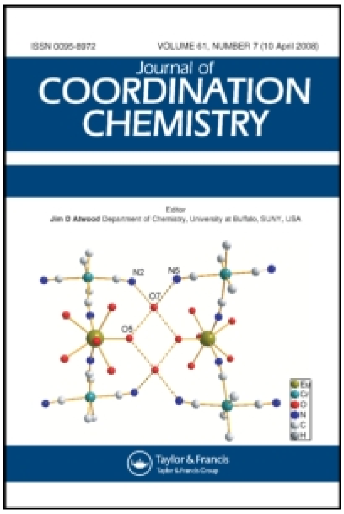

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A linear trinuclear complex of copper(II) with *N*,*N*′-bis(2-hydroxy-5-methoxybenzelidene)-1,3-diiminopropane

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The synthesis and X-ray crystal structure of a linear phenolate-bridged Cu(II) complex **1** with a Cu–Cu bond distance of 2.9260(5) Å is reported. The complex consists of three Cu(II) ions with two molecules of the *N*,*N*′-bis(2-hydroxy-5-methoxybenzelidene)-l,3-diiminopropane ligand and two nitrate ions in such a manner that one ligand is connected with two Cu(II) ions. The complex is monoclinic, space group $P2_1/n$, with $a = 10.6305(5)$, $b = 13.0719(7)$, $c = 14.6336(8)$ Å and $\beta = 102.549(1)^\circ$ at 293 K, $Z = 2$. The structure shows deprotonation of the phenolate oxygen to form a μ_2 bridge. The magnetic moment (1.627 BM per Cu_3 unit) at 300 K reveals that the spin doublet state is the ground state.

Keywords: Copper(II); Trinuclear complex; Phenolate bridge; X-ray structure

1. Introduction

Investigations concerning the structural configuration and chemical properties of polynuclear transition metal compounds have aroused considerable interest mainly because of their implications for topics such as the nature of orbital interactions, electron transfer in redox processes, and biological electron transport chains. Considerable attention has focussed on the chemistry of polynuclear Cu(II) complexes due to the presence of multicopper active sites in blue copper oxidases (e.g., laccase, ascorbate oxidase, and ceruloplasmin) [1–5] and in the development of new inorganic materials showing molecular ferromagnetism [6]. Cumulative spectroscopic and azide bonding studies of *Rhus vernicifera* laccase have focussed on the presence of the trinuclear active site composed of two types of metal centres [2, 5–7]. The crystal structure of ascorbate oxidase from zucchini has shown this type of arrangement

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of three copper atoms in a pattern approximating an isosceles triangle [5]. Four arrangements of the copper atoms in trinuclear Cu(II) complexes have been found, equilateral triangular [8–16], isosceles triangular [17–26], scalene triangular [27] and linear [28–43].

In the present work, we report the synthesis and structural characterization of a novel oxygen-bridged linear trinuclear Cu(II) complex with a moderate copper–copper distance (2.9260(5) Å). The complex has been derived from the tetradentate Schiff base ligand, *N*,*N*′-bis(2-hydroxy-5-methoxybenzelidene)-l,3-diimino-propane.

2. Experimental

2.1. *Materials and physical measurements*

All chemicals used were of reagent grade. Microanalytical data were obtained on a Perkin-Elmer 2400 elemental analyzer. Melting point measurements were carried out on a Buchi 510 analyzer. ^{1}H NMR spectra were recorded on a Bruker AM-400 NMR spectrometer. Infrared spectra were measured on a Jasco FT/IR 300E spectrophotometer and electronic spectra on Hewlett Packard 8452A instrument. Variable-temperature magnetic susceptibility measurements were obtained using a Quantum Design MPMS5 magnetometer.

