A New 1D Coordination Polymer Constructed From a Dissymmetrical Oxamidate Ligand: Structure and Magnetic Properties

Bao Lin Liu, Juan Dang, and Ruo Jie Tao

Institute of Molecular and Crystal Engineering, College of Chemistry and Chemical Engineering, Henan University, Kaifeng 475001, P. R. China

Reprint requests to Prof. Ruo Jie Tao. Fax: +86-378-3881960. E-mail: rjtao@henu.edu.cn

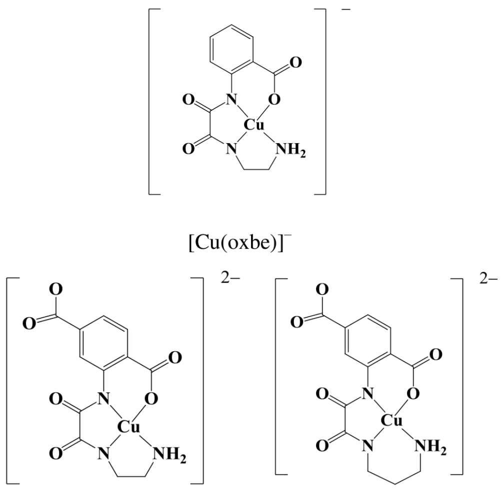
Z. Naturforsch. **2011**, *66b,* 275 – 278; received November 15, 2011

A new complex $\{\{[Cu(oxbe)]Cu(tmen)\}_2{\cdot}2ClO_4\}_n$ (H_3oxbe = *N*-benzoato-*N*′-(2-aminoethyl)-oxamido, tmen = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) has been synthesized and characterized by IR spectroscopy, elemental analysis, and single-crystal X-ray diffraction, and by its magnetic properties. It crystallizes in the triclinic system, space group $P\bar{1}$, with a = 1.364(2), b = 1.379(2), c = 1.516(3) nm, α = 64.402(3), β = 66.098(3), γ = 89.604(3)°, V = 2.301(7) nm^3, Z = 2, $D_{\text{calcd.}}$ = 1.71 g cm^{-3}. The structure of **1** consists of tetranuclear units. Through *syn-anti* carboxylate bridges, the complex features a chain structure.

Key words: Oxamidate Ligand, Crystal Structure, Magnetic Propertie

Introduction

The field of molecular magnetism has developed rapidly in the past two decades. One of the challenges in the area of molecular and supramolecular magnetism is to design materials exhibiting expected magnetic properties [1–4]. To obtain homometallic or heterometallic complexes, a successful strategy is the "complex as ligand" approach, *i. e.*, utilizing a metal complex as a ligand to coordinate an appropriate additional metal ion [5–9]. Along this line, the use of mononuclear oxamidato complexes as ligands toward other metal ions constitutes a step further to obtain high-nuclearity metal complexes [10–12]. Up to date, a number of symmetrical oxamidato complexes have been reported [13–15]. However, owing to synthetic difficulties only few dissymmetrical oxamidato coordination polymers have been published [16–18]. With these facts in mind, we have recently described three mononuclear copper(II) complexes $[CuL]^{n-}$ with the bridging ligands L = *N*-benzoate-*N*′-(2-aminoethyl)oxamido (oxbe) and 2-(2-(2-aminoethylamino)-2-oxoacetamido)terephthalic acid (aeoe) and its derivative *N*-(2-aminoterephthalic acid)-*N*′-(1,3-propanediamine)oxamidate (aeop) (Fig. 1) as precursors for the preparation of both homo- and heterometallic complexes [19–22]. Here we report on the synthesis and the structure of a new 1D coordination polymer $\{\{[Cu(oxbe)]Cu(tmen)\}_2{\cdot}2ClO_4\}_n$, as well as on its magnetic properties.



$[Cu(oxbe)]^-$

$[Cu(aeoe)]^{2-}$ $[Cu(aeop)]^{2-}$

Fig. 1. Mononuclear copper(II) complexes.

Experimental Section

Materials

The copper precursor ($Na[Cu(oxbe)]{\cdot}1.5H_2O$) was prepared as described in the literature [22]. $Cu(ClO_4)_2{\cdot}6H_2O$ was prepared as an in-house reagent. Other chemicals were of commercial reagent grade and used without further purification.

Caution! Perchlorates are potentially explosive, thus only a small amount of material should be prepared and handled with care.

0932–0776 / 11 / 0300–0275 $ 06.00 © 2011 Verlag der Zeitschrift für Naturforschung, Tübingen · http://znaturforsch.com

Table 1. Crystal data and parameters pertinent to data collection and structure refinement for complex **1**.

