for eclipsed systems about Fe(1) and 3.04° for the staggered systems about Fe(2).

An orange Fe_4Cu_2 complex [56] consists of a dimer copper unit bridged by two 1,1'-dimethyl-P-phenyl-2,2'-bis(ferrocenylmethylene) phosphonothionic dihydrazide ligands. The molecule possesses an inversion center, which is the middle of the Cu-Cu vector. Each ligand is coordinated via the two N atoms of the imino groups, to two different copper atoms and via the sulphur atom that bridges the Cu-Cu vector (Cu-Cu, 2.727(2)Å). Each iron atom is sandwiched (FeC_{10}).

The structure of yellow Fe_3Cu_3 complex [57] contains well separated NEt_4^+ cations and the $[(CO)_4Fe_3Cu_3]^{3-}$ anion. The structure of the anion consists of a planar triangular Cu_3 core bridged on all three edges by $Fe(CO)_4$ groups. The mean Fe-Cu and Cu-Cu bond distances are 2.421 and 2.601Å. Another yellow orange Fe_3Cu_3

complex [58] results from the assemblage of three $\{(\text{cp})\text{Fe}\{\text{C}_5\text{H}_3(1\text{-PPh}_2)(2\text{-CH}(\text{Me})\text{S})\text{Cu}\}$ fragments and shows approximate C_3 overall symmetry. The core of the complex is constituted by a Cu_3S_3 ring, which adopts a chair-like conformation. (Fig. 6). The substituents attached to this ring are pseudo – equatorially arranged. Each copper(I) atom has a slightly distorted trigonal planar (CuS_2P) and iron atoms are sandwiched (FeC_{10}). There are two categories of $\text{Cu}\dots\text{Cu}$ separations with the values of 3.194 and 3.356 Å (av.), respectively. The Cu-S-Cu bridge angles reflect the separations, longer separation more open the respective angles, 92.3 vs 97.7°, respectively.

There are two heteroheptameric, (FeCu_6 and FeCu_2Ru_4) complexes (Table 4). The structure of the dark purple FeCu_6 complex [59] consists of an iron(II) center connected by cyano bridges to six copper(II) centers forming spherical units of

$[\text{Fe}\{(\mu\text{-}\eta^2\text{-CN})\text{Cu}(\eta^3\text{-tpa})\}_6]^{8+}$. The $\text{Fe}\dots\text{Cu}$ separations range from 4.899(4) to 4.929(4) Å, which excluded the bond. Each $\text{Cu}(\text{II})$ atom is four- CuN_4 (square planar) and iron atom is six- FeC_6 coordinated. The structure of the dark red FeCu_2Ru_4 complex [60] adopts a capped trigonal bipyramidal skeletal geometry. The four ruthenium atoms form a tetrahedron, with the one Ru_3 face $[\text{Ru}(1)\text{Ru}(2)\text{Ru}(3)]$ capped by a copper atom $[\text{Cu}(1)]$ and the $\text{Cu}(1)\text{Ru}(2)\text{Ru}(3)$ face of the CuRu_3 tetrahedron so formed, further capped by a second copper atom. The $\text{Fe}(\text{C}_5\text{H}_4\text{PPh}_2)_2$ ligand is attached to the two copper atoms and both $\text{Cu}(1)\text{Ru}(1)\text{Ru}(2)$ and $\text{Cu}(1)\text{Ru}(1)\text{Ru}(3)$ faces of the metal skeleton are capped by a triple bridging hydrido ligand. The Cu-Cu bond distance is 2.528(2) Å. The mean Cu-Ru bond distance of 2.724(2) Å is about 0.148 Å shorter than the mean Ru-Ru bond distance (2.872(1) Å).

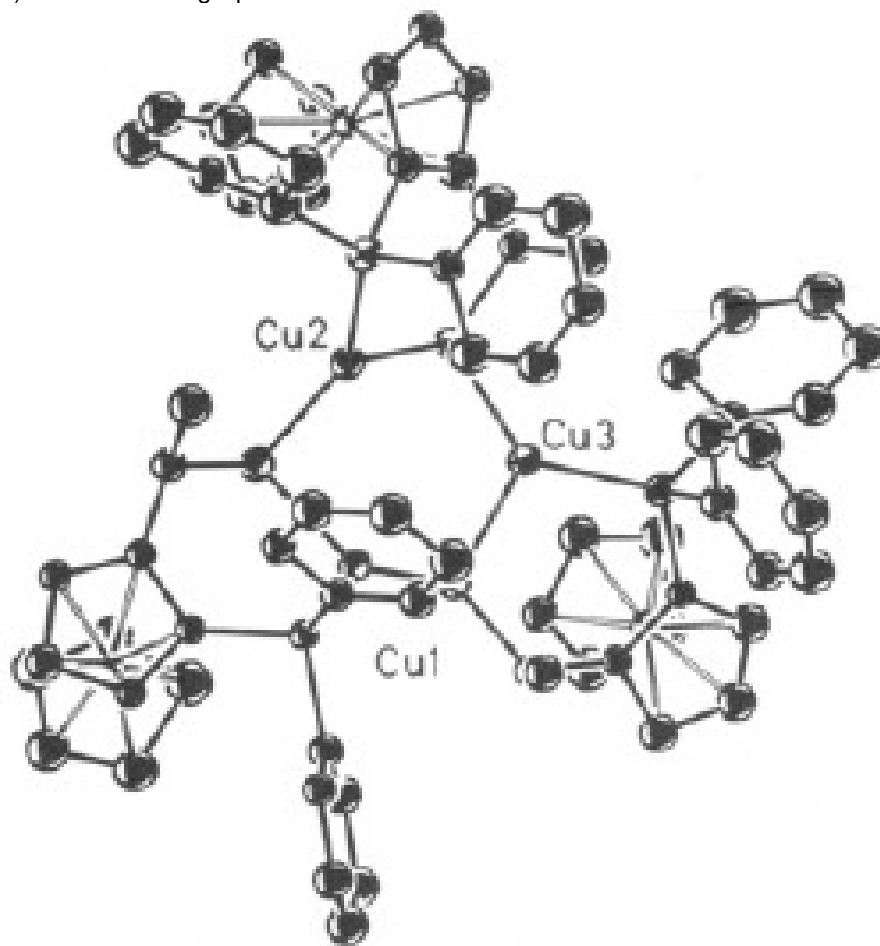


Fig. 6. Structure of $[(\text{cp})\text{Fe}\{\text{C}_5\text{H}_3(\text{PPh}_2)(\text{CH})(\text{Me})\text{S}\}\text{Cu}]_3$ [58]

Inspection of the data in (Table 4) reveals that there are heterometallic complexes with the Fe_4Cu [52,53], Fe_3CuTe [54], Fe_4Cu_2 [29,55,56], Fe_3Cu_3 [57,58], FeCu_6 [59] and FeCu_2Ru_4 [60] cores. The inner coordination sphere around iron atoms are: FeC_6 , FeC_4Cu_2 , FeC_4CuFe , $\text{FeC}_4\text{TeFe}_2$, $\text{FeC}_3\text{CuFe}_3$, $\text{FeC}_3\text{TeCuFe}_2$ and FeC_{10} . The inner coordination spheres around copper atoms are: CuPFe , CuS_2P , CuClFe_2 , CuN_4 , CuN_2S_2 , CuPFe_3 , CuPRu_2Cu , CuPRu_3Cu , CuO_5Cu and CuN_4O_2 . The ruthenium atoms are six- RuC_3Ru_3 and seven- $\text{RuC}_3\text{Cu}_2\text{Ru}_2$ and $\text{RuC}_3\text{CuRu}_3$ coordinated. The mean Fe-C bond distance elongated in the order: 1.76\AA (CO) < 2.04\AA ($\eta^5\text{CL}$), and Cu-L bond distance: 2.05\AA (ter-NL) < 2.21\AA (PL) < 2.37\AA (OL). There are heterodonor ligands which serve as bridge/s between Fe vs Cu in the manners: $\eta^1\text{CN}$: $\eta^1\text{NC}$; $\eta^4\text{C}$: $\eta^1\text{PL}$; $\eta^5\text{C}$: $\eta^1\text{OL}$; $\eta^5\text{C}$: $\eta^1\text{SL}$; $\eta^{10}\text{C}$: $\eta^2\text{NL}$; and $\eta^{10}\text{C}$: $\eta^2\text{SL}$. The mean M-M bond distance elongated in the order: 2.492\AA (Fe-Te) < 2.494\AA (Fe-Cu) < 2.622\AA (Cu-Cu) < 2.704\AA (Fe-Fe) < 2.752\AA (Cu-Ru) < 2.852\AA (Ru-Ru). The complexes crystallized in triclinic (5 examples), monoclinic (4 examples) and orthorhombic (1 example) crystal classes.

6. HETEROOLIGO- AND HETEROPOLYMERIC COMPLEXES

There are four heterooligo- Fe_4Cu_4 (2 examples), Fe_4Cu_5 and Fe_6Cu_5 complexes (Table 5). The core molecular structure of $\{[(\text{cp})\text{Fe}(\text{C}_5\text{H}_4\text{CH}_2\text{NMe}_2\text{Cu})_4(\mu_4\text{-O})(\mu\text{-Cl})_6]$ (Fig. 7) [61] consists of a central oxo group that is tetrahedrally coordinated to four Cu(II) centers. Each Cu(II) carries monodentate $(\text{cp})\text{Fe}(\text{C}_5\text{H}_4\text{CH}_2\text{NMe}_2)$ ligand and is bridged to three other Cu(II) centers by chlorine ligands. The coordination sphere about copper centers is trigonal bipyramidal (CuCl_3ON), with three chlorine donors occupying the equatorial position and the axial sites defined by the central oxo group and the amine donor group of the $\{(\text{cp})\text{Fe}(\text{C}_5\text{H}_4\text{CH}_2\text{NMe}_2)\}$ moiety. The copper atom is displaced 0.17\AA from the Cl plane in the direction of the amine donor. Each iron is sandwiched (FeC_{10}). In $\{[(\text{cp})\text{Fe}(\text{C}_5\text{H}_4\text{CH}_2\text{NMe}_2\text{Cu})_4]$ [62] four Cu(I) atoms form plane square $\{\text{CuN}_2\text{Cu}_2\}$. Each $\{(\text{cp})\text{Fe}(\text{C}_5\text{H}_4\text{CH}_2\text{NMe}_2)\}$ moiety serve as bridge between two Cu(I) atoms by amine donor. Unfortunately, structural parameters are not available.

Structure of yellow Fe_4Cu_5 complex [57] contains well separated $(\text{NEt}_4)^+$ cations and $\{[(\text{CO})_4\text{Fe}]_4\text{Cu}_5\}^{3-}$ anion. In the complex anion the

metal atoms to be arranged in a nearly perfect 3×3 rhombus with $\text{Fe}(\text{CO})_4$ groups occupying the four corners and copper atoms located in the remaining position. The metal atoms thus form a small section of a close-packed surface. There are two different types of iron and copper atoms in the cluster, the central copper atom having six nearest neighbors in the plane. The central copper is apart of $2.627(3)\text{\AA}$ from the copper atom on the adjacent edge, whereas the edge lying coppers are $2.691(4)\text{\AA}$ from the copper atom on the adjacent edge. The two iron atoms, which defined the short diagonal of the rhombus bridge three coppers and are, located $2.410(3)\text{\AA}$ from the Cu's on the edge and $2.491(3)\text{\AA}$ from the central copper atom. The remaining two iron atoms bridge two Cu's with a Fe-Cu bond distance of 2.39\AA .

Structure of dark red Fe_6Cu_5 cluster [63] contains well separated $(\text{NEt}_4)^+$ cation, $\{[(\text{CO})_{12}\text{Fe}_6(\mu\text{-CO})_6(\mu_4\text{-S})\text{Cu}_5(\text{PPh}_3)_2]^-$ anion and MeCN molecule. Structure of the complex anion is shown in (Fig. 8). The cluster consists of a central Cu_5 core in trigonal bipyramidal arrangement with the equatorial plane units chelating to the copper atoms of the central Cu_5 along the pseudo- D_3 axis through the Cu(4) and Cu(5) atoms to the trigonal bipyramidal resulting in pseudo- D_3 symmetry. There are fifteen M-M bonds, including six Cu-Fe of 2.710\AA , three Fe-Fe bonds of 2.525\AA and six Cu-Cu of 2.604\AA .

7. HETEROPOLYMERIC COMPLEXES

There are eleven colored polymeric $\{\text{FeCu}\}_n$ complexes and their crystallographic and structural data are gathered in (Table 5). The structure of dark green monoclinic $\text{Fe}(\text{CN})_6\text{Cu}_2(\text{dien})_2 \cdot 6\text{H}_2\text{O}$ [64] consists of a polymer $\{\text{Fe}(\text{CN})_6\}^{4-}$ and $\text{Cu}_2(\text{dien})^{2+}$ ions linked together via 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^- group are bonded to Cu(II) atoms of adjacent $\{\text{Cu}(\text{dien})\}^{2+}$ units giving rise to linear Fe-CN-Cu linkages and are coordinated in the equatorial plane of the square pyramidal configuration, and the remaining two CN^- groups coordinate to Cu(II) of adjacent $\{\text{Cu}(\text{dien})\}^{2+}$ units in the apical positions of the pyramid, leading to the non-linear Fe-CN-Cu chains. The mean Fe-C bond distances are $1.90(1)\text{\AA}$ (CN) and $1.91(1)\text{\AA}$ ($\mu\text{-CN}$). The mean Cu-N bond distance elongated in the order: 1.97\AA ($\mu\text{-NCEq}$) < $2.03(1)\text{\AA}$ (ter-dien) < 2.21\AA ($\mu\text{-NCap}$). Another

two $\{\text{FeCu}\}_n$ complexes [65,66] have similar polymeric structures as in [64].

