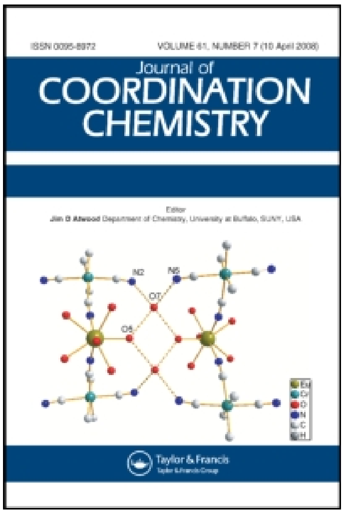

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

SYNTHESIS AND CRYSTAL STRUCTURE OF A BINUCLEAR COPPER (II) COMPLEX BRIDGED BY OXAMIDATO, Cu_2(μ-*CIS*-OXPN)(PHEN)$(NO_3)_2$

Jingjing Nie[a]; Cungen Zhang[b]; Duanjun Xu[a]
[a] Department of Chemistry, Zhejiang University, Hangzhou, P.R. China [b] Department of Applied Chemistry, Jiaotong University, Shanghai, P.R. China

To cite this Article Nie, Jingjing , Zhang, Cungen and Xu, Duanjun(2000) 'SYNTHESIS AND CRYSTAL STRUCTURE OF A BINUCLEAR COPPER (II) COMPLEX BRIDGED BY OXAMIDATO, Cu_2(μ-*CIS*-OXPN)(PHEN)$(NO_3)_2$', Journal of Coordination Chemistry, 52: 2, 151 — 157
To link to this Article: DOI: 10.1080/00958970008022583
URL: http://dx.doi.org/10.1080/00958970008022583

J. Coord. Chem., 2000, Vol. 52, pp. 151-157
Reprints available directly from the publisher
Photocopying permitted by license only

SYNTHESIS AND CRYSTAL STRUCTURE OF A BINUCLEAR COPPER (II) COMPLEX BRIDGED BY OXAMIDATO, $Cu_2(\mu\text{-}CIS\text{-}OXPN)(PHEN)(NO_3)_2$

JINGJING NIE[a], CUNGEN ZHANG[b] and DUANJUN XU[a,]*

[a]*Department of Chemistry, Zhejiang University, Hangzhou 310027, P.R. China;* [b]*Department of Applied Chemistry, Jiaotong University, Shanghai 200240, P.R. China*

(Received 20 December 1999)

The complex $[Cu_2(\mu\text{-}cis\text{-oxpn})(phen)(NO_3)_2]$, where oxpn = *N,N′*-bis(3-aminopropyl) oxamidato and phen = 1,10-phenanthroline, has been synthesized and its crystal structure determined by X-ray methods. The structure consists of binuclear copper (II) molecules in which the Cu(II) atoms are bridged by oxamidato group in the *cis* conformation, the Cu—Cu distance being 5.205(10) Å. The coordination geometry around Cu (II) atoms is square pyramidal; the apex is occupied by a more weakly bonded O atom from a nitrate group. Electron delocalization is observed in the bridging oxamide moiety. The co-planarity of bridge ligand and basal plane around Cu (II) atoms may benefit spin super-exchange between two Cu (II) atoms. IR spectra of the binuclear complex are discussed.

Keywords: Copper (II); Binuclear; Crystal structure; Oxamide; Bridging ligand

INTRODUCTION

Recently, intense efforts have been concentrated on multinuclear transitional metal complexes bridged by some conjugated molecule because of possible unusual magnetic or electrical properties of those complexes [1, 2]. Oxamide is a well-known conjugated molecule and a suitable bridging ligand. Some multinuclear complexes bridged by oxamide or its derivatives have been synthesized and display stronger anti-ferromagnetic interactions

---

*Corresponding author.

[3–6]. The study of spin super-exchange interactions in multinuclear metal complexes has been engaged for several years in our group [7–9]. *N*, *N′*-bis(3-aminopropyl) oxamide (H_2oxpn) is a multidentate derivative of oxamide and we have reported a binuclear copper (II) complex bridged by oxpn [10]. Recently another binuclear copper (II) complex bridged by oxpn, [(μ-*cis*-oxpn)Cu_2(phen)$(NO_3)_2$] has been obtained. We present here its preparation and X-ray molecular structure to compare with the previous complex.

