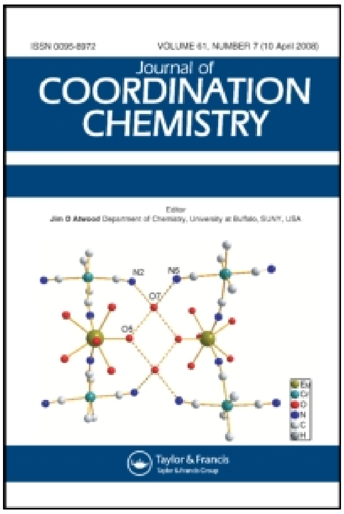
This article was downloaded by:
On: *23 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis, Structure and Characterization of the Cyano-Bridged Heteropolymer Poly{[Bis(Trimethylenediamine)Copper(II)][Hexacyanocobalt(III)]} Perchlorate Dihydrate with a Two-Dimensional Framework

Baolong Li[a]; Xiaoping Shen[a]; Kaibei Yu[b]; Zheng Xu[a]
[a] Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing, P.R. China [b] Chengdu Center of Analysis and Measurement, Academia Sinica, Chengdu, P.R. China

Online publication date: 15 September 2010

To cite this Article Li, Baolong , Shen, Xiaoping , Yu, Kaibei and Xu, Zheng(2002) 'Synthesis, Structure and Characterization of the Cyano-Bridged Heteropolymer Poly{[Bis(Trimethylenediamine)Copper(II)][Hexacyanocobalt(III)]} Perchlorate Dihydrate with a Two-Dimensional Framework', Journal of Coordination Chemistry, 55: 10, 1191 — 1198

To link to this Article: DOI: 10.1080/0095897021000025228

URL: http://dx.doi.org/10.1080/0095897021000025228

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

J. Coord. Chem., 2002, Vol. 55, No. 10, pp. 1191–1198

Taylor & Francis
Taylor & Francis Group

SYNTHESIS, STRUCTURE AND CHARACTERIZATION OF THE CYANO-BRIDGED HETEROPOLYMER POLY{[BIS(TRIMETHYLENE-DIAMINE)COPPER(II)][HEXACYANOCOBALT(III)]} PERCHLORATE DIHYDRATE WITH A TWO-DIMENSIONAL FRAMEWORK

BAOLONG LI[a], XIAOPING SHEN[a], KAIBEI YU[b] and ZHENG XU[a,*]

[a]*Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, P.R. China;* [b]*Chengdu Center of Analysis and Measurement, Academia Sinica, Chengdu 610041, P.R. China*

(Received 16 May 2001; Revised 29 October 2001; In final form 4 April 2002)

The complex $[Cu(tn)_2]_2[Co(CN)_6](ClO_4)\cdot 2H_2O$ (tn = trimethylenediamine) has been prepared and characterized by elemental analysis, IR, electronic and electronic spin resonance spectra and magnetic properties. The x-ray structure analysis shows that each $[Co(CN)_6]^{3-}$ ion coordinates to four $[Cu(tn)_2]^{2+}$ cations through four cyano nitrogen atoms in the same plane, providing a two-dimensional square network structure, formed from Co–CN–Cu(tn)$_2$–NC–Co linkages.

Keywords: Crystal structure; Cyano bridged; Copper(II); Hexacyanocobalt(III)

INTRODUCTION

For years, chemists have devoted their efforts to assemble compounds by using building units and connecting units as a bricklayer would erect a building. Due to the development of crystallography and synthetic chemistry, the time for the assembly of polymer compounds [1–13] on the basis of simply adding building units and connecting units is upon us. Recently, a successful example of this process is the cyano bridging complexes [14–34] in which the cyanometallate anion behaves as a bridging moiety to build up a multidimensional structure with the second coordination centers. These complexes are usually composed of a cyanometallate $[M(CN)_n]^{m-}$ (building block), and a guest molecule and/or a complementary ligand. The major part of these systems has been constructed from transition metal complexes with two available coordination sites of the type NiN_4^{2+} (N_4 = bis(diamine) or tetraamine macrocyclic ligand) and