In blue monoclinic $\{\text{FeCu}\}_n$ complex [67] the Cu(II) atoms are in square-pyramid arrangement (CuN_4O) with the four N atoms of porphyrine ligand in the square plane and water in an axial position. The porphyrins are stacked in a regular sandwich array, with interporphyrine distance of 3.85Å and Cu...Cu separation of 5.95Å. There are two types of ferrocyanide ions in the structure. The first type (one per porphyrine) is in the water rich regions and appears to form a dimer ($\text{Fe}\dots\text{Fe}$, 8.68Å) held together by hydrogen bond water sitting at the intersection of the CN vectors. The second type of $\{\text{Fe}(\text{CN})_6\}^{4-}$ (0.5 per porphyrine situated on an inversion

center) is embedded in the hydrophobic region of the structure. The two types of ferrocyanide units are bonded via hydrogen bonded waters.

The dication $[\{\text{Cu}(\text{Mesalen})\}_3\text{Fe}(\text{acac})]^{2+}$ of the (Cu_3Fe) system has a polymeric structure (Fig. 9) [68]. The asymmetric unit is formed by trimeric $\{\text{Cu}(\text{Mesalen})\}_2\text{Fe}(\text{acac})$ unit plus a $\{\text{Cu}(\text{Mesalen})\}$ unit. The asymmetric units are related one to the other by binary axis passing respectively through the Fe(1) or the Cu(2) atoms (Fig. 9). The Fe(II) atoms are six (FeO_6) and Cu(II) are five- (CuO_3N_2) square pyramidal coordinated. The Fe...Cu and Cu...Cu distances are 3.033(2)Å and 3.654(2)Å, respectively.

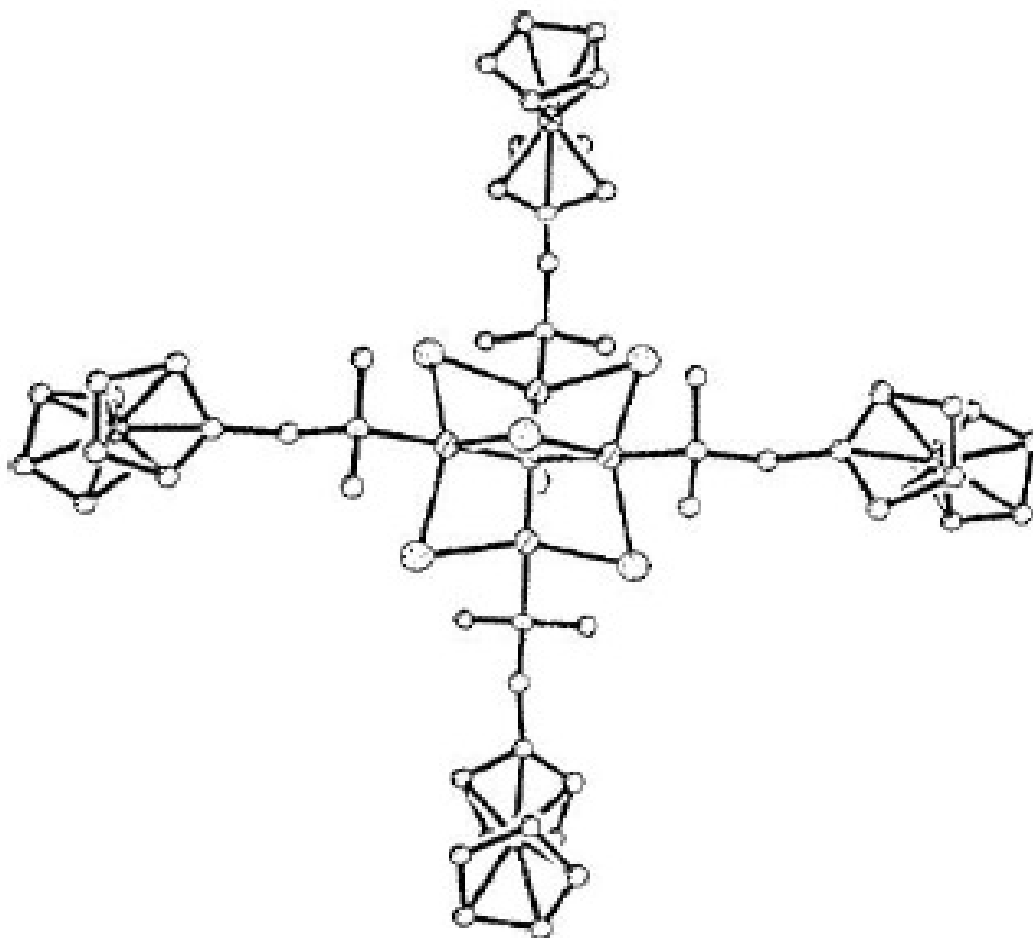


Fig. 7. Structure of $[\{(\text{cp})\text{Fe}(\text{C}_5\text{H}_4\text{CH}_2\text{NMe}_2)\text{Cu}\}_4(\mu_4\text{-O})(\mu\text{-Cl})_6]$ [61]

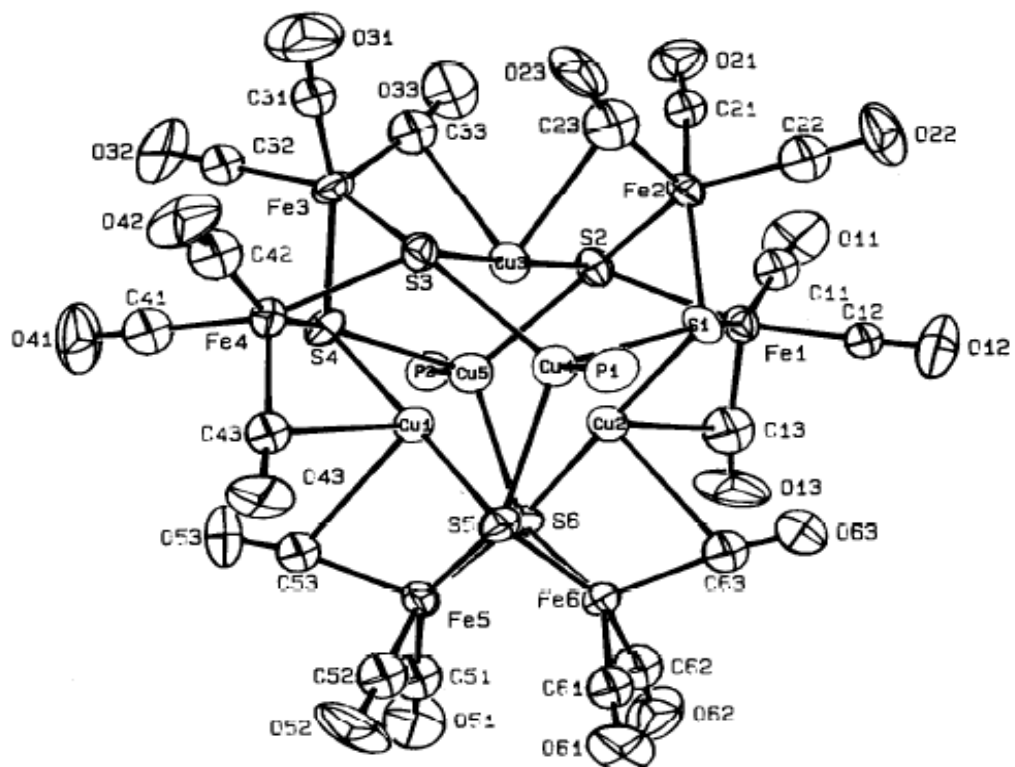


Fig. 8. Structure of $[(\text{CO})_{12}\text{Fe}_6(\text{CO})_6(\mu_4\text{-S})_6\text{Cu}_5(\text{PPh}_3)_2]$ [63]

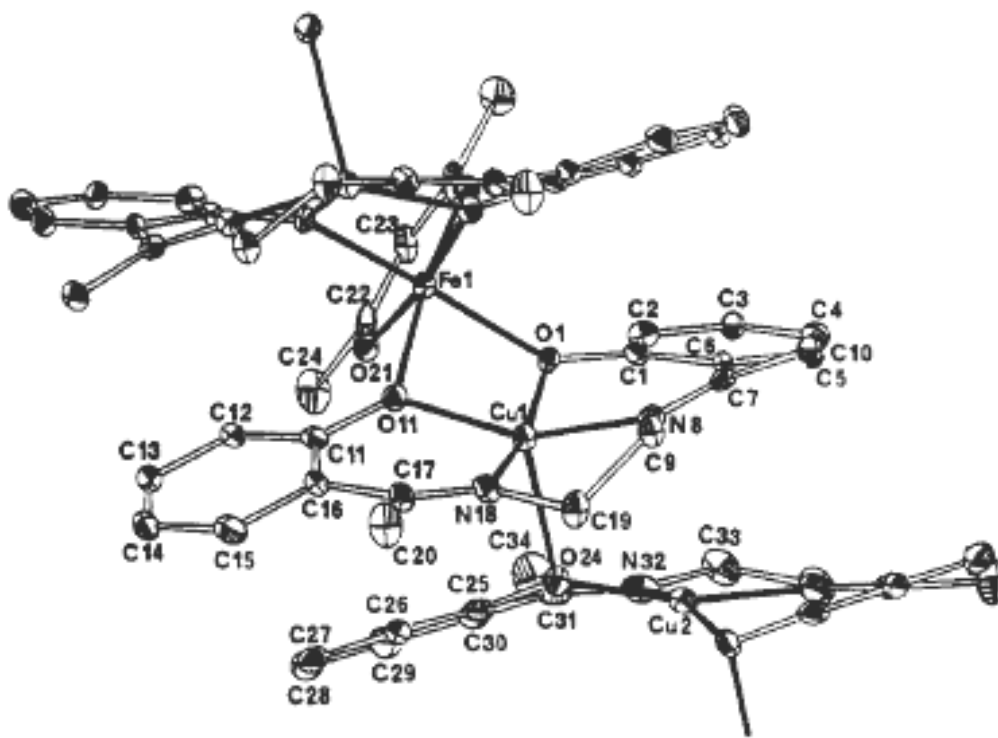


Fig. 9. Structure of $[\{\text{Cu}(\text{mesalem})\}_3\text{Fe}(\text{acac})]_n^{2+}$ [68]

Another blue monoclinic $[(\text{Fe}(\text{edta}))_2\text{Cu}(\text{en})_2(\text{H}_2\text{O})_2(\mu\text{-O})]_n$ [69] is a three – dimensional polymer consisting of a $\{(\mu\text{-oxo})\text{Fe}(\text{edta})\}$ dimers connected with two different $\text{Cu}(\text{en})_2$ moieties $\{\text{Cu}(1)$ and $\text{Cu}(2)\}$ sitting on non-equivalent inversion centres. In one case the edta ligand provides a carboxylate group that coordinate axially to the $\text{Cu}(2)$ atom. In the other, a water molecule axially coordinated to $\text{Cu}(1)$ forms a hydrogen bond with a carboxylate coordinated to the $\text{Fe}(\text{III})$ atom. Each $\text{Cu}(1)$ atom is connected with four $\text{Fe}(\text{III})$ atoms via hydrogen bonds. The $\text{Cu}(2)$ is linked to an iron atom through a covalent iminoacetate group ($-\text{NCH}_2\text{COO}-$). This connection is reproduced by symmetry, and an ordered trimetallic chain of the type $\{\dots\text{Cu}(2)\dots\text{Fe}\dots\text{Fe}\dots\}$ is formed. Some relevant intermetallic distances are: $\text{Fe}\dots\text{Fe}$ 3.533(1)Å, $\text{Fe}\dots\text{Cu}(1)$ 5.734(1), 5.986(1)Å and $\text{Fe}-\text{Cu}(2)$ 6.681(1)Å.

Inspection of the data in (Table 5) reveals that there are four heterooligomers with the Fe_4Cu_4 [61,62], Fe_4Cu_5 [57], and Fe_6Cu_5 [63] cores, and eleven heteropolymers $\{\text{FeCu}\}_n$ [64-72].

