Assembly of an interpenetrating three-dimensional mixed-valence Cu^{II}/Cu^{I} coordination polymer ☆

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Abstract

A novel cyano-bridged three-dimensional mixed-valence Cu(II)/Cu(I) compound [Cu$_2$(oxpn)][Cu(CN)$_2$]$_2$ (oxpn^{2-} = dianion of N,N'-bis(3-aminopropyl)oxamide) has been synthesized and structurally characterized. Single crystals of **1** formed by diffusion of Cu$_2$(oxpn)Cl$_2$ and K$_3$[Cr(CN)$_5$(NO)] in H$_2$O for two months. The structure of the title compound consists of threefold interpenetrating 3D frameworks. In each 3D network, oxamidato-bridged dimeric [Cu$_2$(oxpn)]$^{2+}$ units connect 1D polymeric [Cu(CN)$_2$]$^{-}$ anions giving rise to a 3D structure. Room temperature magnetic measurement shows the presence of strong magnetic coupling between the Cu(II) ions. Electronic paramagnetic resonance spectrum measurements show the transitions due to the excited triplet state.
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1. Introduction

Coordination polymers formed with metal cyanides have received extensive attention because of their potential as porous materials for use in molecule separations and catalysis and as molecule-based magnetic materials [1,2]. Hexacyanometallate anions [M(CN)$_6$]$^{4-/3-}$ (M = Fe, Co, Ru and Os), octacyanometallate precursors [M(CN)$_8$]$^{4-}$ (M = Mo and W), [M(CN)$_4$]$^{2-}$ (M = Ni, Pt, Pd) and [M(CN)$_2$]$^{-}$ (M = Cu, Ag, Au) have been structurally investigated [1]. Various-dimensional polymers have been reported, some of which consist of intriguing framework topologies and guest molecules in the network. In our attempt to prepare a cyano- and oxamidato-bridged complex using [Cu$_2$(oxpn)]$^{2+}$ and [Cr(CN)$_5$(NO)]$^{3-}$, we isolated a new three-dimensional coordination polymer {[Cu$_2$(oxpn)][Cu(CN)$_2$]$_2$}$_\infty$ (**1**). Polymeric [Cu(CN)$_2$]$_n^{n-}$ was formed from the reduction of Cu^{2+} with CN^{-}. It is worth noting that stable cyano-bridged mixed-valence Cu(II)/Cu(I) complexes are rare [3–5]. Especially, the synthesis of mixed-valence Cu^{II}/Cu^{I} complexes is significant since they are of great biological importance and electronic properties [6].

2. Experimental

2.1. Materials and physical measurements

KCN and CuCl$_2$·4H$_2$O were purchased from commercial sources and used as received. Cu(oxpn) and K$_3$[Cr(CN)$_5$(NO)]·H$_2$O were prepared according to the literature method [7,8]. **Caution!** KCN is extremely toxic. Only a small amount of material should be used, and it should be handled with care.

Elemental analyses of carbon, hydrogen, and nitrogen were carried out with an Elementar Vario EL. The infrared spectroscopy was performed on a Magna-IR 750 spectrophotometer in the 4000–650 cm^{-1} region. The electron paramagnetic resonance (EPR) powder spectra were recorded at X-band with a Bruker ER 200B spectrometer. Room-temperature magnetic susceptibility measurement was performed on a Faraday magnetic balance.

2.2. Syntheses of 1

A blue aqueous solution (20 cm^3) of Cu$_2$(oxpn)Cl$_2$ (0.25 mmol) prepared in situ by mixing equimolar Cu(oxpn) and CuCl$_2 \cdot$4H$_2$O was diffused slowly in an H-tube into an aqueous solution (30 cm^3) of K$_3$[Cr(CN)$_5$ (NO)]$\cdot$H$_2$O (0.25 mmol) at room temperature. Well-shaped black single crystals of **1** formed after a couple of months. Complex **1** is insoluble in the usual organic and inorganic solvents and stable in air. Yield: 20% based on Cu. IR (cm^{-1}): v(C≡N), 2135 sh, 2117 s, 2102 s, v(C=O), 1612 s. *Anal*. Calc. for C$_{12}$H$_{16}$Cu$_4$N$_8$O$_2$: C, 25.81; H, 2.89; N, 20.06. Found: C, 26.0; H, 2.8; N, 19.8.

