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Crystal structure and magnetic behaviour of a two-dimensional complex $[Cu(dmen)]_2[Fe(CN)_6]$ (dmen = 2-dimethylaminoethylamine) with an exceptional cyano-bridging

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The cyanide bridged bimetallic assembly $[Cu(dmen)]_2[Fe(CN)_6]$ (dmen = 2-dimethylaminoethylamine) has been prepared and characterized by elemental analyses, infrared and electronic spectroscopy. The crystal structure of the compound consists of a two-dimensional polymeric sheet with two different rings, one a four membered square ring and another a twelve membered hexagonal ring. Each iron(II) ion has two free, two nearly linear bridging and two end-on bridging cyanide groups. In the crystal all the copper(II) ions have a distorted square based pyramidal geometry. From magnetic susceptibility measurements, the complex was found to exhibit a weak ferromagnetic interaction between the nearest copper atoms.

Recently there has been a growing interest in the field of molecular magnetism which has developed over the past decades.[1] Several polymers of bimetallic assemblies having one- (1-D), two- (2-D), or three-dimensional(3-D) structure with their various magnetic properties are known.[2–14] Until now, several ferromagnetic compounds have been developed with critical temperatures ranging from 0.6 to 450 K.[15–17] Among them, the cyanide system based on Prussian Blue and its analogous forms[18–27] is particularly useful and has drawn considerable interest.

In particular much effort has been made for the design of highly ordered structures by the reaction of metal (especially copper and nickel) amine complexes with $[Fe(CN)_6]^{4-}$ or $[M(CN)_6]^{3-}$ (M = Fe, Mn, Co or Cr). Various magnetic properties and structures have been observed by the variation of amines and paramagnetic metal centers.[8,12]

As copper(II) normally possesses four-, five- or six-coordination, so the coupling of the copper amine complexes with Fe^{II} or Fe^{III} can create a novel family of magnetic compounds with potential control over the structure of the crystal lattice. We therefore examined the reaction of $[Cu(dmen)_2][NO_3]_2$ with $[Fe(CN)_6]^{4-}$, from where the compound $[Cu(dmen)]_2[Fe(CN)_6]$ (dmen = 2-dimethylaminoethylamine) easily crystallized out. The compound possesses a two-dimensional structure with an interesting bonding mode of cyanide.

Experimental

Physical measurements

Elemental analyses were carried out using a Perkin-Elmer 2400 II elemental analyzer. The infrared spectrum was recorded on a Perkin-Elmer 883-Instrument from KBr pellets and the electronic spectrum on a Hitachi U-3400 (UV-VIS-NIR) spectrophotometer from aqueous solution. Magnetic susceptibility measurements of the polycrystalline sample have been carried out using a MPMS SQUID magnetometer in the temperature range 2.0–300 K. The contribution of the sample holder was determined separately in the same temperature range and field. Diamagnetic corrections were estimated from Pascals constants. The electronic spin resonance spectrum of the polycrystalline compound has been recorded at X-band frequency using a Bruker ESP 300E automatic spectrometer from room temperature to 4 K.

Materials

The compounds $K_4[Fe(CN)_6]\cdot 3H_2O$ (Loba Chemie, India), $Cu(NO_3)_2\cdot 3H_2O$ (Lancaster) and 2-dimethylaminoethylamine (Fluka) were of reagent grade and used as such.

Preparation of $[Cu(dmen)]_2[Fe(CN)_6]$ 1

An aqueous solution of $K_4[Fe(CN)_6]\cdot 3H_2O$ (1 mmol, 422.2 mg) was added very slowly to an aqueous solution of $[Cu(dmen)_2][NO_3]_2$ (2 mmol, 727.6 mg), prepared by mixing $Cu(NO_3)_2\cdot 3H_2O$ (1 mmol, 241.6 mg) and dmen (2 mmol, 0.218 cm^3) in methanol, and was kept in a dark place. After a few minutes blue crystals suitable for X-ray diffraction were formed, which were collected by filtration, washed with water and dried *in vacuo* over $CaCl_2$. The results of elemental analyses (found C, 32.56; H, 4.70; N, 27.32. $C_{14}H_{24}Cu_2FeN_{10}$ requires C,32.63; H, 4.69; N, 27.18%) were consistent with the formula of the sample used for X-ray analysis.