EXPERIMENTAL

Preparation

The mononuclear complex [Cu(oxpn)] was prepared according to the method reported previously [11]. The title complex, [Cu_2(μ-*cis*-oxpn)(phen)$(NO_3)_2$]·CH_3OH·$2H_2O$ was prepared in a manner similar to the complex [Cu_2(bipy)(μ-*cis*-oxpn)$(H_2O)_2$]·$2NO_3$ [12]. $Cu(NO_3)_2 \cdot 4H_2O$ [2.60 g, 10 mmol] was dissolved in 40 cm^3 of methanol, followed by addition of phenanthroline [1.80 g 10 mmol] with stirring. The mixture solution was heated at 60°C for 1 h, then 20 cm^3 of a methanol solution containing 2.64 g (10 mmol) of [Cu(oxpn)] was slowly added with stirring. After reaction at 60°C for 0.5 h, the resulting solution was filtered and slowly cooled to room temperature. Well-shaped single crystals were obtained from the filtrate by standing the solution for several days.

IR spectra of the title complex, together with the mononuclear complex of Cu(oxpn) for comparison, were recorded on a Perkin Elmer Paragon 1000 spectrophotometer with KBr discs.

Crystal Structure Determination

A dark-green single crystal of the title complex with approximate dimensions 0.20 × 0.26 × 0.32 mm was mounted on a Rigaku AFC7R diffractometer with graphite-monochromated MoKα radiation. Cell parameters were obtained from a least-squares refinement using the setting angles of 20 carefully centred reflections. The reflection data were collected up to $2\theta_{max}$ of 51° using the ω-2θ scan technique. Among 2874 reflections collected, 2734 were unique ($R_{int} = 0.014$). Usual Lp and experience absorption corrections were performed. The structure was solved by direct methods and expanded using Fourier technique.

Non-H atoms were refined anisotropically, except disordered O atoms of a nitrate group with isotropic thermal parameters, using 2283 observed reflections [$I > 2\sigma(I)$], and H atoms were included in structure factor calculations but not refined. All computations were performed using the SHELX93 program package [13]. Scattering factors used were taken from *International Tables for X-ray Crystallography* [14].

Crystal Data

$C_{20}H_{24}Cu_2N_8O_8 \cdot 2H_2O \cdot CH_3OH$, FW = 699.7, monoclinic, $C2/m$, $a = 14.834(2)$, $b = 11.241(2)$, $c = 17.142(2)$ Å, $\beta = 103.661(8)°$, $V = 2777.5(7)$ Å^3, $Z = 4$, $D_x = 1.67$ Mg·m^{-3}, μ(Mo-Kα) = 1.67 mm^{-1}, $R_1 = 0.047$, $wR_2 = 0.1368$, GOF = 1.074, No. of variable = 202, $(\Delta/\sigma)_{max} = 0.02$, $(\Delta\rho)_{max} = 1.59$ e Å^{-3}.

RESULTS AND DISCUSSION

Crystal Structure

Final atomic fractional coordinates and equivalent isotropic thermal parameters for non-H atoms are listed in Table I. Selected bond distances and angles are presented in Table II. The molecular structure of the title complex is illustrated in Figure 1. The complex crystallizes in space group $C2/m$ with four molecules in a unit cell. The complex molecule has C_s crystallographic symmetry, both Cu(1) and Cu(2) atoms being located on a mirror plane. Coordination geometry around the Cu(1) atom is square pyramidal with one O atom of a nitrate group in the apical site while two O atoms of an oxamidato and two N atoms of a phenanthroline form the basal plane. The Cu(1)—O(2) distance of 2.287(5) Å in the apical direction is 0.34 Å longer than the Cu(1)—O(1) distance of 1.948(3) Å in the basal plane. The Cu(1) atom is displaced by 0.221(2) Å out of the basal plane towards the apical position, as expected. Phenanthroline chelates to the Cu(1) atom with normal bond distances and angles. Geometry around the Cu(2) atom is also considered as square pyramidal with a nitrate group in the apical site, but the Cu(2)—O(6) distance (2.627(10) Å) in the apical direction is 0.34 Å longer than the corresponding distance (2.287(5) Å) in the apical direction of the Cu(1) atom and about 0.68 Å longer than Cu(1)—O(1) (1.948(3) Å) in the basal plane around the Cu(1) atom. The Cu(2) atom is displaced by 0.094(3) Å only out of the basal plane defined