2.3. X-ray crystallography

Crystal data for **1**: C$_{12}$H$_{16}$Cu$_4$N$_8$O$_2$, $M_w = 558.49$, $T = 293$ K, monoclinic, space group $C2/c$, $a = 10.341(2)$, $b = 11.771(2)$, $c = 14.306(3)$ Å, $\beta = 103.10(3)°$, $U = 1696.0(6)$ Å^3, $Z = 4$, $\mu = 4.974$ mm^{-1}, $2\theta_{max} = 55°$, λ (Mo K$_\alpha$) $= 0.71073$ Å, 3664 measured reflections, 1935 unique reflections, 1346 observed reflections ($I > 2\sigma(I)$). $R1 = 0.0299$, $wR2 = 0.0488$ (all data), GOF $= 0.924$ based on 118 parameters. X-ray diffraction data were collected on a Rigaku IP diffractometer using graphite-monochromated Mo K$_\alpha$ radiation ($\lambda = 0.71073$ Å) at 293 K. The structure was solved by the direct method and refined by full matrix least-squares on F^2. Anisotropic thermal parameters were used for the non-hydrogen atoms. CCDC-213074 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

3. Results and discussion

3.1. Syntheses

With the original intent of obtaining a cyanide-bridged Cu(II)–Cr(I) complex, slow diffusion of Cu$_2$(oxpn)Cl$_2$ and K$_3$[Cr(CN)$_5$(NO)] in H$_2$O gave rise to crystals of **1**. The formation of [Cu(CN)$_2$]$^-$ is a consequence of the high stability of the [Cu(CN)$_2$]$^-$ ion. The mechanism of the reaction is illustrated by Eqs. (1)–(3). The resulting [Cu(CN)$_2$]$^-$ anion acts as a building block for formation of the cyanide-bridged Cu(II)–Cu(I) coordination polymer.

$$[Cr(CN)_5(NO)]^{3-} \rightleftharpoons [Cr(CN)_4(NO)(H_2O)]^{2-} + CN^-$$
(1)

$$2Cu^{2+} + 6CN^- = 2[Cu(CN)_2]^- + (CN)_2$$
(2)

$$Cu_2(oxpn)]^{2+} + 2[Cu(CN)_2]^- = [Cu_2(oxpn)][Cu(CN)_2]_2$$
(3)
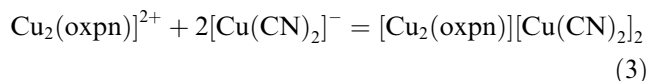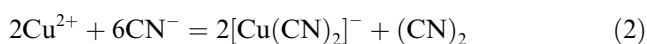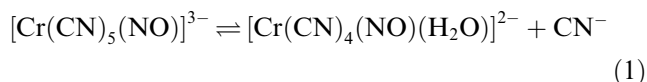
According to this mechanism, the title complex can be alternatively prepared by the reaction of Cu$_2$(oxpn)Cl$_2$ with KCN. We have found that complex **1** can be produced by this method with a lower yield (2%), though. This shows that the rate of dissociation of [Cr(CN)$_5$(NO)]$^{3-}$ plays an important role in formation of **1**. This result reemphasizes the less stability of [Cr(CN)$_5$(NO)]$^{3-}$ than [Fe(CN)$_5$(NO)]$^{2-}$ since similar reaction by using [Fe(CN)$_5$(NO)]$^{2-}$ instead of [Cr(CN)$_5$(NO)]$^{3-}$ affords the 2D bimetallic {[Cu$_2$(oxpn)] [Fe(CN)$_5$(NO)]$_2$}$_\infty$ [9].