---

*Corresponding author. Fax: 86 25 3314502. E-mail: zhengxu@nju.edu.cn and profzxu@jlonline.com

ISSN 0095-8972 print: ISSN 1029-0389 online
DOI: 10.1080/0095897021000025228

$[M(CN)_6]^{3-}$ ($M = Cr^{III}$ or Fe^{III}). Since copper(II) complexes exhibit great stereochemical plasticity, they are expected to give rise to a large variety of assembled compounds with hexacyanometalate. Nevertheless, only a few fully structurally characterized cyanide-bridged bimetallic complexes constructed from copper(II) complexes and hexacyanometalates have been reported so far [35–40]. The most commonly employed building-blocks are the anions $[Fe(CN)_6]^{3-}$ and $[Cr(CN)_6]^{3-}$. We report here the crystal structure and characteristics of a heterometallic complex $[Cu(tn)_2]_2[Co(CN)_6](ClO_4) \cdot 2H_2O$ (**1**) (tn = trimethylenediamine) obtained using $[Co(CN)_6]^{3-}$ as a template.

EXPERIMENTAL

Materials

All chemicals were commercial products of reagent grade and used without purification. $K_3[Co(CN)_6]$ was prepared using literature methods [41].

Preparations

$[Cu(tn)_2]_2[Co(CN)_6](ClO_4) \cdot 2H_2O$ (**1**) Trimethylenediamine (tn) (4 mmol) was added to an aqueous solution (20 mL) of $Cu(ClO_4) \cdot 6H_2O$ (2 mmol) with stirring for 20 min, then the solution was mixed with an aqueous solution (20 mL) of $K_3[Co(CN)_6]$ (1 mmol). The resulting solution was filtered, and the filtrate was placed on the bench-top for one week in the dark at room temperature. Green crystals, suitable for x-ray diffraction analysis, were obtained. Anal. Calcd. for $C_{18}H_{44}ClCoCu_2N_{14}O_6$ (%): C, 27.93; H, 5.73; N, 25.34. Found: C, 27.43; H, 5.51; N, 24.56. The same compound was obtained when the mole ratio of $K_3[Co(CN)_6] : Cu(ClO_4)_2 \cdot 6H_2O : tn = 1 : 1 : 2$.

Caution! *Perchlorate salts are potentially explosive and should be handled in small quantities.*

Physical Measurements

The elemental analyses of carbon, hydrogen, and nitrogen were performed on a Perkin–Elmer 240C analyzer. Infrared spectra were obtained for KBr pellets on a Nicolet 170SX FT-IR instrument. Electronic spectra were recorded in H_2O on a Shimadzu 3100 spectrophotometer. An ESR spectrum was recorded in the solid state on an Er2000-SRC instrument. Magnetic susceptibilities were measured in the solid state using a CAHN-2000 Faraday balance with $[Ni(en)_2]S_2O_3$ as a standard at 6000 G magnetic filed.

X-Ray Crystallography

A green single crystal with dimension of 0.48 × 0.48 × 0.34 mm was placed on a glass fiber. All the x-ray data were collected on a SIEMENS P4 four-circle diffractometer. The unit-cell parameters were obtained by least squares refinement of the values of 29 selected reflections $3.05 < \theta < 14.76°$. The data were collected at 290(2) K using