TABLE I Atomic fractional coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [$Å^2 \times 10^3$] of non-H atoms. $U(eq)$ is defined as one third of the trace of the orthogonalized U_{ij} tensor

Atom	*x/a*	*y/b*	*z/c*	*U(eq)*
Cu(1)	1712(1)	0	−323(1)	34(1)
Cu(2)	2045(1)	0	−3278(1)	42(1)
O(1)	1863(2)	1177(2)	−1116(2)	40(1)
O(2)	3253(3)	0	309(3)	57(1)
O(3)	3067(4)	0	1521(3)	68(1)
O(4)	4431(4)	0	1315(4)	81(2)
O(5)	295(7)	541(9)	−3872(6)	87(3)
O(6)	−1129(6)	419(7)	−4349(5)	86(3)
O(7)	−112(10)	−1073(14)	−4131(8)	127(4)
O(8)	−1185(12)	−5000	−5248(10)	104(4)
O(9)	519(9)	−5000	−3169(8)	80(3)
Ow	−731(3)	−3297(5)	−4043(3)	90(1)
N(1)	1256(2)	1178(3)	362(2)	34(1)
N(2)	2010(2)	1167(3)	−2425(2)	40(1)
N(3)	2207(3)	1255(5)	−4072(2)	60(1)
N(4)	3587(4)	0	1051(3)	44(1)
N(5)	−398(4)	0	−4156(3)	52(1)
C(1)	1248(3)	2349(4)	327(2)	42(1)
C(2)	904(3)	3041(4)	866(3)	50(1)
C(3)	586(3)	2504(4)	1466(3)	47(1)
C(4)	600(3)	1271(4)	1528(2)	38(1)
C(5)	935(2)	632(3)	955(2)	32(1)
C(6)	292(3)	595(4)	2133(2)	44(1)
C(7)	1952(2)	672(4)	−1760(2)	34(1)
C(8)	1964(4)	2470(4)	−2473(3)	51(1)
C(9)	2406(4)	2944(5)	−3130(3)	62(1)
C(10)	1957(4)	2503(6)	−3953(3)	66(2)
C(11)	−362(19)	−5000	−5165(20)	128(10)
C(12)	−224(17)	−5000	−2888(15)	102(7)

by four N atoms of the oxpn ligand, in agreement with the longer Cu(2)—O(6) distance. These facts suggest there is only very weak coordination between Cu(2) and the O(6) atom of the nitrate group. Deprotonation of N atoms of oxpn is considered to be the main reason for different coordination modes between two nitrate groups as discussed below.

Cu(1) and Cu(2) atoms are bridged by oxpn in *cis* configuration to form the binuclear complex, the Cu—Cu distance being 5.205(10) Å. The deprotonated N atoms of an oxpn ligand chelate to the Cu(2) atom with a significant shorter distance of 1.974(3) Å, compared to 2. 014(4) Å between Cu(2) and N(3) from the neutral amino group. This is in agreement with similar oxpn complexes. It seems that the deprotonated N atoms balance the positive charge of the Cu(2) atom and decrease the coordination interaction of the nitrate group in the apical direction.

