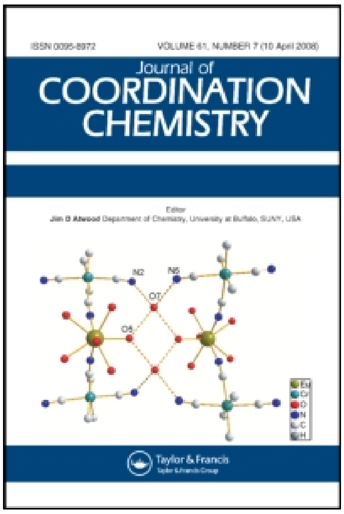

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The assembly, synthesis and properties of a trinuclear cyano-bridged Cu^{II}-Mo^{IV}-Cu^{II} complex

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The assembly, synthesis and properties of a trinuclear cyano-bridged Cu^{II}–Mo^{IV}–Cu^{II} complex

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A new trinuclear cyano-bridged Cu^{II}–Mo^{IV}–Cu^{II} compound has been prepared, characterized spectroscopically (UV–Vis and IR) and its structure determined by X-ray crystallography. The title complex **1** exhibits an antiferromagnetic exchange interaction between copper(II) ions mediated by $[Mo(CN)_8]^{4-}$ diamagnetic units.

Keywords: Cyano-bridged complex; Crystal structure; Magnetic property

1. Introduction

There has been interest in photo-magnetic materials based on octacyanometalate precursors [1–5]; octacyanomolybdate(IV) ions, which act as good building blocks, have played an important role in bimetallic assemblies of photo-magnetic materials [6–12]. Recently, a photomagnetic high-spin molecule, $[Mo(IV)(CN)_2(CN–CuL)_6](ClO_4)_8$ (L = *tris*(2-aminoethyl)amine) was synthesized by treating potassium octacyanomolybdate(IV) with a mononuclear copper(II) complex generated in situ from tris(2-aminoethyl)amine and Cu(II) perchlorate [13]. The reaction of Cu^{2+}, tn, and $[Mo(CN)_8]^{4-}$ produced **1** (tn = 1,3-diaminopropane). We present the crystal structure and characterization of a trinuclear **1** $[Cu(tn)_2]_2[Mo(CN)_8]$.

2. Experimental section

The chemicals $CuCl_2 \cdot 2H_2O$ and 1,3-diaminopropane (tn) were used as supplied by Aldrich. Potassium octacyanomolybdate(IV) has been obtained according to published procedure [14].

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2.1. *Physical measurements*

Infrared spectrum was recorded (in the 4000–400 cm^{-1}) as KBr disks on a Bruker 1600 FTIR spectrometer. The electronic spectra both in solid and aqueous solution were recorded on a Hitachi U-3010 (UV–Vis) spectrophotometer. Magnetic susceptibility data for powder samples were collected in the temperature range 2–300 K with a Quantum Design SQUID Magnetometer MPMS XL-7. Effective magnetic moments were calculated by the equation $\mu_{eff} = 2.828(\chi_M T)^{1/2}$, where χ_M is the molar magnetic susceptibility.

2.2. *Synthesis of 1*

$[Mo(CN)_6(CN–Cu(tn)_2)_2] \cdot 2H_2O$. A solution of 1,3-diaminopropane (0.30 g, 4 mmol) in water (5 ml) was added to a solution of $CuCl_2 \cdot H_2O$ (0.34 g, 2 mmol) in water (5 ml). The mixture was stirred for 2 min before the addition of potassium octacyanomolybdate(IV) (0.497 g, 1 mmol) dissolved in a minimum of water. After filtration, the solution was left standing for several days, which led to formation of green needles. They were collected by filtration and dried in air (0.56 g, 73%). The elemental analysis results (Found C, 31.67; H, 5.74; N, 29.88. $C_{20} H_{44} Cu_2 Mo N_{16} O_2$ requires C, 31.42; H, 5.77; N, 29.33) were in agreement with the formula of the sample used for X-ray analysis. IR (KBr pellet): 2116 (s) 2091 (s) cm^{-1} (ν_{CN}).