TABLE I Crystal parameters for **1**

Compound	$[Cu(tn)_2]_2[Co(CN)_6](ClO_4) \cdot 2H_2O$
Color/shape	Green/prismatic
Empirical formula	$C_{18}H_{44}ClCoCu_2N_{14}O_6$
Formula weight	774.13
Temperature	290(2) K
Crystal system	Triclinic
Space group	$P\bar{1}$
No. of reflection used for unit Cell determination (2θ range)	29(7.10°–29.52°)
a (Å)	8.8080(10)
b (Å)	10.0780(10)
c (Å)	10.1720(10)
α (°)	88.30(2)
β (°)	79.330(1)
γ (°)	67.891(4)
V (Å^3)	821.3(2)
Z	1
D_{calc} (g · cm^{-3})	1.565
μ(MoKα) (cm^{-1})	19.18
F(000)	400
Radiation	MoK$_\alpha$ ($\lambda = 0.71073$ Å) graphite monochromated
Scan type	ω-2θ
$2\theta_{max}$	50.00°
No. of reflection measured	Total: 3223; unique: 2898 ($R_{int} = 0.0167$)
No. of observations [$I > 2\sigma(I)$]	2496
No. variables	226
S	1.067
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0261$ $wR2 = 0.0708$
Max. peak in final diff. Map	0.46 eÅ^{-3}

$W = 1/[\sigma^2(Fo^2) + (0.0415P)^2 + 0.17P]$, $P = [Fo^2 + 2Fc c^2]/3$.

the ω-2θ scan technique in the range of $4.08 < 2\theta < 50.00°$, using MoK$_\alpha$ radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods and refined with full-matrix least-squares technique using SHELX 97 [42]. The positions of all remaining non-H atoms were obtained from successive Fourier syntheses. The positions of hydrogen atoms were calculated using idealized geometry. The parameters of the crystal, data collection and refinement are given in Table I. The atomic coordinates for non-hydrogen atoms are listed in Table II. Bond lengths and angles are shown in Table III.

RESULTS AND DISCUSSION

Crystal Structure

Figure 1 shows on ORTEP drawing of the Cu_2Co trinuclear unit of (**1**) (the asymmetric unit corresponds to one half of the trinuclear unit). All the metal ions are at special equivalent positions [Co (1/2, 1/2, 0), Cu(1) (1/2, 1/2, 1/2), Cu(2)(1, 0, 0)]. Each $[Co(CN)_6]^{3-}$ ion coordinates to four $[Cu(tn)_2]^{2+}$ cations through four cyano nitrogen atoms [N(1), N(2), N(1A), N(2A)] on the same plane, providing a two-dimensional square network structure with Co–CN–$Cu(tn)_2$–NC–Co linkages (Fig. 2).

TABLE II Selected atomic positional parameters($\times 10^4$) and isotropic temperature factors ($\text{Å}^2 \times 10^3$) for **1**

	x	*y*	*z*	*U*(*eq*)
Cu(1)	5000	5000	5000	30(1)
Cu(2)	10000	0	0	35(1)
Co	5000	5000	0	23(1)
N(1)	7258(2)	4907(2)	5234(2)	36(1)
N(2)	3906(2)	7012(2)	5837(2)	39((1)
N(3)	10355(3)	1342(2)	−1444(2)	47(1)
N(4)	10977(3)	909(2)	1189(2)	46(1)
N(5)	5426(3)	6002(2)	2648(2)	42(1)
N(6)	7029(3)	2014(2)	813(2)	44(1)
N(7)	8317(2)	4967(2)	−1545(2)	46(1)
C(1)	7717(3)	6175(3)	5213(3)	47(1)
C(2)	6413(3)	7481(3)	5995(3)	49(1)
C(3)	4772(3)	8011(2)	5525(3)	44(1)
C(4)	12006(4)	1453(3)	−1733(3)	62(1)
C(5)	12369(4)	2042(3)	−549(3)	69(1)
C(6)	12540(4)	1103(3)	614(3)	61(1)
C(7)	5274(3)	5685(2)	1623(2)	29(1)
C(8)	6210(3)	3113(2)	500(2)	30(1)
C(9)	7064(3)	5026(2)	−944(2)	29(1)
O(1)	10880(2)	6065(2)	−2434(2)	54(1)
Cl	154(6)	10027(6)	4867(5)	50(1)
O(2)	363(8)	9119(9)	5952(6)	154(4)
O(3)	1685(5)	9560(8)	3950(4)	137(3)
O(4)	−305(10)	11461(6)	5312(10)	191(5)
O(5)	−1098(6)	9944(8)	4227(7)	123(3)