Crystallography

Crystal data: $C_{14}H_{24}Cu_2FeN_{10}$, $M = 515.25$, monoclinic, space group $P2_1/c$, $a = 11.11(2)$, $b = 8.969(10)$, $c = 10.73(2)$ Å, $\beta = 112.48(11)°$, $U = 988(3)$ Å^3, $Z = 2$, $\mu = 8.487$ mm^{-1}, final $R_{wF} = 0.1746$, $R1 = 0.0662$ and number of parameters = 124.

A blue square shaped crystal of complex **1** was mounted on a glass fibre. Intensity data were measured at 293(2) K on a Syntex P2(1)/c 4-circle diffractometer using graphite monochromated Cu-Kα radiation, $\lambda = 1.54178$ Å. A total of 998

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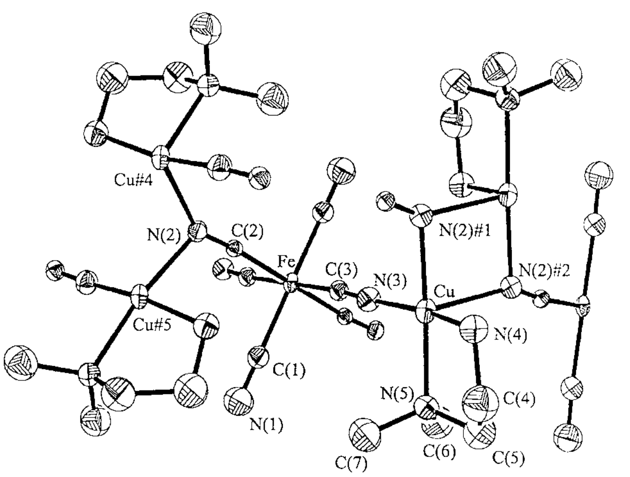

Fig. 1 The crystal structure of complex **1** showing the atom numbering schemes.

reflections measured in the θ range 4.30–49.99° using ω scans were considered unique. The structure was solved by direct methods using SHELXTL-PLUS[28] and refined by a full-matrix least-squares procedure based on F^2 using SHELXL 93.[29]

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Results and discussion

Crystal structure

Crystal structure of the hexanuclear unit Cu_4Fe_2 of $[Cu(dmen)]_2[Fe(CN)_6]$ is shown in Fig. 1. Selected bond distances and angles are listed in Table 1. A new interesting feature is the mixed Cu–cyanide–Fe bridging mode. A 1,2 end-to-end cyanide bridging is usual evidence for bimetallic assemblies with $[M(CN)_6]^{n-}$ building blocks[2–14] and 1,1 end-on type bridging is generally observed in azido or thiocyanato bridged complexes.[30,31] The stereochemistry of the copper(II) ions is best described as a distorted square pyramid with a geometrical factor[32] $\tau = 0.07$. The N(3)–Cu [1.918(9)], N(2)#1–Cu [2.061(9)], N(4)–Cu [1.974(9)] and N(5)–Cu [2.061(9) Å] are the equatorial linkages whereas N(2)#2–Cu [2.297(8) Å] is the axial one. The deviation of Cu from the least squares plane N(4) N(5)N(3)N(2)#1 is 0.17(1) Å. Two copper centres are linked by alternate short [N(2)–Cu#4 2.061(9) Å] and long [N(2)–Cu#5 2.297(8) Å] bonds to the cyanide bridges, which gives rise to the orthogonality between the copper magnetic orbitals.