Empirical formula	$C_{34}H_{48}N_{10}O_{16}Cu_4Cl_2$
Formula weight	1181.92
Crystal system	triclinic
Space group	$P\bar{1}$
a, Å	13.641(2)
b, Å	13.788(2)
c, Å	15.156(3)
α, deg	64.402(3)
β, deg	66.098(3)
γ, deg	89.604(3)
V, Å^3	2301.0(7)
Z	2
$D_{\text{calcd.}}$, g cm^{-3}	1.71
μ(MoK_α), mm^{-1}	2.0
T, K	293(2)
Index ranges	$-15 \le h \le 16$, $-14 \le k \le 16$, $-18 \le l \le 17$
Total / independ. refl. / R_{int}	11805 / 7921 / 0.0535
Ref. parameters	603
$R1$ / $wR2$ [$I \ge 2\,\sigma(I)$]^a	0.0772 / 0.1981
$R1$ / $wR2$ (all data)^a	0.1164 / 0.2135
Goodness-of-fit^b	1.063
$\Delta\rho_{\text{fin}}$ (max / min), e Å^{-3}	1.44 / −0.82

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{1/2}$, $w = [\sigma^2(F_o{}^2)+(AP)^2+BP]^{-1}$, where $P = (\text{Max}(F_o{}^2, 0)+2F_c{}^2)/3$; [b] $\text{GoF} = [\Sigma w(F_o{}^2 - F_c{}^2)^2/(n_{\text{obs}} - n_{\text{param}})]^{1/2}$.

Table 2. Selected bond lengths (Å) and angles (deg) for complex **1**^{a}.

Cu1–O1	1.894(6)	Cu1–N2	1.914(7)
Cu1–N1	1.965(7)	Cu1–N3	2.017(8)
Cu2–O4	1.948(6)	Cu2–O3	1.975(6)
Cu2–N4	1.996(7)	Cu2–N5	2.022(7)
Cu2–O2$^{\#1}$	2.293(6)	Cu3–O5	1.883(6)
Cu3–N7	1.906(7)	Cu3–N6	1.973(7)
Cu3–N8	2.031(8)	Cu4–O8	1.950(6)
Cu4–N9	1.997(8)	Cu4–O7	1.994(5)
Cu4–N10	2.037(7)	Cu4–O6$^{\#2}$	2.270(6)
O1–Cu1–N2	179.0(3)	O1–Cu1–N1	94.3(3)
N2–Cu1–N1	84.8(3)	O1–Cu1–N3	98.7(3)
N2–Cu1–N3	82.2(3)	N1–Cu1–N3	167.0(3)
O4–Cu2–O3	84.5(3)	O4–Cu2–N4	169.5(3)
O3–Cu2–N4	93.4(3)	O4–Cu2–N5	92.3(3)
O3–Cu2–N5	170.3(3)	N4–Cu2–N5	88.0(3)
O4–Cu2–O2$^{\#1}$	95.4(3)	O3–Cu2–O2$^{\#1}$	92.1(2)
N4–Cu2–O2$^{\#1}$	95.0(3)	N5–Cu2–O2$^{\#1}$	97.4(3)
N7–Cu3–N6	84.9(3)	O5–Cu3–N8	98.3(3)
N7–Cu3–N8	82.4(3)	N6–Cu3–N8	163.0(3)
O5–Cu3–N7	178.8(3)	O5–Cu3–N6	94.7(3)
O8–Cu4–N9	170.6(3)	O8–Cu4–O7	84.1(3)
N9–Cu4–O7	93.6(3)	O8–Cu4–N10	92.4(3)
N9–Cu4–N10	88.3(4)	O7–Cu4–N10	170.0(3)
O8–Cu4–O6$^{\#2}$	95.0(3)	N9–Cu4–O6$^{\#2}$	94.1(3)
O7–Cu4–O6$^{\#2}$	91.5(2)	N10–Cu4–O6$^{\#2}$	98.1(3)

[a] Symmetry codes: $^{\#1}$ $-x+2, -y+1, -z+1$; $^{\#2}$ $-x+1, -y+1, -z+1$.