TABLE III Selected bond lengths (Å) and angles (°) for **1**

Cu(1)–N(1)	2.0508(18)	Cu(1)–N(2)	2.0232(18)
Cu(1)–N(5)	2.587(2)	Cu(2)–N(4)	2.0215(19)
Cu(2)–N(3)	2.0283(19)	Cu(2)–N(6)	2.637(2)
Co–C(7)	1.898(2)	Co–C(9)	1.902(2)
Co–C(8)	1.905(2)		
N(1)–Cu(1)–N(2)	89.80(8)	N(1)#1–Cu(1)–N(2)	90.20(8)
N(2)–Cu(1)–N(5)	90.71(7)	N(2)#1–Cu(1)–N(5)	89.29(7)
N(1)–Cu(1)–N(5)	93.11(7)	N(1)#1–Cu(1)–N(5)	86.89(7)
N(4)–Cu(2)–N(3)	88.28(9)	N(4)#2–Cu(2)–N(3)	91.72(9)
N(4)–Cu(2)–N(6)	89.98(8)	N(4)#2–Cu(2)–N(6)	90.02(8)
N(3)–Cu(2)–N(6)	86.55(8)	N(3)#2–Cu(2)–N(6)	93.45
C(7)–Co–C(9)	92.53	C(7)#3–Co–C(9)	87.47(9)
C(7)–Co–C(8)	87.54(9)	C(7)#3–Co–C(8)	92.46(9)
C(9)–Co–Co(8)	87.72(9)	C(9)#3–Co–C(8)	92.28(9)
C(1)–N(1)–Cu(1)	121.26(15)	C(3)–N(2)–Cu(1)	118.83(15)
C(4)–N(3)–Cu(2)	117.09(17)	C(6)–N(4)–Cu(2)	118.08(16)
C(7)–N(5)–Cu(1)	132.61(17)	C(8)–N(6)–Cu(2)	139.12(18)

Symmetry transformation used to generate equivalent atoms: #1, $-x+1$, $-y+1$, $-z+1$; #2, $-x+2$, $-y$, $-z$; #3, $-x+1$, $-y+1$, $-z$.

Cu(1) and Cu(2) both take an elongated octahedron geometry, with four nitrogen atoms from two tn ligands at the equatorial positions (Cu(1)–N(1), 2.0508(18); Cu(1)–N(2), 2.0232(18); Cu(2)–N(3), 2.0283(19); Cu(2)–N(4), 2.0215(19) Å) and two nitrogen atoms from bridging cyanides of $[\text{Co(CN)}_6]^{3-}$ at the axial positions (Cu(1)–N(5), 2.587(2); Cu(2)–N(6), 2.637(2) Å). The Jahn–Teller effect is obvious. The complex cation $[\text{Cu(tn)}_2]^{2+}$ takes a chair geometry. The planes defined by the Cu(1), N(1), N(2),

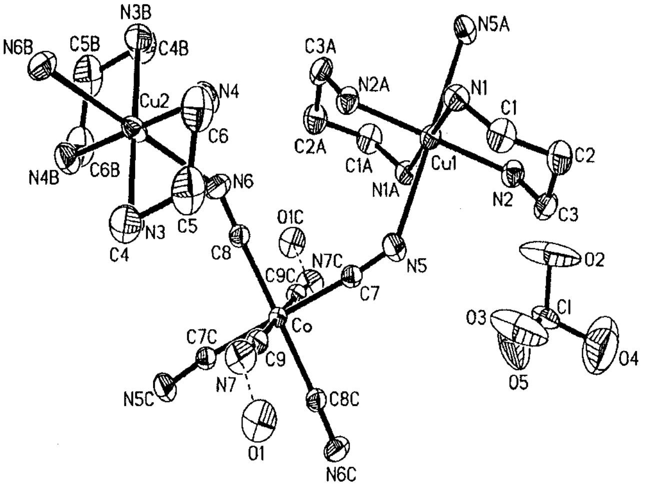


FIGURE 1 ORTEP view of the Cu_2Co unit of **1**.