Fig. 2 represents the 2-D sheet along the z axis, having a parallelogram with iron at its corners in the y–z plane. The interplanar Fe · · · Fe distance is the crystallographic a lattice constant, and the orthogonal interplanar distance ($a \cdot \sin \beta$) is 10.265 Å. The short Cu · · · Cu distance is 3.12(1) Å, and the two Fe–Cu (*via* N2) distances are 4.27(2) and 5.18(2) Å respectively. The next Fe · · · Cu distance (*via* N3) is 4.96(2) Å.

In the two-dimensional sheet each $[Fe(CN)_6]^{4-}$ ion coordinates to six adjacent copper(II) ions [Fig. 2]. The two cyano nitrogens N(3), N(3)# are in 1,2 end-to-end bridging mode and other two cyano nitrogens N(2), N(2)# are in 1,1 end-on bridging mode and are linked to the copper(II) ions in a plane to form a twelve membered pseudo hexagonal ring. The end-to-end copper–cyanide linkage is almost linear and the bond angle of Cu–N(3)–C(3) is 175.4(8)°. The end-on cyanide group is linked to the copper(II) ion in a considerably bent fashion, which gives the bond angles of 116.2(7) and 149.7(8)° for Cu#4–N(2)–C(2) and Cu#5–N(2)–C(2) respectively. The interior bond angles of the square ring are 88.7(3)° for N(2)#1–Cu–N(2)#2 and 91.3(3)° for Cu#4–N(2)–Cu#5. The building block $[Fe(CN)_6]^{4-}$ assumes an octahedral geometry with six CN^- groups, where each of the equatorial CN^- groups co-ordinates to the copper(II) ions in a mixed end-to-end and end-on fashion, and the axial CN^- groups are free. The Fe–C bond lengths range from 1.864(11) to 1.919(12) Å and the bond angles of Fe–C(3)–N(3) and Fe–C(2)–N(2) are 174.9(9) and 172.2(9)° respectively.

Table 1 Selected bond lengths (Å) and bond angles (°) for complex **1**

Cu–N(3)	1.918(9)	Cu–N(4)	1.974(9)
Cu–N(2)#1	2.061(9)	Cu–N(5)	2.061(9)
Cu–N(2)#2	2.297(8)	Fe–C(3)	1.864(11)
Fe–C(2)	1.881(10)	Fe–C(1)	1.919(12)
N(3)–C(3)	1.186(14)	C(1)–N(1)	1.147(13)
C(2)–N(2)	1.169(12)	N(2)–Cu#4	2.061(9)
N(2)–Cu#5	2.297(8)		
N(3)–Cu–N(4)	166.9(4)	N(3)–Cu–N(2)#1	91.7(3)
N(4)–Cu–N(2)#1	88.3(3)	N(3)–Cu–N(5)	92.6(4)
N(4)–Cu–N(5)	85.8(4)	N(2)#1–Cu–N(5)	171.3(3)
N(3)–Cu–N(2)#2	97.9(3)	N(4)–Cu–N(2)#2	95.2(3)
N(2)#1–Cu–N(2)#2	88.7(3)	N(5)–Cu–N(2)#2	98.2(3)
C(1)#3–Fe–C(1)	179.999(1)	C(3)–N(3)–Cu	175.4(8)
N(3)–C(3)–Fe	174.9(9)	N(1)–C(1)–Fe	177.0(10)
N(2)–C(2)–Fe	172.2(9)	C(2)–N(2)–Cu#4	116.2(7)
C(2)–N(2)–Cu#5	149.7(8)	Cu#4–N(2)–Cu#5	91.3(3)

Symmetry transformations used to generate equivalent atoms: #1 $x, -y + \frac{1}{2}, z - \frac{1}{2}$; #2 $-x, y - \frac{1}{2}, -z + \frac{1}{2}$; #3 $-x, -y, -z + 1$; #4 $x, -y + \frac{1}{2}, z + \frac{1}{2}$; #5 $-x, y + \frac{1}{2}, -z + \frac{1}{2}$.

