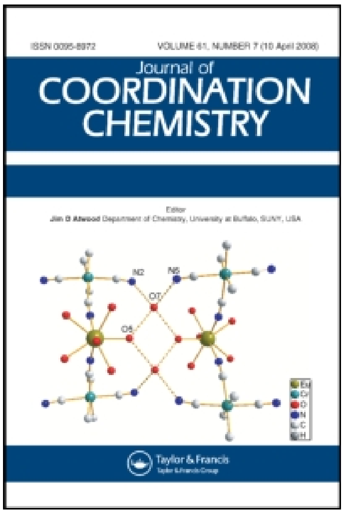

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Huey Lih Shyu[a]; Ho-Hsiang Wei[b]
[a] Chung-Tai Junior College, Taichung, Taiwan [b] Department of Chemistry, Tamkang University, Tamsui, Taiwan

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PREPARATION, CRYSTAL STRUCTURE AND MAGNETIC PROPERTIES OF CYANO-BRIDGED $[Cu(bpy)_2][Fe(CN)_5(NO)]3H_2O$ AND $[Cu(en)_2][Fe(CN)_5(NO)]$

HUEY LIH SHYU[a] and HO-HSIANG WEI[b,*]

[a] *Chung-Tai Junior College, Taichung, Taiwan;* [b] *Department of Chemistry, Tamkang University, Tamsui, Taiwan*

(Received 22 March 1998)

Two new double complexes $[Cu(bpy)_2][Fe(CN)_5(NO)]3H_2O$ (**1**) and $[Cu(en)_2][Fe(CN)_5(NO)]$ (**2**) have been prepared from the reaction of mixture of $Cu(ClO_4)_2 \cdot 6H_2O$ and $Na_2[Fe(CN)_5(NO)] \cdot 2H_2O$ in water with bipyridine (bpy) and ethylenediamine (en) in ethanol, respectively, and have been characterized by X-ray analysis, IR, EPR, Mössbauer spectroscopy and magnetic measurements. The structure of complex **1** consists of a cyano-bridged binuclear complex, in which the Cu(II) and Fe(II) centres are linked by a CN group. The structure of complex **2** consists of two moieties of cation $[Cu(en)_2]^{2+}$ and a cyano-bridged anion $[Fe(CN)_4(NO)(CN)\text{–}Cu(en)_2\text{–}(NC)Fe(CN)_4(NO)]^{2-}$. Cryomagnetic investigations (4–300 K) revealed an intermolecular ferromagnetic interaction with $J = 5.04\,cm^{-1}$ for **1** and a weak intermolecular antiferromagnetic interaction obeying the Curie–Weiss law with $J' = -1.96\,cm^{-1}$ for **2**.

Keywords: Cu(II); Fe(II); amines; X-ray structures; magnetic properties

INTRODUCTION

The chemistry of transition metal cyanide complexes containing a nitrosyl ligand has become of remarkable interest in recent years due to their unusual electronic structures[1–4] magnetic behaviour[5] and in the still unravelled role of NO in diverse physiological processes.[6] Tang and coworkers[5] reported an antiferromagnetic 2-D cyano-bridged polymeric $[Cu_2(oxpn)]\text{-}[Fe(CN)_5(NO)]_2$ complex, in which a nitrogen atom of a cyano group of $[Fe(CN)_5(NO)]^{2-}$ coordinated to one of the adjacent Cu(II)

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[*] Corresponding author.

ions of $Cu_2(oxpn)$[oxpn = *N*,*N*′-bis(3-aminopropyl)oxamide]. Very recently, Fujishima and co-workers[7] reported photo-induced magnetic spin coupling of nickel nitroprusside, $Ni[Fe(CN)_5(NO)] \cdot 5.3H_2O$. We have reported[8] two double complexes, $[Ni(bpy)_3][Fe(CN)_5(NO)] \cdot 3H_2O$ with paramagnetism and a weak antiferromagnetic one-dimensional chain $[Ni(en)_2][Fe(CN)_5(NO)] \cdot H_2O$. These studies revealed that the formation of discrete or cyano-bridged polymeric double complexes of $[M(L)_n]^{2+}$ with $[Fe(CN)_5(NO)]^{2-}$ is dependent on the nature of the ligand L of the cations.

As the intention of these studies was to clarify more fully the structural correlation with magnetic properties of double complexes with the $[Fe(CN)_5(NO)]^{2-}$ anion, we have prepared two new double complexes, cyano-bridged $[Cu(bpy)_2][Fe(CN)_5(NO)] \cdot 3H_2O$ (**1**) (bpy = 2,2′-bipyridine) and $[Cu(en)_2][Fe(CN)_5(NO)]$ (**2**) (en = ethylenediamine). Here the results of crystal structure analysis, IR, EPR, Mössbauer spectroscopy, and cryomagnetic properties of these species are described.

EXPERIMENTAL

Materials

$Na_2[Fe(CN)_5(NO)] \cdot 2H_2O$, bipyridine (bpy), ethylenediamine (en), and other materials of analytical grade (Aldrich Co.) were used as supplied.