The complexes crystallized in the following crystal classes: monoclinic (6 examples), tetragonal (3 examples) and hexagonal (1 example). The inner coordination sphere about iron atoms are: FeX_6 ($X = \text{O}, \text{N}$ or C), FeO_4N_2 , FeN_3C_3 , FeC_4Cu_2 , $\text{FeC}_3\text{S}_2\text{CuFe}$ and FeC_{10} . The copper atoms are CuS_3P , CuN_2Cu_2 , CuFe_2Cu_2 , CuN_5 , CuN_4O , CuO_3N_2 , CuCl_3ON , CuN_4O_2 , CuFe_2Cu_4 , and $\text{CuC}_2\text{S}_2\text{Fe}_2\text{Cu}_4$ coordinated. The mean $\text{Fe}-\text{L}$ bond distance elongated in the order: 1.77Å ($\mu\text{-O}$) < 1.805Å (CO) < 1.925Å (CN) < 1.97Å ($\text{tetra} - \text{OL}$) < 1.975Å (ter-NL) < 2.025Å ($\text{penta} - \text{CL}$). The mean $\text{Cu}-\text{L}$ bond distance elongate in the order: 1.92Å ($\mu_4\text{-O}$) < 2.00Å ($\text{tetra} - \text{NL}$) < 2.015Å ($\text{bi} - \text{NL}$) < 2.02Å ($\text{ter} - \text{NL}$) < 2.03Å (NL) < 2.245Å (PPh_3) < 2.41Å ($\mu\text{-Cl}$) < 2.54Å (OH_2). The heterodentate ligands which serve as bridge/s ($\text{Fe}:\text{Cu}$) in the manner: $\eta^1\text{C}:\eta^1\text{C}(\text{CO})$; $\eta^1\text{C}:\eta^1\text{N}$ (CN); $\eta^1\text{N}:\eta^1\text{N}$ (N_3); $\eta^1\text{O}:\eta^2\text{O}\eta^1\text{N}(\text{L})$; $\eta^5\text{C}:\eta^1\text{N}(\text{L})$. The mean $\text{M}-\text{M}$ bond distance elongated in the order: 2.525 ($\text{Fe}-\text{Fe}$) < 2.537Å ($\text{Fe}-\text{Cu}$) < 2.650Å ($\text{Cu}-\text{Cu}$). Both steric and electronic factors associated with the donor atom appear to influence the $\text{L}-\text{M}-\text{L}$ bond angles of the macrocyclic rings. The mean $\text{L}-\text{Fe}-\text{L}$ bond angle opens in the order: 75.4° ($-\text{NC}_2\text{N}-$) < 80.2° ($-\text{OC}_2\text{N}-$); and $\text{L}-\text{Cu}-\text{L}$ bond angle: 84.8° ($-\text{NC}_2\text{N}-$) < 95.8° ($-\text{OC}_3\text{N}-$).

Structure of brown monoclinic $\{\text{FeCu}\}_n$ [70] consists of one $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ anion, two $[\text{Cu}^{\text{II}}(\text{tn})]^{2+}$

cations, one K^+ , one Cl^- and five H_2O molecules. The copper(II) atoms exhibit a CuN_5 inner coordination sphere, which created in both cases by bidentate tn ligand and by three N atoms of the cyano groups. While coordination geometry about the $\text{Cu}(\text{II})$ is intermedial between the two ideal geometries (trigonal bipyramidal and square pyramidal). The $\text{Cu}(2)$ atom is located in an approximately square-pyramidal geometry. The $\text{Fe}(\text{II})$ atom is hexacoordinated FeC_6 . The $[\{\text{Cu}(\text{tn})\}_2\{\text{Fe}(\text{CN})_6\}]$ forms an infinite lamellar structure (2D layered). The shortest $\text{Cu}\dots\text{Cu}$ distance is 6.845(1)Å and mean $\text{Fe}-\text{Cu}$ distance is 5.045Å.

Structure of black also monoclinic $\{\text{FeCu}\}_n$ [70] consist of one $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ anion, two $[\text{Cu}^{\text{II}}(\text{tn})]^{2+}$ cation and two H_2O molecules. The $\text{Cu}(\text{II})$ atom (CuN_5) has a trigonal bipyramidal distorted square-pyramid. The inner coordination sphere is created by non-chelating three tn ligand and by two N atoms of cyano groups. The $\text{Fe}(\text{II})$ atom is hexacoordinated (FeC_6). The mean $\text{Fe}-\text{Cu}$ distances 5.073Å. The polymeric structure of the complex displays a 3D layer.

Structure of dark green $\{\text{FeCu}\}_n$ [70] consists of one $[\text{Fe}(\text{CN})_6]^{4-}$ anion, and $[\text{Cu}(\text{tnH})_2(\text{H}_2\text{O})_2]^{4+}$ cation and water molecule. The $\text{Cu}(\text{II})$ atom has a strongly elongated centrosymmetric environment with four almost equivalent $\text{Cu}-\text{N}$ bonds involving two N atoms of CN groups (1.961(4)Å) and two N atoms of tnH 92.044(2)Å and two elongated $\text{Cu}-\text{O}$ bonds (2.633(4)Å). The $\text{Fe}(\text{III})$ has an almost perfect octahedral FeC_6 environment ($\text{Fe}-\text{C} = 1.914(5) - 1.921(4)\text{Å}$). The structure can be described as being formed by linear chains with the alternating $[\text{Cu}(\text{tnH})_2(\text{H}_2\text{O})_2]^{4+}$ and $[\text{Fe}(\text{CN})_6]^{4-}$ units linked by a CN bridge. The shortest $\text{Cu}-\text{Fe}$ and $\text{Cu}\dots\text{Cu}$ intrachain distances are 10.058Å.

Molecular structure of monoclinic $[(\text{tp})\text{Fe}(\text{CN})_3\text{Cu}(\text{dien})]\text{ClO}_4\cdot\text{H}_2\text{O}$ [71] consists of a one-dimensional cationic polymer, with free ClO_4 counteranions. The zig-zag chain is made by up of a cyano-bridged alternating $\{(\text{tp})\text{Fe}(\text{CN})_3\}^-$ and $\{\text{Cu}(\text{dien})\}^{2+}$ fragment. The former fragment uses two cis-CN groups to connect with two $\{\text{Cu}(\text{dien})\}^{2+}$ units, while each $\{\text{Cu}(\text{dien})\}^{2+}$ unit is linked to two $\{(\text{tp})\text{Fe}(\text{CN})_3\}^-$ ions at cis-positions. The $\text{Fe}(\text{III})$ atom is six coordinated (FeN_3S_3) and $\text{Cu}(\text{II})$ atom adopts a distorted square-pyramidal geometry (CuN_5). The mean $\text{Cu}\dots\text{Fe}$ separations within the chain are 5.051Å. The shortest interchain distances are 8.169(2)Å ($\text{Fe}\dots\text{Fe}$), 13.345(2)Å ($\text{Cu}\dots\text{Cu}$) and 11.062(4)Å ($\text{Fe}\dots\text{Cu}$) respectively.

Table 1. Crystallographic and structural data for heterodimeric Fe Cu complexes^a

Complex (colour)	Crys.cl Sp. Gr Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromo-phore	M-L [Å]	Fe-Cu [Å] Fe-L-Cu [°]	L-M-L [°]	Ref
Double salts								
[FeCl ₄][Cu(PPh ₃) ₃] (gold yellow)	m P2 ₁ /n 4	19.146(2) 23.388(2) 11.452(1)	98.683(3)	Fe ^{III} Cl ₄ Cu ^I P ₃	Cl ^o 2.154(3,21) Ph ₃ P 2.295(2,8)		Cl,Cl ^p 109.5(1,4.3) P,P 119.4(1,3.8)	3
[FeCl ₄][Cu(PPh ₃) ₃] (dark brown)	tr P $\bar{1}$ 2	13.233(4) 18.108(3) 12.669(4)	101.13(2) 117.29(2) 94.29(2)	Fe ^{III} Cl ₄ Cu ^I P ₃	Cl 2.178(2,20) Ph ₃ P 2.304(2,24)		Cl,Cl 109.5(1,2.8) P,P 118.1(7,3.4)	3
[Fe(cp ⁺) ₂][Cu(η^2 -mnt) ₂] (black)	tr P $\bar{1}$ 1	9.713(5) 11.417(4) 11.958(5)	109.90(2) 113.20(5) 92.66(3)	FeC ₁₀ Cu ^{II} S ₄	cp ⁺ C not given S 2.271(2,9)		C,C not given S,S 90.67(5)	4
[Fe(η^4 -tpp)(Him) ₂]. [Cu(η^2 -mnt) ₂].(thf) ₄ (dark)	tr P $\bar{1}$ 1	10.012(4) 11.604(6) 15.902(7)	71.42(4) 87.12(3) 78.45(4)	Fe ^{III} N ₆ Cu ^{III} S ₄	η^4 N 1.982(3,1) imN 2.016(3,0) η^2 S 2.173(2,5)		N,N 91.1(1,2) ^c S,S 92.8(1) ^c	5
Fe Cu dimers								
[(PEtPh ₂)Fe(μ -H) ₃ . Cu(PEtPh ₂)] (red orange) (at 233 K)	m P2 ₁ 2	10.872(2) 18.512(4) 12.647(3)	94.10(3)	Fe ^{II} H ₃ P ₃ . Cu Cu ^I H ₃ P ₃ .Fe	μ H 1.52(-,15) P 2.182(1,2) μ H 1.60(-,1) 1.89 P 2.182(3,2)	Cu 2.319(2) H 81.9 98.3(-,7.0)	P,P 105.9(2,5.1) P,Cu 109.5(1) 114.9(1,1.0) P,Fe 179.3(1)	6
{Si(OMe) ₃ (OC)Fe. (μ -CO) ₂ (μ - η^1 : η^1 - dppm)Cu(AsPh ₃) (yellow)	m P2 ₁ /c 4	11.582(1) 8.650(1) 21.919(2)	94.24(1)	FeC ₃ P. SiCu Cu ₂ P. AsFe	OC 1.75(1) P 2.224(3) Si 2.282(3) μ OC 1.74(1) μ OC 2.45(1,7) P 2.259(3) As 2.355(1)	Cu 2.497(2) C not given	C,C 111.9(5,3) 133.3(4) C,P 95.4(4,1.9) Si,P 177.2(2) C,Cu 67.7(3,2.1) 175.9(4) P,Cu 89.6(1) Si,Cu 93.2(1) C,As 110.8(2) 129.6(2) P,As 118.9(1) C,Fe 41.4(3,6) P,Fe 103.86(8) As,Fe 137.27(6)	7
[(OC) ₂ Fe(μ - η^1 : η^1 - Ph ₂ Ppy) ₂ (μ -CO). Cu(ac)]ClO ₄ .	m C2/c 8	26.600(5) 14.815(3) 26.075(5)	108.75(5)	FeC ₃ P ₂ Cu CuN ₂ O. CFe	OC 1.780(11,2) μ OC 1.815(11) μ LP 2.211(3,2)	Cu 2.501(2) C 74.4(4)	C,C 109.4(5,5.1) 141.2(4) P,P 165.7(1)	8

1.75Me ₂ CO (gold yellow)					μLN 2.055(10,6) AcO 2.117(8) μOC 2.276(11)		C,Cu 61.2(3) 80.0(3) 165.5(3) N,N 123.6(4) N,O 99.8(3,9.8) N,C 113.6(4) N,Fe 98.2(2,4) O,Fe 139.8(3)	
[(OC) ₂ Fe(μ-η ¹ :η ¹ - Ph ₂ Ppy) ₂ (μ-CO). Cu(H ₂ O)]ClO ₄ (orange)	tr Pī 2	12.388(1) 13.473(1) 14.248(1)	103.01(1) 91.02(1) 100.39(1)	FeC ₃ P ₂ . Cu CuN ₂ OC.Fe	OC 1.780(6,11) μOC 1.778(6) μLP 2.214(2,0) μLN 2.037(5,12) H ₂ O 2.245(6) μOC 2.320(6)	Cu 2.512(2) C 74.3(2)	C,C 111.9(3,2,5) 136.2(3) P,P 169.0(1) C,Cu 68.2(2,5.4) 172.1(2) N,H 135.0(2) N,O 96.0(2) N,Fe 98.8(2,3) O,Fe 140.5(2)	8
{P(NMe ₂) ₂ (OMe)}(OC) ₃ . Fe{μ-η ² -Si(OMe) ₂ . (NMe)}.Cu(PPh ₃) (yellow)	tr Pī 2	9.653(9) 11.977(11) 16.05(2)	100.55(7) 96.14(7) 95.03(8)	FeC ₃ P. SiCu CuNPFe	OC 1.750(5,6) P 2.194(2) Si 2.268(2) N 2.151(4) Ph ₃ P2.198(2)	Cu 2.530(2)	C,C 111.5(2,2.1) 135.4(2) P,Si 178.04(5) Si,Cu 70.23(7) N,P 123.88(12) N,Fe 90.80(12) P,Fe 145.22(5)	9
{Si(OMe) ₃ } ₂ (OC) ₃ Fe. (μ-η ² -dppm)Cu(PPh ₃) (not given)	m P2 ₁ /c 4	11.542(5) 18.567(7) 21.230(7)	94.67(2)	FeC ₃ P. SiCu CuP ₂ Fe	OC 1.712(12) 1.751(13,3) η ² P 2.226(3) Si 2.271(4) η ² P 2.278(3) Ph ₃ P 2.263(3)	Cu2.540(2)	C,C 112.1(6,1) 133.2(5) C,P 95.2(4,7) C,Si 84.5(4,2.7) C,Cu 67.3(4,3.1) 174.0(4) P,Cu 90.7(1) Si,Cu 93.1(1) P,Si 176.3(2) P,P 119.9(1) P,Fe 101.4(1) 138.6(1)	10
[(H ₂ O)ClFe{μ-η ⁴ :η ⁴ - (fsa) ₂ en}Cu(MeOH)]. MeOH	m P2 ₁ /c 4	10.619(6) 11.698(4) 18.429(9)	101.6(1)	FeO ₅ Cl CuO ₃ N ₂	η ⁴ O 1.930(7,9) η ⁴ μO 2.028(7,22) H ₂ O 2.150(7)	O 100.1(3,7)	O,O 77.5(2) 87.2(3,3) ^c 98.8(3,8.5)	11

