Pergamon

0277-5387(94)00293-2

Polyhedron Vol. 14, No. 5, pp. 639–642, 1995

0277-5387/95 $9.50+0.00

X-RAY CRYSTAL STRUCTURE, SPECTRAL AND MAGNETIC PROPERTIES OF A MIXED-LIGAND DINUCLEAR COMPLEX [Cu(Phen)(Sa)(ClO_4)]$_2$

MING LI, JIANG-ZHONG ZOU, ZHENG XU* and XIAO-ZENG YOU

Coordination Chemistry Institute, National Key Laboratory of Coordination Chemistry,
Nanjing University, Nanjing (210093), P.R.C.

and

XIAO-YIN HUANG

Fujian Institute of Research on the Structure of Matter, Chinese Academy of Science,
Fuzhou (350002), P.R.C.

(*Received* 25 *April* 1994; *accepted* 15 *July* 1994)

Abstract—The mixed-ligand dinuclear complex [Cu(Phen)(Sa)(ClO_4)]$_2$ (where Phen = 1,10-phenanthroline and Sa = salicylaldehyde) has been synthesized and characterized by IR and ESR spectra and magnetic susceptibility measurements, which obey the Curie–Weiss law with $\theta = -10$ K. The crystal structure of the title complex has been determined and is a dimer in which two monomeric units are bridged by two oxygen atoms of phenolate groups.

It has been suggested that under certain conditions copper phenanthroline complexes play an important role in the cleavage of DNA and the differences in the chemical arrangement of the complexes can result in very striking differences in biopharmacological activity.[1] A few interesting papers have been published on ternary complexes containing phenanthroline and amino acids. These complexes have a potential application as a model for the interaction of enzyme–metal ion and substrate and may be related to a transport process of copper in human serum.[2-4]

In order to extend further the study of such complexes, we synthesized [Cu(Phen)(Sa)(ClO)$_4$]$_2$ and determined the crystal structure, magnetic susceptibility, EPR, IR and reflectance electronic spectra.

EXPERIMENTAL

Physical measurements

Carbon, hydrogen and nitrogen were determined on a Perkin–Elmer 240C microanalyser. IR absorption spectra, as KBr pellets, were recorded on a Nicolet FTIR 170X spectrophotometer. The electronic reflectance spectrum was recorded on a Shimadzu UV-240 spectrophotometer equipped with the standard reflectance accessory. Magnetic susceptibilities were measured in the temperature range 75–300 K by the Faraday method with a DSM-5 susceptometer. Corrections for the diamagnetism of the ligands were applied. The EPR spectra were obtained in X-band using a Bruker ER 200D-SRC.

Preparation of the complex [Cu(Phen)(Sa)(ClO_4)]$_2$

To the solution of salicylaldehyde (122 mg, 1 mmol) and 1,10-phenanthroline monohydrodate (198 mg, 1 mmol) in ethanol (15 cm^3) was added solid $Cu(ClO_4)_2 \cdot 6H_2O$ (371 mg, 1 mmol) with stirring. After refluxing for 1 h, the mixture was filtered off while hot, washed with hot ethanol and air-dried. A green solid was obtained with a yield of 78%. Found: C, 48.8; H, 2.9; N, 5.9. Calc. for $CuC_{19}H_{13}N_2O_6$: C, 49.1; H, 2.8; N, 6.0%.

X-Ray structure determination of the complex

A dark-green crystal with dimensions of 0.70 × 0.50 × 0.40 mm was mounted on an Enraf–

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* Author to whom correspondence should be addressed.

Table 1. Crystallographic data for $[Cu(Phen)(Sa)(ClO_4)]_2$

Formula	$CuClO_6N_2C_{19}H_{13}$
Formula weight	464.32
Crystal system	Triclinic
Space group	P1
Unit cell constants	
a (Å)	9.151(5)
b (Å)	9.303(3)
c (Å)	11.714(5)
α (°)	96.19(3)
β (°)	111.05(4)
γ (°)	97.12(4)
V (Å^3)	910.9(7)
Z	2
D_c(g cm^{-3})	1.69
μ (cm^{-1})	13.88
F (000)	470
Scan speed (° min^{-1})	5.5
Scan width (°)	$0.5+0.35 \tan \theta$
$2\theta_{max}$ (°)	49.9
No. of data collected	3413
No. of reflections used in the refinement	$2999[I > 3\sigma(I)]$
No. of refined parameters	314
R^a	0.033
$R_W{}^b$	0.048
GOF	1.71
ω	$1/\sigma^2F$
ρ_{max}, ρ_{min}(e Å^{-3})	0.058, −0.038

$^a R = \Sigma[|F_0| - |F_c|]/\Sigma|F_0|$.