3.2. Crystal structure

An ORTEP view of the units of **1** with the atomic numbering scheme is shown in Fig. 1. Selected bond distances and angles of **1** are listed in Table 1. The structure of **1** consists of a threefold equivalent three-dimensional network. Each 3D framework is composed of [Cu$_2$(oxpn)]$^{2+}$ moieties connected by polymeric [Cu(CN)$_2$]$^-$ anions, as shown in Figs. 1 and 2. The 3D framework can also be regarded as 1D [Cu(CN)$_2$]$^-$ chains connected by dimeric [Cu$_2$(oxpn)]$^{2+}$ cations. The Cu^{II} ion, Cu(1) in [Cu$_2$(oxpn)]$^{2+}$ group, assumes a distorted square planar coordination with three atoms of the *trans*-oxamidato ligand and one nitrogen atom from the bridging cyano-ligand. The largest deviation from
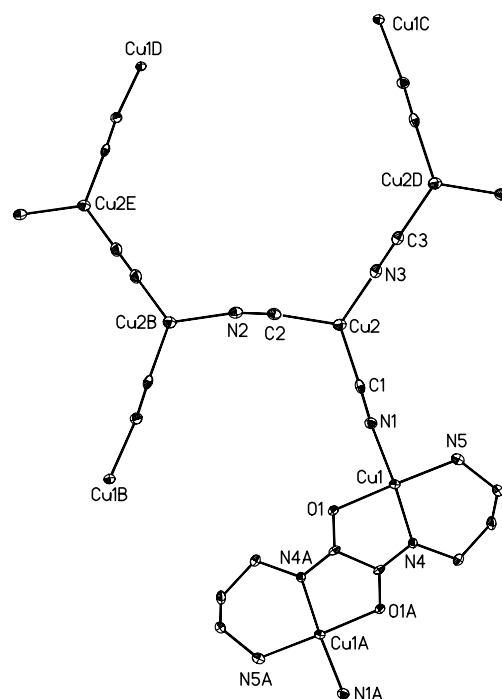

Fig. 1. Illustration showing the coordination sphere of Cu^{II} and Cu^I.

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

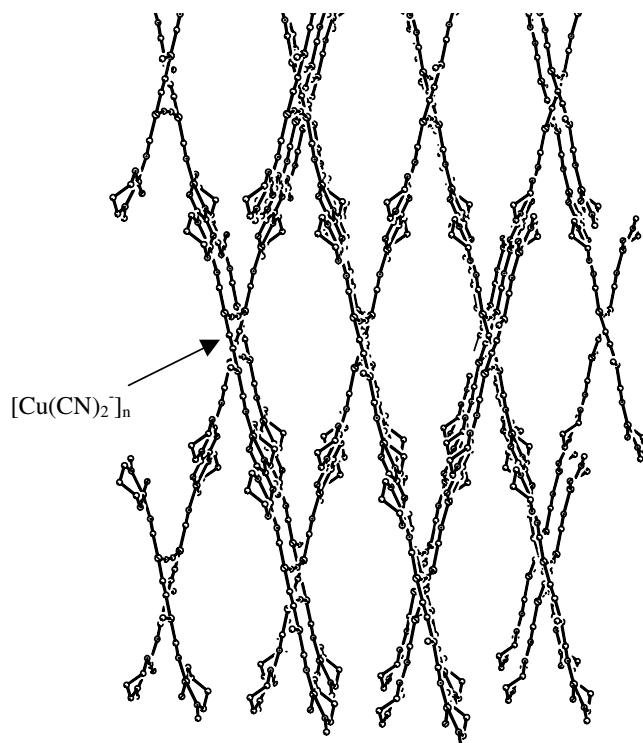| Cu(1)–N(4)	1.943(3)	Cu(2)–C(1)	1.925(3)
Cu(1)–N(1)	1.961(3)	Cu(2)–C(2)	1.964(3)
Cu(1)–O(1)	1.982(2)	Cu(2)–C(3)	1.921(3)
Cu(1)–N(5)	2.009(3)		
C(1)–N(1)–Cu(1)	172.6(3)	N(1)–C(1)–Cu(2)	177.8(3)
C(3)–Cu(2)–C(1)	127.2(1)	C(3)–Cu(2)–C(2)	113.7(1)
C(1)–Cu(2)–C(2)	117.4(1)	N(3)#3–C(3)–Cu(2)	177.7(4)
N(2)#2–C(2)–Cu(2)	167.6(3)		