Synthesis of the complex {{[Cu(oxbe)]Cu(tmen)}$_2$·2ClO$_4$}$_n$ (1)

1 mmol (0.362 g) of Na[Cu(oxbe)]·1.5H_2O was dissolved in 15 mL of water, and 20 mL of an aqueous solution containing 1 mmol (0.116 g) of tmen and 1 mmol (0.371 g) of Cu(ClO$_4$)·6H_2O was added under constant stirring. The resulting violet solution was filtered, and finally well-shaped dark-green single crystals suitable for X-ray crystal analysis were obtained by slow evaporation of the solution (yield 69 %). Anal. for $C_{34}H_{52}N_{10}O_{16}Cu_4Cl_2$: calcd. C 34.62, H 4.37, N 11.89; found C 34.55, H 4.43, N 11.85 %. – IR (KBr): $\nu_{C=O}$ 1668 cm^{-1}.

Physical measurements

Elemental analyses for carbon, hydrogen and nitrogen were performed on a Perkin-Elmer 2400II elemental analyzer. The infrared spectra were recorded on an Avatar-360 spectrometer using KBr pellets in the range of 400–4000 cm^{-1}. Variable temperature magnetic susceptibility data were obtained on microcrystalline samples from 5 to 300 K in a magnetic field of 10 kG, using a Quantum Design MPMS-7 SQUID magnetometer. Diamagnetic corrections were made with Pascal parameters for all constituent atoms.

X-Ray analysis

A single crystal was selected for data collection of compound **1** and mounted on a Bruker Smart APEX diffractometer with a CCD detector using graphite-monochromatized MoK_α radiation (λ = 0.71073 Å). Lorentz and polarization corrections were applied, and an absorption correction was performed using the program SADABS [23]. The crystal structure was solved using SHELXTL and refined using full matrix least-squares techniques [24]. The the hydrogen atoms were positioned geometrically and included in the final cycles of refinement in a riding model along with the attached carbon atoms. A summary of the crystallographic data is given in Table 1. Selected bond lengths and angles are given in Table 2.

CCDC 800752 contains the supplementary crystallographic data for **1**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Results and Discussion

IR spectra

The IR spectra of the ligand H$_3$oxbe and the mononuclear complex Na[Cu(oxbe)]·1.5H_2O have been reported [22]. The strong $\nu_{C=O}$ (oxamido) band at 1649 cm^{-1} in the spectrum of the mononuclear precursor is replaced by a strong band at 1668 cm^{-1} for complex **1**. Such a hypsochromic shift indicates that the oxamidate C=O group is coordinated to the copper ion. In addition, the ν(NH$_2$) vibration at *ca.* 3307 cm^{-1}

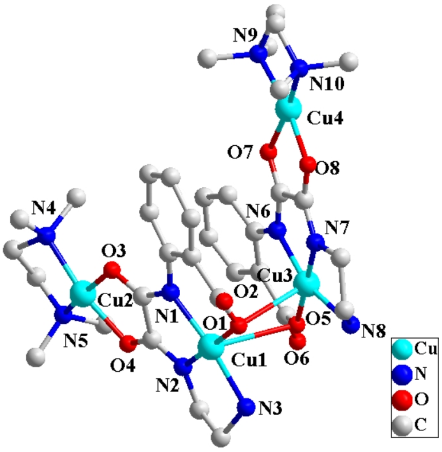


Fig. 2. Tetranuclear unit of complex **1**. Hydrogen atoms and perchlorate anions are omitted for clarity.

for H_3oxbe is still present for complex **1** with a small shift to 3315 cm^{-1} [22]. Such a blue shift indicates that the nitrogen atom of -NH_2 is coordinated to the copper ion. A broad strong band at *ca.* 1119 cm^{-1} is characteristic of a perchlorate ion.

Description of the crystal structure

The X-ray single-crystal structure analysis has revealed that complex **1** crystallizes in the space group $P\bar{1}$. As shown in Fig. 2, complex **1** consists of a tetranuclear unit and two perchlorate anions. In the tetranuclear unit, the four Cu(II) ions are all in a distorted square-pyramidal coordination. The Cu1 and Cu3 ions are coordinated by one oxygen atom and three nitrogen atoms from oxamidate bridges. The axial positions are filled with one oxygen atom from other oxamidate bridges. The square-planar environments of Cu2 and Cu4 are formed by two nitrogen atoms from the tmen ligand and two oxygen atoms from the oxamidate bridges. The apical position is occupied by another carboxylate oxygen atom with the Cu–O bond length 2.293(6) Å, which is comparable with the values found in another complex reported by us [22]. The Cu–N distances are distributed in the range 1.906(7) – 2.031(8) Å, and the Cu–O distances are in the range 1.883(6) – 2.293(6) Å, similar to the values reported in the literature [22]. The Cu$\cdots$Cu distance through the oxamido bridge is 5.202(2) Å.

These tetranuclear units are linked by coordinative bonds between carboxylic oxygen atoms and Cu ions to form a new 1D coordination polymer, as illustrated in Fig. 3.

