One Novel Racemic Cu–Co Cyano-Bridged Complex: Synthesis, Characterization, Crystal Structure, and Magnetic Properties

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One novel racemic Cu–Co cyano-bridged complex $[C_{38}H_{38}CoCu_2N_{14}O]^+[C_{22}H_{18}CoCuN_{10}]^- \cdot 7H_2O$ where [L = *N*,*N′*-bis(2-pyridylmethylene)butane-1,4-diamine] has been prepared and characterized by elemental analyses, spectroscopic study, single crystal X-ray crystallography, and variable temperature magnetic susceptibility measurements. The compound crystallises as a 57/43 racemic twin and contains two different, one binuclear and one trinuclear, complex species. A low temperature magnetic susceptibility measurement showed the existence of very weak antiferromagnetic interactions.

In the past few years, there has been an increasing interest in metal assemblies constructed with paramagnetic metal complexes with the aim to provide molecular based magnets exhibiting spontaneous magnetization.[1–5] An enormous amount of research has been devoted to the study of cyanide containing metal complexes because of their structural richness, unique spectroscopic properties, peculiar reactivity, electron transition properties,[6] and biological relevance.[7–9] Cyano-bridged bimetallic assemblies based on hexacyanometallate building blocks, $[M(CN)_6]^{n-}$, provide a rich variety of magnetic materials with structures ranging from clusters to 3D extended networks and interesting magnetic, electron transfer,[1,10–14] and magnetooptical properties.[1,15–29] Electron transfer is a fundamental and important chemical process with important applications in the fields of photosynthesis, disease control, and catalysis.[6] Initial efforts have been focussed on the preparation of 3D prussian blue analogues in which two metal centres are paramagnetic.[30] One route to bimetallic cyanide bridged extended arrays is that of using hexacyanometallate building blocks with transition metal complexes containing polydentate ligands.[1,10,14,25,30–37] In this approach, hexacyanometallate ions can adopt different bridging modes from η^1 to η^6 to form bimetallic assemblies of various network structures.[1] This approach has afforded cyano-bridged complexes with 1D, 2D, and 3D extended structures as well as discreate polynuclear species.[30]

Recently, we have reported one 2D-polymeric compound with an exceptional 1,1 end-on cyano bridge[38] and one pentanuclear complex $[(CuL)_4Fe(CN)_6]\cdot 16H_2O$ [L = *N*,*N*-dimethyl-*N′*-(α-methyl-salicylidene)ethane-1,2-diamine].[39] We have also recently reported one cyano-bridged trinuclear complex $[(CuL)_2Fe(CN)_6]ClO_4\cdot 2CH_3OH\cdot H_2O$ where L = *N*,*N*-bis(2-pyridylimine)propane-1,3-diamine[40] and cyano-bridged polynuclear and trinuclear Cu–Co complexes with 1-dimethylamino-2-propyl amine.[41]

Combining Schiff base cationic complexes with hexacyanometallate ions generates large variations in structures and magnetic properties.[41] Previous investigations varied[42–46] in i) Schiff base ligands, ii) the nature of the counter anions, and iii) the transition metal couple. However, the progress concerning the analysis and comprehension of the structural information for such mixed valence and mixed metal complexes is still limited,[7] and so by investigating the structure and magnetic properties of these species, we hope to improve the design of multinuclear complexes. Focussing our interest in this area, we have synthesized one cationic complex of Cu(II) with the neutral tetradentate Schiff base ligand L, where L = *N*,*N′*-bis(2-pyridylmethylene)butane-1,4-diamine. These types of ligands have been used to design Cu_2Zn_2SOD (SOD = superoxide dismutase) model complexes.[46,47] We are interested in preparing a cyano-bridged bimetallic assembly from hexacyanocobaltate $[Co(CN)_6]^{3-}$ ion (building block) and a four coordinated cationic $[CuL]^{2+}$ complex (connecting block).

In this paper, we report the synthesis, characterization, single crystal X-ray analysis, and magnetic properties of one cyano-bridged racemic complex comprised of two different species. To the best of our knowledge, this is the first example of a crystallographically characterized racemic cyano-bridged Cu–Co mixed-metallic complex having two different species in the crystal.

Experimental

Preparation. Reagent grade pyridine-2-carboxaldehyde, 1,4-diaminobutane, $K_3[Co(CN)_6]$ (Fluka), and $Cu(ClO_4)_2\cdot 6H_2O$ (Aldrich) were obtained commercially and used as received. **Caution**: Perchlorate salts are potentially explosive and should be handled in small quantities.