Preparation of $[Cu(bpy)_2][Fe(CN)_5(NO)] \cdot 3H_2O$, (1) and $[Cu(en)_2][Fe(CN)_5(NO)]$, (2)

To a solution of $Cu(ClO_4)_2 6H_2O$ (1 mmol in 20 cm^3 of water) and 2,2′-bipyridine (2 mmol in 10 cm^3 of ethanol) or ethylenediamine (2 mmol in 10 cm^3 of ethanol) was slowly added a solution of $Na_2[Fe(CN)_5(NO)] \cdot 2H_2O$ (1 mmol) in 20 cm^3 of water. The solution turned blue for complex **1** and violet for complex **2**. After several days, the resulting blue crystals of complex **1** (85% yield) and violet crystals of complex **2** (80% yield) were filtered off, and air dried. The crystals were suitable for X-ray diffraction analysis. *Anal.* found: C, 46.38; H, 3.29; N, 21.23%. Calc. for $C_{25}H_{22}N_{10}O_4FeCu$ (**1**): C, 46.45; H, 3.41; N, 21.67%. Found: C, 27.11; H, 3.97, N, 34.79%. Calc. for $C_9H_{16}N_{10}OFeCu$ (**2**): C, 27.04; H, 4.01; N, 35.06%.

Physical Measurements

IR spectra were recorded on a Bio-Rad FTS 40FTIR spectrophotometer using KBr pellets in the 4000–400 cm^{-1} region. X-band EPR spectra at

300 K for the powdered complexes were recorded on a Bruker ECS-106 spectrometer. Mössbauer spectra at 298 K were recorded on a conventional Austin S-600 Mössbauer spectrometer. ^{57}Co(Rh) was used as the source and all isomer shifts are represented with respect to iron foil. Temperature dependence of the magnetic susceptibilities of the polycrystalline samples was measured between 4 and 300 K at field 1 T using a Quantum Design MPMS computer-controlled SQUID magnetometer. Corrections for the diamagnetism of complexes **1** and **2** were estimated from Pascal's constants.[9]

X-ray Crystal Structure Analysis

Crystallographic data for complexes **1** and **2** were collected on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromatized Mo K_α radiation at 25°C. The reflections were in the range $17.56 \leq 2\theta \leq 22.20°$ for complex **1** and $15.38 \leq 2\theta \leq 25.62°$ for complex **2**. Details of data collection, crystallographic data, and reduction are summarized in Table I. The structures were solved by the heavy-atom method and refined by full-matrix least-squares based on F. Reliability factors were defined as $R_f = \sum(|F_0| - |F_c|)/\sum|F_0|$ and the function minimized $R_w = [\sum w(|F_0| - |F_c|)^2/\sum|F_0|^2]^{1/2}$, where in the final least-squares calculation the weight scheme $1/\sigma(F_0)^2$ was used. The atoms except for hydrogen were refined with isotropic thermal parameters.

TABLE I Crystallographic data for $[Cu(bpy)_2][Fe(CN)_5(NO)]3H_2O$ (**1**) and $[Cu(en)_2][Fe(CN)_5(NO)]$ (**2**)

	1	**2**
Formula	$C_{25}H_{22}N_{10}O_4FeCu$	$C_9H_{16}N_{10}OFeCu$
M	645.90	399.68
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$	$P\bar{1}$
a (Å)	11.355(5)	7.161(3)
b (Å)	13.836(3)	8.883(4)
c (Å)	18.467(5)	13.403(4)
α (°)		88.54(3)
β (°)	93.45(3)	87.96(3)
γ (°)		75.83(3)
V(Å^3)	2896.1(16)	862.1(6)
Z	4	2
D_c(g cm^{-3})	1.481	1.607
F(000)	1319	407
μ(Mo K_α) (cm^{-1})	12.762	21.855
Crystal size (mm)	0.10 × 0.15 × 0.25	0.13 × 0.15 × 0.25
No. of data used	1568	2130
R_f	0.052	0.030
R_w	0.050	0.030

All refinement calculations were performed using the NRCVAX computer program.[10]

RESULTS AND DISCUSSION

IR Spectra

The most important aspects concerning the IR spectra of complexes **1** and **2** concern the vibrational stretching frequencies of NO and CN ligands. In general, IR absorption bands in the region 2200–1900 cm^{-1} are due to CN^{-} and NO^{+} vibrations.[11,12] Nitric oxide has an extra electron, occupying a π^* antibonding orbital, which is relatively easily lost. In the case of terminally bound NO, simple MO theory predicts that whilst M–NO^{+} will be linear, M–NO^{-} may be bent bond.[13–15] It is well-known that ν(NO) is sensitive to medium effects; thus, different alkaline and alkaline-earth hydrated salts of $[Fe(CN)_5(NO)]^{2-}$ show different values in the range 1965–1900 cm^{-1}.[1,16,17] Strong singlet peaks at 1936 for complex **1** and at 1938 cm^{-1} for complex **2** are assigned to NO stretching, thus implying that the Fe–N–O bonds are nearly linear.[12]

Structure of Complex 1

An ORTEP[18] drawing of complex **1** with the atom numbering scheme and unit cell packing are shown in Figures 1 and 2, respectively. Selected bond distances and angles are given in Table II.

