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Synthesis and structural characterisation of Fe(II) and Cu(I) complexes of a new tetrafunctional N-donor ligand with dodecahedral or tetrahedral binding domains†

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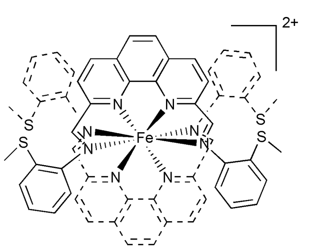
The tetrafunctional N-donor ligand 1 is able to form homoleptic complex cations with dodecahedral ($[Fe\{C_{12}H_6N_2(CHNC_6H_4SMe)_2\}_2]^{2+}$ 2) or tetrahedral ($[Cu_2\{C_{12}H_6N_2(CHNC_6H_4SMe)_2\}_2]^{2+}$ 3) binding domains.

Polyfunctional ligands which are able to either act as fully chelating systems towards one metal ion or to divide their donor functions into separate domains to bind different metal ions offer fascinating perspectives in the synthesis of complexes with complementary topological properites.[1–3]

Though principally ambivalent in this sense, 1,10-phenanthroline systems normally act in a chelating fashion due to steric hindrances caused by the polycyclic aromatic system.[4,5] We report herein the first instance where a Schiff-base derivative of 1,10-phenanthroline containing four nitrogen donor functions—namely $C_{12}H_6N_2(CHNC_6H_4SMe)_2$ **1**—behaves in an ambivalent fashion towards different metal ions in homoleptic bis-ligand complex cations and describe the structural properties of $[Fe\{C_{12}H_6N_2(CHNC_6H_4SMe)_2\}_2]^{2+}$ **2** and of $[Cu_2\{C_{12}H_6N_2(CHNC_6H_4SMe)_2\}_2]^{2+}$ **3**.

Ligand **1** (ESI†) was synthesised from 2,9-diformylphenanthroline[6] and 2-methylmercaptoaniline. The mononuclear iron(II) complex cation **2** was obtained by reaction of **1** with $FeCl_2·4H_2O$ and isolated as $[Fe\{C_{12}H_6N_2(CHNC_6H_4SMe)_2\}_2]_2[Cl_3FeOFeCl_3][ClO_4]_2·4DMF$.‡ The dinuclear copper(I) cation **3** was obtained by reaction of **1** with $Cu(MeCN)_4BF_4$[7] or with $Cu(ClO_4)_2·6H_2O$ and isolated as $[Cu_2\{C_{12}H_6N_2(CHNC_6H_4SMe)_2\}_2][BF_4]_2$ or as $[Cu_2\{C_{12}H_6N_2(CHNC_6H_4SMe)_2\}_2][ClO_4]_2·3DMF$ respectively.



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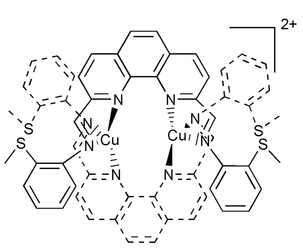

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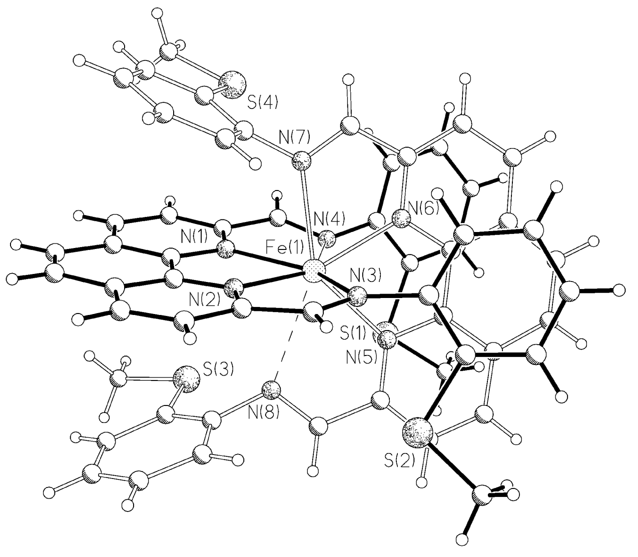

Fig. 1 Structure of $[Fe\{C_{12}H_6N_2(CHNC_6H_4SMe)_2\}_2]^{2+}$ **2** in crystals of $[Fe\{C_{12}H_6N_2(CHNC_6H_4SMe)_2\}_2]_2[Cl_3FeOFeCl_3][ClO_4]_2·4DMF$. Selected bond distances (Å): Fe(1)–N(1) 2.246(3), Fe(1)–N(2) 2.178(3), Fe(1)–N(3) 2.397(3), Fe(1)–N(4) 2.809(3), Fe(1)–N(5) 2.238(3), Fe(1)–N(6) 2.183(3), Fe(1)–N(7) 2.399(3), Fe(1)–N(8) 2.729(3).