(dark red)					Cl 2.303(3) MeHO 2.277(7) $\eta^4\mu\text{O}$ 1.929(7,3) $\eta^4\text{N}$ 1.911(8,4)		162.9(3,6) O,O 82.3(3) 95.9(3,1.5) N,N 85.8(4) ^d O,N 95.7(3,2.1) ^c 167.2(3,5)	
(hfa) ₂ Fe{ μ -(prpn) ₂ en}Cu (not given)	m P2 ₁ /c 4	13.576(7) 20.365(5) 12.606(7)	97.70(5)	FeO ₆ CuO ₂ N ₂	hfaO 2.07(1,3) μO 2.15(1,4) μO 1.88(1,1) N 1.94(1,3)	O 96.1(5,9)	O,O 85.5(5,3) ^c 70.9(4) 93.3(5,11.5) 169.1(5,4.7) O,O 83.0(5) N,N 89.5(6) ^d O,N 93.7(5,1.6) 174.8(6,3.3)	12
(hfa) ₂ Fe(μ -prpn) ₂ pr}Cu (not given)	tr P $\bar{1}$ 2	11.630(4) 12.443(6) 13.897(4)	90.83(5) 95.26(5) 116.19(4)	FeO ₆ CuO ₂ N ₂	hfaO 1.922(12) 2.062(1,51) μO 2.086(13,13) μO 1.913(11,4) N 1.933(10) 2.072(12)	O 100.0(4,2)	O,O 85.8(4,1) 69.3(4) 93.6(5,10.0) 168.1(5,6.3) O,O 76.6(6) N,N 97.2(4) ^c O,N 94.9(6,4.9) 166.6(6,3.0)	12
[(H ₂ O)Fe(μ - η^4 : η^4 - nprh)(μ -Cl)Cu]. (ClO ₄) ₂ .H ₂ O (brown)	or P4/n 2	15.96(1) 14.36(1)		Fe ^{III} N ₄ . OCl Cu ^{II} N ₄ Cl	$\eta^4\text{N}$ 2.01(7) H ₂ O 2.081(13) μCl 2.55(5) $\eta^4\text{N}$ 2.16(6) μCl 2.41(5)		not given not given	13
Fe(μ - η^2 : η^1 -mao) ₃ . Cu(PPh ₃) (not given)	tr P $\bar{1}$ 2	9.854(5) 12.765(4) 17.506(4)	94.37(5) 108.84(4) 102.47(3)	Fe ^{II} N ₆ Cu ^I O ₃ P	N 1.913(4,16) 1.953(4,14) O 2.064(3) 2.124(3,3) Ph ₃ P 2.145(2)	Cu 3.394(1)	N,N 78.5(2,7) ^d 94.1(2,6.1) 167.3(2,3.2) O,O 93.7(1,2.0) O,P 122.4(1,6.7)	14
[(η^4 -oep)Fe(μ -F). Cu(η^3 -bnpy)(OCIO ₃)]. PF ₆ (black) (at 173 K)	tr P $\bar{1}$ 2	16.673(3) 13.832(4) 16.901(5)	93.69(105.64(2) 92.91(2)	Fe ^{III} N ₄ F Cu ^{II} N ₃ FO	$\eta^4\text{N}$ 2.049(4,7) μF 1.865(3) $\eta^3\text{N}$ 1.977(4,8) 2.041(4) μF 2.101(3)	Cu 3.956(1) F 171.9(1)	N,N 88.2(1,5) ^c 158.6(5,9) N,F 100.8(5,6) N,N 93.7(2) ^c 96.1(2) ^e N,F 90.0(1,8)	15

					O ₃ ClO 2.139(3)		106.5(1) N,O 84.9(2,8) 156.8(1) F ₂ O 96.7(1)	
[(η^4 -oep)Fe(μ -F). Cu(η^3 -bnpy)(MeCN). (ClO ₄)(PF ₆).MeCN (dark brown) (at 173 K)]	tr P $\bar{1}$ 2	13.96(1) 14.-08(1) 18.49(2)	106.1(1) 100.54(8) 111.74(8)	Fe ^{III} N ₄ F Cu ^{II} N ₄ F	η^4 N 2.04(1,3) μ F 1.86(1) η^3 N 2.00(1,1) 2.08(1) MeCN 2.01(1) μ F 2.22(1)	Cu 4.047(3) F 166.2(5)	N,N 88.0(5,6) 158.6(5,9) N,F 100.8(5,6) N,N 87.6(5) ^c 96.7(6) ^e 87.7(6,2.0); 172.7(6,1.9) N,F 92.3(5,5.6)	15
[(η^4 -oep)Fe(μ -O). Cu(η^4 -Me ₆ tren)]. ClO ₄ thf (violet) (at 173 K)]	or Pnma 4	15.044(2) 18.296(3) 20.051(3)		Fe ^{III} N ₄ O Cu ^{II} N ₄ O	η^4 N 2.10(5A) μ O 1.747(7) η^4 N 2.024(5,0) 2.162(7,4) μ O 1.828(4)	Cu 3.575(1) O 178.2(3)	N,N 86.0(1,2) ^c 149.3(2,8) N,O 105.5(2,1.4) N,N 84.3(2,3) ^c 118.6(3,1.4) N,O 95.7(2,1) 179.6(2)	16
[(η^4 -oep)Fe(μ -O). Cu(η^4 -Me ₆ tren)]. ClO ₄ .MeCN ^f (violet) (at 173 K)]	m P2 ₁ /n 8	17.847(3) 25.085(4) 25.356(4)	108.95(1)	Fe ^{III} N ₄ O Cu ^{II} N ₄ O Fe ^{III} N ₄ O Cu ^{II} N ₄ O	η^4 N 2.110(6,13) μ O 1.745(4) η^4 N 2.086(7,22) 2.150(7,1) μ O 1.829(4) η^4 N 2.113(6,11) μ O 1.783(4) η^4 N 2.083(6,38) 2.168(7,11) μ O 1.830(4)	Cu 3.570(1) O 175.2(3) Cu 3.572(1) P 176.6(3)	N,N 85.7(2,3) ^c 148.4(2,2) N,O 105.8(2,1.0) N,N 84.8(3,1.5) ^c 119.3(3,4.4) N,O 95.2(2,6) 178.5(3) N,N 85.7(2,2) ^c 148.1(2,2) N,O 106.0(2,1.7) N,N 84.5(3,8) ^c 119.1(4.2-4) N,O 95.5(2,1.5) 179.3(2)	16
[(η^2 -mac)Fe(μ - η^4 : η^1 - bpm)Cu(η^2 -acac) ₂]. (ClO ₄) ₂ (purple)]	m P2 ₁ /n 4	8.943(3) 24.332(8) 15.954(5)	100.77(4)	FeN ₆ Cu ^{II} O ₄ N	macN not given bpmN not given η^2 O not given N not given		not given not given	17
[(η^4 -oep)Fe(μ - η^2 -NC). Cu(η^3 -Me ₅ -dien)].	tr P $\bar{1}$ 2	12.265(3) 15.361(3)	98.69(2) 107.20(2)	Fe ^{III} N ₅	η^4 N 2.040(3,5) μ NC 1.859(3)	Cu 4.90	N,N 88.3(2) ^c 99(1)	18

ClO ₄ (black)		15.066(1)	104.93(2)	Cu ^I N ₃ C	η ³ N 2.157(4,72) μNC 1.859(3)		N,N 85.2(1,1) ^c 113.0(2) N,C 111.8(2,1.6) 146.7(2)	
[(η ⁴ -oep)(py)Fe. (μ-η ² -CN)Cu. (η ³ -bnpy).(otf)](otf) (violet)	tr Pī 2	14.960(6) 15.374(7) 16.233(5)	82.22(3) 69.23(3) 84.63(4)	Fe ^{III} N ₅ C Cu ^{II} N ₄ O	η ⁴ N 1.95(2,2) pyN 2.07(1) μNC 1.86(3) η ³ N 1.99(14,0) 2.09(1) μCN 2.02(2) otfO 2.34(1)	Cu 4.94	N,N 90.0(6) ^c 87.(2) N,C 174.2(6) N,N 91.9(5,3.1) ^c 88.7(5,1.2) 153.9(7) 175.9(6) N,O 95.8(5,10.0)	18
[(η ⁴ -oep)(py)Fe. (μ-η ² -CN)Cu(η ³ - Me ₅ dien)(Me ₂ CO)]. (SbF ₆) ₂ .Me ₂ CO (violet)	tr Pī 2	12.152(2) 13.658(3) 22.108(4)	82.04(3) 89.41(3) 67.11(3)	Fe ^{III} N ₅ C Cu ^{II} N ₄ O	η ⁴ N 1.991(7,11) pyN 2.052(6) μNC 1.905(8) η ³ N 2.044(9,9) μCN 1.937(7) Me ₂ CO 2.294(6)	Cu 4.98	N,N 90.0(2) ^c 90.9(2) N,C 176.4(3) N,N 86.8(3,2) ^c 91.9(1,3) 154.8(3) N,O 97.8(3,7.4)	18
[(η ⁴ -oep)(py)Fe. (μ-η ² -CN)Cu(η ⁴ -tim)]. (PF ₆) ₂ .2Me ₂ CO (blue)	m P2 ₁ /c 4	17.083(3) 18.220(4) 23.300(5)	109.40(3)	Fe ^{III} N ₅ C Cu ^{II} N ₅	η ⁴ N 1.974(5,3) pyN 2.072(5) μNC 1.912(7) η ⁴ N 1.970(6,8) μCN 2.171(7)	Cu 5.02	N,N 90.0(2) ^c 90(2) N,C 178.3(2) N,N 80.8(2,1) ^d 97.8(2,1) 166.8(3,1.9)	18
[(η ⁴ -oep)(py)Fe. (μ-η ² -CN)Cu. (η ⁴ -cyclops)]SbF ₆ (red)	m P2 ₁ /c 4	13.619(3) 16.866(4) 26.053(4)	94.69(2)	Fe ^{III} N ₅ C Cu ^{II} N ₅	η ⁴ N 1.991(9,13) pyN 2.11(1) μNC 1.92(1) η ⁴ N 1.965(1,15) μCN 2.13(1)	Cu 5.11	N,N 90.0(4) ^c 90.2(7) N,C 179.1(4) N,N 80.9(4,2) ^d 95.2(4,2.6) 158.5(4,7)	18
[(η ⁴ -oep)(py)Fe. (μ-η ² -CN)Cu. (η ⁴ -Me ₆ tren)]. (SbF ₆) ₂ .Me ₂ CO ^f (not given) (at 223 K)	tr Pī 4	13.833(3) 16.552(4) 31.532(6)	94.90(2) 94.66(2) 112.52(2)	Fe ^{III} N ₅ C Cu ^{II} N ₅ Fe ^{III} N ₅ C	η ⁴ N 1.99(1,1) pyN 2.057(9) μNC 1.88(1) η ⁴ N 2.01(1) 2.14(1,0) μCN 1.91(1) η ⁴ N 2.00(1,2) pyN 2.05(1)	Cu 4.93	N,N 90.0(4,8) ^c 91(1) N,C 89(1),178.9(5) N,N 86.7(2,1.9) ^d 94.3(5,1.6) 119.4(6,7) N,N 90.0(4,3) ^c 91.1(3)	19

				Cu ^{II} N ₅	μNC 1.92(2) η ⁴ N 1.99(1) 2.14(2,1) μCN 1.88(1)		N,C 89(1),178.0(5) N,N 86.4(6,1.4) ^d 93.6(6,5) 119.6(7,1.3)	
[(η ⁴ -oep)(py)Fe. (μ-η ² -CN)Cu. (η ³ -Me ₅ dien). (otf)](otf) (not given) (at 223 K)	tr Pī 2	11.941(2) 13.576(3) 19.280(5)	84.08(2) 80.38(2) 70.60(2)	Fe ^{III} N ₅ C Cu ^{II} N ₄ O	η ⁴ N 1.989(5,5) pyN 2.066(4) μNC 1.898(5) η ³ N 2.019(4) 2.052(4,4) μCN 1.949(5) otfO 2.239(6)	Cu 4.98	N,N 90.0(2,8) ^c 91.(1) N,C 89(2),178.1(2) N,N 86.5(2,1) ^d 91.3(2) 164.4(2,8.1) N,O 97.7(2,6.8)	19
[(η ⁴ -oep)Fe(μ-η ¹ :η ¹ -ac). Cu(η ³ -Me ₅ dien)]. (ClO ₄) ₂ .CH ₂ Cl ₂ (violet) (at 223 K)	tr Pī 2	13.777(3) 13.847(3) 17.608(4)	96.82(3) 108.06(3) 114.32(3)	Fe ^{III} N ₄ O Cu ^{II} N ₃ O	η ⁴ N 2.040(8,16) acO 1.961(7) η ³ N 2.01(1,3) acO 1.936(8)	Cu 4.430	N,N 88.1(4) ^c N,O 98.3-101.6(3) N,N 86.2(5,7) ^d 165.1(4) N,O 93.7(4,1.9) 177.8(4)	20
[(η ⁴ -oep)Fe(μ-η ¹ :η ¹ - OCHO)Cu(η ³ -Me ₅ dien). (OCIO ₃)ClO ₄ (red) (at 223 K)	tr Pī 2	9.016(3) 15.377(5) 19.253(5)	78.12(3) 86.30(4) 76.23(3)	Fe ^{III} N ₄ O Cu ^{II} N ₃ O ₂	η ⁴ N 2.042(6,3) η ¹ O 1.968(5) η ³ N 2.033(7,22) η ¹ O 1.976(6) O ₃ ClO 2.282(7)	Cu 5.860	N,N 88.3(2) ^c N,O 97.5-102.7(2) N,N 86.5(3,2) ^d 160.0(7) O,O 96.6(2) N,O 97.5(2,6.9) 168.8(7)	20
(OC) ₃ Fe(μ-η ⁴ :η ³ - B ₅ H ₈)Cu(PPh ₃) ₂ (yellow) (at 183 K)	tr Pī 2	11.113(5) 14.670(8) 15.034(7)	95.60(4) 121.01(3) 106.29(4)	FeC ₃ B ₃ H CuB ₂ P ₂ H	OC not given η ⁴ B 2.115(7,40) H 1.56(6) η ³ B 2.219(8,55) H 1.96(7) Ph ₃ P not given		not given P,P 127.57(8)	21
(Fe(μ-OEt)(μ-η ⁴ :η ⁴ - hbp)Cu]ClO ₄ (dark)	m P2 ₁ /c 4	18.113(2) 13.903(2) 14.426(2)	115.85(1)	Fe ^{III} O ₄ N Cu ^{II} N ₃ O ₂	μEtO 1.971(6) η ⁴ O 1.853(7,6) η ⁴ μO 1.945(6) η ⁴ μN 2.184(4) η ⁴ N 1.984(10,28) η ⁴ μO 2.322(6) μEtO 1.930(7)	Cu 3.122(2) O 93.6(2) 106.3(3)	μO,μO 83.8(3) μO,μO 75.8(3)	22
[Fe(μ-η ⁴ :η ⁴ -bpmp). (μ-η ² -EtCO ₂)Cu].	or Pnma 4	20.849(6) 17.411(4)		Fe ^{III} O ₃ N ₃	η ⁴ N 2.14(2,2) η ⁴ μO 1.93(1)	Cu 3.401(4) O 119.3(5)	not given	23