As depicted in Figure 1, complex **1** consists of a cyano-bridged bimetallic complex. Cu(II) has a five a co-ordination sphere with distorted pryamidal

TABLE II Selected bond distances (Å) and angles (°) for complex 1

Fe–N(6)	1.626(9)	Fe–C(1)	1.936(10)
Fe–C(2)	1.928(12)	Fe–C(3)	1.948(12)
Fe–C(4)	1.948(11)	Fe–C(5)	1.941(13)
Cu–N(1)	1.989(8)	Cu–N(7)	1.979(9)
Cu–N(8)	2.119(9)	Cu–N(9)	2.076(9)
Cu–N(10)	1.978(9)		
Fe–N(6)–O(1)	176.9(9)	Fe–C(1)–N(1)	175.1(10)
Fe–C(2)–N(2)	177.1(11)	Fe–C(3)–N(3)	178.5(9)
Fe–C(4)–N(4)	176.8(12)	Fe–C(5)–N(5)	179.1(10)
Cu–N(1)–C(1)	163.7(9)	N(1)–Cu–N(7)	94.7(4)
N(1)–Cu–N(8)	114.3(4)	N(1)–Cu–N(9)	138.9(4)
N(1)–Cu–N(10)	93.4(3)	N(7)–Cu–N(10)	171.9(4)
N(7)–Cu–N(8)	80.4(4)	N(9)–Cu–N(10)	80.4(4)
N(8)–Cu–N(9)	106.8(3)	N(8)–Cu–N(10)	95.6(4)

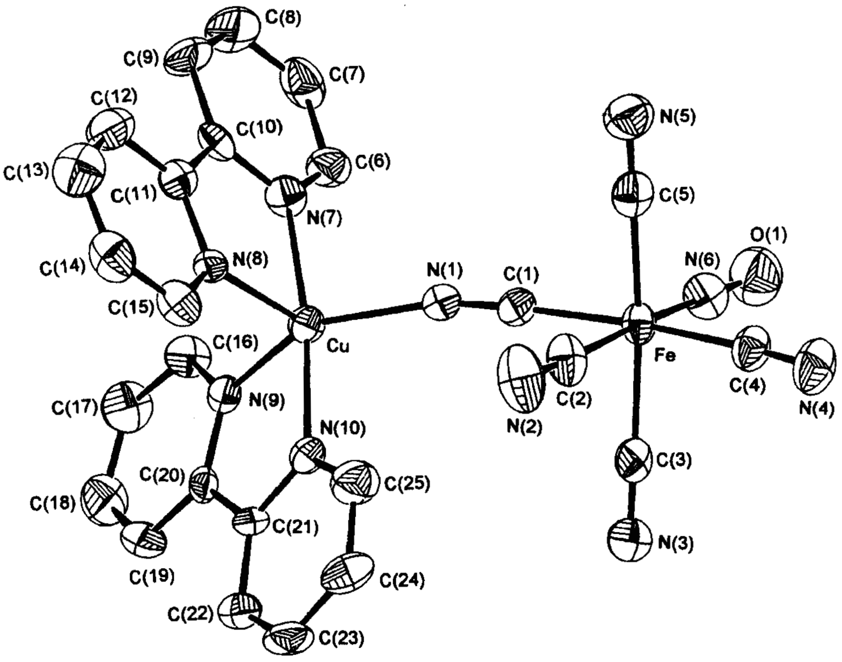

FIGURE 1 ORTEP stereoview of $[Cu(bpy)_2][Fe(CN)_5(NO)]3H_2O$ (**1**) (without H_2O; 30% probability thermal ellipsoids).

symmetry. The average Cu–N (bipy) bond length of 2.038 Å is slightly longer than Cu–N(1) (CN) of 1.989(8) Å. The mean Fe–C, Fe–N, C–N and N–O bond lengths in the $[Fe(CN)_5(NO)]^{2-}$ moiety are 1.940, 1.626(9), 1.137, and 1.131(13) Å, respectively. These values are in accordance with reported values for other nitroprusside metal salts.[1,3,8,19,20] The bond angle Fe–N–O (176.9(9)°) is nearly linear.

According to the unit-cell packing (Figure 2), one crystalling water molecule ($H_2O(4)$) locates at the centre of two $Cu(bpy)_2$ sites, which has short contact distances of O(4)···C(19) (3.40(3) Å) and Cu(II)···O(4) (4.795(22) Å); Cu(II)···Cu(II) is (6.898(3) Å). These contact distances may play an important role in magnetic exchange interactions between Cu(II) ions in complex **1**.

