Crystal Structure and Magnetic Properties of a 2D Sheetlike μ-Cyanido- and μ-Oxamidato-Bridged Fe(III)−Cu(II) Bimetallic Complex

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Introduction

Coordination metal complexes with one-dimensional polymeric structures have been actively investigated because of their unusual properties.[1] One of the ways to illustrate bulk magnetic properties consists of increasing the dimensionality of the complexes by appropriately choosing the constituent molecules.[2,3] Although some 2D or 3D transition metal-containing compounds have been synthesized to date, most of them are homometallic.[4−8] Furthermore, although a few 2D or 3D heteronuclear complexes have been obtained,[2,3] to our knowledge, very few of them have been characterized by single-crystal X-ray diffraction.[9−11]

Recently, N,N′-disubstituted oxamides stimulated a considerable number of theoretical and experimental studies in the design of polymetallic species exhibiting potentially unusual magnetic properties[12] because of their easy *cis*−*trans* conformational change. The bis-terdentate character of these ligands in the *trans*-conformation allows the formation of *trans*-oxamidato-bridged copper(II) dimers which can be linked by bridging ligands such as azide,[13a] cyanate,[13b] and acetate[14] to form 1D homometallic alternating chains. In order to extend this study, our work is devoted to obtaining the bimetallic polymeric compounds in dimensionality larger than 1. With this purpose in mind, cyanide was chosen as the second bridging ligand to link *trans*-oxamidato-bridged dimers to synthesize 2D or 3D heterometallic compounds. We report here the X-ray crystal structure of $[Cu_2(oxpn)Fe(CN)_5(NO)]_n$ (where oxpn is the dianion of *N,N′*-bis(3-aminopropyl)oxamide) together with a description of its magnetic properties.

Table 1. Crystal Data for $[Cu_2(oxpn)Fe(CN)_5(NO)]_n$

formula	$C_{13}H_{16}N_{10}O_3Cu_2Fe$	V/Å^3	1963.8(3)
fw	543.2	Z	4
color	dark green	D_c/g cm^{-3}	1.837
cryst syst	orthorhombic	T/°C	22
space group	*Pnma*	μ(Mo Kα)/cm^{-1}	29.201
a/Å	11.413(4)	R^a	0.047
b/Å	22.242(5)	$R_w{}^b$	0.054
c/Å	7.736(2)		

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum(|F_o| - |F_c|)^2/\sum|F_o|^2]^{1/2}$.

Experimental Section

The ligand H_2oxpn and its mononuclear compound Cu(oxpn) were prepared according to the literature.[15]

Synthesis of $[Cu_2(oxpn)Fe(CN)_5(NO)]_n$. To an aqueous solution of Cu(oxpn) (1 mmol, 30 mL) was added an aqueous solution of copper perchlorate (1 mmol, 10 mL) with stirring. Then an aqueous solution of sodium nitroferricyanide dihydrate ($Na_2Fe(CN)_5(NO)\cdot 2H_2O$) (1 mmol, 10 mL) was added dropwise to the solution obtained above, affording a green precipitate, which was filtered off, washed with water, and dried in a desiccator containing silica gel, yield 92%. Anal. Calcd for $C_{13}H_{16}N_{10}O_3Cu_2Fe$: C, 28.72; H, 2.97; N, 25.77; Cu, 23.39; Fe, 10.28. Found: C, 28.54; H, 3.02; N, 25.48; Cu, 23.48; Fe, 10.41. Well-shaped single crystals of this complex were obtained by the slow-diffusion method using an H-tube in the dark. The starting materials were aqueous solutions of sodium nitroferricyanide dihydrate in one arm and Cu(oxpn) and copper perchlorate in 1:1 molar ratio in the other arm of the H-shaped tube.

Magnetic Susceptibility Measurements. Magnetic measurements on powder samples were carried out with a CF-1 type extracting sample magnetometer in the temperature range 1.5−300 K. Correction for the diamagnetism of the complex was estimated from Pascal's constants to be -230×10^{-6} cm^3 mol^{-1}. Effective magnetic moments were calculated from the equation $\mu_{eff} = 2.828(\chi_M T)^{1/2}$, where χ_M is the molar magnetic susceptibility corrected for the diamagnetism of the constituent atoms. The powder EPR spectra were recorded on a Bruker 2000-SRC spectrometer.