$^b R_w = [w(F_0 - |F_c|)^2/\Sigma w(F_0)^2]^{1/2}$.

Nonius CAD4 diffractometer for data collection using graphite-monochromated Mo-K_α radiation at 23°C. The crystallographic data are summarized in Table 1.

The structure was solved by Patterson methods followed by Fourier syntheses and refined by full-matrix least squares with anisotropic thermal parameters for the non-hydrogen atoms. All the hydrogen atoms were located on the difference Fourier maps and assigned isotropic thermal parameters. Selected distances and angles are listed in Tables 2 and 3. Atomic scattering factors were taken from Ref. 5. The calculations were performed on MICRO-VAX 3100 using the TEXSAN plus version 2.01 programs.

RESULTS AND DISCUSSION

As shown in Fig. 1, the centrosymmetric structure of the dimer consists of two [Cu(phen)

Table 2. Intramolecular distances (Å)

Cu—O(1)	1.904(2)	Cu—O(2)	1.953(2)
Cu—N(1)	1.999(2)	Cu—N(2)	2.005(2)
Cu—O(3)	2.497(2)	Cu—O(1)*	2.625(2)
Cu—Cu	3.379(2)	Cl—O(6)	1.400(3)
Cl—O(5)	1.409(2)	Cl—O(4)	1.427(2)
Cl—O(3)	1.437(2)	O(1)—C(21)	1.310(3)
O(2)—C(27)	1.242(3)	N(1)—C(1)	1.336(3)
N(1)—C(6)	1.343(3)	N(2)—C(10)	1.335(3)
N(2)—C(11)	1.350(3)		

Table 3. Intramolecular bond angles involving non-hydrogen atoms (°)

O(1)—Cu—O(1)*	84.83(7)	O(3)—Cu—O(1)*	175.09(5)
O(2)—Cu—O(3)	82.54(8)	O(1)*—Cu—N(2)	90.65(8)
O(3)—Cu—N(2)	86.95(8)	Cl—O(3)—Cu	127.6(1)
O(1)—Cu—O(2)	93.39(8)	O(1)—Cu—N(1)	92.43(8)
O(1)—Cu—N(2)	172.99(6)	O(2)—Cu—N(1)	173.92(7)
O(2)—Cu—N(2)	92.22(9)	N(1)—Cu—N(2)	82.12(9)
C(21)—O(1)—Cu	123.4(1)	C(27)—O(2)—Cu	122.3(2)
C(10)—N(2)—Cu	129.1(2)	C(1)—N(1)—Cu	128.6(2)
C(6)—N(1)—Cu	112.9(2)	C(11)—N(2)—Cu	112.3(2)
O(2)—Cu—O(1)*	93.28(7)	O(1)—Cu—O(3)	97.95(8)
O(1)*—Cu—N(1)	89.00(7)	O(3)—Cu—N(1)	94.91(8)
Cu—O(1)—Cu*	95.17(7)	Cu—O(1)*—C(21)*	112.1(1)
Cu*—O(1)*—C(21)*	123.4(1)		

$(Sa)(ClO_4)]$ units linked by two oxygen atoms from two phenolate groups. The coordination of the copper atom is an elongated octahedron. The copper atom is located on the equatorial plane of the octahedron, which consists of the two O atoms of Sa and the two N-atoms of the phen; their deviations from the best-fit plane are from +0.09 to −0.04. The axial position of the elongated octahedron are occupied by two oxygen atoms from perchlorate and phenolate. The bond distances of the axial Cu—O are 2.497(2) and 2.625(2)Å, respectively; the former is shorter than that of catena-bis-(2,2′-bipyridyl)-μ-perchlorato-copper(II) complex [2.512(5) Å and 2.746(5) Å],[6] due to the different coordination forms of the ClO_4^- ion in the two complexes. Bond distances and angles within the phen molecule and Sa ligand are normal. The dihedral angle between the mean planes of phen molecule and the Sa ligand is 160°. The Cu···Cu separation is 3.379(2) Å.