Structure of Complex 2

An ORTEP drawing of complex **2** with the atom numbering scheme is given in Figure 3. Relevant bond distances and angles are given in Table III. The

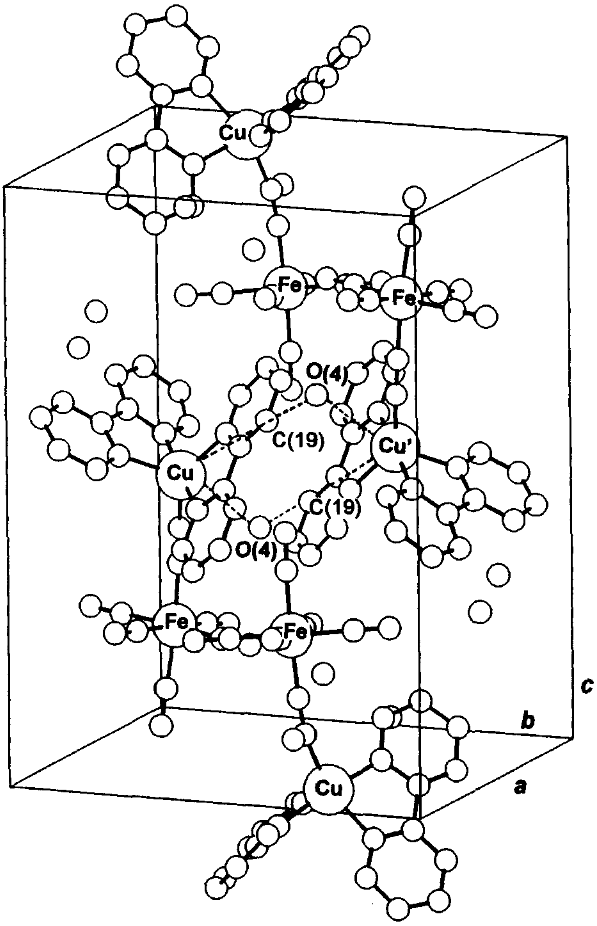

FIGURE 2 View of the packing of the molecules in complex **1**. Hydrogen atoms are omitted for clarity. Short contacts between the oxygen atoms, O(4), of crystalline H_2O and Cu(II) ions or C(19) atoms are drawn by dotted lines.

structure of complex **2** shows that asymmetric unit consists of one isolated $[Cu(en)_2]^{2+}$ cation and one $[Cu(en)_2][\{Fe(CN)_5(NO)\}_2]^{2-}$ anion. In the anion moiety, two cyano nitrogens (N(1)) from $Fe(CN)_5(NO)$ moieties in the *trans* mode are coordinated to the adjacent central Cu(1) ions to make a six-coordination sphere, CuN_6.

The average bond lengths Cu(1)–N (N(7) and N(8) of en), 2.017, is somewhat shorter than Cu(1)–N(1) (bridging CN), 2.491(3) Å. The bond angles N(1)–Cu(1)–N(1) (179.9) and Fe-C(1)–N(1) (178.8(3)°) are nearly linear, but the bond angle Cu(1)–N(1)–C(1) is 136.5(3)°. The mean bond lengths

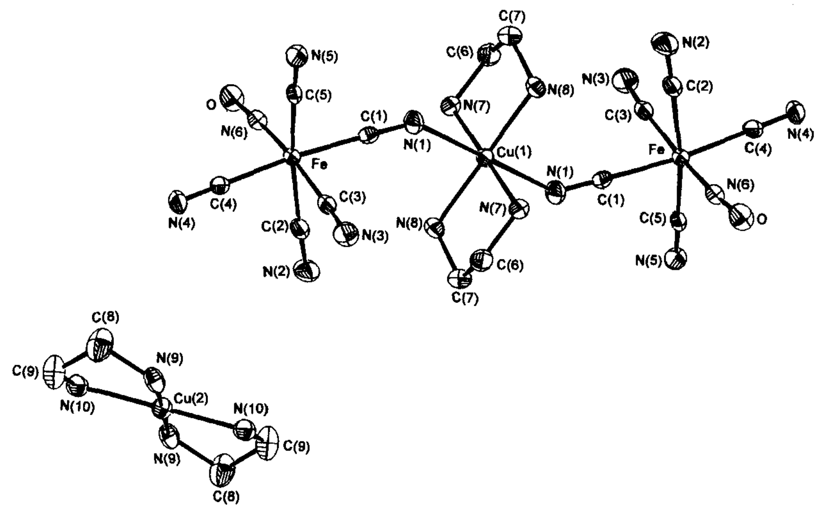

FIGURE 3 ORTEP stereoview of $[Cu(en)_2][Fe(CN)_5(NO)]$ (**2**) (30% probability thermal ellipsoids).