2.3. *X-ray crystallography*

The X-ray diffraction measurement for $[Mo(CN)_6(CN–Cu(tn)_2)_2] \cdot 2H_2O$ was performed on a Bruker Smart 1000 CCD diffractometer using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at room temperature. The structures were solved using direct methods and the non-hydrogen atoms were refined anisotropically. All the hydrogen atoms of the ligands were placed in calculated positions with fixed isotropic thermal parameters and included in the structure factor calculations in the final stage of full-matrix least-squares refinement. The hydrogen atoms of the water molecules were located in the difference Fourier map and refined isotropically. All calculations were performed using the SHELXTL program [15]. Details of the crystal parameters, data collection and refinement for complex $[Mo(CN)_6(CN–Cu(tn)_2)_2] \cdot 2H_2O$ are listed in table 1, and selected bond distances and angles are given in table 2.

3. Results and discussions

3.1. *Synthesis and characterization*

The new trinuclear cyano-bridged complex **1** $[Mo(CN)_6(CN–Cu(tn)_2)_2] \cdot 2H_2O$ has been prepared by reacting 2 equiv of the Cu complex with 1 equiv of octacyanomolybdate(IV). The formation of cyanide bridges in the trinuclear complex was evidenced by the IR spectrum in the region of the stretching vibration of the cyanide ligands. The IR spectrum of **1** shows strong bands at 2116 and 2091 cm^{-1}, assigned to the terminal CN group and the intermetallic $Cu^I–C\equiv N–Cu^{II}$ bond

Table 1. Crystal data and structure refinement for **1**.

Empirical formula	$C_{20}H_{44}Cu_2MoN_{16}O_2$
Formula weight	763.73
Temperature (K)	273(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$C2/c$
a (Å)	15.8257(11)
b (Å)	10.9453(7)
c (Å)	19.4533(18)
α (°)	90
β (°)	110.437(1)
γ (°)	90
V (Å^3)	3157.5(4)
Z	4
D_c (Mgm^{-3})	1.607
Absorption coefficient (mm^{-1})	1.773
F(000)	1568
Crystal size (mm^3)	0.38 × 0.25 × 0.23
θ range for data collection (°)	2.31 to 27.49
Limiting indices	$-20 \le h \le 19$, $-13 \le k \le 14$, $-25 \le l \le 21$
Reflections collected/unique	9676/3617 [$R_{(int)} = 0.0165$]
Max. and min. transmission	0.6890 and 0.5538
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3617/3/195
Goodness-of-fit on F^2	1.072
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0622$, $wR_2 = 0.1489$
R indices (all data)	$R_1 = 0.0647$, $wR_2 = 0.1509$
Extinction coefficient	0.0090(5)
Largest diff. peak and hole (e.A^{-3})	5.412 and −3.459

Table 2. Selected bond distances (Å) and angles (°) for **1**.

Bond distances (Å)			
Mo(1)–C(10)	2.165(5)	Mo(1)–C(8)	2.166(5)
Mo(1)–C(7)	2.166(5)	Mo(1)–C(9)	2.168(5)
Cu(1)–N(3)	2.004(4)	Cu(1)–N(2)	2.016(5)
Cu(1)–N(4)	2.027(4)	Cu(1)–N(1)	2.046(5)
Cu(1)–N(5)	2.413(5)	N(5)–C(7)	1.163(6)
N(6)–C(8)	1.151(7)	N(7)–C(9)	1.147(7)
N(8)–C(10)	1.146(8)		
Bond angles (°)			
C(10)#1–Mo(1)–C(10)	79.8(3)	C(8)#1–Mo(1)–C(8)	78.1(3)
C(7)–Mo(1)–C(7)#1	141.6(3)	C(9)#1–Mo(1)–C(9)	141.9(3)
N(3)–Cu(1)–N(4)	93.34(19)	N(2)–Cu(1)–N(1)	85.1(2)
C(7)–N(5)–Cu(1)	141.6(4)	N(5)–C(7)–Mo(1)	178.9(5)
N(6)–C(8)–Mo(1)	179.4(5)	N(7)–C(9)–Mo(1)	177.6(5)
N(8)–C(10)–Mo(1)	179.5(6)	N(3)–Cu(1)–N(2)	176.3(2)
N(4)–Cu(1)–N(1)	155.5(2)		

Symmetry transformations used to generate equivalent atoms: #1 $-x, y, -z+1/2$.

(νC≡N(b)), respectively. The shift of ν(C≡N) to lower wavenumber compared with that of $K_4[Mo(CN)_8]$ (ν_{CN} 2129 cm^{-1}) is consistent with the formation of C≡N bridges as revealed by the X-ray analysis. Bignozzi *et al.* have discussed electronic effects on the stretching frequencies in bridging cyanide ligands, a withdrawal of charge from the nitrogen to the second metal (Cu^{2+}) leads to a decrease in ν_{CN} [16].

