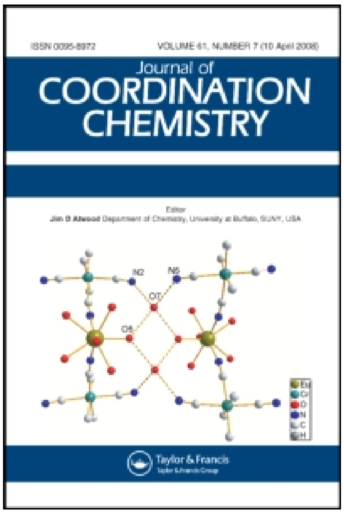

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

SYNTHESIS AND CHARACTERIZATION OF OXIDIZED PRODUCTS OF CuX (X = CI, Br) AND *N,N*-DIMETHYL-BENZENEETHANETHIOAMIDE

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To cite this Article Hegen, Zheng , Tianniu, Chen , Xiangrong, Ye , Xinquan, Xin , Wing-Tak, Wong and Wa-hung, Leung(1999) 'SYNTHESIS AND CHARACTERIZATION OF OXIDIZED PRODUCTS OF CuX (X = CI, Br) AND *N,N*-DIMETHYL-BENZENEETHANETHIOAMIDE', Journal of Coordination Chemistry, 46: 4, 425 — 431

To link to this Article: DOI: 10.1080/00958979908054906

URL: http://dx.doi.org/10.1080/00958979908054906

J. Coord. Chem., 1999, Vol. 46, pp. 425–431
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Printed in Malaysia.

SYNTHESIS AND CHARACTERIZATION OF OXIDIZED PRODUCTS OF CuX (X = Cl, Br) AND *N,N*-DIMETHYL-BENZENEETHANETHIOAMIDE

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(Received 10 April 1997)

The binuclear complexes $Cu_2(C_{10}H_{12}ONS)_2X_2$, where X = Cl, Br, have been synthesized and characterized and the X-ray structure determination of $Cu_2(C_{10}H_{12}ONS)_2Br_2$ is reported. The ligand originally prepared has been oxidized (along with the metal ion) and changed into a bidentate ligand. Copper(II) has a distorted square planar coordination with Cu–S 2.242(2) Å and Cu–Br 2.318(1) Å. In the structure, two Cu atoms are linked by bridging oxygen atoms with Cu–O 1.908(4) Å and Cu–Cu 3.042 Å.

Keywords: Synthesis; X-ray structure; copper; oxidization

INTRODUCTION

In an attempt to imitate the polydentate species MO_nS_{4-n} (M = Mo, W) with thioamide and to synthesize thioamide-containing Cu(Ag)–Mo(W)–S clusters,[1] we prepared the ligand *N,N*-dimethylbenzeneethanethioamide.[2] A series of air-oxidized binuclear copper(II) complexes were obtained accidentally. In this paper we report their synthesis and characterization as well as the X-ray crystal structure determination of $Cu_2(C_{10}H_{12}ONS)_2Br_2$. The

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[*] Corresponding author.

prospective application to selective oxidation of the α-site of thioamides is discussed.

EXPERIMENTAL

Materials

The chemicals were AR or CP grade reagents and were used without further purification.

Physical Measurements

Carbon, hydrogen and nitrogen analyses were performed with a Perkin-Elmer 240C elemental analyzer. Infrared spectra were measured on a Bruker IFS 66V instrument.

Preparation of the Starting Ligand

N,*N*-Dimethyl-2-phenylthioacetamide were prepared according to Ref. [2]. The product was obtained in the form of a yellow-brown solid, m.p. 79–81°C; yield: 80%.

Preparation of Complexes

A well-ground mixture of CuX (X = Cl, Br, 1 mmol) and $C_{10}H_{13}NS$ (0.179 g, 1 mmol) was placed in a reaction tube. A black solid was generated by heating the mixture at 90°C for 12 h under pure nitrogen. A solution obtained by extracting the product with CH_3CN (40 cm^2), was allowed to evaporate in air slowly; crystals appeared several days later. The compositions of both complexes obtained confirmed by elemental analysis (Table I).