TABLE III Selected bond distances (Å) and (°) for complex **2**

Fe-N(6)	1.659(3)	Fe-C(1)	1.937(4)
Fe-C(2)	1.950(4)	Fe-C(3)	1.949(4)
Fe-C(4)	1.940(4)	Fe-C(5)	1.937(4)
Cu(1)-N(1)	2.491(3)	Cu(1)-N(7)	2.008(3)
Cu(1)-N(8)	2.026(3)	Cu(2)-N(9)	2.026(3)
Cu(2)-N(10)	1.999(3)	N(6)-O	1.129(4)
Fe-N(6)-O	176.5(3)	Fe-C(1)-N(1)	178.8(3)
Fe-C(2)-N(2)	176.7(4)	Fe-C(3)-N(3)	176.3(3)
Fe-C(4)-N(4)	179.7(3)	Fe-C(5)-N(5)	178.4(3)
Cu(1)-N(1)-C(1)	136.5(3)	N(1)-Cu(1)-N(1)	179.9
N(7)-Cu(2)-N(7)	180.0	N(8)-Cu(1)-N(8)	180.0
N(7)-Cu(1)-N(8)	95.43(13)	N(7)-Cu(1)-N(8)	84.57(13)
N(9)-Cu(2)-N(9)	180.0	N(10)-Cu(2)-N(10)	180.0
N(9)-Cu(2)-N(10)	84.61(14)		

Fe-C, Fe-N, C-N and N-O in the $[Fe(CN)_5(NO)]^{2-}$ moiety are in accordance with corresponding observed values in complex **1**. The bond angle Fe-N(6)-O (176.5(3)°) is nearly linear. The shortest contact distance between two Cu(II) ions in two adjacent $[Cu(2)(en)_2]^{2+}$ units is 7.161 Å.

EPR and Mössbauer Spectra

The X-band (9.8 GHz) EPR spectra of polycrystalline powders recorded at 300 K for complexes **1** and **2** show typical absorption for Cu(II) with a spin state of $S=\frac{1}{2}$, and with $g=2.12$ for complex **1** and 2.10 for complex **2**.

$[Fe(CN)_5(NO)]^{2-}$ is diamagnetic and thus no EPR signal can be observed for it.

Mössbauer spectra at 298 K for complexes **1** and **2** show a quadrupole doublet with parameters of isomer shift (IS), −0.28 for **1**, $-0.27\,\mathrm{mm\,s^{-1}}$ for **2** and quadrupole splitting (QS) of 1.58 for **1**, and of $1.88\,\mathrm{mm\,s^{-1}}$ for **2**. For comparison, the Mössbauer spectrum at 298 K for sodium nitroprusside was measured and has IS = −0.65 and $QS = 1.74\,\mathrm{mm\,s^{-1}}$. The negative IS values of **1** and **2** are somewhat lower than that of $-0.65\,\mathrm{mm\,s^{-1}}$ for sodium nitroprusside indicating that total s-electron density at the iron nucleus of $[Fe(CN)_5(NO)]^{2-}$ in complexes **1** and **2** is lower than that of sodium nitroprusside. This can be interpreted by the additional shielding effect of the 3d-electron at the iron atom by donating a 3d-electron from the copper(II) ion to the iron through the bridging CN ligand.[21]

Magnetic Susceptibility Studies

In the plots of χ(per Cu) and χT *versus* T shown in Figure 4 for the complex **1**, the χT value increases with decreasing temperature down to 10 K, indicating a ferromagnetic exchange interaction, but decreases below it. In the

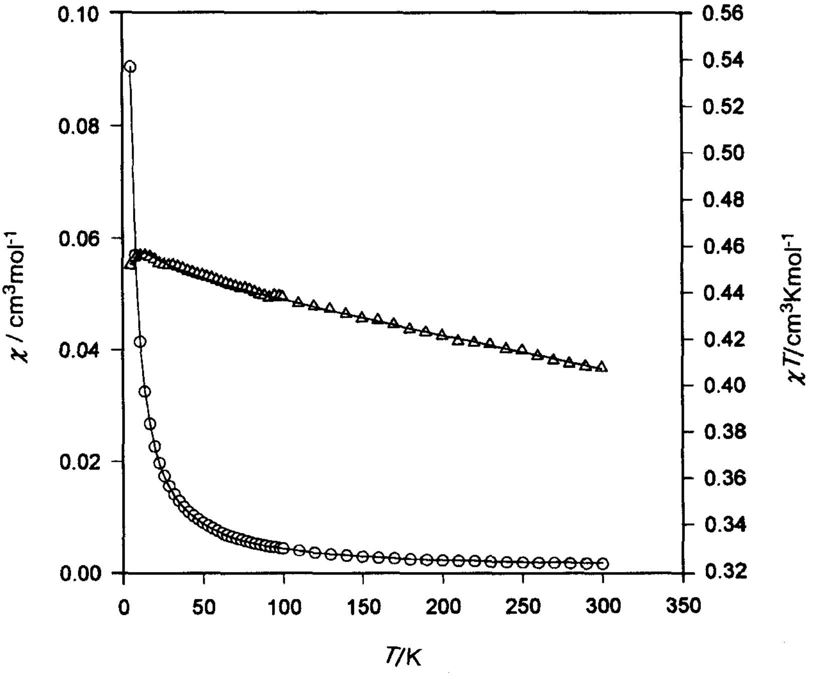

FIGURE 4 Plots of χ(○) and χT(△) versus T for complex **1**. The solid line curve was calculated from equation (*1*) with $g = 2.05$ and $J = 5.04\,\mathrm{cm^{-1}}$.

low-temperature region below 10 K, magnetic interaction occurs between two nearest neighbour paramagnetic Cu(II) ions. According to the structural results, the unit-cell packing of complex **1**, one crystalline H_2O molecule located at the centre of two $[Cu(bpy)_2]^{2+}$ sites, has short contact distances of O(4)···C(19) (3.40 Å), Cu···O(4) (4.79 Å), and Cu···Cu′ (6.99 Å). The short contact between O(4) and C(19) is a pathway for hydrogen bonding, O(4)···H–C(19). Therefore, weak magnetic interaction between Cu···Cu′ could be caused through the oxygen of H_2O molecules.