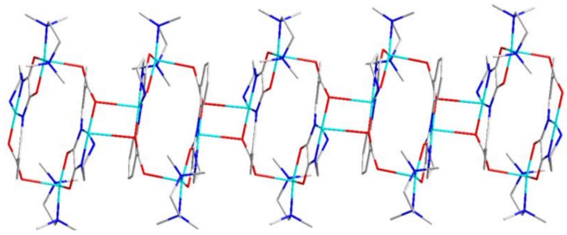


Fig. 3. Visualization of the new chain structure of complex **1**. Hydrogen atoms and perchlorate anions are omitted for clarity.

Magnetic properties

The magnetic susceptibility of the complex was measured in the range of 5 – 300 K. The curves of χ_M and μ_{eff} *versus* T are shown in Fig. 4. At room temperature, the μ_{eff} value of complex **1** is 2.38 μ_B, which is slightly lower than that expected for uncoupled binuclear ions (2.45 μ_B). Upon cooling, the μ_{eff} value of the complex decreases regularly, approaching a minimum around 5 K with μ_{eff} = 0.89 μ_B, which possibly is due to antiferromagnetic interactions between the tetranuclear units.

The magnetic analysis was carried out by using the theoretical expression of the magnetic susceptibility deduced from the spin Hamiltonian $H = -2J\hat{S}_{Cu1}\hat{S}_{Cu2}$. The expression of the magnetic susceptibility for a Cu(II)-Cu(II) binuclear unit is $\chi_M = \frac{2Ng^2\beta^2}{KT}\left[\frac{1}{3+\exp(-2J/KT)}\right] + N\alpha,\ N\alpha = 120\times10^{-6}$ cm^3 mol^{-1}.

The molecular field approximation (zj') to deal with magnetic exchange interactions between binuclear units gives the expression $\chi_M{}' = \frac{\chi_M}{1-(2zj'/Ng^2\beta^2)\chi_M}$.

In order to overcome the paramagnetic impurities, we have introduced ρ to take into account the

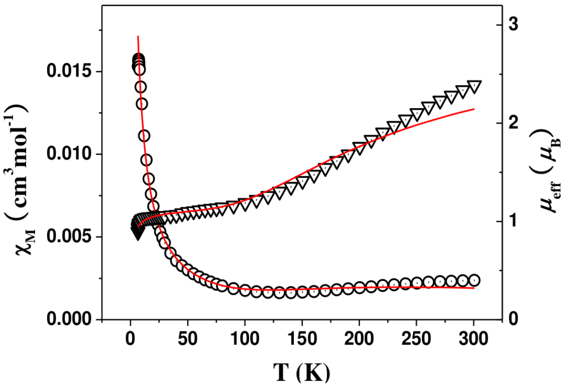


Fig. 4. χ_M and μ_{eff} *versus* T plots for complex **1**.

presence of such impurities. Thus, the expression of the magnetic susceptibility for this system becomes $\chi_M{}' = \chi_M(1-\rho) + \frac{Ng^2\beta^2}{3KT}\sum S_i(S_i+1)\rho$, where J is the exchange integral between two copper ions in the binuclear moiety and N_α is the temperature-independent paramagnetism. The best-fit parameters are $J = -170.8$ cm^{-1}, $g = 2.24$, $\rho = 0.08$, and z $j' = -6.3$ cm^{-1}. The agreement factor $R = \Sigma(\chi_{\mathrm{obsd}} - \chi_{\mathrm{calcd}})^2/\Sigma\chi_{\mathrm{obsd}}{}^2 = 2.49 \times 10^{-3}$ is satisfactory as seen in Fig. 4. The negative J and zj' values suggest that the interactions between Cu(II) ions and between binuclear systems are all antiferromagnetic. To our knowledge, no formula is available in the literature to reproduce the magnetic susceptibility of such a complex system. Therefore, its magnetic properties are interpreted only tentatively. The susceptibility data show a slight unexplained deviation in the high-temperature part (250 – 300 K).

Acknowledgement

We acknowledge the generous financial support of the Natural Science Foundation of Henan Province (No. 092300410031).

---

[1] O. Kahn, *Angew. Chem.* **1985**, *97*, 837 – 853; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 834 – 850.

[2] J. S. Miller, A. J. Epstein, *Angew. Chem.* **1994**, *106*, 399 – 432; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 385 – 415.

[3] S. Ferlay, T. Mallah, R. Ouahés, P. Veillet, M. Verdaguer, *Nature* **1995**, *378*, 701 – 703.