3.2. *Electronic spectra*

UV/Vis spectra of **1** recorded both in the solid state and for aqueous solution show similar features, indicating **1** is stable in aqueous solution. The lowest energy band at $\lambda_{max} = 597\,nm$ ($\varepsilon = 641\,mol^{-1}dm^3\,cm^{-1}$) figure 1, can be assigned to electron transfer from Cu^{II} to cyanide. This shift to lower energy with respect to the mononuclear parent complex $[Cu(dipn)]^{2+}$ (580 nm) ($\varepsilon = 27\,mol^{-1}dm^3cm^{-1}$) can be explained on the basis of bridge formation Cu–NC–Mo. The higher energy band at $\lambda_{max} = 370\,nm$ ($\varepsilon = 691\,mol^{-1}\,dm^3\,cm^{-1}$), characteristic of $[Mo(CN)_8]^{4-}$ [17], is attributed to d–d and metal-to-ligand charge transfer (MLCT) electronic transitions.

3.3. *Crystal structure of 1*

The crystal structure of $[Mo(CN)_6(CN{-}Cu(tn)_2)_2]\cdot 2H_2O$ is shown in figure 2. **1** comprises a $[Mo(CN)_8]^{4-}$ connected by cyanide bridges to two identical Cu(II) cations, and two water molecules. Because the solid state structure of **1** is constrained by crystallographically-imposed C2 symmetry, the two Cu centers are symmetry related and therefore structurally equivalent. Each $[Cu(tn)_2]^{2+}$ unit exhibits a *trans* N-based conformation with Cu–N bond lengths ranging from 2.004(4) to 2.046(4) Å. In accord with the (pseudo) Jahn-Teller effect [18], the axial Cu–N bond distance (Cu1–N5) is longer than those of the equatorial ones (Cu1–N1, Cu1–N2, Cu1–N3, and Cu1–N4) as shown in table 2. The axial bond distance (Cu1–N5) and Cu1–N5≡C7 bond angle are 2.413(5) and 141.6(4)°. Another interesting feature is that the Mo–CN coordinate bonds are not sensitive to whether the CN ligand is terminal (Mo–C8 = 2.166(5), Mo–C9 = 2.168(5), Mo–C10 = 2.165(5) Å) or bridging (Mo–C7 = 2.166(5) Å. The two independent bridging Mo–CN coordinate bonds are significantly similar to those of the six terminally coordinated cyano ligands. The Mo atom is coordinated by eight CN groups, with Mo–C distances ranging from 2.165(5) to 2.168(5) Å in a distorted bicapped trigonal prism. The mean bridging and non-bridging CN bond distances are 1.163(6), 1.151(7), 1.147(7), and 1.146(8) Å, in agreement with the spectroscopic differences

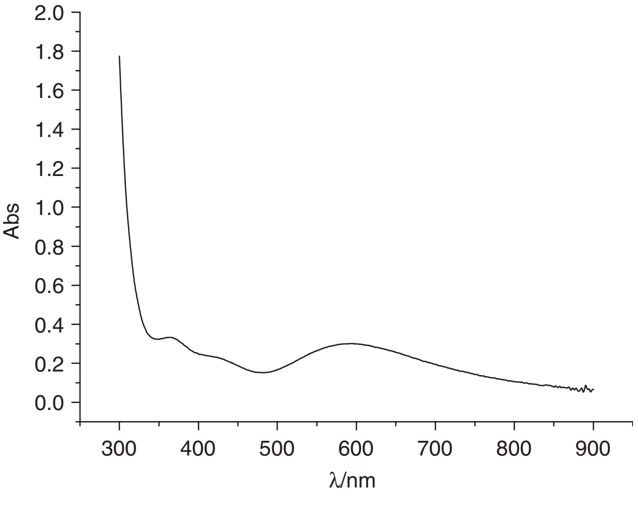

Figure 1. UV–Vis spectra of $[Mo(CN)_6(CN{-}Cu(tn)_2)_2]\cdot 2H_2O$ in water. Concentrations ca. $4.7\times 10^{-4}\,mol\,dm^{-3}$.

between terminal and bridging CN-moieties. Each $Mo^{IV}(CN)_8^{4-}$ group connects two Cu atoms (Cu1 and Cu1A) via two cyano bridges (C7–N5 and C7A–N5A) with the Cu–N_{CN} distance 2.413(5) Å. Cyano bridges are distorted with Mo–C–N angle 177.6(5)°, and the C–N–Cu angle of 141.6(4)°. The shortest metal$\cdots$metal distance for Mo$\cdots$Cu is 5.325(1) Å.