We have attempted to reproduce theoretically the experimental susceptibility of complex **1** by using the Bleaney–Bowers expression:[22]

$$\chi = [2Ng^2\mu_B^2/kT][1 + (1/3)\exp(-2J/kT)]^{-1} + N_\alpha \qquad (1)$$

where N_α is the temperature-independent paramagnetism. The best fits gave values of $g = 2.12$ (from EPR), $J = 5.04\,\mathrm{cm}^{-1}$ and $N\alpha = 60 \times 10^{-6}\,\mathrm{cm}^3\,\mathrm{mol}^{-1}$.

Figure 5 is the plot of χ (per Cu) and χT *versus* T in the range 4–300 K for complex **2**. The χT value slightly decreases from $0.43\,\mathrm{cm}^3\,\mathrm{K\,mol}^{-1}$ with decreasing temperature down to a value of $0.36\,\mathrm{cm}^3\,\mathrm{K\,mol}^{-1}$ at 4 K,

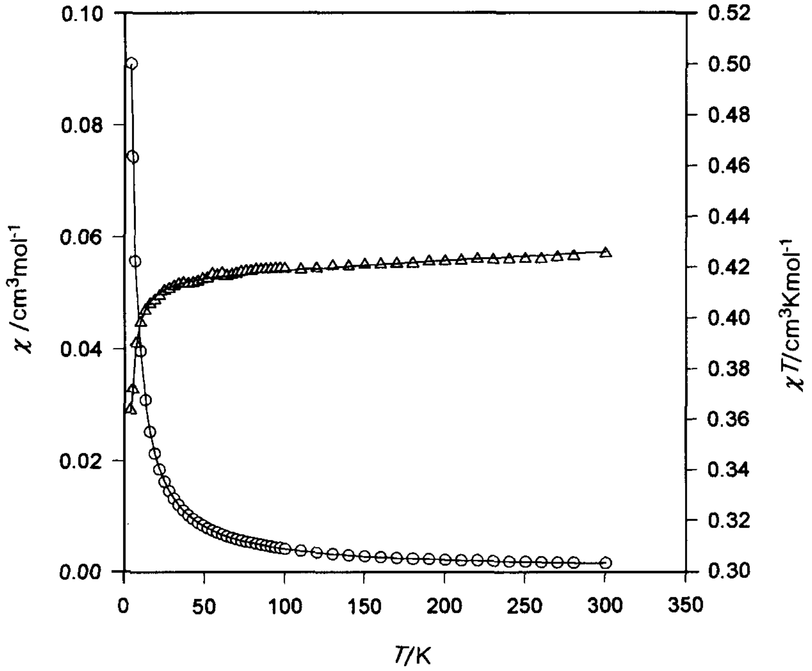

FIGURE 5 Plots of χ(○) and χT(△) versus T for complex **2**. The solid line curve was calculated from equation (2) with $g = 2.12$ and $J = -1.96\,\mathrm{cm}^{-1}$.

indicating a weak antiferromagnetic interaction. In **2** there is a large Cu···Cu′ (7.161 Å) separation. Although an unambiguous interpretation of the cryomagnetic data of complex **2** was not obtained, since the inverse susceptibility plot of complex **2** is linear as a function of temperature, under the approximation of the mean molecular field, the following Curie–Weiss equation[23] was used to fit the data:

$$\chi = Ng^2\mu_B^2S(S+1)/k(T-\theta) \qquad (2)$$

TABLE IV Atomic coordinates and equivalent isotropic thermal parameters for **1**