TABLE I Analytical data for the Cu(II) complexes

Compound	*Empirical formula*	*Color*	*Yield* (%)		*Elemental analyses* (%) C	H	N
(1)	$Cu_2S_2Cl_2N_2C_{20}H_{24}O_2$	Dark red	36%	found	40.04	4.18	4.74
				calc.	40.89	4.09	4.77
(2)	$Cu_2S_2Br_2N_2C_{20}H_{24}O_2$	Dark red	43%	found	35.38	3.55	4.15
				calc.	35.40	3.54	4.14

RESULTS AND DISCUSSIONS

Infrared Spectra

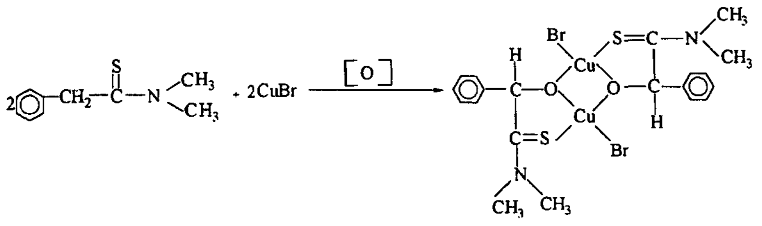
IR data are given in Table II. In the spectrum of $Cu_2S_2X_2N_2C_{20}H_{24}O_2$ ($X = Cl$, Br), bands attributable to ν(C–N) at 1450 cm^{-1} do not change with respect to the free ligand, while the bands attributed to ν(C=S) (1384 cm^{-1}) and $\nu(CH_2)$ (2890 cm^{-1}) are shifted to lower frequencies. This suggest that the ligand is changed during the growth of the crystals and it is nitrogen not sulfur, that participates in coordination. Furthermore, the appearance of new bands attributed to ν(Cu–X),[3] ν(Cu–S),[4] and $\nu(Cu–(\mu\text{-}O)_2–Cu)$[5] reveals that the α-site of $C_{10}H_{13}NS$ is oxidized (Scheme 1) and the coordination of halide ion helps copper(II) complete four-coordination.

X-ray Crystallography

Unfortunately, we didn't obtain good single crystals of $Cu_2S_2Cl_2N_2C_{20}H_{24}O_2$, so only the crystals structure of $Cu_2S_2Br_2N_2C_{20}H_{24}O_2$ was determined. Unit cell parameters and intensity data for $Cu_2S_2Br_2N_2C_{20}H_{24}O_2$ were obtained at 300 K using a CAD4 diffractometer operating in the ω-2 mode with graphite-monochromated Mo*K*α radiation. The structure was solved by direct methods (SIR92) and refined by full-matrix least-squares techniques. Anisotropic temperature factors were applied to all non-hydrogen atoms. Hydrogen atoms were positioned geometrically

TABLE II Selected IR data (cm^{-1}) for the complexes

	$\nu(-CH_2)$	ν(C–N)	ν(C=S)	ν(Cu–X)	ν(Cu–S)	$\nu(Cu–(\mu\text{-}O)_2–Cu)$
$C_{10}H_{13}NS$	2924	1454	1384			
(1)	2875	1450	1360	350	375	756
(2)	2868	1456	1355	250	370	754



SCHEME 1

and not refined. The weighting scheme $w=\sigma_c^2(F_o+P^2F_o^2/4)^{-1}$ was used. Goodness of fit is 1.54, the maximum peak in final difference map was $0.31\,e\,Å^{-3}$, while the minimum of that was $-0.36\,e\,Å^{-3}$. Experimental details are summarized in Table III. Final atomic coordinates are given in Table IV.

Crystal Structure of the Complex

The structure and atom numbering of the molecule are indicated in Figure 1. Selected bondlengths and angles are given in Table V. The structure consists of a binuclear molecule which is centrosymmetric. Two copper(II) ions are coordinated by two bidentate groups, $C_{10}H_{13}ONS$, and two terminal bromide ions. The bridging mode is constructed *via* two oxygen atoms on the α-sites of two $C_{10}H_{12}ONS$ molecules. Coordination geometry is a distorted square plane. Two of the four coordination sites are occupied by a sulfur atom of the bidentate group and a bromide atom. Cu–S and Cu–Br

TABLE III Crystal data and details of intensity measurements and structure refinement