(PF ₆) ₂ (not given)		12.587(3)		Cu ^{II} O ₃ N ₃	η ² O 2.00(1,11) η ⁴ N 2.10(1,11) η ⁴ μO 2.01(1) η ² O 1.94(1) 2.31(2)		not given	
[(MeO)Fe(μ-η ⁴ : η ⁴ - bpmp) (μ-η ² -ac)Cu]. (BPh ₄) ₂ .0.22acH (red green)	tr Pī 2	13.135(3) 13.503(3) 20.940(5)	93.62(2) 93.8(2) 92.78(2)	Fe ^{III} O ₃ N ₃ Cu ^{II} N ₃ O ₂	MeO 1.849(1) η ⁴ μO 1.975(4) η ⁴ N 2.154(5,22) 2.255(5) acO 2.016(4) η ⁴ N 1.975(5) 2.020(5,14) η ⁴ μO 2.176(4) acO 1.945(4)	Cu 3.641(1) O 122.5(2)	not given not given	23
[Fe(μ-η ⁴ : η ⁴ -bpmp). (μ-η ² -ac) ₂ Cu]. (ClO ₄) ₂ .0.5MeOH (not given) (at 233 K	m P2 ₁ /n 4	12.677(2) 22.059(2) 16.269(2)	94.184(1)	Fe ^{III} O ₃ N ₃ Cu ^{II} O ₃ N ₃	acO 1.934(1) 2.142(5) η ⁴ μO 1.984(3) η ⁴ N 2.126(5,60) acO 1.960(4) 2.178(4) η ⁴ μO 2.006(3) η ⁴ N 2.129(5,71)	Cu 3.149(2) O 118.0(2)	O, O 93.5(2,5.5) N, N 79.1(2,9) ^d 96.7(2) O, N 90.8(2,5.2) O, O 93.4(2,5.5) N, N 79.5(2,9) ^d O, N 90.8(2,8.1)	24
[Fe(μ-η ⁵ : η ¹ -mpyc) ₂ . Cu]BF ₄ (dark red) (at 173 K)	tr Pī 2	7.586(2) 11.338(3) 16.041(3)	71.06(1) 89.37(2) 75.22(2)	FeC ₁₀ Cu ^I N ₂	η ⁵ C 2.071(3,14) η ¹ N 1.862(3,0)	Cu 3.231	not given N, N 178.28(11)	25
[Fe(μ-η ⁵ : η ¹ -mpyc) ₂ . Cu][CuCl ₂] (red) (at 173 K)	or Pna2 ₁ 4	21.238(4) 8.773(1) 14.257(1)		FeC ₁₀ Cu ^I N ₂ Cu ^{II} Cl ₂	η ⁵ C 2.07(3,4) η ¹ N 1.925 Cl 2.348(-,11)	Cu 3.292	not given N, N 171.4(6) Cl, Cl 178.9(3)	25
[Fe(μ-η ⁵ : η ¹ -C ₅ H ₄ P. (Ph ₂)S]Cu]BF ₄ . CH ₂ Cl ₂ (yellow)	or Pna2 ₁ 4	26.387(9) 12.286(5) 11.055(3)		FeC ₁₀ Cu ^I S ₂	η ⁵ C not given η ¹ S 2.142(5,2)		not given S, S 171.5(2)	26

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

Table 2. Crystallographic and structural data for heterotrimeric Fe₂Cu, FeCu₂ and FeCuMo complexes^a

Complex (colour)	Crys.cl Sp. Gr Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromo-phore	M-L [Å]	M-M [Å] M-L-M [°]	L-M-L [°]	Ref
Fe₂Cu								
[{(OC) ₃ Fe(μ-CO). (μ-PPh ₂)Fe(CO) ₃] {μ-Cu(PPh ₃)}] (red)	tr	11.081(3)	76.41(2)	FeC ₄ P.	OC ^b 1.782(8,33)	Cu 2.495(1,14)	C,P ^b 80.8(2)	28
	Pt	12.190(3)	87.03(2)	CuFe	μOC 1.973(7,7)	Fe 2.627(1)	μC,Cu 95.1(2,3)	
	2	15.808(4)	80.48(2)	Cu ^I PFe ₂	μP 2.228(2,6) Ph ₃ P 2.218(2)	C 83.5(3) P 72.3(1)	μC,Fe 48.3(2,3) P,Cu 87.6(1,3) P,Fe 53.9(1,2) Cu,Fe 58.2(1,5) P,Fe 148.2(1,3) Fe,Fe 63.5(1)	
[{(OC) ₄ Fe ₂ Cu. (Pcy ₃)PPh ₄ . 0.5thf (red)	tr	10.717(2)	90.62(2)	FeC ₄ Cu.Fe	OC 1.77(1,3)	Cu 2.495(2,8)	C,C 89.0-140.8(4)	29
	Pt	11.703(2)	92.32(2)	Cu ^I PFe ₂		Fe 2.900(2)	C,Cu 71.0(3,8.4)	
	2	24.130(7)	115.53(2)		Ph ₃ P 2.213(2)		C,Fe 79.7(3,2) 91.6(3,4.1), 169.8(3,5.2) Cu,Fe 54.22(4) P,Fe 144.5(1,2.2) Fe,Fe 71.05(5)	
[{(pab) ₃ Fe(μ-η ¹ :η ¹ - pab) ₃] ₂ Cu].2CH ₂ Cl ₂ (dark)	m	14.538(7)	108.89(4)	Fe ^{II} N ₆	N 1.909(7,15)	Cu 3.283(1)	N,N 78.5(3,6) ^c	30
	P2 ₁ /c	13.019(8)		Cu ^{II} O ₆	1.951(7,15)		94.2(3,8.2) 167.0(2,3)	
	2	22.673(1)			O 1.923(4,0) 2.014(6,0) 2.412(4,20)		O,O 86.6(2,7) 93.4(2,1.0) 180.0(1)	
[{(η ³ -C ₉ H ₂₁ N ₃)Fe]. (μ-η ¹ :η ¹ :η ² -dmg) ₃ Cu]. (ClO ₄) ₂ .0.5MeOH (not given)	m	29.144(5)		Fe ^{III} O ₃ .N ₃	dmgO 1.928(5,12)	Cu 3.58	not given	31
	C2/c	12.330(3)	119.22(1)	Cu ^{II} N ₆	η ³ N 2.215(4,20) η ² N 2.022(5,47) 2.324(4) 2.523(6)		N,N 64.1(2) ^c 78.5(2,6) ^c 80.5, 160.3(2)	
	4	14.860(2)						
[(py)(η ⁴ -oep)Fe. (μ-η ² -CN) ₂ Cu. (η ⁴ -cyclam)]. (SbF ₆) ₂ (black)	m	16.862(5)	112.68(2)	Fe ^{III} N ₅ C	η ⁴ N 1.989(9,15)	Cu 5.15	N,N 90.2(5,2)	18
	P2 ₁ /n	17.419(3)			pyN 2.07(1)		N,C 178.5(4)	
	2	18.646(4)		Cu ^{II} N ₆	μNC 1.91(1) η ⁴ N 2.015(10,5) μCN 2.45(1,0)		N,N 90.0(5,3.5)	
[{(cp)Fe(μ-η ⁵ :η ² - C ₁₂ H ₁₈ NS ₂) ₂ Cu]. PF ₆ ^e	tr	21.775(13)	62.82(4)	FeC ₁₀	C not given	Cu 5.781(4)	not given	32
	Pt	20.167(6)	67.72(4)	Cu ^I S ₄	S 2.273(6,7)	6.234(3)	S,S 93.5(2,5) ^d	
	6	18.545(8)	61.42(4)	FeC ₁₀	2.359(5,10)	Cu 5.809(4)	100.7,123.2(2,3)	

(orange)				Cu ^I S ₄ FeC ₁₀ Cu ^I S ₄	C not given S 2.278(6,2) 2.353(4,7) C not given S 2.288(7,3) 2.337(5,11)	6.322(3) Cu5.843(4) 7.802(5)	not given S,S 94.3(2,2) ^d 97.3,123.7(2,1.5) not given S,S 93.0(2,2) ^d 105.7,122.1(2,1.4)	
[(cp)Fe] ₂ (μ-η ⁵ :η ² -C ₅ H ₄ CO ₂) ₂ Cu(py) ₂] (yellow brown) (at 163 K)	m P2 ₁ /c 2	14.761(5) 5.922(2) 15.913(6)	102.69(3)	FeC ₁₀ Cu ^{II} O ₄ N ₂	C not given η ² O 2.123(5,0) η ² O 2.304(5,0) pyN 1.977(5,0)		not given O,O 59.4(2) ^f O,N 89.5(2,6)	33
[(cp)Fe] ₂ (μ-η ⁵ :η ² -C ₅ H ₄ CO ₂) ₂ Cu(py) ₂] (yellow brown)	tr Pī 1	5.986(2) 8.038(2) 15.512(3)	104.42(2) 93.11(2) 99.95(2)	FeC ₁₀ Cu ^{II} O ₄ N ₂	C not given η ² O 1.975(3,0) η ² O 2.53(0,0) pyN 1.998(5,0)		not given O,N 89.5(2)	33
[(cp)Fe] ₂ (μ-η ⁵ :η ² -C ₅ H ₄ CO ₂) ₂ Cu(im) ₂] (yellow brown) (at 163K)	tr Pī 1	7.475(3) 9.296(3) 10.090(3)	111.05(2) 92.38(4) 101.69(3)	FeC ₁₀ Cu ^{II} O ₄ N ₂	C not given η ² O 1.957(9,0) η ² O 2.76(-,0) imN 1.953(9,0)		not given O,N 88.8(4)	33
[(cp)Fe(μ-η ⁵ :η ² -C ₁₂ H ₁₅ NO) ₂ Cu] (yellow) (at 180 K)	m P2 ₁ /c 4	11.511(2) 19.613(2) 14.493(2)	88.32(2)	FeC ₁₀ Cu ^{II} O ₂ N ₂	C not given O 2.564(4,47) N 1.960(4,7)		not given O,O 66.4(2) N,N 163.1(2) O,N 79.1(2,9) ^c	34
[(cp)Fe(μ-η ⁵ :η ² -C ₁₂ H ₁₄ NO) ₂ Cu] (dark brown)	m P2 ₁ /c 4	12.668(2) 19.422(2) 20.921(3)	91.10(1)	FeC ₁₀ Cu ^{II} O ₂ N ₂	C not given O 1.890(4,10) N 1.973(4,20)		not given O,O 137.0(2) N,N 138.3(2) O,N 95.2(2,2.5) ^d 99.8(2,3.5)	35
[(cp)Fe(μ-η ⁵ :η ¹ -C ₅ H ₄ CO ₂) ₂ Cu. (1.2-Me ₂ im) ₂] (green) (at 155 K)	tr Pī 2	9.468(2) 9.849(2) 16.011(4)	90.44(2) 94.85(2) 90.47(2)	FeC ₁₀ Cu ^{II} O ₂ N ₂	C not given O 1.973(4,11) N 1.996(5,6)		not given O,O 91.8(2) N,N 93.7(2) O,N 89.8(2,1) 162.3(2,4.5)	36
[(cp)Fe(μ-η ⁵ :η ¹ -C ₅ H ₄ CO ₂) ₂ Cu. (N-Meim) ₂ .H ₂ O] (gold brown) (at 155 K)	m C2/c 4	21.145(3) 7.858(1) 18.573(3)	114.61(1)	FeC ₁₀ Cu ^{II} O ₂ N ₂	C not given O 1.985(4,0) N 1.973(4,0)		not given O,N 89.0(2)	36
[Fe(μ-η ⁵ :η ¹ -C ₅ H ₄ PPh ₂) ₂ . {μ-η ⁵ :η ¹ -C ₅ H ₄ P(Ph) ₂ O} ₂]	m P2 ₁ /n	22.590(2) 15.916(2)	105.15(2)	FeC ₁₀ C ⁰ O ₂ P ₂	C not given O 2.113(7,2)		not given O,O 102.1(6)	37