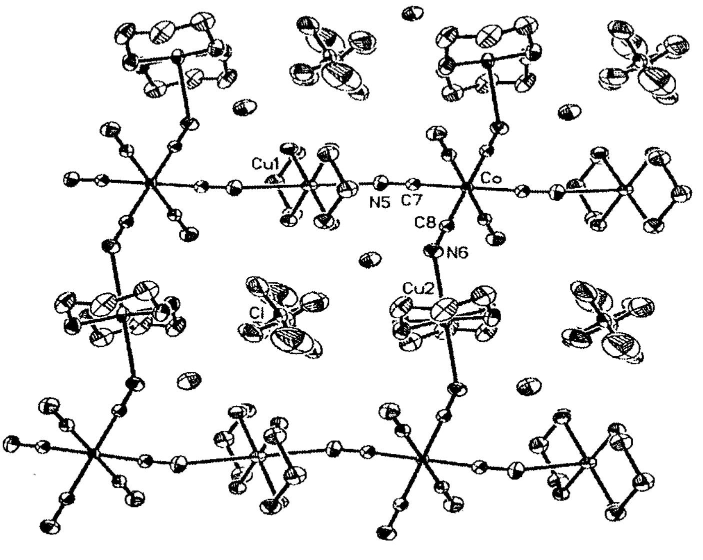


FIGURE 2 View along *c* axis of 2D network showing the $Cu_4^{II}Co_4^{III}$ squares of **1**.

N(1)A and N(2)A atoms are perfectly planar. C(1), C(2) and C(3) are 0.7571, 0.4564 and 0.8562 Å, respectively, below the mean plane, while C(1)A, C(2)A and C(3)A are above the mean plane. Figure 2 shows a two-dimensional network composed of the Cu_4Co_4 squares with the size 10.172(1) × 10.599(1) Å. Perchlorate ion resides in each square and takes two positions with the occupancy factor 0.5 on the basis of the peak heights.

The two-dimensional sheets align along the *c* axis to form the crystal (Fig. 3). The intersheet Co–Co separation along *c* is 8.808(5) Å. The nearest intersheet Co–Cu(1) and Co–Cu(2) separations are 9.320(4) and 7.842(4) Å, respectively. Thus there are no obvious intersheet Co–Co and Co–Cu interactions. Water molecules exist between

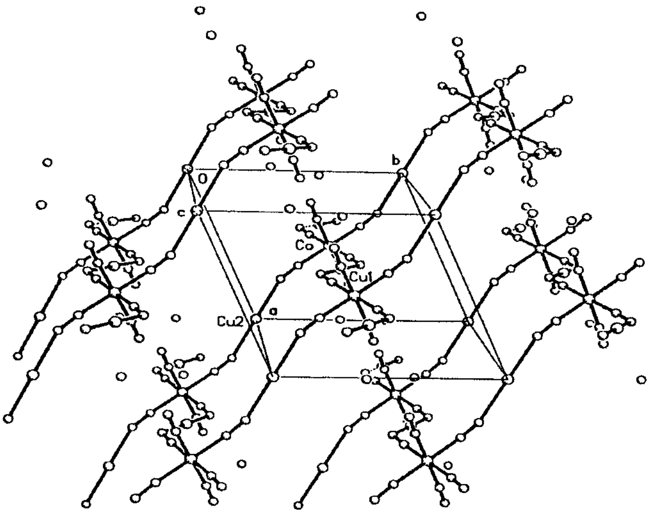


FIGURE 3 The packing mode of two-dimensional sheets of **1**.