Compound	$Cu_2(C_{10}H_{12}ONS)_2Br_2$
Empirical formula	$Cu_2S_2Br_2N_2C_{20}H_{24}O_2$
Molecular weight	675.44
Crystal system	monoclinic
a (Å)	8.663(1)
b (Å)	7.417(1)
c (Å)	18.786(2)
β (°)	102.05(2)
Volume (Å^3)	1180.5(3)
Space group	$P2_1/n$
Z	2
D_c (g cm^{-1})	1.900
Radiation	MoK_α ($\lambda=0.71069$ Å) graphite monochromated
μ (cm^{-1})	53.93
F(000)	668.00
2θmax	44.9
Temperature (K)	300
No. of reflections measured	Total: 1818 Unique: 1717 ($R_{int}=0.024$)
No. observations ($I > 3.00\sigma(I)$)	1038
No. variables	136
Weighting scheme parameter *p* in $w=\sigma_c^2(F_o+p^2F_o^2/4)^{-1}$	0.0000
Final *R*	0.030
Final R_w	0.025

TABLE IV Atomic coordinates and equivalent isotrotropic thermal parameter (Å^2)

Atom	*x/a*	*y/b*	*z/c*	B_{eq}
Br(1)	0.11908(8)	0.5480(1)	0.88121(4)	4.63(2)
Cu(1)	0.33519(8)	0.4374(1)	0.96374(4)	2.74(2)
S(1)	0.2334(2)	0.1714(3)	0.98725(10)	3.90(5)
O(1)	0.5099(4)	0.3750(6)	1.0398(2)	3.0(1)
N(1)	0.3652(6)	−0.0462(8)	1.0923(3)	2.9(1)
C(1)	0.3722(7)	0.1099(9)	1.0607(3)	2.6(2)
C(2)	0.5016(7)	0.2448(9)	1.0938(3)	2.6(2)
C(3)	0.4677(7)	0.3307(9)	1.1622(3)	2.4(2)
C(4)	0.3221(7)	0.4039(9)	1.1631(3)	2.8(2)
C(5)	0.2949(7)	0.4974(9)	1.2230(4)	3.2(2)
C(6)	0.4140(9)	0.5150(10)	1.2834(4)	3.9(2)
C(7)	0.5574(8)	0.436(1)	1.2846(4)	4.3(2)
C(8)	0.5841(7)	0.346(1)	1.2245(4)	3.6(2)
C(9)	0.4830(8)	−0.1102(9)	1.1551(4)	4.0(2)
C(10)	0.2381(9)	−0.173(1)	1.0648(4)	4.5(2)

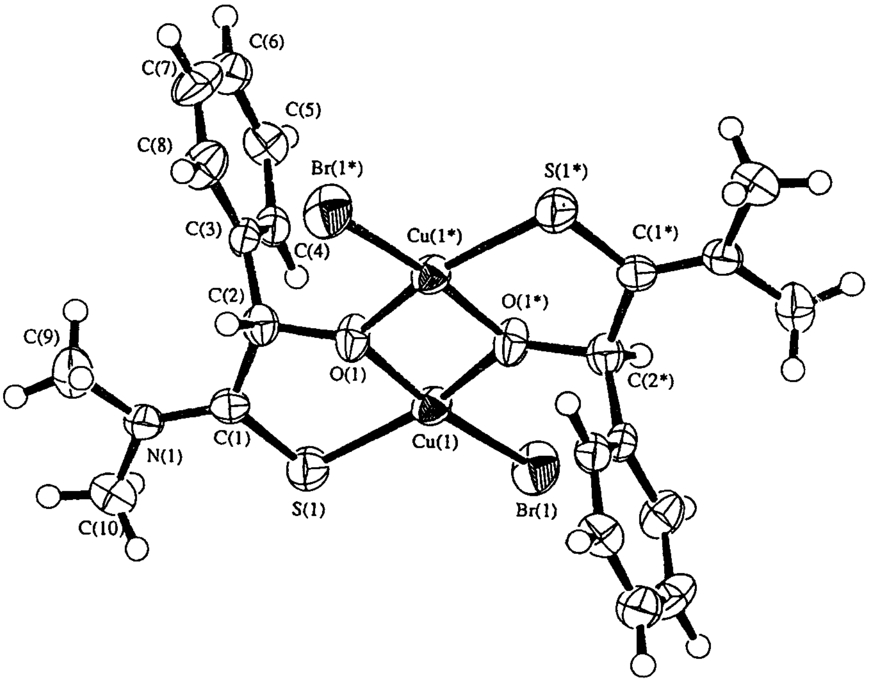


FIGURE 1 Crystal structure of the complex.