Cu].BF ₄ (yellow)	4	19.274(2)			P 2.271(4,4)		P,P110.1(4)		
[Fe(μ-η ¹⁰ :η ² - C ₁₃ H ₁₄ S ₂) ₂ Cu]. ClO ₄ .2CH ₂ Cl ₂ (orange red)	tr	11.024(4)	105.04(2)	FeC ₁₀	C not given		not given	38	
	P1	12.480(3)	93.17(1)	Cu ₂ S ₄	S not given		not given		
	2	14.698(2)	107.02(2)						
[Fe(μ-η ¹⁰ :η ² - C ₁₀ H ₆ S ₆) ₂ Cu]. BF ₄ (orange)	m	24.816(5)	90.95(2)	FeC ₁₀	C not given		not given	39	
	l2/a	12.634(1)		Cu ₂ S ₄	S 2.353(3,6)		S,S 92.9(1) ^d		
	12	27.250(4)					106.6(1) 145.4(2)		
[Fe ₂ (μ-η ⁵ :η ¹ -C ₁₇ H ₁₄ OP) ₄ . Cu(EtOH)](BF ₄) ₂ .EtOH (orange)	m	19.484(2)	93.9(1)	FeC ₁₀	C not given		not given	40	
	P2 ₁ /c	13.450(2)		CuO ₅	O 1.947(7,14)		O,O 85.5(4)-		
	4	25.477(2)			2.031(7,45) EtHO 2.023(8)		133.3(4) 172.3(4)		
[Fe ₂ (μ-η ⁵ :η ¹ -C ₁₇ H ₁₆ OP) ₄ . Cu](BF ₄) ₂ .2MeNO ₂ (dark green)	m	12.325(2)	108.7(2)	FeC ₁₀	C not given		not given	40	
	P2 ₁ /c	33.137(3)		CuO ₄	O 1.93(1,1)		O,O 93.1(5,1.1)		
	4	17.608(2)					153.4(4,6)		
FeCu₂									
[(Ph ₃ P) ₂ CuFe(CO) ₄ . Cu(PPh ₃) ₂] (yellow)	m	10.723(3)	99.31(3)	FeC ₄ Cu ₂	OC 1.81(2,10)	Cu 2.511(4,12)	C,C 96.6(9)-	41	
	P2 ₁ /c	39.960(14)		CuP ₂ Fe	Ph ₃ P 2.287(7,13)		126.5(9)		
	4	15.283(6)					Cu,Cu 168.7(2) P,P 118.1(3,3,3)		
[(η ⁴ -Me ₆ tren)Cu. (μ-NC) ₂ Fe(η ⁴ -oep)]. (SbF ₆) ₃ (dark violet) (at 223 K)	or	13.093(4)		Fe ^{III} N ₄ C ₂	η ⁴ N 1.995(8,1)	Cu 4.99	N,N 90.0(3,4) ^d	19	
	Pbcn	28.064(8)		Cu ^{II} N ₅	μNC 1.94(1,0)		N,C 88.3-91.7(4)		
	4	21.243(4)			η ⁴ N 1.99(1) 2.16(1,2) μCN 1.94(1)		N,N 85.6(4,4) ^c 94.8(4,1.2) 119.4(4,1.0) 178.8(4)		
[(η ⁴ -Me ₆ tren)Cu(μ- OCHO)Fe(η ⁴ -oep)(μ- OCHO)Cu(η ⁴ -Me ₆ tren)]. (ClO ₄) ₂ .SbF ₆ (violet)	or	12.517(6)		Fe ^{III} N ₄ O ₂	η ⁴ N 2.045(10,5)	Cu 5.422	N,N90.0(4,6) ^d	20	
	Pbcn	29.45(1)		Cu ^{II} N ₄ O	O 2.103(9,0)		N,O 90.0(4,2.0)		
	4	21.569(8)			η ⁴ N 2.00(1) 2.15(1,2) O 1.923(9)		N,N 84.8(5,3) ^c 119.2(5,2.9) N,O 876.2(5) 99.9(5,2.9) 170.2(5)		
[(η ⁴ -tpp)Fe(μ-η ¹ :η ³ - schb) ₂ Cu ₂].B ₁₁ CH ₁₂ . 3dmf.3H ₂ O (not given)	tr	14.403(8)	76.58(5)	Fe ^{III} N ₆	η ⁴ N 2.00(3,0)	Cu 6.0	not given	42	
	P1	17.682(12)	73.54(5)	Cu ^{II} N ₃ O	η ¹ N 1.98(1,0)		not given		
	2	21.577(12)	84.80(5)		η ³ N 1.92(1) 1.98(1,0)				

[Fe(μ - η^5 : η^1 -mpyc) ₂ . Cu ₂ Cl ₂] (red) (at 173(2) K)	or Pna2 ₁ 4	21.238(4) 8.773(1) 14.257(1)		FeC ₁₀ Cu ¹ N ₂ Cu Cu ¹ Cl ₂ Cu	O 1.86(1) C not given η^1 N 1.90(2) 1.95(2) Cl 2.096(7,30)	Cu 2.810(2)	not given N,N 171.4(6) N,Cu 94.3(4,7) Cl,Cl 176.9(3) Cl,Cu 89.1(2,4.2)	43
FeCuMo								
(NEt ₄)[Cl ₂ Fe(μ -S) ₂ . Mo(μ -S) ₂ Cu(PPh ₃) ₂] (red)	tr Pī 2	13.429(3) 15.284(4) 12.285(3)	105.50(2) 93.21(2) 101.54(2)	FeCl ₂ S ₂ MoS ₄ CuS ₂ P ₂	Cl 2.214(4,3) μ S 2.277(4,5) μ S 2.181(3,1) 2.226(3,3) μ S 2.320(4,10) Ph ₃ P 2.326(3,5)	Mo 2.769(2) S 75.(1,2) Cu 2.786(2) S 76.4(1,2)	Cl,Cl 111.2(2) S,S 102.5(1) Cl,S 110.7(2,1.4) Cl,Mo 124.4(1,4) S,S 109.5(1,3.7) S,Cu 54.1(1,3) 127.1(1,1.4) S,Fe 53.0(1,2) 126.0(1,2) S,S 99.1(1) P,P 115.4(1) S,P 110.3(1,4.5) S,Mo 49.58(9) 123.3(1) P,Mo 49.51(9) 121.2(1)	44

a. Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis 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 five-membered metallocyclic ring. d. The six-membered metallocyclic ring. e. There are three crystallographically independent molecules. f. There are four-membered metallocyclic ring

Table 3. Crystallographic and structural data for heterotetrameric complexes^a

Complex (colour)	Crys.cl Sp.Gr Z	a [Å]b [Å]c [Å]	α [°] β [°] γ [°]	Chro-mo-phore	M-L [Å]	M-M [Å] M-L-M [°]	L-M-L [°]	Ref
Fe₃Cu								
(CO) ₉ (μ -CO)(μ_3 -CMe)Fe ₃ Cu(PPh ₃) (black)	m P2 ₁ 2	11.828(2) 15.605(3) 8.939(2)	107.85(2)	FeC ₄ Cu. Fe ₂ FeC ₅ Cu. Fe ₂ FeC ₅ Fe ₂ CuPFe ₂	OC ^b 1.792(11,38) μ_3 C 1.912(8) OC 1.790(9,9) μ OC 2.090(8) μ_3 C 1.958(7) OC 1.798(9,10) μ OC 1.930(7) μ_3 C 2.025(9) Ph ₃ P 2.207(2)	Cu 2.494(1) Fe 2.584(2,16) μ_3 C 81.8(3,2.7) Cu 2.564(1) Fe 2.568(2,31) μ C 74.8(3,3.5)	Cu,Fe ^d 60.4(3) Fe,Fe 58.82(4) Cu,Fe 57.78(3) Fe,Fe 59.98(4) Fe,Fe 61.20(4) P,Fe 148.6(1,5.1) Fe,Fe 61.52(4)	45
(ppn) ₂ [(CO) ₃ Fe] ₃ . (μ_4 -CCO)CuI] (dark brown) (at 153 K)	tr P1 2	13.863(2) 14.248(4) 23.807(2)	75.33(2) 87.36(2) 88.03(2)	FeC ₄ Cu. Fe ₂ FeC ₄ Cu. Fe FeC ₄ Fe CuClFe ₂	OC 1.774(6,5) μ_4 C 1.971(5) OC 1.760(6,5) μ_4 C 1.955(5) OC 1.748(3) 1.784(6,2) μ_4 C 2.045(5,5) μ_4 C 2.008(2) I 2.4377(8)	Cu 2.551(1) μ_4 C 79.8(2) Fe 2.590(1,15) μ_4 C 81.4(2,1.7) Cu 2.552(1) μ_4 C 80.2(2) Fe 2.605(1) Fe 2.554(1) μ_4 C 79.3(2)	Cu,Fe 59.33(3) Fe,Fe 59.07(3) Cu,Fe 59.33(3) Fe,Fe 59.07(3) C,I 151.0(2) C,Fe 134.7(4,3.8) I,Fe 147.37(4,2.3) Fe,Fe 61.39(7)	46
[NMe ₃ (CH ₂ Ph)] ₂ . [Cl ₃ Fe ₃ Cu(μ -SP ^r) ₆] (orange brown)	m P2 ₁ /n 4	10.846(1) 12.018(5) 41.23(1)	94.97(2)	FeS ₃ Cl CuS ₃	μ S 2.345(5,11) Cl 2.314(4,7) μ S 2.241(4,20)	Cu 3.145(3) 3.235(3,1) S 88.7(2,1.6) Fe 3.852(3,5) S 110.4(2,1)	S,S 103.5(2,3.6) 119.3(2,3) S,S 120.0(2,7.6)	47
Fe₂Cu₂								
[(Co) ₄ FeCu(Pcy ₃)] ₂ (yellow)	m P2 ₁ /c 4	11.042(2) 17.321(3) 24.824(6)	92.32(2)	FeC ₄ . Cu ₂ Fe Cu ^r PFe ₂	OC 1.783(6,29) cy ₃ P 2.228(1,1)	Cu 2.477(1,5) 2.593(1,13) Fe 2.862(1)	C,C 88.5-153.2(3) Cu,Cu 105.2(1,5) Cu,Fe 55.6(1,2,3) P,Fe 145.6(1,4.1) Fe,Fe 68.7(1,1)	29
[(CO) ₄ FeCu(PBu ^t) ₃] ₂ (yellow) (at 213 K)	or P2,2,2, 4	8.881(3) 14.208(3) 31.114(6)		FeC ₄ . Cu ₂ Fe CuPFe ₂	OC 1.781(7,30) Bu ^t ₃ P 2.260(1,8)	Cu 2.511(1) 2.556(1,8) 2.638(1) Fe 2.850(1)	C,C 88.9-153.6(3) Cu,Cu 101.0(3,1.9) Cu,Fe 56.3(1,2,3) P,Fe 146.1(1,1.9) Fe,Fe 67.5(1,3)	48
[Fe(μ - η^5 : η^1 -	m	20.173(4)	103.48(2)	FeC ₁₀	η^5 C 2.023(9)	O 104.9(3)	not given	49