2D sheets and form hydrogen-bonds with N(7) and N(4) [O(1)–N(7), 2.864(3); O(1)–N(4), 3.048(3) Å]. This two-dimensional network is similar to the reported two-dimensional network $[Ni(Pn)_2]_2[Fe(CN)_6]ClO_4 \cdot 2H_2O$ (Pn = 1,2-diaminopropane) [43]. $[Cu(dien)]_3[Fe(CN)_6]_2 \cdot 6H_2O$ (dien = diethylenetriamine) has a step-shaped two-dimensional network [35]; $[\{Cu(dien)\}_2\{Cr(CN)_6\}]_n$ $[Cu(dien)(H_2O)Cr(CN)_6]_n \cdot 4nH_2O$ [36] and $[\{(Cu(dien))_2Co(CN)_6\}_n]$ $[Cu(dien)(H_2O)Co(CN)_6]_n \cdot 5H_2O$ [40] have one-dimensional cationic chains and a binuclear anion; $[Cu(edma)]_3Cr(CN)_6]$ [36] (edma = ethylenediaminemonoacetate) is a tetranuclear complex and $[Fe\{(CN)Cu(tpa)\}_6]ClO]_4]_8 \cdot 3H_2O$ [37] (tpa = tris(2-pyridylmethyl)amine) is a heptanuclear complex; $K[Cu(cyclam)][Fe(CN)_6] \cdot 4H_2O$ (cyclam = 1,4,8,11-tetraazacyclotetradecane) has a one-dimensional chain [39].

Infrared Spectrum

An IR Spectrum of complex **1** shows the following bands 3561 s, 3329 vs, 3271 s, 3163 s, 2969 s, 2942 s, 2891 s, 2788 w, 2126 s, 2117 s, 2077 w, 1640 m, 1615 s, 1589 s, 1460 w, 1443 m, 1404 m, 1323 w, 1287 s, 1252 w, 1182 s, 1094 vs, 1061 w, 1027 s, 912 m, 898 m, 814 w, 673 s, 628 s, 559 w, 491 m, 418 cm^{-1}. A strong single peak at 3561 cm^{-1} belongs to water. The characteristic IR active bands for ν(NH) [44] of the NH_2 groups appeared at 3329, 3271 and 3163 cm^{-1}. The two sharp bands at 2126 and 2117 cm^{-1} are assigned to CN stretching vibrations of bridging and terminal cyanide groups, respectively [32]. The band at 1094 cm^{-1} is attributed to ClO_4^- [45].

Electronic Spectrum

The aqueous solution electronic spectrum of complex **1** shows two broad peaks at 251 and 574 nm. The high-energy peak is assigned as a *d–d* transition of copper(II) ions and the low-energy absorption is assigned to cobalt(III)–copper(II) charge transfer [44].

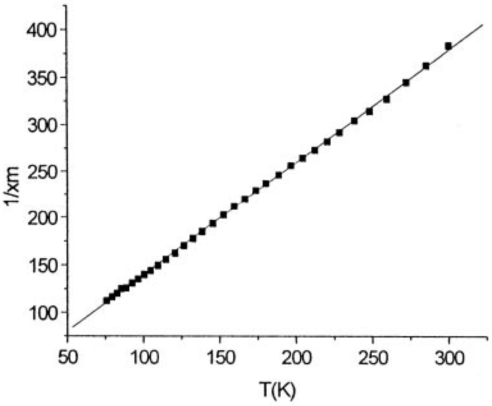


FIGURE 4 Plot of $1/\chi_m$ *vs.* T for the compound (**1**).

Electronic Spin Resonance Spectrum

The solid state ESR spectrum of complex **1** shows a symmetric feature with $g_{\|} = 2.176$ and $g_{\perp} = 2.059$. The ESR spectrum of the complex is typical for copper(II), and the data suggest elongated octahedral geometry with $g_{\|} > g_{\perp} > g_e$, and the unpaired electron occupies the $d_{x^2-y^2}$ orbital [44], which is consistent with the crystal structure.

Magnetic Properties

The magnetic moment of complex **1** at 300 K is 2.50 B.M. in good agreement with the spin-only value 2.45 B.M. for two Cu(II) ($S = 1/2$) and one diamagnetic $S = 0$ spins. No magnetic interaction is presumed within the two-dimensional network because of the diamagnetic nature of Co(III) [32]. The magnetic moment exhibits continuous slight decrease with the decreasing temperature to 2.32 B.M. at 76 K. This may be attributed to a weak antiferromagnetic interaction. Variable-temperature magnetic susceptibility studies in the temperature range 75 ~ 300 K, showed that compound (**1**) obeys the Curie–Weiss law, $\chi_m = C/(T - \theta)$, with values of $\theta = -16.89$ K, $C = 0.8361$ emu K mol^{-1} (Fig. 4) [32,46]. It indicates that the title compound is a "Curie–Weiss" paramagnetic compound.