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Synthesis of the Ligand and Complex: The tetradentate Schiff base ligand [*N*,*N′*-bis(2-pyridylmethylene)butane-1,4-diamine] was prepared by the condensation of a methanol solution of 1,4-diaminobutane (0.441 g, 5 mmol) with pyridine-2-carboxaldehyde (1.07 g, 10 mmol) for half an hour. The resulting brown coloured solution was used for complex formation without further purification.

$[CuL](ClO_4)_2$ was prepared by the addition of the above ligand solution to a solution of $Cu(ClO_4)_2\cdot 6H_2O$ (0.370 g, 10 mmol) in 50 mL methanol.

Preparation of $[C_{38}H_{38}CoCu_2N_{14}O]^+[C_{22}H_{18}CoCuN_{10}]^-\cdot 7H_2O$: The hexacyanometallate ion has the tendency to decompose during heating and irradiation with light. So an aqueous solution of $K_3[Co(CN)_6]$ (0.664 g, 2 mmol) was added very slowly to a solution of $[CuL](ClO_4)_2$ (1.05 g, 3 mmol) in 50 mL methanol. The resulting solution was kept in a dark place. Light blue rhombic shaped crystals suitable for X-ray diffraction were formed after 1 day and were collected by filtration, washed with a minimum volume of ethanol and dried in air. Yield: Approximately 70%. The results of the elemental analyses (Anal. Found: C, 46.1; H, 4.6; N, 21.6%; Calcd. for $[C_{38}H_{38}CoCu_2N_{14}O]^+[C_{22}H_{18}CoCuN_{10}]^-\cdot 7H_2O$ requires C, 46.0; H, 4.5; N, 21.5%) were consistent with the formula obtained from X-ray analysis.

Measurements. Elemental analyses were carried out using a Perkin-Elmer 2400 II elemental analyser. The infrared spectrum was recorded on a Perkin-Elmer FT-IR instrument in KBr pellets and the electronic spectrum was recorded on a Perkin-Elmer Lambda-40 (UV–vis) spectrophotometer in the solid state with nujol. Magnetic measurements were carried out on polycrystalline samples (20 mg) with a Quantum Design MPMS SQUID magnetometer operating at a magnetic field of 0.1 T between 2 and 300 K. The magnetic data were corrected with the values of the sample holder and the diamagnetic corrections were evaluated using Pascal's constants. Magnetization measurements were carried out at 2 K between 0 and 7 T. ESR spectra were recorded on powder samples at an X-band frequency with a BRUKER 300E automatic spectrometer, varying the temperature between 4 and 300 K.

X-ray Crystal Structure Analysis. Crystal data: Empirical formula $C_{60}H_{70}Co_2Cu_3N_{24}O_8$, $[C_{38}H_{38}CoCu_2N_{14}O]^+[C_{22}H_{18}CoCuN_{10}]^-\cdot 7H_2O$, fw 1563.88, $T = 150(2)$ K, Bruker Nonius kappa CCD area detector, Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å, monoclinic, space group Pn, $a = 18.6659(5)$, $b = 10.0924(4)$, $c = 20.6321(8)$ Å, $\beta = 116.367(2)^\circ$, $V = 3482.4(2)$ Å^3, $Z = 2$, D(calcd) $= 1.491$ Mg/m^3, $m = 1.437$ mm^{-1}, 10226 reflections collected, 7657 independent [R(int) $= 0.0429$], final $R1/wR2$ [$I > 2\sigma(I)$] 0.0483/0.1229, (all data) 0.0623/0.1411, absolute structure parameter $= 0.42(2)$.

The structure was solved by direct methods (SHELX-S) and refined on F^2 using SHELXL-97 and all unique data. Attempts to solve the structure in a centrosymmetric space group $P2/n$ or $P21/n$ were unsuccessful. Further, with $Z = 2$, both the cationic and anionic species would be required to have a crystallographic symmetry in order to crystallise in a centrosymmetric space group, which is highly unlikely. The structure was therefore solved and successfully refined by assuming the non-centrosymmetric monoclinic space group Pn. The Flack parameter in SHELXL-97 was finally refined to 0.43(2), indicating that the crystal is a 57/43 racemic twin.