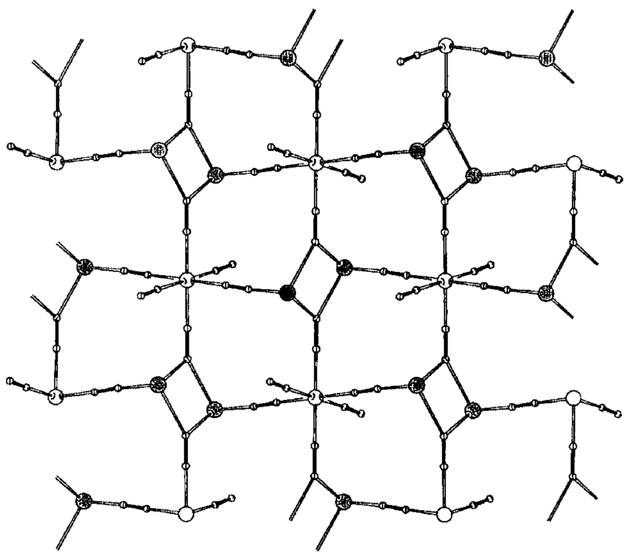

Fig. 2 Projection of the polymeric chain structure along the z axis.

Infrared spectrum

The bimetallic assembly of complex **1** shows IR bands at 3327 and 3275 cm^{-1} due to N–H stretching of the NH_2 group and several weak bands in the range 2980–2807 cm^{-1} can be assigned to the aliphatic C–H stretching vibration. It shows three well resolved bands at 2001, 2071, and 2108 cm^{-1} indicating the existence of three types of cyanide groups in the crystal lattice. The lower wavenumber band can be assigned to a non-bridging cyanide group. The band at 2071 cm^{-1} is attributed to the intermetallic linear cyanide bridge stretching vibration. The higher wavenumber band at 2108 cm^{-1} can be ascribed to the end-on bridging mode of cyanide. The intensities of the three bands are almost equal, which suggests the presence of equal contributions of three different cyanide modes to the bulk structure of the assembly.

Electronic spectrum

The solution electronic spectrum of the complex shows a strong absorbance at 480 nm[2] which is assigned to electron transfer Fe^{2+} $d_{yz}(B_2) \rightarrow Cu^{2+}$ $d_{x^2-y^2}(A_1)$ and an intense shoulder at 690 nm, due to d–d transitions of copper(II) ion.

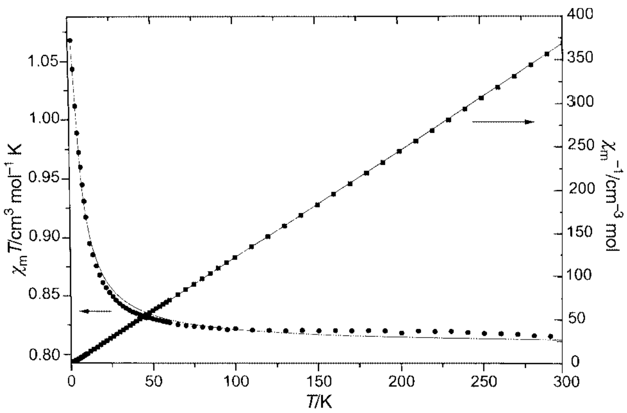

Fig. 3 Plot of the temperature dependence of $\chi_m T$ for complex **1** (per Cu_2Fe).