Acknowledgments

This work was supported by the National Nature Science Foundation of China for Key Project No. 29823001 and Funds of the State Key Laboratory of Structure Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Science.

Supplementary Material

Crystallographic data for structure **1** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-139265.

References

[1] K. Biradha, D. Dennis, V.A. MacKinnon, C. Seward and M.J. Zaworotko (1999). In: G. Tsoucaris (Ed.), *Current challenges on large scale supramolecular assemblies.* NATO Advanced Research Workshop, pp. 115–132. Kluwer Academic Publishers, Dordrecht, The Netherlands.
[2] D.M.L. Goodgame, D.A. Grachvogel and D.J. Williams (1999). *Angew. Chem. Int. Ed. Engl.*, **38**, 153.
[3] T.M. Reineke, M. Eddaoudi, M. Fehr, D. Kelley and O.M. Yaghi (1999). *J. Am. Chem. Soc.*, **121**, 1651.
[4] H. Gudbjartson, K. Biradha, K.M. Poirier and M. Zaworotko (1999). *J. Am. Chem. Soc.*, **121**, 2599.
[5] J. Heo, S. Kim, D. Whang and K. Kim (1999). *Angew. Chem. Int. Ed. Engl.*, **38**, 641.
[6] B.F. Abrahams, S.R. Batten, M.J. Grannas, H. Hamit, B.F. Hoskins and R. Robson (1999). *Angew. Chem. Int. Ed. Engl.*, **38**, 1475.
[7] S.S.-Y. Chui, S.M.-F. Lo, J.P.H. Charmant, A.G. Orpen and I.D. Williams (1999). *Science*, **283**, 1148.
[8] S.R. Batten and R. Robson (1998). *Angew. Chem. Int. Ed. Engl.*, **37**, 1460.
[9] O.M. Yaghi, H. Li, D. Davis, D. Richardson and T.L. Groy (1998). *Acc. Chem. Res.*, **31**, 474.
[10] L.R. MacGillivary, R.H. Groeneman and J.L. Atwood (1998). *J. Am. Chem. Soc.*, **120**, 2676.
[11] H. Li, M. Eddaoudi, T.L. Groy and O.M. Yaghi (1998). *J. Am. Chem. Soc.*, **120**, 8571.
[12] H. Li, C.E. Davis, T.L. Groy and O.M. Yaghi (1998). *J. Am. Chem. Soc.*, **120** 2186.
[13] S. Kitagawa and M. Kondo (1998). *Bull. Chem. Soc. Japan.*, **71**, 1739.
[14] G.A. Bowmaker, B.J. Kennedy and J.C. Reid (1998). *Inorg. Chem.*, **37**, 3968.
[15] M.A. Omary, T.R.Webb, Z. Assefa, G.E. Shankle and H.H. Patterson (1998). *Inorg. Chem.*, **37**, 1380.
[16] A.M. Ibrahim, E. Siebel and R.D. Fisher (1998). *Inorg. Chem.*, **37**, 3521.
[17] D.J. Cromer (1957). *J. Phys. Chem.*, **61**, 1388.
[18] D.J. Chesnet and J. Zubieta (1998). *Chem. Commun.*, 1707.
[19] T. Iwamoto (1996). In: D.D. MacNiicol, F. Toda, and R. Bishop (Eds.), *Supramolecular Chemistry in Cyanometallate System in Comprehensive Supramolecular Chemistry*, Vol. 6, Ch. 19, pp. 643–690. Pergamon, Oxford.