The non-hydrogen atoms were anisotropic. The hydrogen atoms on the organic ligands were included in calculated positions (riding model). Only seven of the 16 hydrogen atoms on the water molecules were obtained from difference mapping and these were included in the model unrefined. The remaining hydrogen atoms of the water molecules were ignored. Crystallographic data has been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk]. Copies can be obtained on request, free of charge, by quoting the publication citation and deposition number 208964.

Results and Discussion

Infrared Spectrum. The complex shows a broad peak in the range 3540–3210 cm^{-1}, indicating the presence of water molecules in the lattice and also the ν(N–H) frequency.[48] It shows one band at 2129 cm^{-1} which can be assigned to the intermetallic cyanide bridging.[6] The lower wave number band that appeared at 2101 cm^{-1} was assigned to the terminal ν(C=N) stretching mode.[41] The band at 1646 cm^{-1} is assigned as imine stretching, which is slightly higher than other reported complexes, where it has appeared between 1610 and 1630 cm^{-1}.[49,50]

Electronic Spectrum. The electronic spectrum in the solid state of the title complex showed bands with maxima at 672 and 384 nm. The sharp band at 384 nm can not be easily assigned, as several transitions with different origins can be expected. Several bands in the region 380 to 300 nm can be interpreted as charge transfers from ligand to cobalt and charge transfers between copper and cobalt in either direction.[43] The band at 672 nm is due to the d–d transition.

Description of the Structures. The compound crystallises as a 57/43 racemic twin and contains two different, one binuclear and one trinuclear, complex species. The crystal structure of **1** consists of two different complex species $[C_{22}H_{18}CoCuN_{10}]^-$ (**A**) and $[C_{38}H_{38}CoCu_2N_{14}O]^+$ (**B**), and seven water molecules (lattice) in one asymmetric unit. The water molecules participate in O–H···O/N hydrogen bonding to stabilise the crystal structural framework. The crystal structures of (**A**) and (**B**) with atomic numbering schemes are presented in

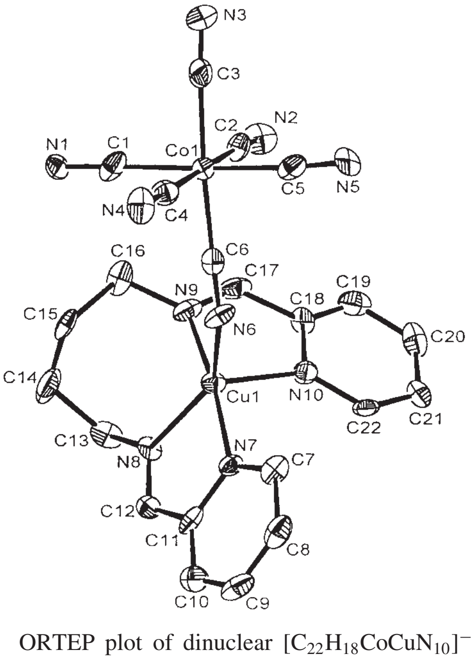

Fig. 1. ORTEP plot of dinuclear $[C_{22}H_{18}CoCuN_{10}]^-$ unit (**A**). (Displacement ellipsoids are drawn at 50% probability level.)

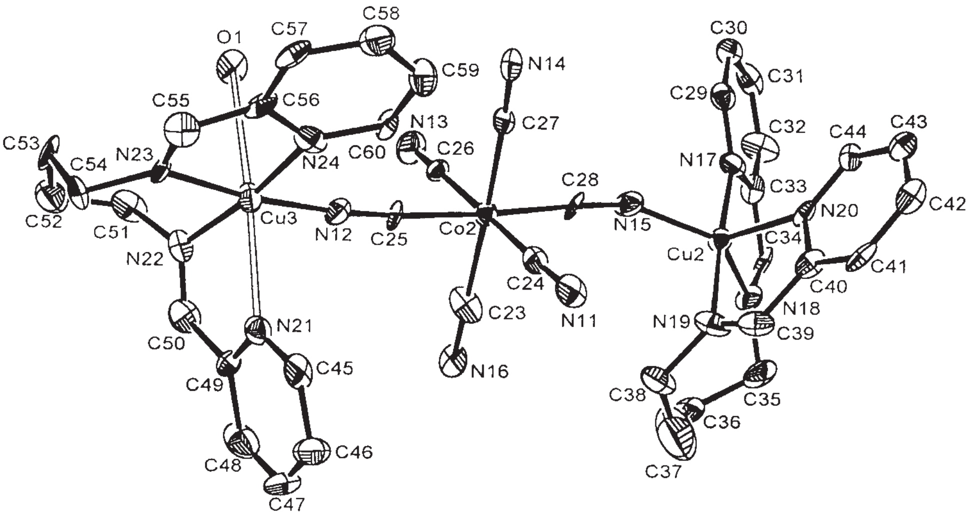

Fig. 2. ORTEP plot of trinuclear $[C_{38}H_{38}CoCu_2N_{14}O]^+$ unit (**B**). (Displacement ellipsoids are drawn at 50% probability level.)