The crystal structure of **2**§ (Fig. 1) shows that the eight nitrogen donor atoms of the two ligands define a distorted triangulated dodecahedron around Fe(II) which is composed of two sets of trapezoidal arrangements in perpendicular orientations. These sets belong to different ligands and form two interpenetrating tetrahedra, a flattened one consisting of N(1), N(2), N(5) and N(6) and an elongated one defined by N(3), N(4), N(7) and N(8). The shortest Fe–N bonds [N(2), N(6): 2.180 Å; N(1), N(5): 2.242 Å] are formed by the aromatic donor functions which define the flattened tetrahedron. The elongated tetrahedron is composed of the imine donor functions and makes two slightly longer $Fe–N_{imino}$ bonds [N(3), N(7): 2.389 Å] and two substantially longer ones [N(4), N(8): 2.769 Å]. According to this distance distribution, the overall coordination around iron(II) should be described as a distorted 4 + 2 + 2 dodecahedral geometry. The two phen moieties are planar within experimental error (mean deviation 0.026 and 0.037 Å, respectively) and nearly perpendicular (interplanar angle 100.7°) to each other. The complex anion $[Cl_3FeOFeCl_3]^{2-}$ has crystallographically imposed inversion symmetry resulting in an apparently linear Fe–O–Fe bridge [Fe–O 1.759(1) Å]. From an inspection of the atomic displacement parameters, however, it cannot be ruled out that the linear bridge represents only the mean geometry of slightly bent molecules which are distributed throughout the crystal in a disordered fashion. This dinuclear iron(III) species has been described frequently in the literature in compounds with a variety of different counter cations.[8]

The structure of **3** is shown in Fig. 2. Though the spatial distribution of the nitrogen donor functions within the complex cation is closely related to that observed in **2**, the overall symmetry is remarkably higher in this case. Cation **3** belongs to the point group D_2 with the principal twofold axis passing through the Cu atoms. The second rotation axis passes through

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† Electronic supplementary information (ESI) available: synthesis, characterisation, Mössbauer and NMR data, structure of **1**. See http://www.rsc.org/suppdata/cc/b0/b005671p/

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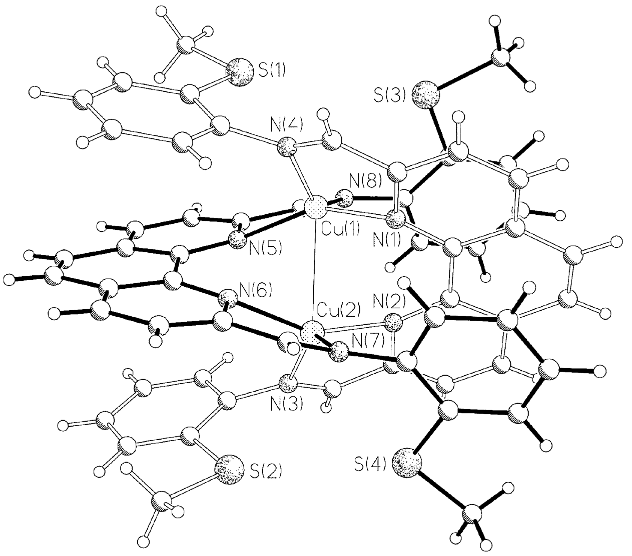

Fig. 2 Structure of $[Cu_2\{C_{12}H_6N_2(CHNC_6H_4SMe)_2\}_2]^{2+}$ **3** in crystals of $[Cu_2\{C_{12}H_6N_2(CHNC_6H_4SMe)_2\}_2][ClO_4]_2\cdot 3DMF$. Selected bond distances (Å): Cu(1)–N(1) 2.052(2), Cu(1)–N(4) 2.044(2), Cu(1)–N(5) 2.057(2), Cu(1)–N(8) 2.048(2), Cu(2)–N(2) 2.060(2), Cu(2)–N(3) 2.041(2), Cu(2)–N(6) 2.061(2), Cu(2)–N(7) 2.046(2).

the midpoints of the homonuclear six-membered carbon rings of the phenanthroline systems, and the third axis is normal to the others. None of these axes is crystallographically imposed. The dodecahedral (bitetrahedral) nitrogen framework around iron in **2** is now split into two distinct sub-sites hosting the copper ions in a fashion completely different from the mononuclear iron complex. Each copper ion is in a highly distorted tetrahedral environment formed by two phenanthroline-type and two imine-type nitrogen atoms from different ligands each. The angles defined by those CuN_2 triangles which are bisected by the principal twofold axis are 74.8° for Cu(1) and 74.3° for Cu(2), and the corresponding N–Cu–N angles within these triangles are 152.1(1) and 138.0(1)° for Cu(1) and 154.1(1) and 137.0(1)° for Cu(2). The N-donor functions of both phen systems are bonded to two different metal atoms each which are located at opposite sides of the aromatic plane. This type of bonding introduces steric strain to the ligand and leads to a significant twisting of the individual rings of the polycyclic aromatic system. Consequently, the N–C–C–N fragments are no longer planar, and the corresponding torsion angles are 9.4° [N(1), N(2)] and 10.4° [N(5), N(6)] respectively. The copper atoms are 2.695(1) Å apart from each other. Cation **3** is an extremely rare example of a complex containing 1,2-bifunctional nitrogen donor ligands with phenanthroline-like rigid geometries which do not act as chelating groups towards metal ions. To our knowledge, the only other example is the binuclear complex cation $[Cu_2\{C_{12}H_6N_2(CHNC_6H_4F)_2\}_2]^{2+}$.[4]