Crystallographic Data Collection and Structure Determination. A dark green block-shaped crystal with dimensions $0.15 \times 0.1 \times 0.1$ mm was mounted on an Enraf-Nonius CAD-4 diffractometer equipped with a graphite-monochromated Mo Kα radiation by using the $\omega-2\theta$ scan technique. Cell parameters were determined by a least-squares fit of 25 reflections with θ angles ranging between 5.8 and 14.4°. Cell dimensions and structure refinement data are listed in Table 1. Intensity data were collected in the 2θ range 4−48°. The intensity was corrected for Lorentz−polarization and empirical absorption effects. Due to the rather small volume of our crystals, of the 1583 measured independent reflections, only 682 were observed with $I > 3\sigma(I)$ and used for the structure refinement.

The structure was solved by direct methods with the MULTAN package[16] of programs and refined by full-matrix least-squares methods. The final R and R_w values were 0.047 and 0.054, respectively. Final coordinates for non-hydrogen atoms are listed in Table 2, and selected bond distances and angles are gathered in Table 3. Full crystallographic data, anisotropic thermal parameters, and hydrogen coordinates are presented as supplementary material.

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Table 2. Positional and Isotropic Thermal Parameters for the Non-Hydrogen Atoms of $[Cu_2(oxpn)Fe(CN)_5(NO)]_n$

atom	x	y	z	$B_{eq}{}^{a}$/Å^2
Cu	0.3770(2)	0.0968(1)	0.4228(2)	2.45(3)
Fe	0.3805(3)	0.250	−0.0576(3)	2.15(5)
N(1)	0.396(1)	0.1549(4)	0.229(1)	2.3(2)
N(2)	0.412(1)	0.1556(5)	0.654(1)	3.0(3)
N(3)	0.232(2)	0.250	−0.060(2)	3.2(4)
N(4)	0.650(2)	0.250	−0.032(2)	4.2(5)
O(3)	0.134(1)	0.250	−0.045(3)	7.9(6)
O(10)	0.5406(9)	0.0655(4)	0.390(1)	3.0(2)
N(11)	0.207(1)	0.1197(5)	0.429(2)	3.4(3)
N(12)	0.3548(9)	0.0190(5)	0.533(1)	2.6(2)
C(10)	0.522(1)	0.0139(6)	0.460(1)	1.7(3)
C(11)	0.137(1)	0.0902(7)	0.570(2)	4.9(3)
C(12)	0.137(2)	0.0239(8)	0.559(2)	6.8(4)
C(13)	0.245(2)	−0.0059(9)	0.609(2)	6.0(5)
C(1)	0.390(1)	0.1901(5)	0.120(2)	2.4(3)
C(2)	0.394(1)	0.1894(6)	0.761(2)	2.7(3)
C(4)	0.549(2)	0.250	−0.050(3)	3.7(5)

[a] $B_{eq} = (4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Table 3. Selected Bond Distances (Å) and Angles (deg) for $[Cu_2(oxpn)Fe(CN)_5(NO)]_n$

	Bond Distances (Å)		
Cu−N(1)	1.99(1)	Cu−N(2)	2.25(1)
Cu−O(10)	2.01(1)	Cu−N(11)	2.01(2)
Cu−N(12)	1.95(1)	Fe−N(3)	1.69(2)
Fe−C(1)	1.91(2)	Fe−C(2)	1.95(2)
Fe−C(4)	1.93(3)		
	Bond Angles (deg)		
N(1)−Cu−N(2)	101.7(5)	N(1)−Cu−O(10)	91.8(5)
N(1)−Cu−N(11)	87.5(7)	N(1)−Cu−N(12)	157.1(5)
N(2)−Cu−O(10)	97.9(5)	N(2)−Cu−N(11)	90.2(6)
N(2)−Cu−N(12)	101.0(5)	O(10)−Cu−N(11)	171.8(6)
O(10)−Cu−N(12)	82.4(5)	N(11)−Cu−N(12)	95.1(6)
N(3)−Fe−C(1)	93.6(8)	N(3)−Fe−C(2)*	94.1(8)
N(3)−Fe−C(4)	179.(1)	C(1)−Fe−C(1)*	88.2(8)
C(1)−Fe−C(2)*	172.3(8)	C(1)−Fe−C(4)	85.5(9)
C(2)−Fe−C(2)*	87.4(9)	C(2)*−Fe−C(4)	86.8(9)