C ₅ H ₄ PPPh ₂) ₂ . Cu(μ-ONO ₂) ₂] ₂ (yellow)	P2 ₁ /c 4	12.767(3) 24.355(5)		CuO ₂ P ₂	2.052(10) μO 2.163(6,9) η ¹ P 2.259(6,5)		O,O 72.6(3) P,P 117.8(1) O,P 109.3(4,9.0) 130.0(4)	
[Fe(μ-η ⁵ :η ¹ - C ₅ H ₄ PPPh ₂) ₂ . Cu(μ-I)] ₂ (golden)	tr Pī 1	12.684(2) 12.807(3) 13.876(3)	87.90(2) 114.06(2) 111.78(2)	FeC ₁₀ CuP ₂ l ₂	η ⁵ C 2.046(4) 2.058(5) η ¹ P 2.28(1,0) 2.649(6) μI 2.736(7)	I 81.8(2)	not given P,P 111.2(4) I,I 98.2(2) P,I 102.3(4,7.8) 118.4(4,7)	49
[Fe(μ-η ⁵ :η ¹ - C ₅ H ₄ PPPh ₂) ₂ . Cu(μ-η ² -OCO)] ₂ (yellow)	tr Pī 1	8.654(1) 11.725(2) 14.895(2)	98.44(1) 103.90(1) 96.62(1)	FeC ₁₀ CuO ₂ P ₂	η ⁵ C 2.042(5) 2.047(5) η ² O 2.083(4,28) η ¹ P 2.260(1)	Cu 4.561	not given O,O 98.1(2) P,P 110.8(1) O,P 108.5(1,8) 121.5(1)	49
Fe₂CuM								
[{(Si(OMe) ₃ (CO) ₃ Fe) ₂ Hg(μ-η ² - dppm) ₂ Cu]PF ₆ . 4CH ₂ Cl ₂ (orange)	m P2/n 2	15.663(6) 12.120(3) 22.620(7)	107.78(3)	FeC ₃ P. SiHg HgFe ₂ Cu CuP ₂ Hg	OC1.784(6,10) P 2.260(2) Si 2.330(2) P 2.228(2,0)	Hg 2.613(2) Cu 2.689(2)	P,Si 175.49(7) P,Hg 95.92(6) Si,Hg 82.97(6) Fe,Fe 176.62(4) Fe,Cu 91.96(2) P,P 160.16(9)	50
[{(CO) ₃ Fe] ₂ (μ ₃ -S). Co(CO) ₂ (PPh ₃). Cu(PPh ₃)] (not given)	tr Pī 2	12.184(3) 13.422(5) 13.484(2)	104.96 91.84 93.54	FeC ₃ S. CuCoFe CuPCo. Fe ₂ CoC ₂ SP. CuFe ₂	OC 1.749(8,31) μ ₃ S 2.19(2) Ph ₃ P 2.233(2) OC 1.718(7,14) μ ₃ S 2.170(2) Ph ₃ P 2.208(2)	Cu 2.582(1,1) Co 2.595(2,3) S 73.04(6,8) Fe 2.624(2) S 73.56(6) Co 2.521(1)	S,Cu 99.7(1,3) S,Co 53.1(1,4) Cu,Co 58.23(4) Cu,Fe 59.46(4,3) Co,Fe 59.58(4,15) P,Co 140.18(7) P,Fe 145.8(1,2) Co,Fe 61.14(4,6) Fe,Fe 61.08(4) S,P 94.39(7) S,Cu 102.18(6) S,Fe 53.85(6,4) P,Cu 162.90(7) P,Fe 132.2(1,2.9) Cu,Fe 60.59(4,1) Fe,Fe 60.72(4)	51

a. Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis is e.s.d., and the second is maximum deviation from the mean; b. The chemical identity of the coordinated atom or ligand is specified in these columns

Table 4. Crystallographic and structural data for heteropenta-, heterohexa- and heteroheptameric complexes^a

Complex (colour)	Crys.cl Sp. Gr Z	a [Å]b [Å]c [Å]	α [°] β [°] γ [°]	Chro-mo- phore	M-L [Å]	M-M[Å] M-L-M [°]	L-M-L [°]	Ref
Heteropenta-								
(ppn)[(CO) ₁₃ Fe ₄ . Cu(PPh ₃)] (black)	tr P $\bar{1}$ 2	16.352(5) 15.169(6) 13.811(4)	99.06(2) 78.17(7) 76.88(3)	FeC ₃ Cu. Fe ₃ CuPFe ₃	OC ^b not given Ph ₃ P 2.211(8)	Cu 2.556(5,30) Fe 2.606(6,39)	Cu,Fe ^p 59.3(1,1.6) 108.2(2,1.6) Fe,Fe 60.2(1,1.6) P,Fe 143.7(3,3.3)	52
[{(η ⁵ -cp) ₂ Fe ₂ (μ- η ¹⁰ :η ² -ema)} ₂ . Cu(ONO ₂) ₂]. 2MeOH (yellow)	tr P $\bar{1}$ 1	7.520(2) 11.047(2) 16.186(5)	101.93(2) 97.24(2) 104.95(1)	FeC ₁₀ CuN ₄ O ₂	μ ⁵ C 2.041(7,10) η ¹⁰ C2.035(10,15) η ² N 2.047(5,6) O ₂ NO 2.515(6)	Cu 6.042(2) 6.211(2)	not given N,N84.6(7) ^c 95.4(2) N,O 90.2(2,3.1)	53
(ppn) ₂ [CO] ₉ (μ ₃ -Te). Fe ₃ (μ-CuCl)] (deep purple) (at 223(2) K)	or Pbca	24.274(5) 21.634(4) 30.363(6)		FeC ₃ Te. CuFe ₂ (x2) FeC ₄ Te. Fe ₂ CuClFe ₂	OC not given OC not given Cl 2.150(4)	Te 2.489(2,4) Cu2.485(1,7) Fe 2.648(2,9) 2.738(3) Te 2.493(2)	C,C 99.4(7,9.9) Te,Cu 100.9(1,2) Te,Fe 57.2(1,5) Fe,Fe 58.9(1,3) Cu,Fe 56.5(1,1) 111.4(1,5) C,C 98.5(7,39) Te,Fe 58.1(1) Fe,Fe 62.2(1) C,Fe 146.5(2,5.1) Fe,Fe 66.85(8)	54
Heterohexa-								
[PPh ₄] ₂ {(CO) ₈ Fe ₂ }. (μ ₄ -η ² -Cu ₂ (dchpe)]. 0.4ñ5thf (not given)	tr P $\bar{1}$ 1	10.810(1) 11.976(1) 18.254(2)	91.11(1) 82.32(1) 71.40(1)	FeC ₄ Cu. Fe CuPFe (x2)	OC ^b 1.765(5,32) P 2.2276(8)	Cu 2.4781(6) 2.5310(5) Fe 2.8238(6)	C,C 91.6-127.9(2) C,Cu 58.6-87.5(1) C,Fe 81.2(1,4.5) 100.9(1,5.1) 163.3(2,5.8) P,Fe 134.22(3) 156.89(3) Fe,Fe 58.62(2)	29
[{(η ⁵ -cp)Fe] ₄ (μ- η ⁵ :η ¹ -C ₅ H ₄ COO) ₄ . Cu ₂ thf ₂] (black green)	tr P $\bar{1}$ 1	9.584(1) 10.118(1) 13.631(1)	92.46(1) 91.86(1) 104.95(1)	FeC ₁₀ (x4) CuO ₅ Cu (x2)	η ⁵ C 2.034(15,36) μLη ⁵ C2.041(11,27) η ² O 1.947(7,19) thf O 2.226(6)	Cu 2.605(1)	not given O,O 81.5-102.1(2) 169.4(3,2)	55
[{(η ⁵ -cp)Fe] ₂ (μ- η ¹⁰ :η ³ -dmppCu) ₂].	tr P $\bar{1}$	12.381(2) 14.029(1)	106.24(1) 117.66(1)	FeC ₁₀ (x4) CuN ₂ S ₂	η ⁵ C not given μLC not given	Cu 2.727(2)	not given N,N 141.5(3)	56

(CF ₃ SO ₃) ₂ .EtOH (orange)	2	14.232(2)	78.53(1)	(x2)	μLN 1.997(9,0) μS 2.428(3,21)	S 68.3(8)	S,S 111.69(8) N,S 89.0(2) 104.6(3,8.8)	
(NEt ₄) ₃ [(CO) ₄ Fe] ₃ Cu ₃ (yellow)	m P2 ₁ /n 4	12.946(3) 18.894(4) 19.031(6)	93.91(2)	FeC ₄ Cu ₂ (x3) CuFe ₂ Cu ₂ (x3)	OC 1.75(1,4)	Cu2.421(2,21) Cu 2.582(2) 2.611(2,2)	C,C 97.5-131.2(5) Cu,Cu 64.98(5,68) Fe,Fe 174.67(7,56) Cu,Cu 60.00(5,75) Fe,Cu 57.51(5,96) 117.40(7,1.37)	57
[(η ⁵ -cp)Fe{μ-η ⁵ :η ² - C ₅ H ₃ (1-PPh ₂)(CH). (Me)S}Cu] ₃ (yellow orange)	m P2 ₁ 2	13.276(1) 18.221(2) 16.028(1)	113.13(1)	FeC ₁₀ (x3) CuS ₂ P	not given P 2.225(6,23) μS 2.191(5,13) 2.251(6.1)	Cu 3.194(9) S 92.3(2) Cu 3.356(4,16) S 97.7(2.5)	not given S,S 116.5(2,3) S,P 105.1(2,2.0) 136.9(2,3.4)	58
Heterohepta-								
[Fe{(μ-η ² -CN)Cu. (η ³ -tpa)} ₆ (ClO ₄) ₈ . 3H ₂ O (dark purple)	m P2 ₁ 2	16.673(2) 24.909(3) 18.060(3)	114.74(1)	FeC ₆ CuN ₄ (x6)	μNC 1.87(2,3) μCN 1.92(1,3) η ³ N 2.04(1,3) 2.06(2,9)	Cu 4.899(4)- 4.929(4)	C,C 90.0(7,2.3) 177.(2,2) N,N 81.8(6,1.9) ^c 97.9(6,1.8)	59
[Fe(μ-η ⁵ :η ¹ - C ₅ H ₄ PPh ₂) ₂ Cu ₂ . (μ ₃ -H) ₂ Ru ₄ (CO) ₁₂]. (dark red)	m P2 ₁ /n 4	17.045(2) 15.727(2) 18.093(2)	94.583(2)	FeC ₁₀ CuPRu ₃ . Cu CuPRu ₂ . Cu RuC ₃ . Cu ₂ Ru ₂ (x2) RuC ₃ . CuRu ₃ RuC ₃ Ru ₃	η ⁵ C 2.051(8,31) η ¹ P 2.237(4) η ¹ P 2.224(4) OC 1.843(18)- 1.998(14) OC 1.843(18)- 1.898(14) OC 1.843(18)- 1.898(14)	Ru 2.713(2) 2.803(2,27) Cu2.528(2) Ru 2.637(2) 2.663(2) Cu 2.637(2)- 2.830(2) Ru 2.808(2) 2.946(2,39) Cu 2.777(2) Ru 2.782(2)- 2.986(2) Ru 2.781(2)- 2.812(2)	not given P,Ru 141.8(1,8.6) P,Cu 113.4(1) Ru,Ru 64.1(1,1.8) Ru,Cu 64.7(1,1.3) P,Ru 144.3(1,7.3) P,Cu 134.2(1) Ru,Ru 66.5(1) Ru,Cu 66.0(1) Cu,Cu 56.4(1) Ru,Ru 58.7(1,1.4) Cu,Ru 58.3(1,2.1) 107.6(1,5.0) Cu,Ru 57.6(1,1.7) 105.2(1) Ru,Ru 58.5(1,4) Ru,Ru 63.4(1,1.2)	60

a. Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis is e.s.d., and the second is maximum deviation from the mean value. b. The chemical identity of the coordinated atom or ligand is specified in these columns. c. The five-membered metallocyclic ring

Table 5. Crystallographic and structural data for heterooligo- and heteropolymeric complexes^a

Complex (colour)	Crys.cl Sp.Gr Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chro mo-phore	M-L [Å]	M-M[Å] M-L-M [°]	L-M-L[°]	Ref
Oligomeric								
$[(\eta^5\text{-cp})\text{Fe}(\mu\text{-}\eta^5\text{:}\eta^1\text{-C}_5\text{H}_4\text{CH}_2\text{NMe}_2)\text{Cu}]_4$ ($\mu_4\text{-O})(\mu\text{-Cl})_6$) (not given) (at 233 K)	tg P42 ₁ c 2	16.930(6) 13.084(7)		FeC ₁₀ CuCl ₃ ON	$\eta^5\text{C}^b$ 1.996(17,8) 2.056(16,27) μCl 2.410(4,27) $\mu_4\text{O}$ 1.921(2) $\eta^1\text{N}$ 2.032(10)	Cl 91.1(2,2) O 109.5(1,7)	C, C ^b not given Cl, Cl 119.1(2,23) N 177.4(3) Cl, O 84.6(1,6) Cl, N 95.4(3,2.7)	61
$[(\eta^5\text{-cp})\text{Fe}(\mu\text{-}\eta^5\text{:}\eta^1\text{-C}_5\text{H}_4\text{CH}_2\text{NMe}_2)\text{Cu}]_4$ (not given)	tg P42 ₁ c 2	15.389 10.278		FeC ₁₀ CuN ₂ Cu ₂				62
$(\text{NEt}_4)_3[\{(\text{CO})_4\text{Fe}\}_4\text{Cu}_5]$ (yellow)	tg P42 ₁ / mnn 2	13.553(2) 14.650(2)		FeC ₄ Cu ₂ CuFe ₂ Cu ₄ CuFe ₂ Cu ₂ (x4)	OC 1.77(2,5)	Cu 2.410(3,13) Fe 2.491(3,0) Cu 2.527(2,0) Cu 2.527(2) 2.691(4)	C, C 103.8(11,4.5) 135.2(10,2.4) Cu, Cu 65.1(/1,3.3) 123.0(1) Fe, Fe 180.0 Cu, Cu 64.4, 115.6(1) 180.0 Cu, Cu 57.8(1) Fe, Fe 174.0(1) Cu, Fe 58.1(1,2.3) 115.4(1,1.8)	57
$(\text{NEt}_4)[(\text{CO})_{12}\text{Fe}_6$ ($\mu\text{-CO})_6(\mu_4\text{-S})_6$ Cu ₅ (PPh ₃) ₂ MeCN (dark red)	m Pn 2	12.426(3) 15.572(4) 20.709(4)	90.14(2)	FeC ₃ S ₂ CuFe CuC ₂ S ₂ Fe ₂ Cu ₄ (x3) CuS ₃ P (x2)	OC 1.84(2,5) μOC 1.80(2,0) $\mu_4\text{S}$ 2.318(5,35) μOC not given $\mu_4\text{S}$ 2.245(5,11) $\mu_4\text{S}$ 2.452(4,41) Ph ₃ P 2.245(5,46)	Cu 2.710(3,22) S 62.5- 136.7(2) Fe 2.525(3,8) S 66.0(1,3) Cu 2.574- 2.809(3) S 67.1(1,1.1)	S, S 85.0(2,3) S, Cu 52.3(1,5) 69.7(1,1.0) S, Fe 56.9(1,9) Cu, Fe 90.5(1,5) Fe, Fe 131.4(1,1.2) Cu, Cu 57.9(1,2.6) Fe, Cu 90.7(1,7.4) 113.7-145.1(1) S, S 114.6(2,1.9) S, P 103.7(2,3.7) Cu, Cu 65.2(1,1.0)	63
Polymeric								
$[(\text{NC})_2\text{Fe}(\mu\text{-}\eta^2\text{-CN})_4$ {Cu($\eta^2\text{-dien}$)} ₂].6H ₂ O	m C2/c	27.438(3) 7.778(1)	100.9(1)	Fe ^{II} C ₆ Cu ^{II} N ₅	NC 1.90(1,1) μNC 1.91(1,0)		C, C 87.9(5,2.8) N, N 83.5(5,4) ^c	64