3.4. *Magnetic properties*

The magnetic properties of **1** were investigated in the temperature range 2–300 K for molar susceptibility and in the range 0–70 kOe for magnetization. The magnetic behavior of **1** is shown in figure 3 in the form of $\chi_M T$ *versus* T. From room temperature down to 100 K, the $\chi_M T$ remains constant at 0.9985 $cm^3 K mol^{-1}$ (2.82 μ_B), close to the expected value of 1.0 $cm^3 K mol^{-1}$ (2.83 μ_B) for two isolated Cu(II) ($S = 1/2$) ions. Below 100 K, the $\chi_M T$ decreases, reaching a value of 0.511 $cm^3 K mol^{-1}$ at 2 K. This antiferromagnetic behavior has been confirmed by the field dependence of the magnetization (0–70,000 Oe) measured at 2 K as shown in figure 4 in the form of $M/N\mu_B$ *versus* H. The magnetization curve showed a gradual increase with applied field and reached a value of 2.06 N μ_B at 70,000 Oe, which is smaller than the expected value for two Cu(II) ($S = 1/2$) ions (2.828 μ_B), indicating the presence of antiferromagnetic coupling between two separated Cu^{2+} centers at high field.

Supplementary data

CCDC 609490 contains the supplementary crystallographic data of **1**. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

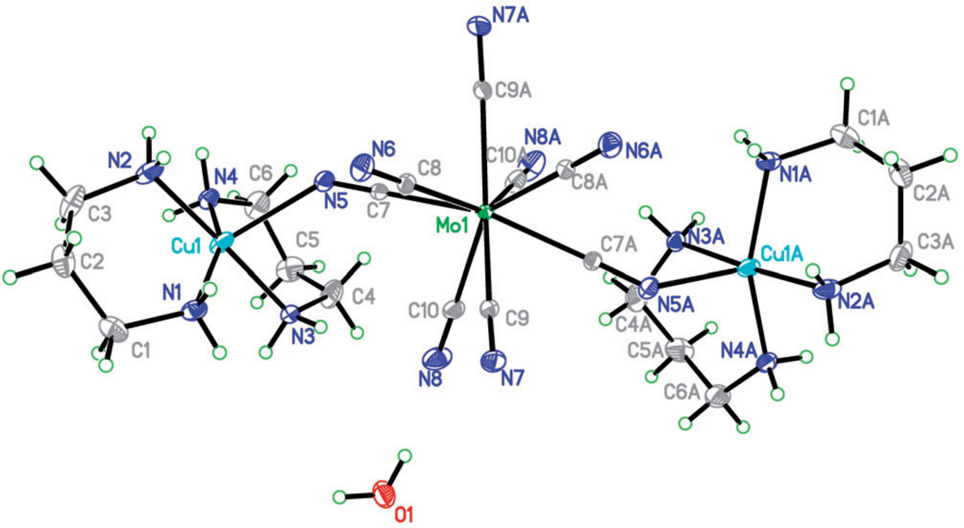

Figure 2. The ORTEP view of $[Mo(CN)_6(CN–Cu(tn)_2)_2] \cdot 2H_2O$.

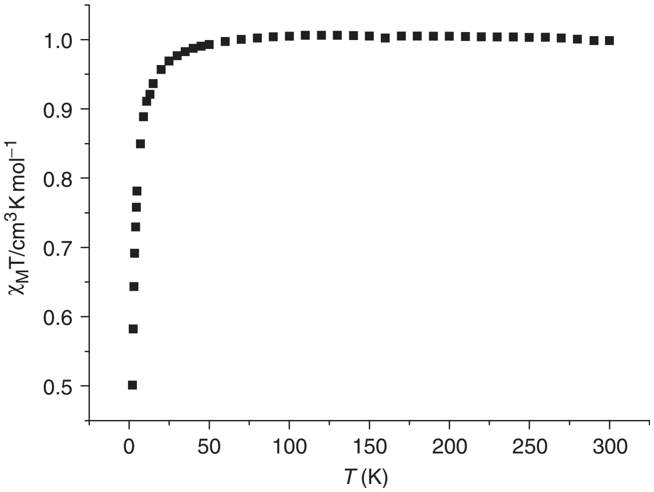

Figure 3. Temperature dependence of $\chi_M T$ at an applied field of 1000 Oe for $[Mo(CN)_6(CN–Cu(tn)_2)_2] \cdot 2H_2O$.