Table 1. Selected Bond Lengths [Å] and Angles [deg] for Complex **1**

Cu(1)–N(9)	1.955(8)	Cu(1)–N(7)	1.994(7)
Cu(1)–N(8)	2.001(7)	Cu(1)–N(6)	2.014(9)
Cu(1)–N(10)	2.111(8)	Cu(2)–N(17)	1.973(8)
Cu(2)–N(15)	1.979(9)	Cu(2)–N(19)	1.998(8)
Cu(2)–N(18)	2.031(8)	Cu(2)–N(20)	2.117(8)
Cu(3)–N(12)	1.946(8)	Cu(3)–N(23)	1.971(7)
Cu(3)–N(22)	2.021(7)	Cu(3)–N(24)	2.037(7)
Cu(3)–N(21)	2.371(7)	Cu(3)–O(1)	2.591(7)
Co(1)–C(4)	1.871(11)	Co(1)–C(5)	1.876(11)
Co(1)–C(1)	1.884(11)	Co(1)–C(2)	1.888(11)
Co(1)–C(6)	1.891(10)	Co(1)–C(3)	1.898(12)
Co(2)–C(25)	1.863(9)	Co(2)–C(24)	1.869(10)
Co(2)–C(28)	1.877(10)	Co(2)–C(23)	1.881(10)
Co(2)–C(27)	1.907(9)	Co(2)–C(26)	1.922(10)
N(9)–Cu(1)–N(7)	172.7(3)	N(9)–Cu(1)–N(8)	91.4(3)
N(7)–Cu(1)–N(8)	81.3(3)	N(9)–Cu(1)–N(6)	89.9(3)
N(7)–Cu(1)–N(6)	95.6(3)	N(8)–Cu(1)–N(6)	143.1(3)
N(17)–Cu(2)–N(15)	96.4(3)	N(17)–Cu(2)–N(19)	175.2(4)
N(15)–Cu(2)–N(19)	88.3(4)	N(17)–Cu(2)–N(18)	81.1(3)
N(15)–Cu(2)–N(18)	136.9(3)	N(19)–Cu(2)–N(18)	94.6(3)
N(12)–Cu(3)–N(23)	173.3(3)	N(12)–Cu(3)–N(22)	92.6(3)
N(23)–Cu(3)–N(22)	92.4(3)	N(12)–Cu(3)–N(24)	93.6(3)
N(23)–Cu(3)–N(24)	81.3(3)	N(22)–Cu(3)–N(24)	173.3(3)
N(12)–Cu(3)–O(1)	88.1(3)	C(4)–Co(1)–C(5)	92.9(4)
C(4)–Co(1)–C(1)	86.4(4)	C(5)–Co(1)–C(1)	177.6(5)
C(4)–Co(1)–C(2)	176.7(5)	C(5)–Co(1)–C(2)	89.8(4)
C(1)–Co(1)–C(2)	91.0(4)	C(4)–Co(1)–C(6)	91.2(4)
C(5)–Co(1)–C(3)	86.5(4)	C(1)–Co(1)–C(3)	91.3(5)
C(2)–Co(1)–C(3)	89.8(4)	C(6)–Co(1)–C(3)	175.7(4)
C(6)–N(6)–Cu(1)	150.3(7)		
C(25)–N(12)–Cu(3)	170.7(7)	C(28)–N(15)–Cu(2)	156.5(8)

Figs. 1 and 2, respectively. Selected bond distances and angles are given in Table 1.

The complex **A** is a binuclear compound formed from one $[Co(CN)_6]^{3-}$ and one $[Cu(C_{16}H_{18}N_4)]^{2+}$ unit, the two metal centers being linked through a cyano group.