Fig. 2. One single 3D framework showing the non-planar $[Cu(CN)_2]^-$ chains connected by $[Cu_2(oxpn)]^{2+}$ units.

the least-square plane defined by N(1)N(4)N(5)O(1) is 0.126 Å at O(1), and Cu(1) lies 0.0441 Å out of the plane. The Cu–O and Cu–N_{oxpn} bond distances are comparable to those in $[Cu_2(oxpn)]^{2+}$-related compounds [10–12]. In the polymeric $[Cu(CN)_2]^-$ chain, the Cu^I ion [Cu(2)] is in an approximately trigonal-planar coordination with the C–Cu–C or C–Cu–N bond angles are 127.2(1)°, 117.4(1)° and 113.7(1)°, respectively (the sum of the total angles is 358.3°). The Cu(I) ion is above the coordination plane by 0.143 Å. Based on the crystal structures of M[Cu(CN)_2] (M = Na+ or K+), the three-coordinate Cu(I) ion is surrounded by one nitrogen and two carbon atoms of three cyano-ligands [13,14]. The bridging cyano-ligands within the infinite $[Cu(CN)_2]^-$ chain are fully disordered whereas the cyano-ligand bridging Cu^I and Cu^{II} can be discriminated unambiguously. Unlike the planar structure of the $[Cu(CN)_2]^-$

chain in [Cu(CN)(dien)][Cu(CN)_2] [4], that in **1** is not planar: successive Cu^I sites are related by inversion centers at the middle of the cyano-carbon–nitrogen bonds that bridge Cu^I ions (Fig. 2). Consequently, $[Cu_2(oxpn)]^{2+}$ groups connect the non-planar $[Cu(CN)_2]^-$ chains to extend generating a 3D network with large cavities, as shown in Fig. 3.

The cavities (Fig. 3) are filled by the other two identical 3D networks giving rise to an interpenetrating framework. Fig. 4 shows two interpenetrating 3D networks. The three sets of 3D networks are connected through weak coordination bonds of Cu(1)–N(1)#1 (2.831(1) Å), Cu(1)–N(1)#1 (3.055(1) Å, #1: 0.5−x, 0.5−y,−z), Cu(2)–N(1)#2 (3.047(1) Å, #2: −x,−y,−z) and Cu(2)–C(1)#2 (3.087(1) Å) (Fig. 5, top). The interaction between Cu(2) and the CN− ligand of adjacent 3D framework can be assigned to the d–π orbital overlap as shown at the bottom of Fig. 5.
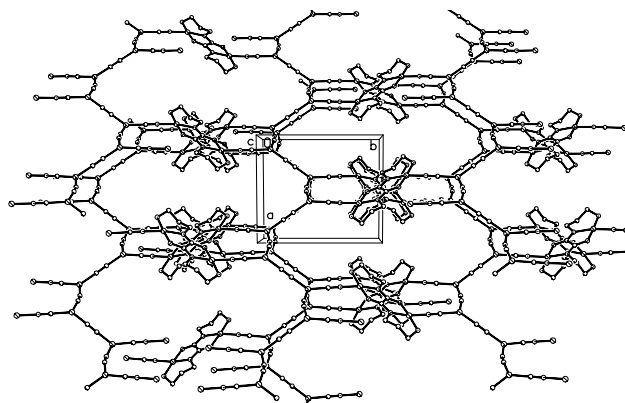