Magnetic properties

The magnetic behaviour of the compound in a 0.2 T field is shown in Fig. 3, as a $\chi_m T$ *vs.* T plot. At room temperature the $\chi_m T$ value is 0.815 cm^3 K mol^{-1} (2.55μ_B per Cu_2Fe with $g = 2.08$). The expected value for two uncoupled copper(II) ions is 0.74 cm^3 K mol^{-1} for $g = 2$. $\chi_m T$ increases smoothly down to *ca.* 100 K and then sharply at lower temperature reaching a maximum value of 1.07 cm^3 K mol^{-1} (2.92μ_B) at 2.0 K. The $1/\chi_m$ *vs.* T plot in the range 2.0–100 K obeys the Curie–Weiss law with a positive Weiss constant $\theta = +1.49$ K. The magnetic behaviour below 100 K indicates a weak ferromagnetic coupling which can result from the interaction of the copper(II) ions as follows. (1) The intervening diamagnetic iron(II) ions lead to the same situation observed in the Prussian blue compound[33–35] and in the recently reported $[Ni(en)_2]_3[Fe(CN)_6](PF_6)_2$.[11] The interaction has been rationalized by taking into account the Goodenough and Kanamori rules, in particular when a magnetic orbital overlaps an empty one the result of the interaction is ferromagnetic [$Fe^{II}(e_g^0)$ and $Cu^{II}(e_g^3)$]. (2) Through the double end-on cyanide bridge. So far, there is not enough information available [copper(II) ions linked by the nitrogen atom of NC bridges] to permit the construction of a complete magneto-structural correlation, but for similar bridges, like azide, it has been shown that the magnetic behaviour is related to the Cu–N–Cu angles in azide-bridged copper(II) complexes. These complexes show an antiferromagnetic exchange interaction when the Cu–N–Cu angle is greater than 108°.[35,36] On the contrary, in our case the Cu–N–Cu angle is close to 91.3° which leads to orthogonality between the copper(II) magnetic orbitals, which is responsible for the ferromagnetism of the compound.

Consequently, the application of the Bleaney–Bowers expression for an isotropically coupled pair of $S = \frac{1}{2}$ ions[37] is relevant, using as a criterion of best fit the minimum value of $R = \Sigma_i (\chi T_i^{calc} - \chi T_i^{exp})^2/(\chi T_i^{exp})^2$. The results of the fit are shown as the solid line in Fig. 3, where $J = 4.4$ cm^{-1}, $g = 2.07$ with $R = 2.6 \times 10^{-5}$. During the regression analysis the temperature independent paramagnetism was fixed as zero.

The field dependence of magnetization (0–5 T) measured at 2 K is shown in Fig. 4, in the form of $M/N\mu_B$ (per Cu_2Fe unit) *vs.* H. The magnetization reaches a value of 1.92 $N\mu_B$ at 5 T which is close to the expected $S = 1$ value of 2 $N\mu_B$ for the Cu_2Fe system, indicating the presence of ferromagnetic interaction between the nearest copper(II) ions.

Electronic spin resonance spectrum

The ESR spectrum of the polycrystalline compound has been recorded from room temperature to 4 K. In this range the spectrum remains unchanged and no signals at half field were detected. It showed a broad band with three g values at 2.043, 2.091 and 2.213, typical for copper(II) ions with rhombic distortion.

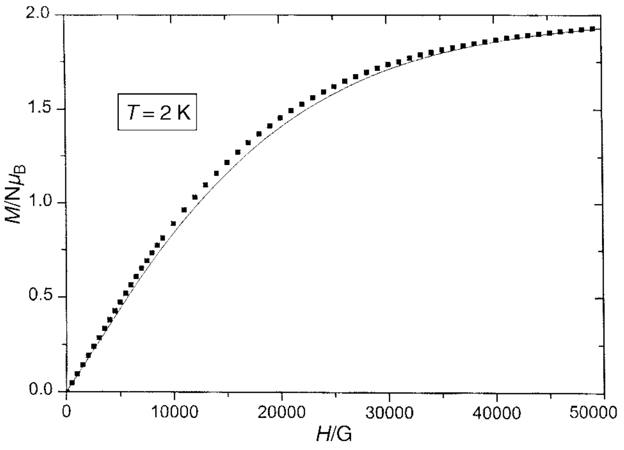

Fig. 4 The field dependence of magnetization at 2 K for complex **1** (per Cu_2Fe).

Conclusion

A two-dimensional copper(II)–iron(II) array has been obtained from the reaction of the $[Cu(dmen)_2]^{2+}$ cation and the $[Fe(CN)_6]^{4-}$ anion. The assembly of the two components occurs through both the 1,2 end-to-end and the unusual 1,1 end-on cyanide bridging mode and is also due to the co-ordination properties of the copper ion. The magnetic measurements show a weak ferromagnetic coupling.

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