The Co(1) atom in **A** has the expected octahedral arrangement with slight distortions as indicated by the variations of the *cis* angles [86.5(4)–92.9(4)°] and *trans* angles [175.7(4)–177.6(4)°] from the ideal values of 90 and 180°, respectively. The Co–C and C–N distances are grouped together in the narrow ranges 1.871(11)–1.898(12) Å and 1.126(13)–1.182(13) Å, respectively. The Co–C–N groups are almost linear, as indicated by the angles 173.9(8)–178.0(10)°.

The Cu(1) centre in **A** is pentacoordinated. This coordination number is very common for Cu(II) with either square-based pyramidal (SP) or trigonal-bipyramidal (TBP) geometry. Recently, some complexes have been reported in which the Cu(II) ion adopts a geometry that is intermediate between SP and TBP.[51a,14] Several parameters are used to specify the geometry, one of which is the Addison distortion index τ.[43] The value of τ is 0.495 for **A**, which indicates that the coordination environment of the copper atom is trigonal-bipyramidal (TBP). The mean basal plane is constructed by the coordination of two nitrogen atoms N(8) and N(10) from the tetradentate Schiff base and one nitrogen atom N(6) of the coordinated cyanide group. The Cu(1)–N(10), Cu(1)–N(8), and Cu–N(6) distances are 2.111(8), 2.001(7), and 2.014(9) Å, respectively. The axial positions are occupied by the other two nitrogen atoms N(7) and N(9) of the Schiff base ligand, and the Cu–N bonds involving these atoms 1.994(7) and 1.955(8) Å, respectively, are only marginally shorter than the equatorial bonds. The deviation of the Cu(1) from the mean basal plane formed by N(6), N(8), N(10) is 0.065(4) Å towards N(7). The bond angles and bond distances of **A** are close to the values in other related pentacoordinated complexes.[13,14,51] The bond angle of C(6)–N(6)–Cu(1) at 150.3(7)° indicates a non-linear linkage between the nitrogen atom of the cyanide ligand and the copper(II) atom.

The complex **B** is a trimetallic compound formed from one $[Cu(C_{16}H_{18}N_4)]^{2-}$ and one $\{Cu(C_{16}H_{18}N_4)(H_2O)\}^{2-}$ unit linked by one central $Co(CN)_6$ unit, through two CN groups in the *trans* positions. The cobalt(III) ion in this species is also octahedral, with the Co(2)–C and C–N distances ranging from 1.863(9)–1.922(10) and 1.125(10)–1.176(12) Å, respectively. All the bond distances and angles around Co(2) compare well with the corresponding values in **A**, and also in other similar complexes.[45]

The two independent copper ions in **B**, Cu(2) and Cu(3), have different coordination numbers and different geometries. Both are bonded to four N atoms of a Schiff base ligand and to one N atom from the bridging CN group. However, Cu(3) is additionally bonded to a coordinated water molecule [O(1)] resulting in a coordination number of six, in contrast to Cu(2) which has a coordination number of five. Cu(2) has a distorted trigonal bipyramidal geometry ($\tau = 0.63$),[43] whilst the geometry around Cu(3) is distorted octahedral.

For the Cu(2) centre, the basal plane is formed by the N(18) and N(20) atoms of the Schiff base and the N(15) atom of the bridging cyanide, while the axial sites are occupied by the N(19) and N(17) atoms of the Schiff base [N(17)–Cu(2)–N(19) = 175.2(4)°]. The Cu(2) centre is displaced out of the basal plane by 0.052(5) Å towards N(17). For the octahedral Cu(3) centre, the equatorial positions are occupied by the atoms N(22), N(23), and N(24) from the Schiff base and N(12) from the bridging cyanide, while the axial positions are occupied by the other N atom, N(21), from the Schiff base and a water molecule O(1). The equatorial atoms are planar within ±0.018(4) Å, with the Cu(3) atom being displaced by 0.059(4) Å towards the N(21) axial atom. The Cu–N distances involving Cu(2) vary from 1.973(8)–2.117(8) Å and those involving Cu(3) from 1.946(8)–2.037(7) Å in the equatorial plane. The Cu(3)–N(21) axial bond at 2.371(7) Å is significantly longer than the Cu–N equatorial bonds. The Cu(3)–O(H_2O) axial bond is much longer with a value of 2.591(7) Å. Similar values for Cu–O bonds in distorted octahedral complexes are quite common. The *trans* angles N(17)–Cu(2)–N(19), N(12)–Cu(3)–N(23), and N(22)–Cu(3)–N(24) have values of 175.2(4), 173.3(3), and 173.3(3)°, respectively, and are close to linear. The two Cu–N–C angles involving the bridging CN groups are significantly different, with a nearly linear coordination for Cu(3) [Cu(3)–N(12)–C(25) = 170.7(7)°] and a nonlinear coordination for Cu(2) [Cu(2)–N(15)–C(28) = 156.5(8)°].