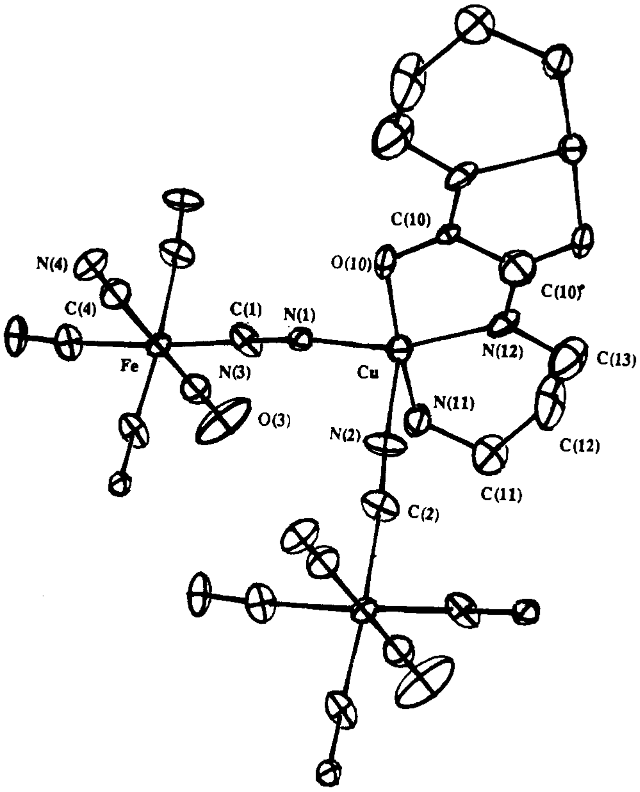

Figure 1. Perspective view of $[Cu_2(oxpn)Fe(CN)_5(NO)]_n$ with the atom-labeling scheme.

Results and Discussion

Description of the Crystal Structure. The structure is made up of parallel sheets, each consisting of a 2D array of Cu(II) and Fe(III) centers bridged by both oxpn and cyanide; the former behaves as a bis-terdentate ligand in a *trans*-conformation to form Cu(II) dimers, while the latter bridges Cu(II) and Fe(III) ions in bis-monodentate end-to-end fashion, spreading out along the *bc* plane to form an infinite network. A perspective view of the asymmetric unit along with the atom-labeling scheme and of one symmetry-related unit is depicted in Figure 1. A crystallographic inversion center is located at the middle of a C−C bond of an amide.

The asymmetric unit is a Cu(II)−Fe(III) dinuclear fragment in which the copper atom has a CuN_4O chromophore and adopts a (4+1) square pyramidal surrounding, whereas the iron atom is in a (4+2) distorted octahedral environment. The basal plane around the copper(II) ion is formed by the N(11), N(12), and O(10) atoms of the *trans*-oxamidate ligand, by a nitrogen atom, N(1), of the cyanide group, and by a nitrogen atom, N(2), of another cyanide group occupying in the apical position. The average deviation of N(1), N(11), N(12), and O(10) from the mean basal plane is 0.16 Å. The copper(II) ion is displaced toward the apical site by 0.26 Å. The Cu−N(2) apical bond length is 2.25(1) Å. A trigonal bipyramidal description would place N(1), N(2), and N(12) in the equatorial plane and N(11) and O(10) in the axial positions. The copper(II) ion deviates only by 0.042 Å from this trigonal plane, and the trigonal axis does not show too much distortion from linearity, N(11)−Cu−O(10) being 171.8(6)°. However, the angles in the trigonal plane depart significantly from the theoretical 120° value, with values of 157.1(5), 101.7(5), and 101.0(5)°. As for the Fe(III) ion, the coordination geometry is that of a tetragonally compressed octahedron. The equatorial plane is defined by four cyanide carbon atoms, and the two axial sites are occupied by a cyanide carbon atom and a nitrosyl nitrogen atom, respectively.