[20] H. Yuge, Y. Noda and T. Iwamoto (1996). *Inorg. Chem.*, **35**, 1842.
[21] T. Kitazawa (1999). *Chem. Commun.*, **891**.
[22] K.-M. Park, R. Kuroda and T. Iwamoto (1993). *Angew. Chem. Int. Ed. Engl.*, **32**, 884.
[23] T. Yuge and T. Iwamoto (1994). *J. Chem. Soc., Dalton Trans.*, 1237.
[24] D.W. Knoeppel and S.G. Shore (1996). *Inorg. Chem.*, **35**, 1747.
[25] I. Muga, J.M. Gutierrez-Zorrilla, A. Luque, P. Roman and F. Loret (1997). *Inorg. Chem.*, **36**, 743.
[26] D.W. Knoeppel, J. Lin, E.A. Meyers and S.G. Shore (1998). *Inorg. Chem.*, **37**, 4828.
[27] T. Niu, J. Lu, X. Wang, J.D. Korp and A. Jacobson (1998). *Inorg. Chem.*, **37**, 5324.
[28] H. Miyasaka, H. Okawa, A. Miyazali and T. Enoki (1998). *Inorg. Chem.*, **37**, 4878.
[29] N. Re, R. Crescenzi, C. Floriani, H. Miyasaka and N. Matsumto (1998). *Inorg. Chem.* **37**, 2717
[30] M. Ohba, N. Usuki, N. Fukita and H. Okawa (1999). *Angew. Chem. Int. Ed. Engl.*, **38**, 1795.
[31] N. Fukita, M. Ohba, H. Okawa, K. Matsuda and H. Iwamura (1998). *Inorg. Chem.*, **37**, 842.
[32] M. Ohba, N. Usuki, N. Fukita and H. Okawa (1998). *Inorg. Chem.*, **37**, 3349.
[33] M. Ohba, N. Maruono, H. Okawa, T. Enoki and J.-M. Latour (1994). *J. Am. Chem.*, **116**, 11566.
[34] M. Ohba, N. Fukita and H. Okawa (1997). *J. Chem. Soc., Dalton Trans.*, 1733.
[35] H.-Z. Kou, D.-Z. Liao, P. Cheng, Z.-H. Jiang, S.-p. Yan, G.-L. Wang, X.-K. Yao and H.-G. Wang (1997). *J. Chem. Soc., Dalton Trans.*, 1503.
[36] D.G. Fu, J. Chen, X.S. Tan, L.J. Jiang, S.W. Zhang, P.J. Zheng and W.X. Tang (1997). *Inrog. Chem.*, **36**, 220.
[37] R.J. Parker, D.C. Hockless, B. Moubaraki, K.S. Murray and L. Spiccia (1996). *Chem. Commun.*, 2789.
[38] J.Z. Zou, Z. Xu, X.Y. Huang, W.L. Zhang, X.P. Shen and Y.P. Yu (1997). *J. Coord. Chem.*, **42**, 55.
[39] E. Clacio, J.M. Dominguez-Vera, M. Ghazi, R. Kivekas, J.M. Moreno and A. Pajunen (2000). *J. Chem. Soc., Dalton Trans.*, **505**.
[40] M. Ferbinteanu, S. Tanase, M. Andruh, Y. journaux, F. Cimpoesu, I. Strenger and E. Riviere (1999). *Polyhedron*, 3019.
[41] J.H. Bigelow (1946). *Inorg. Syn.*, **2**, 225.
[42] G.M. Sheldrick (1997). *SHELX-97.* University of Göttingen, Germany.
[43] M. Ohba, H. Okawa, T. Ito and A. Ohto (1995). *J. Chem. Soc., Chem. Commun.*, **1545**.
[44] N. Mondal, M.K. Saha, S. Mitra, V. Gramlich and M.S.E. Fallah (2000). *Polyhedron*, **19**, 1935.
[45] B.J. Hathaway and A.E. Underhill (1961). *J. Chem. Soc.*, **3091**.
[46] B. Yan, H.-D. Wang and Z.-D. Chen (2000). *Inorg. Chem. Commun.*, **3**, 653.