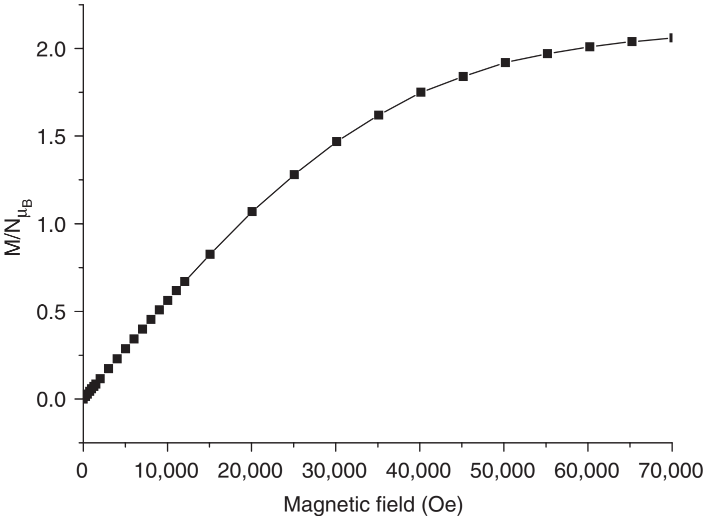

Figure 4. Field dependence of the magnetization at 2 K for complex $[Mo(CN)_6(CN–Cu(tn)_2)_2] \cdot 2H_2O$.

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References

[1] S.I. Ohkoshi, N. Machida, J.Z. Zhong, K. Hashimoto. *Synth. Met.*, **122**, 523 (2001).

[2] Y. Arimoto, S.I. Ohkoshi, N. Machida, J.Z. Zhong, H. Seino, Y. Mizobe, K. Hashimoto. *J. Am. Chem. Soc.*, **125**, 9240 (2003).

[3] A. Dei. *Angew. Chem. Int. Ed. Engl.*, **44**, 1160 (2005).

[4] A.P. de Silva, N.D. McClenaghan. *Eur. J. Chem.*, **10**, 574 (2004).

[5] Special issue "Photochromism: Memories and Swithes" M. Irie (Guest Ed.). *Chem. Rev.*, **100**, 1683 (2000).

[6] C. Mathoniere, R. Podgajny, P. Guionneau, C. Labrugere, B. Sieklucka. *Chem. Mater.*, **17**, 442 (2005).

[7] G. Li, T. Akitsu, O. Sato, Y. Einaga. *J. Am. Chem. Soc.*, **125**, 12396 (2003).

[8] T. Hozumi, K. Hashimoto, S. Ohkoshi. *J. Am. Chem. Soc.*, **127**, 3864 (2005).

[9] D.-F. Li, D.-X. Yang, S.-A. Li, W.-X. Tang. *Inorg. Chem. Commun.*, **5**, 791 (2002).

[10] R. Podgajny, T. Korzeniak, K. Stadnicka, Y. Dromzee, N.W. Alcock, W. Errington, K. Kruczala, M. Balanda, T.J. Kemp, M. Verdaguer, B. Sieklucka. *Dalton Trans.*, 3458 (2003).

[11] Y.S. You, D. Kim, Y. Do, S.J. Oh, C.S. Hong. *Inorg. Chem.*, **43**, 6899 (2004).

[12] G. Rombaut, M. Verelst, S. Golhen, L. Ouahab, C. Mathoniere, O. Kahn. *Inorg. Chem.*, **40**, 1151 (2001).

[13] J.M. Herrera, V. Marvand, M. Verdaguer, J. Marrot, M. Kalisz, C. Mathoniere. *Angew. Chem. Int. Ed. Engl.*, **43**, 5468 (2004).

[14] J.D. Leipoldt, C. Bok, P.J. Cillier. *Z. Anorg. Allg. Chem.*, **409**, 343 (1974).

[15] G. M. Sheldrick. *SHELXS 97, Program for Crystal Structure Refinement*, University of Göttingen, Göttingen, Germany (1997).

[16] C.A. Bignozzi, S. Roffia, C. Creutz, F. Scandola. *J. Am. Chem. Soc.*, **107**, 1644 (1985).

[17] M.F.A. Hendricks, V.S. Mironov, L.F. Chibotaru, A. Ceulemans. *Inorg. Chem.*, **43**, 3142 (2004).

[18] I.B. Bersuker. *The Jahn-Teller Effect*, Cambridge University Press, Cambridge, U. K. (2006).