(dark green)	8	14.869(2)			$\eta^3\text{N}$ 2.03(1,0) μCN 1.99(1,2)	96.6(5,1.9)		
$\{[(\text{NC})_2\text{Fe}(\mu\text{-}\eta^2\text{-CN})_4]_2\cdot\{\text{Cu}(\eta^3\text{-dien})\}_3\cdot(\text{H}_2\text{O})_6\}$ (dark green)	m P2 ₁ /c 4	20.332(6) 14.162(5) 14.932(5)	96.29(3)	$\text{Fe}^{\text{II}}\text{C}_6$ $\text{Cu}^{\text{II}}\text{N}_5$ (x2) $\text{Cu}^{\text{II}}\text{N}_4\text{O}$	NC 1.95(2,2) μNC 1.95(2,4) $\eta^3\text{N}$ 2.01(2,2) μCN 1.98(2,3) 2.31(2,1) $\eta^3\text{N}$ 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)	65	
$\{[(\text{NC})_2\text{Fe}(\mu\text{-}\eta^2\text{-CN})_4]_2\cdot\{\text{Cu}(\eta^3\text{-dien})\}_3\cdot(\text{H}_2\text{O})_3\}$ (dark blue)	m P2 ₁ /a 4	14.896(3) 14.128(5) 20.267(6)	96.31(3)	$\text{Fe}^{\text{II}}\text{C}_6$ $\text{Cu}^{\text{II}}\text{N}_5$ (x2) $\text{Cu}^{\text{II}}\text{N}_4\text{O}$	NC 1.92(1,2) μNC 1.93(1,4) $\eta^3\text{N}$ 2.03(2,1) μCN 2.14(1,15) $\eta^3\text{N}$ 2.03(1,2) μCN 1.96(1) H_2O 2.43(1)	C,C not given N,N not given N,N not givšn	66	
$\{[\text{Fe}(\text{CN})_6]_2\cdot[\text{H}_2\text{Fe}(\text{CN})_6]_{0.5}\cdot[\text{Cu}(\eta^4\text{-tmppor})(\text{H}_2\text{O})]\}_2\cdot 1.5\text{H}_2\text{O}$ (blue)	m C2/c 4	20.756(3) 21.311(3) 30.109(4)	102.79(2)	$\text{Fe}^{\text{II}}\text{C}_6$ $\text{Cu}^{\text{II}}\text{N}_4\text{O}$	NC 1.926(15,22) $\eta^4\text{N}$ 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)	67	
$\{[\eta^4\text{-acac}]\text{Fe}\{\text{Cu}(\mu\text{-Me salen})\}_3\cdot(\text{PF}_6)_2\}$ (dark)	hx P6 ₁ 22 6	14.471(2) 50.372(2)		$\text{Fe}^{\text{II}}\text{O}_6$ $\text{Cu}^{\text{II}}\text{O}_3\text{N}_2$	$\eta^4\text{O}$ 1.967(2,0) $\text{L}\mu\text{O}$ 2.538(7,10) $\text{L}\mu\text{O}$ 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)	68	
$\{[\text{Fe}(\mu\text{-edta})_2\text{Cu}(\eta^2\text{-en})_2(\text{H}_2\text{O})_2(\mu\text{-O})]\}_2$ (blue)	m C2/c 8	16.662(2) 15.254(3) 18.751(3)	102.58(1)	$\text{Fe}^{\text{III}}\text{O}_4\text{N}_2$ $\text{Cu}^{\text{II}}\text{N}_4\text{O}_2$	μO 1.773(1) LO 2.024(2,15) LN 2.236(2,10) $\eta^2\text{N}$ 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(1,6) ^c 86.2(1,3.3) 102.5(1)	69	
$\{\text{K}[\{\eta^2\text{-1,3-tn}\}\text{Cu}(\mu\text{-}\eta^2\text{-})]\}_2$	m	15.1478(2)	109.95(9)	FeC_6	μNC 1.915(6,20)	Cu 4.980(1)-	C,C not given	70

NC ₃ Fe]Cl.5H ₂ O (brown)	P2 ₁ /c 4	14.6941(4) 12.6533(4)		CuN ₅	μCN 2.010(4,17) 2.176(4,54)	5.194(1) Cu 6.845(1)	N,N 141.4(2)- 174.2(2)	
{[(η ² -1,3-tn)Cu(μ-η ² - NC) ₃] ₂ Fe]2H ₂ O} _n (black)	m P2 ₁ /n 2	7.5721(1) 10.721(1) 12.926(2)	90.01(1)	FeC ₆ CuN ₅	μNC 1.913(5,29) μCN 1.994(4,7) 2.228(4) η ² N 2.018(3,17)	Cu 5.035(1,1) 5.149(1) Cu 6.719(1)	C,C not given N,N 142.9(2) 177.0(2)	70 ^d
{[(μ-η ² -1,3-tn)(H ₂ O) ₂ Cu(μ-η ² -NC) ₆ Fe] _n (dark green)	m P2 ₁ /n 2	10.0586(4) 9.0189(3) 11.9833(6)	104.2(1)	FeC ₆ CuN ₅	μNC 1.912(4,9) μCN 1.961(4,0) η ² N 2.044(4,0) H ₂ O 2.633(4,0)	Cu 10.058 Cu 10.058	C,C not given N,N not given	70
{[(η ³ -dien)Cu(μ-η ² -NC) ₃ Fe(η ³ -tp)]ClO ₄ .H ₂ O} _n	m P2 ₁ /c 4	13.902(2) 13.345(2) 15.007(2)	112.98	FeN ₃ C ₃ CuN ₆	η ³ N 1.974(2,4) μNC 1.930(3,9) μCN 1.978(2) 2.443(3) η ³ N 1.989(3,11)	Cu 5.030(2,10) 11.062(4) Fe 8.169(2) Cu 13.345(2)	C,C 88.2(1,2.0) N,N 90.4(1,6.1) 166.0(1,5.6)	71
{[(dppc)(N ₃)Fe] ₂ (μ-η ² - N ₃) ₂ Cu(η ⁴ -tact)] (black)	m P2 ₁ /c 2	9.815(1) 13.197(1) 20.774(1)	95.78(1)	Fe ^{II} N ₆ Cu ^I N ₆	μN ₃ 1.990(2) 2.164(1) η ⁴ N 2.056(1,2) 2.119(1,36) μN ₃ not given η ⁴ N 2.023(2,2)		N,N 76.2-154.2 N,N 90.0(1,4.0) 180.0	72

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

In crystal structures of black $\{\text{FeCu}\}_n$ [72] two fragments $\{\text{Fe}^{\text{II}}(\text{dcpc})_2\}$ and $\{\text{Cu}^{\text{I}}(\text{tac})\}$ are bridged by azide groups in the manner $\mu\text{-}1,3\text{-N}_3$ and form zig-zag one dimensional chain. Each metal atoms Fe(III) and Cu(II) are six coordinated (MN_6). The mean Fe(III)-N bond distance of 2.085Å is somewhat longer than those of Cu(II)-N, will the value of 2.023Å. The stereochemistry about the Fe(III) atom is much higher distorted with the N-Fe-N bond ranging from 76.2 to 154.2° than that about the Cu(II) atom with the bond angle of (86.1°, 93.9° and 180°).

8. CONCLUSION

This review has classified over 100 heterometallic FeCu complexes. There is wide variety of heterometallic cores: FeCu; Fe₂Cu, FeCu₂, FeCuMo; Fe₃Cu, Fe₂Cu₂, Fe₂CuM (M=Hg or Co); Fe₄Cu, Fe₃CuTe; Fe₄Cu₂, Fe₃Cu₃; FeCu₆, FeCu₂Ru₄; Fe₄Cu₄; Fe₄Cu₅; Fe₆Cu₅ and $\{\text{FeCu}\}_n$. The mean M-M bond distance elongate in the sequence: 2.520Å (range 2.319 – 2.732Å, Fe-Cu) < 2.638Å (2.527 – 2.810Å, Cu-Cu) < 2.663Å (2.537 – 2.900Å, Fe-Fe). The most donor ligands for the iron atoms are with C donor sites and for copper atoms with O and N donor sites. The L-Fe-L bond angles of the metallocyclic rings open in the order: 75.4° (-OC₂O-) < 78.8° (-NC₂N-) < 81.2° (-OC₂N-) < 86.0° (-OC₃O-) < 89.4° (-NC₃N-) and for the L-Cu-L bond angles the order is: 59.4° (-OCO-) < 82.4° (-NC₂N-) < 87.4° (-NC₃N-) < 93.0° (-SC₃S-) < 95.8° (-OC₃N-) < 96.4° (-NC₄N-).

The complexes crystallized in the following crystal classes: monoclinic (x46) > triclinic (x39) > orthorhombic (x12) > tetragonal (x3) > hexagonal (x1). There are examples, which exist in two isomeric forms: monoclinic and triclinic $[\text{FeCl}_4][\text{Cu}(\text{PPh}_3)_3]$ [3], monoclinic and orthorhombic $[(\text{oep})\text{Fe}(\text{O})\text{Cu}(\text{Me}_6\text{tren})]\text{ClO}_4$ [16], and monoclinic and triclinic $[(\text{cp})\text{Fe}]_2 \cdot (\text{C}_5\text{H}_4\text{CO}_2)\text{Cu}(\text{py})_2$ [33]. Two crystallographically independent molecule are present in monoclinic $[(\text{oep})\text{Fe}(\text{O})\text{Cu}(\text{Me}_6\text{tren})]\text{ClO}_4$ [16] and triclinic $[(\text{oep})(\text{py})\text{Fe}(\text{CN})\text{Cu}(\text{Me}_6\text{tren})]$. $(\text{SbF}_6)_2 \cdot \text{Me}_2\text{CO}$ [19], and in triclinic $\{[(\text{cp})\text{Fe}(\text{C}_{12}\text{H}_{18}\text{NS}_2)]_2\text{Cu}\}\text{PF}_6$ [32] even three such molecules are present. All the isomers as well as the independent molecules are classical examples of distortion isomerism [27].

Recently, structural parameters of 94 heterometallic FeAu complexes were analyzed and classified [2]. There is somewhat wider variety of the heterometallic cores, than those

found in the heterometallic FeCu complexes. The cores are: FeAu; Fe₂Au, FeAu₂; Fe₃Au, Fe₂Au₂, FeAu₃, Fe₂AuCo, FeAu₂Pt, FeAuCo₂, TeAuCoRu; Fe₄Au, Fe₃Au₂, Fe₂Au₃, Fe₃AuTe, Fe₃AuCo, Fe₂Au₂Ir, Fe₂AuRh₂, FeAuCo₃, FeAuRh₃; Fe₄Au₂, Fe₃Au₃, Fe₂Au₄, FeAu₅; Fe₆Au; Fe₅Au₂, Fe₄Au₃, Fe₃Au₄, Fe₂Au₅; Fe₈Au, Fe₆Au₃, Fe₃Au₆ and Fe₈Au₂K. The inner coordination spheres in FeCu complexes about the iron atoms range from five to seven, and ten which is the most common; and about the copper atoms from two to six, with the most common six. In FeAu complexes, the iron atoms are found from five to ten coordinated, with the most common again ten. The inner coordination spheres about gold atom range from two to six, with the most common four. Noticeable, the complexes FeCu vs FeAu crystallized in the following crystal classes: 45.5 vs 61.7% (monoclinic), 38.6 vs 29.8% (triclinic), 11.9 vs 8.5% (orthorhombic), and in FeCu also tetragonal (3%) and hexagonal (1%). The mean M-M bond distances in the FeCu complexes elongated in the order: 2.520Å (2.319 – 2.732Å) (Fe-Cu) < 2.638 (2.527 – 2.810Å) (Cu-Cu) < 2.663 (2.537 – 2.900Å) (Fe-Fe). In FeAu the order is: 2.668 (2.502 – 2.922Å) (Fe-Fe) < 2.680 (2.438 – 2.975Å) (Fe-Au) < 2.898 (2.630 – 2.992Å) (Au-Au).

Iron and copper elements as well as their complexes are important both from a chemical and biological point of view, and structural information is important for the better understanding of their role in both areas. It is hoped that such review will serve to draw together common structural trends and stimulate activity in areas of particular interest. Also in preparation by us is structural review of heterometallic FeAg complexes.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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