[4] a) W. R. Entley, G. S. Girolami, *Science* **1995**, *268*, 397 – 400; b) H. Iwamura, K. Inoue, N. Koga, *New J. Chem.* **1998**, *22*, 201 – 210; c) O. Kahn, J. Larionova, L. Ouahab, *Chem. Commun.* **1999**, 945 – 952.

[5] R. E. P. Winpenny, *Chem. Soc. Rev.* **1998**, *27*, 447 – 452

[6] O. Kahn, *Acc. Chem. Res.* **2000**, *33*, 647 – 657

[7] B. Q. Ma, S. Gao, G. Su, G. X. Xu, *Angew. Chem.* **2001**, *113*, 448 – 451; *Angew. Chem. Int. Ed.* **2001**, *40*, 434 – 437.

[8] J. K. Tang, Y. Z. Li, Q. L. Wang, E. Q. Gao, D. Z. Liao, Z. H. Jiang, *Inorg. Chem.* **2002**, *41*, 2188 – 2192.

[9] L. Zhang, S. B.Wang, G. M. Yang, J. K. Tang, D. Z. Liao, Z. H. Jiang, S. P. Yan, P. Cheng, *Inorg. Chem.* **2003**, *42*, 1462 – 1466.

[10] L. N. Zhu, N. Xu, W. Zhang, D. Z. Liao, K. Yoshimura, K. Mibu, Z. H. Jiang, S. P. Yan, P. Cheng, *Inorg. Chem.* **2007**, *47*, 1297 – 1304.

[11] Y. Q Sun, L. L Fan, D. Z. Gao, Q. LWang, M. Du, D. Z. Liao, C. X. Zhang, *Dalton Trans.* **2010**, *39*, 9654 – 9661.

[12] E. Pardo, C. Train, R. Lescouezec, K. Boubekeur, E. Ruiz, F. Lloret, M. Verdaguer, *Dalton Trans.* **2010**, *39*, 4951 – 4958.

[13] E. Pardo, E. Pardo, L. Morales-Osoris, M. Julve, F. Lloret, J. Cano, R. Ruiz-García, J. Pasán, C. Ruiz-Pérez, X. Ottenwaelder, Y. Journaux, *Inorg. Chem.* **2004**, *43*, 7594 – 7596.

[14] J. Tercero, C. Diaz, J. Ribas, M. Maestro, J. Mahía, H. Stoeckli-Evans, *Inorg. Chem.* **2003**, *42*, 3366 – 3373.

[15] J. K. Tang, Y. Ou-Yang, H. B. Zhou, Y. Z. Li, D. Z. Liao, Z. H. Jiang, S. P. Yan, P. Cheng, *Crystal Growth & Design* **2005**, *5*, 813 – 819.

[16] J. Larionova, S. A. Chavan, J. V. Yakhmi, A. G. Frøystein, J. Sletten, C. Sourisseau, O. Kahn, *Inorg. Chem.* **1997**, *36*, 6374 – 6381.

[17] Y. Pei, K. Nakatani, O. Kahn, J. Sletten, J. P. Renard, *Inorg. Chem.* **1989**, *28*, 3170 – 3175.

[18] Y. Pei, O. Kahn, K. Nakatani, E. Codjovi, C. Mathoniere, J. Sletten, *J. Am. Chem. Soc.* **1991**, *113*, 6558 – 6564.

[19] W. J. Lou, S. Q. Zang, Q. L. Wang, R. J. Tao, *Inorg. Chim. Acta* **2009**, *362*, 3005 – 3012.

[20] W. J. Lou, S. Q. Zang, W. Zhang, Q. L. Wang, R. J. Tao, *J. Coord. Chem.* **2008**, *61*, 3642 – 3650.

[21] W. J. Lou, Y. Zhang, H. Cui, B. L. Liu, R. J. Tao, *Z. Naturforsch.* **2010**, *65b*, 607 – 610.

[22] S. Q. Zang, R. J. Tao, Q. L. Wang, N. H. Hu, Y. X. Cheng, J. Y. Niu, D. Z. Liao, *Inorg. Chem.* **2003**, *42*, 761 – 766.

[23] G. M. Sheldrick, SADABS, Program for Empirical Absorption Correction of Area Detector Data, University of Göttingen, Göttingen (Germany) **2002**. See also: R. H. Blessing, *Acta Crystallogr.* **1995**, *A51*, 33 – 38.

[24] G. M. Sheldrick, SHELXTL (version 5.1), Bruker Analytical X-ray Systems, Inc., Madison, Wisconsin (USA), **1997**. See also: G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112 – 122.