TABLE V Selected bondlengths (Å) and angles (°) for the complex

Br(1)–Cu(1)	2.318(1)	Cu(1)–S(1)	2.242(2)
Cu(1)–O(1)	1.908(4)	Cu(1)–O(1)	1.944(4)
S(1)–C(1)	1.692(6)	O(1)–C(2)	1.414(7)
N(1)–C(1)	1.308(8)	N(1)–C(9)	1.468(8)
N(1)–C(10)	1.459(8)	C(1)–C(2)	1.535(8)
Br(1)–Cu(1)–S(1)	98.47(6)	Br(1)–Cu(1)–O(1)	172.0(1)
Br(1)–Cu(1)–O(1)	101.0(1)	S(1)–Cu(1)–O(1)	85.5(1)
S(1)–Cu(1)–O(1)	159.9(1)	O(1)–Cu(1)–O(1)	75.7(2)
Cu(1)–S(1)–C(1)	99.0(2)	Cu(1)–O(1)–Cu(1)	104.3(2)
Cu(1)–O(1)–C(2)	123.5(4)	Cu(1)–O(1)–C(2)	130.7(4)
C(1)–N(1)–C(9)	124.1(6)	C(1)–N(1)–C(10)	120.9(6)
C(9)–N(1)–C(10)	115.0(6)	S(1)–C(1)–N(1)	121.1(5)
S(1)–C(1)–C(2)	119.3(5)	N(1)–C(1)–C(2)	119.5(6)
O(1)–C(2)–C(1)	107.2(5)	O(1)–C(2)–C(3)	111.7(5)

TABLE VI Geometrical data for the (Cu–(μ-O)$_2$–Cu) moiety in different complexes

Compounds	*Cu–Cu*	*Cu–O*	*Cu–O–Cu*	*O–Cu–O*
(2)	3.042 Å	1.908(4) Å	104.3°(2)	75.7°(2)
Di-μ-(methoxy)bis-squratocopper(II)[6]	2.74 Å	1.930 Å	90°	90°
$[\{Cu_2(en)_2(OH)_2 \cdot Cu_2(O_2CMe)_4\}(PF_6)_2 \cdot 0.5EtOH]_\alpha$[7]	3.005(3) Å	1.951(4) Å	100.7°(1)	79.3°(1)
$[Cu_2L(C_2HO)(CH_3OH)](ClO_4)_2$[8]	2.924(2) Å	1.970(6) Å	100.8°(3)	80.2°(3)

L: 2,6-disformyl-4-*tert*-butylphenoldi(benzoylhydrazone).

bondlengths are 2.242(2) and 2.318(1) Å, respectively. The other two sites are occupied by two bridging oxygen atoms. Distances and angles in the (Cu–(μ-O)$_2$–Cu) moiety of the complex suggest a longer Cu–Cu bond length as compared with the other compounds (Table VI).

$Cu_2(C_{10}H_{12}ONS)_2X_2$ complexes are prepared by using a method which has been developed and applied in synthesizing more than two hundred cluster and coordination compounds[9] over recent years. The advantage of using this method is that the reaction can take place without solvent and sometimes generates unusual products.[10,11] To date, no literature report of the oxidation of the α-site of thioamide has been found. Oxidized products have been made by the reaction of lithium *N*,*N*-dimethylthioformamide anion, generated *in situ* from LDA and *N*,*N*-dimethylthioformamide in THF, with corresponding aryl aldehyde or ketone at −78°C according to Ref. [12] while the oxidation of *N*,*N*-dimethylbenzeneethanethioamide with H_2O_2 in glacial AcOH led to $PhC(SO)N(CH_3)_2$.[13] In view of this, the above-mentioned structure of complex (2) has inspired us to oxidize the α-site of thioamides selectively *via* formation of complexes, but removal of the metal ion and the terminal ligand is still a problem.

Supplementary Materials

Full lists of atomic positions and thermal parameters, bond distances and angles, and observed and calculated structure factors are available from the authors upon request.

Acknowledgments

This work was supported by the National Natural Science Foundation of China, the State Education Commission of China and the Croucher Foundation of Hong Kong.

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