	x/*a*	*y*/*b*	*z*/*c*	*Beq* (Å^2)
Fe	0.45467 (16)	0.79566 (13)	0.20621 (8)	3.94 (9)
Cu	0.55003 (14)	0.74237 (11)	0.47085 (7)	3.95 (7)
N1	0.4802 (8)	0.7727 (7)	0.3721 (4)	4.3 (5)
N2	0.7179 (10)	0.8433 (9)	0.2258 (6)	8.0 (7)
N3	0.5370 (9)	0.5844 (7)	0.1948 (5)	5.0 (5)
N4	0.4871 (10)	0.8187 (8)	0.0427 (5)	6.8 (7)
N5	0.4144 (10)	1.0151 (8)	0.2215 (5)	6.7 (7)
N6	0.3153 (8)	0.7700 (7)	0.1925 (5)	5.1 (5)
N7	0.4380 (8)	0.8240 (7)	0.5216 (5)	4.2 (5)
N8	0.6681 (7)	0.8489 (6)	0.5146 (4)	3.4 (4)
N9	0.5479 (8)	0.6316 (7)	0.5466 (4)	3.8 (5)
N10	0.6734 (8)	0.6578 (7)	0.4339 (4)	4.0 (5)
C1	0.4655 (10)	0.7825 (8)	0.3108 (6)	4.1 (6)
C2	0.6209 (11)	0.8246 (9)	0.2168 (6)	5.2 (7)
C3	0.5074 (10)	0.6623 (9)	0.1981 (5)	4.4 (6)
C4	0.4725 (11)	0.8120 (9)	0.1027 (6)	4.7 (7)
C5	0.4300 (10)	0.9338 (9)	0.2154 (6)	4.8 (7)
C6	0.3244 (11)	0.8068 (9)	0.5203 (6)	5.2 (7)
C7	0.2490 (11)	0.8549 (11)	0.5658 (6)	6.4 (9)
C8	0.2960 (12)	0.9227 (11)	0.6102 (7)	7.1 (9)
C9	0.4161 (12)	0.9453 (10)	0.6109 (7)	6.5 (8)
C10	0.4849 (10)	0.8934 (8)	0.5657 (5)	4.0 (6)
C11	0.6126 (10)	0.9094 (8)	0.5590 (5)	3.9 (6)
C12	0.6730 (12)	0.9819 (10)	0.5971 (6)	5.9 (8)
C13	0.7919 (13)	0.9916 (10)	0.5867 (7)	6.9 (9)
C14	0.8452 (11)	0.9303 (10)	0.5429 (7)	5.8 (8)
C15	0.7825 (11)	0.8602 (9)	0.5061 (6)	5.1 (7)
C16	0.4768 (11)	0.6238 (9)	0.6013 (6)	4.8 (7)
C17	0.4908 (13)	0.5524 (10)	0.6524 (6)	6.4 (8)
C18	0.5798 (13)	0.4865 (10)	0.6461 (6)	6.7 (9)
C19	0.6538 (12)	0.4946 (9)	0.5884 (6)	5.9 (8)
C20	0.6344 (10)	0.5678 (8)	0.5396 (5)	3.3 (6)
C21	0.7055 (10)	0.5805 (8)	0.4754 (5)	3.5 (6)
C22	0.7940 (11)	0.5215 (9)	0.4590 (6)	4.5 (7)
C23	0.8534 (12)	0.5382 (10)	0.3974 (6)	5.7 (7)
C24	0.8199 (11)	0.6161 (10)	0.3538 (6)	5.7 (7)
C25	0.7304 (13)	0.6740 (10)	0.3734 (6)	6.4 (8)
O1	0.2186 (8)	0.7540 (8)	0.1799 (5)	8.4 (6)
O2	0.5933 (9)	0.3865 (8)	0.1655 (5)	9.1 (6)
O3	0.4306 (14)	0.2817 (16)	0.0777 (8)	22.4 (16)
O4	0.1810 (18)	0.6893 (15)	0.3367 (16)	32.4 (25)

where $\theta = zJ'S(S+1)/3k$, and zJ' is the intermolecular magnetic interaction parameter. The values obtained for g and J' in this manner are 2.12 and $-1.96\,\text{cm}^{-1}$, respectively.

Magnetic susceptibility data for **1** and **2** show ambiguously spin–spin interaction occuring *via* a superexchange pathway or long-range magnetic ordering for rather than a direct metal–metal or short-range interaction. This long-range magnetic ordering of copper complexes also has been demonstrated in previous reports[24,25] which revealed that despite structural data showing a large separation in the region of 7–10 Å between two paramagnetic metal ions, a weak magnetic exchange interaction exists.

As a final comment, we emphasize that this study gives new evidence for the fact that the formation of cyano-bridged double complex of $[CuL_2]^{2+}$ with $[Fe(CN)_5(NO)]^{2-}$ and their crystal structure and magnetic properties are dependent on the nature of the ligands L of the action.

Supplementary Material

Tables containing atom positions, anisotropic thermal parameters, hydrogen atom locations, bond lengths and angles are available from the authors on request. List of atomic positions for the complexes are given in Tables IV and V.