Electron delocalization is observed in the oxpn moiety, the O(1)—C(7) and N(2)—C(7) distances being 1.275(4) Å and 1.290(5) Å, respectively. It

TABLE II Selected bond lengths [Å] and angles [°]

Cu(1)—O(1)	1.948(3)	Cu(1)—N(1)	1.991(3)
Cu(1)—O(2)	2.287(5)	Cu(2)—N(2)	1.974(3)
Cu(2)—N(3)	2.014(4)	Cu(2)—O(5)	2.267(5)
O(1)—C(7)	1.275(4)	N(2)—C(7)	1.290(5)
N(2)—C(8)	1.469(6)	C(7)—C(7)^{a}	1.511(8)
C(8)—C(9)	1.526(6)	C(9)—C(10)	1.496(8)
Ow—O(7)	2.681(10)	Ow—O(8)	2.779(13)
Ow—O(9)	2.834(11)	O(6)—N(3)^{b}	2.954(10)
O(6)—H(3B)^{b}	2.054(9)		
O(1)^{a}—Cu(1)—O(1)	85.6(2)	O(1)—Cu(1)—N(1)	94.06(12)
O(1)—Cu(1)—N(1)^{a}	167.04(13)	N(1)—Cu(1)—N(1)^{a}	83.4(2)
O(1)—Cu(1)—O(2)	93.66(12)	N(1)—Cu(1)—O(2)	99.29(13)
N(2)—Cu(2)—N(2)^{a}	83.3(2)	N(2)—Cu(2)—N(3)^{a}	173.9(2)
N(2)—Cu(2)—N(3)	93.6(2)	N(3)^{a}—Cu(2)—N(3)	88.9(3)
C(7)—O(1)—Cu(1)	110.7(2)	N(4)—O(2)—Cu(1)	126.4(4)
C(10)—N(3)—Cu(2)	119.9(3)	O(1)—C(7)—N(2)	128.0(4)
O(1)—C(7)—C(7)^{a}	116.5(2)	N(2)—C(7)—C(7)^{a}	115.5(2)
N(2)—C(8)—C(9)	111.6(4)	C(10)—C(9)—C(8)	114.0(4)
N(3)—C(10)—C(9)	112.0(4)	O(6)—H(3B)^{b}—N(3)^{b}	177.2(4)

Symmetry code, a: $x, -y, z$; b: $-x, y, -1-z$.

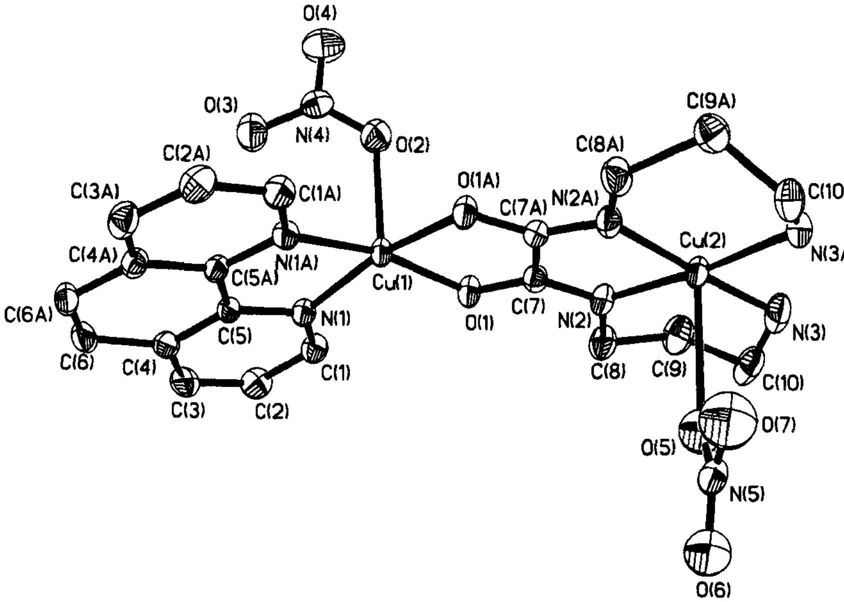

FIGURE 1 Molecular structure of the title complex showing 30% probability displacement ellipsoids. H atoms are omitted for clarity.

is notable that the N(2)—C(7) distance in the present binuclear complex is much shorter than in the mononuclear Cu(oxpn) complex [6] and similar to typical double bond distances between N and C atoms. Atoms of the oxpn ligand are coplanar; the dihedral angles between the oxpn plane and coordination basal planes around the Cu(1) atom and the Cu(2) atoms are 12.37° and 0.32°, respectively. Both coplanar geometry structure and electron delocalization in the bridging ligand are considered to benefit spin super-exchange interactions between neighboring Cu (II) atoms.