Fig. 3. Cell packing diagram along the crystallographic *c* axis showing one set of 3D frameworks and the formed cavities.
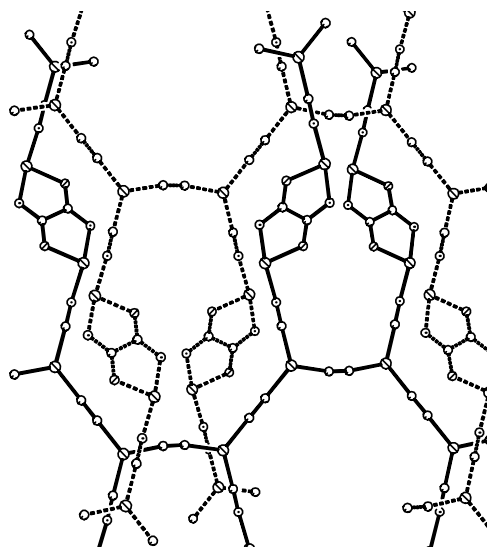

Fig. 4. Two identical interpenetrating 3D networks (some atoms of $oxpn^{2-}$ were omitted for clarity).
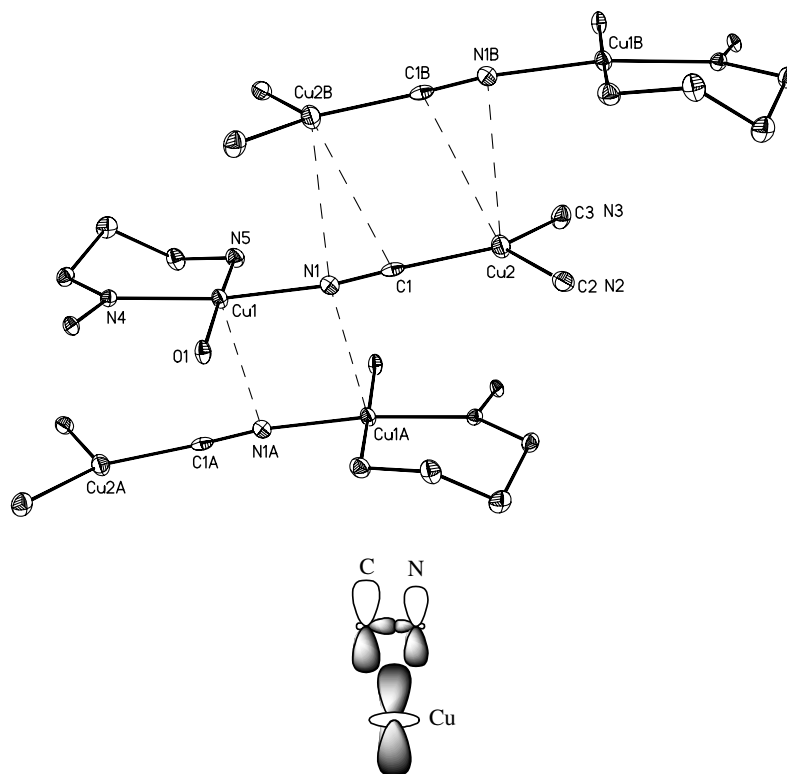
Fig. 5. Top: close contacts between threefold interpenetrating frameworks. Bottom: d–π orbital interaction between Cu^I and the CN^- ligand in complex **1**.

3.3. Spectroscopic properties

The IR spectrum of the complex exhibits three bands at 2135sh, 2117s and 2102s cm^{-1}, which can be attributed to the C≡N stretching vibration. The splitting of ν_{as}C≡N compared with that of $K[Cu(CN)_2]$ (2112 and 2091 cm^{-1} [13,14]) indicates the similar symmetry of $[Cu(CN)_2]^-$ in these related species. The strong absorption at 1612 cm^{-1} is due to the C=O stretching rather than to the NO^+ stretching mode, which is consistent with the structural results.