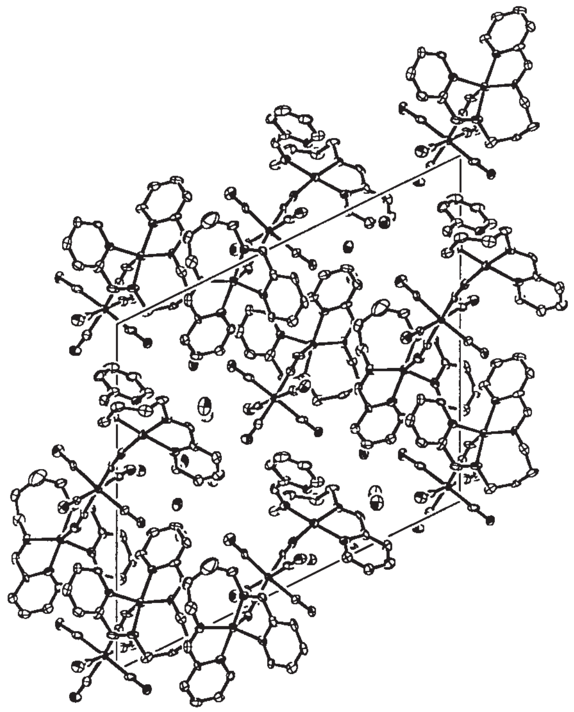

Fig. 3. Molecular packing diagram of complex **1** along *b*-axis.

The crystallographic packing diagram of the complex along the *b*-axis is shown in Fig. 3.

Magnetic Properties. The magnetic properties of the complex **1** in the form of χ_M and $\chi_M T$ vs T plots are shown in Fig. 4, treated as the magnetic susceptibility per three copper(II) ions. The magnetic data have been interpreted taking into consideration that in the crystal net there are two different molecules: one dinuclear Co(III)–Cu(II), thus following the Curie-law because Co(III) is diamagnetic (d^6, spin paired), and one Cu(II)–Co(III)–Cu(II) trinuclear species, with some possible small coupling. For this reason, the susceptibility values are given for three Cu(II) ions. χ_M values start from 0.00421 $cm^3\,mol^{-1}$ at 300 K to 0.54 $cm^3\,mol^{-1}$ at 2.02 K. The value of $\chi_M T$ at room temperature is 1.26 $cm^3\,mol^{-1}$ K. This value corresponds to three independent Cu^{II} ions without coupling ($g > 2.00$). The $\chi_M T$ value decreases monotonically to 2.02 K, attaining a value of 1.10 $cm^3\,mol^{-1}$ K. This global feature is characteristic of the presence of very weak antiferromagnetic interactions between the Cu^{II} ions. A very good fit can be obtained through a combination (1:1) of the Bleaney–Bowers expression for a copper(II) dimer,[5] plus a paramagnetic entity following the Curie law for a Cu(II) ion. The best fit parameters were: $J = -1.04$ cm^{-1}, $g = 2.12$, and $R = 3.0 \times 10^{-5}$ (R is the agreement factor

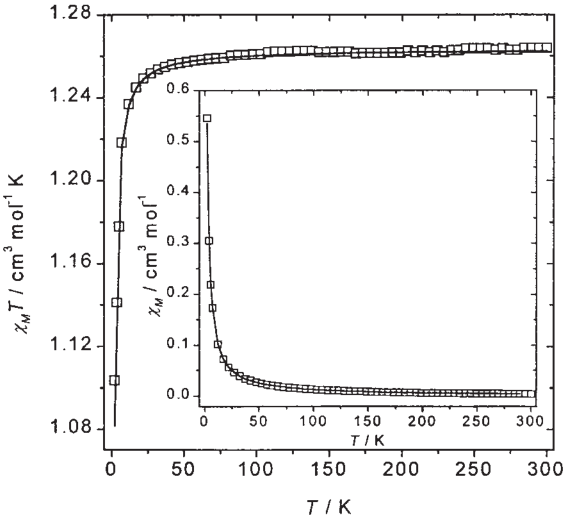

Fig. 4. Plot of temperature dependence of $\chi_M T$ and χ_M (inset) for complex **1**.