The cyanide groups, which act as bis-monodentate ligands to bridge Cu(II)−Fe(III) heterometallic centers in two different ways forming linear and nonlinear Fe—C≡N—Cu sequences, connect the *trans*-oxamidato-bridged dimers to extend an infinite 2D network along *bc* plane as shown in Figure 2. The bridging pathway Cu−N(1)≡C(1)—Fe is linear with the Cu−N(1)−C(1) angles being 170(2)° and the bond Cu−N(1) (1.99(1) Å) in the equatorial plane. In contrast, the bridging unit Cu−N(2)≡C(2)—Fe is nonlinear with Cu−N(2)−C(2) angles 159(1)° and the longer Cu−N(2) (2.25(1) Å) bond in the axial position (see Figure 1). The bond lengths of Fe—C, Fe—N, C≡N, and N≡O are in accordance with the reported values for other nitroprusside metal salts.[17−19] All of Fe—C≡N, Fe—N≡O, and Cu—N≡C angles are quasi-linear, in the range 159−179°.

The deprotonated oxpn ligand adopts the *trans*-conformation with the bis-tridentate character to form one five- and one six-membered chelate ring at each copper center. The bond length for Cu−N(12) (1.95(1) Å), shorter than those for Cu−N(11) (2.01(2) Å) and Cu−O(10) (2.01(1) Å), agrees with those found in other oxamidato-bridged copper(II) complexes.[12−14,20] The

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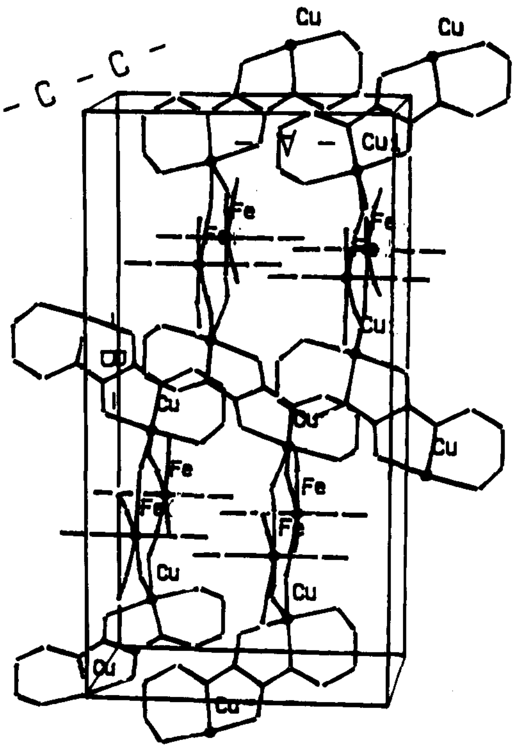

Figure 2. Schematic stereoview of the unit-cell contents for $[Cu_2(oxpn)Fe(CN)_5(NO)]_n$ emphasizing the connections among metal centers.

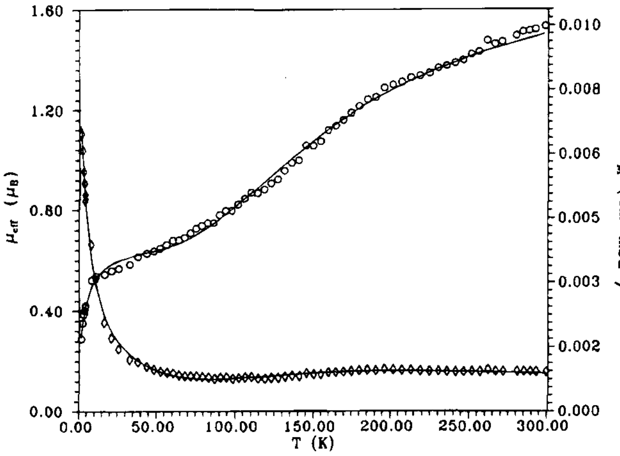

Figure 3. Plot of temperature dependence of the molar susceptibility χ_M (◇) and the effective magnetic moment μ_{eff} (○) for $[Cu_2(oxpn)Fe(CN)_5(NO)]_n$. The solid line represents the best calculated values.