The room-temperature magnetic measurement suggests that **1** has a $\chi_m T$ value of 0.3 emu K mol^{-1} (1.5 μ_B), considerably lower than the expected value of 0.75 emu K mol^{-1} (2.4 μ_B) for a system with two uncoupled $S = 1/2$ ions. This indicates the presence of strong antiferromagnetic interaction between the Cu(II) ions through the oxamidato bridges. The powder X-band EPR spectrum of **1** measured at room temperature shows axial signals with $g_\| = 2.20$ and $g_\perp = 2.04$. The signals have been assigned to the excited triplet state for a magnetically coupled $S_1 = S_2 = 1/2$ dimeric system according to Tang et al. [11]. The EPR spectrum at 100 K shows similar signals with the intensity of the signals weaker than that of the former. This is understandable considering that for the antiferromagnetically coupled system the excited triplet state at 100 K is less populated, which results in a weaker transition signals at 100 K.

4. Conclusion

In conclusion, a novel cyano-bridged mixed-valence Cu^{II}/Cu^I coordination polymer has been synthesized and characterized. It contains a threefold interpenetrating 3D network. The present research provides a possible strategy for the construction of such species.

Acknowledgements

References

[1] K.R. Dunbar, R.A. Heintz, Prog. Inorg. Chem. 45 (1997) 283;
J. Lu, W.T.A. Harrison, A.J. Jacobson, Angew. Chem. Int. Ed. Engl. 34 (1995) 2557;
W. Chen, L. Fenghui, X.Z. You, Chem. Lett. (2002) 734;
D.W. Knoeppel, S.G. Shore, Inorg. Chem. 35 (1996) 5328;
B.F. Hoskins, R. Robson, N.V.Y. Scarlett, Angew. Chem., Int. Ed. Engl. 34 (1995) 1203;
T. Soma, H. Yuge, T. Iwamoto, Angew. Chem., Int. Ed. Engl. 33 (1994) 1665;
E. Siebel, R.D. Fischer, Chem. Eur. J. 3 (1997) 1987.

[2] M. Ohba, N. Maruone, H. Okawa, T. Enoki, J.-M. Latour, J. Am. Chem. Soc. 116 (1994) 11566;
H. Miyasaka, N. Matsumoto, H. Okawa, N. Re, E. Gallo, C. Floriani, Angew. Chem. Int. Ed. Engl. 34 (1995) 1446;
M. Ohba, H. Okawa, Coord. Chem. Rev. 198 (2000) 313;
F. Hulliger, M. Landolt, H. Vetsch, J. Solid State Chem. 18 (1976) 283;
H.-Z. Kou, S. Gao, B.-Q. Ma, D.-Z. Liao, Chem. Commun. (2000) 713.

[3] C. Kappenstein, J. Chem. Soc., Chem. Commun. (1980) 1116;
E. Colacio, R. Kivekas, F. Lloret, M. Sunberg, J. Suarez-Varela, M. Bardaji, A. Laguna, Inorg. Chem. 41 (2002) 5141.

[4] S.F. Huang, H.H. Wei, Y. Wang, Polyhedron 16 (1997) 1747.

[5] R.J. Williams, D.T. Cromer, A.C. Larson, Acta Crystallogr. B 27 (1971) 1701.

[6] M.-L. Tong, L.-J. Li, K. Mochizuki, H.-C. Chang, X.-M. Chen, Y. Li, S. Kitagawa, Chem. Commun. (2003) 428.

[7] W.P. Griffith, J. Lewis, G. Wilkinson, J. Chem. Soc. (1959) 872.

[8] H. Ojima, K. Nonoyama, Z. Anorg. Allg. Chem. 75 (1972) 389.

[9] H.-Z. Kou, D.-Z. Liao, Z.-H. Jiang, S.-P. Yan, Q.-J. Wu, S. Gao, G.-L. Wang, Inorg. Chem. Commun. 3 (2000) 151.

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

[11] Z.N. Chen, W.X. Tang, K.B. Yu, Polyhedron 13 (1995) 783.

[12] J. Ribas, C. Diaz, R. Costa, J. Tercero, X. Solans, M. Font-Bardia, H. Stoeckli-Evans, Inorg. Chem. 37 (1998) 233.

[13] D.T. Cromer, J. Phys. Chem. 61 (1957) 1388.

[14] J.D. Graybeal, G.L. McKown, Inorg. Chem. 5 (1966) 1909.