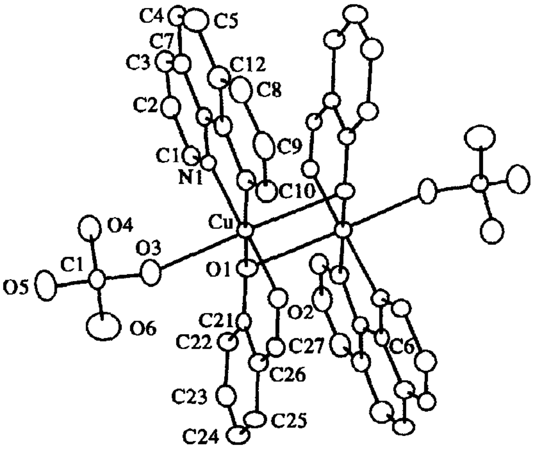

Fig. 1. Molecular structure and atomic numbering of $[Cu(Phen)(Sa)(ClO_4)]_2$.

Magnetic susceptibility measurements of a polycrystalline sample between 75 and 300 K obeyed the Curie–Weiss law $X = C/(T-\theta)$, with $C = 0.5$ emu K mol^{-1} and $\theta = -10 \pm 1$ K, respectively. The decreasing of the effective magnetic moment from 1.89 μ_B at 300 K to 1.77 μ_B at 75 K and the negative Weiss constant may indicate the presence of a weak antiferromagnetic interaction between the two copper atoms in the dimer. Similar behaviour has been found in other dimeric copper(II) complexes.[7–9]

Figure 2 shows that the EPR spectrum obtained for polycrystalline samples at room temperature appeared to show axial symmetry with $g_\perp = 2.05$, $g_\parallel = 2.23$. The values of $g_\parallel \geqslant g_\perp > 2.0$ suggested that the ground state of the dimer was $d_{x^2-y^2}$ and the coordination geometry was octahedral or square pyramidal,[10] and the forbidden transition $\Delta m_s = \pm 2$ was also observed in the $g = 4$ region, which indicated that the complex was dimeric. These results were consistent with the crystal structure.

The IR spectrum of the complex shows an absorption band at 1609 cm^{-1} belonging to the C=O stretching vibration, which, owing to oxygen coordination, is significantly shifted from its position for the free ligand (1700 cm^{-1}). The reflectance spectrum of the complex exhibited a broad *d–d* transition (at 16 200 cm^{-1}) and a charge transfer band at 22 700 cm^{-1}.

Acknowledgement—Financial support given by the National Natural Science Foundation and a key research project from the State Science and Technology Commission of China are acknowledged.

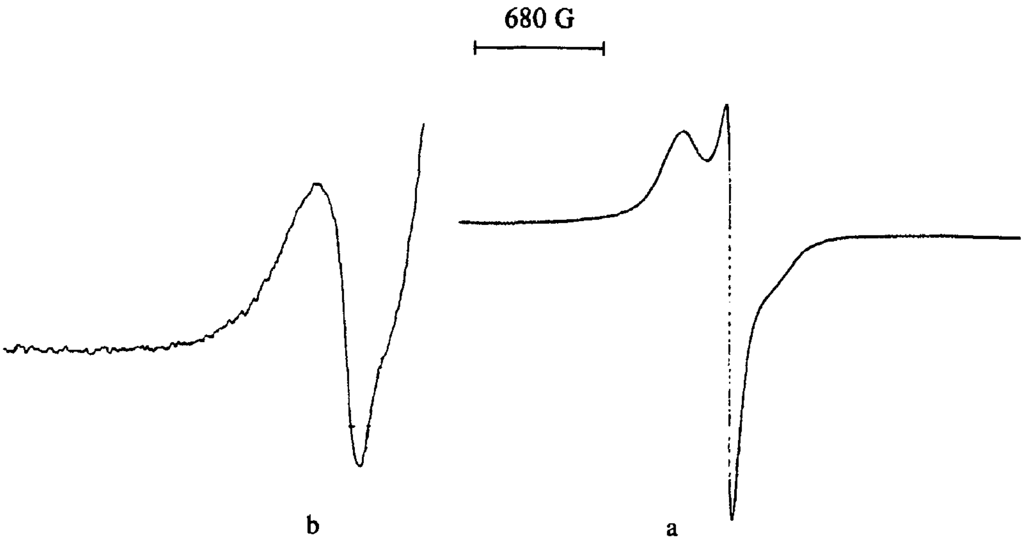

Fig. 2. EPR spectra (X-band) of $[Cu(Phen)(Sa)(ClO_4)]_2$ at room temperature. (a) Full-field region; (b) half-field region amplified 10^3-fold.

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