Cu••Cu(a) and Cu••Fe separations through oxpn and cyanide bridges are 5.28 and 5.04 Å, respectively.

EPR and Magnetic Data. The EPR spectra recorded at room temperature only show a symmetric feature at $g = 2.10$ and no signal at half-field. The spectra do not change on lowering the temperature; they simply decrease in intensity and show no hyperfine splitting.

The temperature dependence of the molar susceptibility (χ_M) and the magnetic moment (μ_{eff}) per copper(II) atom of the title compound is shown in Figure 3. The μ_{eff} for each copper atom is 1.53 μ_B at 300 K, which is lower than expected for a noncoupled paramagnetic system with $s = {}^1/_2$. This fact, together with the smooth decrease of μ_{eff} with T, shows that antiferromagnetic exchange is operative. It is known that $[Fe(CN)_5(NO)]^{2-}$ is diamagnetic[17,21] because the unpaired electron of the low-spin Fe(III) ion and one electron of the nitronyl free radical form an electron pair. Therefore, although $[Cu_2(oxpn)Fe(CN)_5(NO)]_n$ is a Cu(II)–Fe(III) bimetallic compound, the exchange interaction between Cu(II) and Fe(III) ions through the cyanide bridging ligand is negligible. As for the coupling between Cu(II) ions, two exchange pathways are possible: one through the deprotonated oxpn ligand and the other through the $[Fe(CN)_5(NO)]^{2-}$ group. On one hand, oxamidato ligands are known to be effective in transmitting the antiferromagnetic exchange interaction between two copper(II) ions when the magnetic orbitals are in the plane of the oxamidato ligands.[22] On the other hand, the copper••copper separation through the $[Fe(CN)_5(NO)]^{2-}$ group is so large (9.55 Å) that the magnetic orbitals between the two copper(II) ions can not overlap efficiently, and the magnetic exchange transmitted by this pathway is expected to be small.[23,24]

Since the magnetic system of this 2D sheetlike compound is too complicated to develop a suitable model, we attempted to simplify it to be 2D sheets of interacting dimers, Cu(oxpn)Cu, on the assumption that the exchange interaction between Cu(II) ions through the $[Fe(CN)_5(NO)]^{2-}$ group is an interdimer effect in a molecular field approach. So, it should be possible to interpret the data with a modified Bleaney–Bowers equation,[5,25,26] taking into account the intermolecular interactions. Least-squares fitting of the experimental data with eq 1 leads

$$\chi_M = \frac{N\beta^2 g^2}{K(T-\Theta)}\left[3 + \exp\left(-\frac{J}{KT}\right)\right]^{-1}(1-\varrho) + \frac{N\beta^2 g^2}{4K(T-\Theta)}\varrho + N_\alpha \quad (1)$$

to $J = -268.8$ cm^{-1}, $\varrho = 0.013$, and $\Theta = -6$ K by setting $g = 2.10$, which is the average g factor from EPR spectra, with $R = 3 \times 10^{-4}$ where R is defined as $R = \sum(\mu_{obsd} - \mu_{calcd})^2/\sum(\mu_{obsd})^2$.

The antiferromagnetic exchange interaction transmitted by the *trans*-oxamidate group in this compound ($J = -268.8$ cm^{-1}) is very weak compared with that in other *trans*-oxamidato-bridged compounds ($J = 500-600$ cm^{-1}).[27,28] This may be due to the environment of the copper(II) ion in $[Cu_2(oxpn)Fe(CN)_5(NO)]_n$ acquiring some trigonal bipyramidal character, which leads to the two magnetic orbitals in a copper(II) dinuclear unit being unfavorably oriented to overlap from each side of the oxamidate bridge as shown in other oxamidato-bridged copper(II) binuclear compounds.[29]

Supplementary Material Available: Complete tables of crystallographic data and data collection paramerters, bond distances and angles, and general displacement parameters (B's) (5 pages). Ordering information is given on any current masthead page.

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