Disorder exists in the present crystal structure. As mentioned above, two nitrate groups display different coordination modes. While the nitrate group bonded to Cu(1) atom lies on a mirror plane, the nitrate group attached to the Cu (2) atom is disordered, near the mirror plane, with 0.5 site occupancy factor. This results in a larger electron density of 1.59 $eÅ^{-3}$ [0.71 Å to the disordered O(6) atom] in the final difference Fourier map. The crystalline methanol molecule is also disordered in the crystal structure, located on the mirror plane with site occupancy factor of 0.25. An extensive H-bonding network exists between complex molecules and crystalline molecules of water and methanol molecules. The distances between non-H atoms involving H-bonding are presented in Table II.

Infrared Spectrum

Infrared spectra of several binuclear copper (II) complexes with a bridging oxamidato ligand have been investigated, one characteristic feature of those complexes being their amide I band [16]. Compared to the absorption peak of 1640 cm^{-1} in the free H_2oxpn [17], the amide I band in the mononuclear complex shifts by 40 – 90 cm^{-1} towards low wavenumbers, while the amide I band in binuclear complexes reverts to near to its original position [18, 19]. This experimental fact has been used as proof of bridging coordination of the oxamidato dianion. In the present work, the amide I band in the mononuclear and binuclear complexes are observed at 1587 cm^{-1} and 1629 cm^{-1}, respectively, and agree well with data cited above.

Supplementary Material

Full lists of crystallographic data are available from the authors upon request.

Acknowledgements

The project was supported by the National Natural Science Foundation of China (29973036).

References

[1] M. Melnik, *Coord. Chem. Rev.* **36**, 1 (1981).

[2] Y. Sunatsuki, M. Nakamura, N. Matsumoto and F. Kai, *Bull. Chem. Soc. Jpn.* **70**, 1851 (1997).

[3] M. Dominguez-Vera, N. Galvez, E. Colacio, R. Cuesta, P. Costes and J.-P. Laurent, *J. Chem. Soc., Dalton Trans.* p. 861 (1991).

[4] Z. Chen, D. Fu, K. Yu and W. Tang, *J. Chem. Soc. Dalton Trans.* p. 1917 (1994).

[5] Z. Chen, W. Tang and K. Yu, *Polyhedron* **13** 783 (1994).

[6] J. L. Sanz, B. Cervera, R. Ruiz, C. Bois, J. Faus, F. Lloret and M. Julve, *J. Chem. Soc., Dalton Trans.* p. 1359 (1996).

[7] D. Xu, A. Xie, Y. Xu, C. Zhang and W. Chen, *J. Coord. Chem.* **39**, 273 (1996).

[8] C. Chen, D. Xu, Y. Xu, C. Cheng and R. Ling, *Acta Crystallogr.* **C48**, 1231 (1992).

[9] D. Xu, A. Xie, Y. Xu, C. Zhang and W. Chen, *J. Coord. Chem.* **39**, 273 (1996).

[10] C. Zhang, J. Sun, X. Kong and C. Zhao, *J. Coord. Chem.* in press.

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

[12] C. Zhang, P. Zhu, Z. Ma and D. Yang, *J. Coord. Chem.* in press.

[13] G. M. Sheldrick, SHELX93, Program for Crystal Structure Refinement (university of Göttingen, Germany, 1993).

[14] *International Tables for X-ray Crystallograph* (Kynoch Press: Birmingham, England, Present distributor: Kluwer Academic Publishers, Dordrecht, 1974), Vol. IV, p. 72.

[15] H. Ojima and K. Nonoyama, *Coord. Chem. Rev.* **92**, 85 (1988).

[16] F. Lloret, J. Sletten, R. Ruiz, M. Julve, J. Faus and M. Verdaguer, *Inorg. Chem.* **31**, 779 (1992).

[17] Z. Zhang, D. Liao, Z. Jiang, S. Hao, H. Wang and G. Wang, *Inorg. Chim. Acta* **173**, 201 (1991).

[18] D. Liao, B. Lin and G. Wang, *Acta Chim. Sinica* **50**, 269 (1992).