TABLE V Atomic coordinates and equivalent isotropic thermal parameters for **2**

	x/a	*y/b*	*z/c*	*Beq* (Å²)
Cu1	0	0	0	2.56 (3)
Cu2	1	1/2	1/2	3.13 (3)
Fe	0.40021 (7)	− 0.47497 (6)	0.19179 (4)	2.256 (24)
C1	0.2381 (5)	− 0.3542 (4)	0.0910 (3)	2.58 (16)
C2	0.3522 (6)	− 0.2894 (5)	0.2728 (3)	3.24 (19)
C3	0.1638 (6)	− 0.5028 (5)	0.2579 (3)	2.98 (19)
C4	0.5241 (5)	− 6.032 (4)	0.3016 (3)	2.66 (17)
C5	0.3970 (5)	− 0.6595 (4)	0.1185 (3)	2.46 (16)
C6	− 0.2029 (6)	− 0.0346 (5)	0.1816 (3)	4.17 (21)
C7	− 0.0891 (7)	0.0803 (5)	0.2031 (3)	4.22 (22)
C8	0.8655 (8)	0.8267 (6)	0.5114 (4)	6.1 (3)
C9	0.7261 (7)	0.7800 (6)	0.4513 (4)	5.6 (3)
N1	0.1446 (5)	− 0.2812 (4)	0.0318 (3)	3.60 (16)
N2	0.3148 (6)	− 0.1802 (4)	0.3197 (3)	4.91 (20)
N3	0.0306 (5)	− 0.5175 (5)	0.3010 (3)	4.68 (20)
N4	0.5966 (5)	− 0.6778 (4)	0.36628 (24)	3.72 (17)
N5	0.3930 (5)	− 0.7659 (4)	0.0736 (3)	3.53 (16)
N6	0.6077 (5)	− 0.4509 (3)	0.14348 (22)	2.69 (14)
N7	− 0.2381 (4)	− 0.0280 (3)	0.07414 (23)	2.99 (14)
N8	0.0808 (5)	0.0523 (3)	0.13565 (22)	2.97 (15)
N9	1.0528 (5)	0.7126 (4)	0.50270 (24)	3.59 (16)
N10	0.7305 (5)	0.6160 (4)	0.47108 (24)	3.50 (16)
O	0.7517 (4)	− 0.4341 (4)	0.11537 (22)	4.52 (17)

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References

[1] M.M. Vergara, E.L. Varetti, G. Rigotti and A. Navaza, *J. Phys. Chem. Solids* **50**, 951 (1989); *ibid.* **51**, 381 (1990).

[2] H. Zöllner, W. Krasser and T. Woike, *Chem. Phys. Lett.* **161**, 497 (1989).

[3] M.R. Pressprich, M.A. White, Y. Velhter and P. Coppens, *J. Am. Chem. Soc.* **116**, 5233 (1994).

[4] D.A. Estrin, L.M. Baraldo, L.D. Slep, B.C. Barja, J.A. Olabe, L. Paglieri and G. Gorongiu, *Inorg. Chem.* **35**, 3897 (1996).

[5] Z.N. Chen, J.L. Wang, J. Qiu, F.M. Miao and W.X. Tang, *Inorg. Chem.* **34**, 2255 (1995).

[6] J.S. Stamler, D.J. Singel and J. Loscalzo, *Science* **258**, 1898 (1992).

[7] Z.Z. Gu, O. Sato, T. Iyoda, K. Hashimoto and A. Fujishima, *J. Phys. Chem.* **100**, 18289 (1996).

[8] H.L. Shyu, H.H. Wei and Yu Wang, *Inorg. Chim. Acta* **258** 81 (1997).

[9] O. Kahn, *Molecular Magnetism.*, (VCH: New York, 1993), p. 3.

[10] E.J. Gabe, Y. Le Page, J.P. Cherland, F.L. Lee and P.S. White, *J. Appl. Crystallogr.* **22**, 384 (1989).

[11] R.F. Fenske and R.L. DeKock, *Inorg. Chem.* **11**, 437 (1972).

[12] F. Bottomley and F. Grein, *J. Chem. Soc., Dalton Trans.* 1359 (1980).

[13] M. Braga, A.C. Pavao and J.R. Leite, *Phys. Rev. B* **23**, 4328 (1981).

[14] M.M. Vergara and E.L. Varetti, *Spectrochim. Acta* **49A**, 527 (1993).

[15] C.O. Della Vedova, J.H. Lesk, E.L. Varetti, P.J. Aymonino, O.E. Piro, B.E. Rivero, E.F. Aymonino, O.E. Piro, B.E. Rivevo and E.F. Castellano, *J. Mol. Struct.* **170**, 241 (1981).

[16] N.W. Alcok, A. Samotus and J. Szklarzewicz, *J. Chem. Soc., Dalton Trans.* 885 (1993).

[17] P.N. Hawker and M.V. Twigg, in S.G. Wilkinson, R. Gillard and J.A. McCleverty. (eds.), *Comprehensive Coordination Chemistry*, Vol. 4 (Pergamon, Oxford, 1989), p. 1187.

[18] C.K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN (1976).

[19] A.G. Sharpe, *The Chemistry of Cyano Complexes of the Transition Metals* (Academic Press, New York, 1976).

[20] A. Navaza, G. Chevrier, P.M. Alzari and P.J. Aymonino, *Acta Crystallogr.* **C45**, 839 (1989).

[21] N.N. Greenwood and T.C. Gibb, *Mössbauer Spectroscopy*, Chapman and Hall, London, 1971, p. 183.

[22] B. Bleaney and K.D. Bowers, *Proc. R. Soc. London, Ser. A* **214**, 451 (1952).

[23] C.J. O'Connor, *Prog. Inorg. Chem.* **29**, 203 (1982).

[24] F. Tinti, M. Verdaguer, O. Kahn and J.M. Savariault, *Inorg. Chem.* **26**, 2380 (1987).

[25] P. Chaudhuri and K. Oder, *J. Chem. Soc., Dalton Trans.* 1597 (1990).