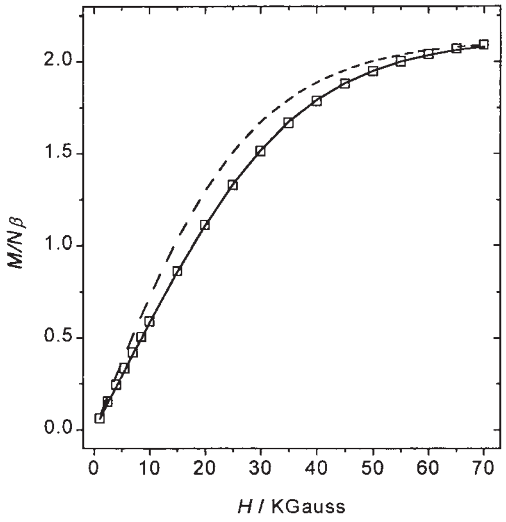

Fig. 5. The field dependence of the reduced magnetization at 2 K for complex **1**.

defined as $\chi_i[(\chi_M T)_{obs} - (\chi_M T)_{calc}]^2/\chi[(\chi_M T)_{obs}]^2)$. This J parameter is very weak, indicating almost no-coupling. To corroborate the order of magnitude of this small antiferromagnetic parameter, a magnetization measurement was carried out at very low temperature (2 K). The reduced magnetization ($M/N\beta$) curve for two Cu^{II} ions vs H (once having subtracted the reduced magnetization for one isolated Cu(II), according to the Brillouin formula) does not follow the Brillouin law (Fig. 5). At intermediate fields, the experimental points are below the theoretical curve, indicating weak antiferromagnetism. At 7 T, the $M/N\beta$ value tends to 2.0, which corresponds to two electrons (close to saturation). The experimental curve has been fit with full-diagonalization methods. A very good fit can be obtained with the following parameters: $J = -1.03$ cm^{-1}, $g = 2.12$, and $R = 7.6 \times 10^{-5}$ (R is the agreement factor defined as $\chi_i[(\chi_M T)_{obs} - (\chi_M T)_{calc}]^2/[(\chi_M T)_{obs}]^2)$. The two J values (from susceptibility and magnetization measurements) are almost identical: -1.04 and -1.03 cm^{-1} respectively. The g value is the same ($g = 2.12$).

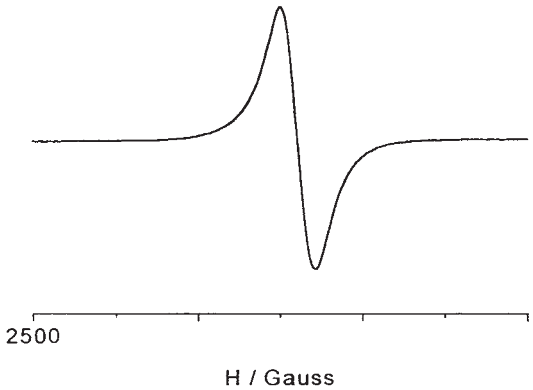

Fig. 6. ESR spectrum of complex **1** at 4 K.

The ESR spectrum has been measured at 4 K (Fig. 6). A broad band, without anisotropy, centered at $g = 2.12$ (in agreement with the susceptibility and magnetization data) was present. Only the intensity and broadness of this band vary with T. This pseudo-isotropic band may due to the presence in the crystal of two types of Cu^{II} ions (dinuclear and mononuclear). Thus, the observed spectrum is an average.

The small J value can be indicative either of intramolecular or intermolecular interactions. In fact, there are a lot of Cu^{II} polynuclear complexes bridged by diamagnetic polycyano metallates, like the present case. In most of these cases, the coupling is weak antiferromagnetic or nil.[52–57] In a few cases, weak ferromagnetic coupling has also been reported.[38,58]

In conclusion, the results indicate a very weak (almost negligible) intramolecular interaction between copper(II) ions through the diamagnetic $[Co(CN)_6]^{3-}$ bridge. Very weak intermolecular interactions, mainly due to hydrogen bonds, are also possible. However, owing to the small J value, this J' value is completely masked. In fact, the calculated parameter could be a mixture of small J (intramolecular) and J' (intermolecular) interactions.

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