The structures of the complex cations **2** and **3** show some striking similarities. The close relationship between them can best be explained by removing the binuclear copper system and placing a divalent iron atom into the centroid of the molecule. This system has a highly symmetrical nitrogen environment around the central metal which can be described in terms of a triangulated dodecahedron with center-to-vertex distances of 2.182 Å (mean of 4) for the compressed tetrahedron and of 2.828 Å (mean of 4) for the elongated one. The hypothetical complex cation thus derived can easily be transformed to the complex cation **2** by a formal relaxation process which shortens two of the four long nitrogen–iron contacts within the elongated nitrogen tetrahedron to *ca.* 2.398 Å. This process is accompanied by a rotation of the methylthio-substituted phenyl rings which are attached to the conserved nitrogen donor functions of the elongated nitrogen tetrahedron around the N–C bond by 180°.

The Mössbauer spectra of a crystalline sample of $[Fe\{C_{12}H_6N_2(CHNC_6H_4SMe)_2\}_2]_2[Cl_3FeOFeCl_3][ClO_4]_2\cdot 4DMF$ in the range 80–300 K show a superposition of two quadrupole doublets (I) and (II) with an intensity ratio of close to unity (48:52) at 80 K. We assign subspectrum (I) to cation **2** and subspectrum (II) to $[Cl_3FeOFeCl_3]^{2-}$. The parameters of the subspectrum (I) (δ 1.18 mm s^{-1}; ΔE_Q = 2.45 mm s^{-1}) are surprisingly close to those typical for ferrous iron in octahedral environments.[9] They do not reflect any particularity in the electronic structure that could be related to the eight-coordination of iron in **2**.

The results presented here indicate that the highly conjugated ligand **1** acts either as a normal chelating tetradentate ligand or as a binucleating bis-didentate ligand depending on the nature of the central metal ion.

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Notes and references

‡ **CAUTION**: perchlorate salts of metal complexes are potentially explosive. Only small amounts of the materials should be handled and this has to be done with great caution.

§ *X-Ray structure analysis*: Siemens P4RA four-circle diffractometer, Mo-Kα radiation (λ = 0.71073 Å), graphite monochromator, rotating anode generator, scintillation counter, 150 K, empirical absorption corrections, SHELXTL-Plus and SHELXL97 programs,[10] direct methods, full-matrix least-squares refinement on F^2, one scaling factor, one isotropic extinction parameter.

Crystal data: for $[Fe\{C_{12}H_6N_2(CHNC_6H_4SMe)_2\}_2]_2[Cl_3FeOFeCl_3][ClO_4]_2\cdot 4DMF$: M = 2857.85, monoclinic, a = 11.760(4), b = 21.356(5), c = 25.690(8) Å, β = 100.66(2)°, V = 6340.6 Å^3, space group $P2_1/c$, Z = 2, D_c = 1.497 g cm^{-3}, μ(Mo-Kα) = 0.819 mm^{-1}, transmission range 0.801–0.688, crystal dimensions *ca.* 0.45 × 0.23 × 0.18 mm, ω scan, $2\theta_{max}$ = 54°, 13 833 unique reflections, $R1(wR2)$ = 0.0589 (0.1297) for 9226 observed reflections [$I > 2\sigma(I)$], 802 variables, non-hydrogen atoms anisotropic, H atoms at idealized positions.

For $[Cu_2\{C_{12}H_6N_2(CHNC_6H_4SMe_3)_2\}_2][ClO_4]_2\cdot 3DMF$: M = 1502.50, triclinic, a = 11.188(3), b = 16.587(4), c = 17.538(4) Å, α = 89.54(2), β = 84.40(2), γ = 87.11(2)°, V = 3234.9 Å^3, space group $P\bar{1}$, Z = 2, D_c = 1.543 g cm^{-3}, μ(Mo-Kα) = 0.94 mm^{-1}, transmission range 0.843–0.707, crystal dimensions *ca.* 0.75 × 0.23 × 0.15 mm, ω scan, $2\theta_{max}$ = 54°, 14 130 unique reflections, $R1(wR2)$ = 0.0435 (0.0929) for 10 639 observed reflections [$I > 2\sigma(I)$], 862 variables, non-hydrogen atoms anisotropic, H atoms at idealized positions.

CCDC 182/1788. See http://www.rsc.org/suppdata/cc/b0/b005671p/ for crystallographic files in .cif format.

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