2.2. *Preparation of the ligand (H_2L)*

The ligand, *N*,*N*′-bis(2-hydroxy-5-methoxybenzelidene)-l,3-diiminopropane, was prepared by direct condensation of 2-hydroxy-5-methoxybenzaldehyde (3.04 g, 20 mmol) and 1,3-diaminopropane (0.74 g, 10 mmol) in ethanol. The reaction mixture in ethanol was stirred for 6 h and then placed in a freezer for 24 h. The precipitate was collected by filtration and washed with cold ethanol. After recrystallization, crystals were collected and dried *in vacuo* (1.81 g, 5.3 mmol, 53% yield, m.p. 102°C). Anal. Calcd for $C_{19}H_{22}N_2O_4$ (%): C, 66.67; H, 6.43; N, 8.19. Found: C, 66.52; H, 6.41; N, 8.17. ^{1}H NMR (δ in $CDCl_3$): 2.09 (t, 2H, $-NCH_2CH_2CH_2N-$), 3.69 (t, 4 H, $-NCH_2CH_2CH_2N-$), 3.73 (s, 6H, $-OCH_3$), 6.74 (d, 2H, 3-aromatic-*H*), 6.89–6.90 (m, 4H, 4- and 6-aromatic-*H*). 8.31 (s, 2H, $-N{=}CH-$).

2.3. *Preparation of Cu(II) complex*

Copper(II) nitrate trihydrate (1.7 g, 7.0 mmol) and the ligand (1.4 g, 4.1 mmol) were dissolved in 95% ethanol and stirred for 1 h at room temperature. The solution was filtered and the filtrate kept in a beaker at 277 K for crystallization. Greenish blue crystals started appearing after 3–4 days and these were collected by filtration (0.19 g, 0.58 mmol, 8.1% yield, based on Cu). Recrystallization was from 95% ethanol Anal. Calcd for $C_{38}H_{40}Cu_3N_6O_{14}$ (%): C, 46.04; H, 4.02; N, 8.45. Found: C, 45.90; H, 3.89; N, 8.42.

2.4. *X-ray structure*

Single crystals suitable for X-ray work were grown by slow evaporation of a solution of the copper(II) complex in ethanol at ambient temperatures. A suitable single crystal of dimensions $0.19 \times 0.20 \times 0.35\,\mathrm{mm}^3$ was selected and mounted on a Bruker SMART CCD diffractometer equipped with a graphite-monochromated Mo-Kα ($\lambda = 0.71073$ Å) radiation. A total of 11,877 [unique data = 4661; $R_{\mathrm{int}} = 0.0359$] reflections was measured and 3115 reflections were assumed observed ($I > 2\sigma(I)$). The structure was solved by direct methods and refined by full-matrix least-squares on F^2. Scattering factors and anomalous dispersion correction terms were taken from *International Tables for X-ray Crystallography*. All H atoms included in the refinement were placed in idealized positions (C–H = 0.96 Å and H–C–H = 109.4°) with U_{iso} constrained to be 0.08 Å^2 after the non-H atoms refined anisotropically. The refinement converged to residual indices R of 0.0523.

3. Results and discussion

3.1. *Synthesis*

The Schiff base ligand was prepared by condensation of 2-hydroxy-5-methoxybenzaldehyde and 1,3-diaminopropane in a 1 : 1 mole ratio in ethanol. The ligand acts as dibasic ONNO tetradentate. The copper(II) complex is soluble in common organic solvents.

3.2. *Crystal structure*

The molecular structure of **1** is shown in figure 1. Crystallographic data, and selected bond lengths and angles, are given in tables 1 and 2. The central copper atom Cu2 which, for simplicity, is arbitrarily chosen to be the origin of the cell is located at the inversion centre. Copper ions are held together by μ_2-bridging phenolate oxygen atoms. The terminal copper, either Cul or Cu1A, is four coordinated with distorted square planar geometry with an N_2O_2 donor by means of two imine nitrogen atoms and two bridging phenolate oxygens, and with bond angles ranging between 76.0 and 98.9°. The short Cu–Cu distance of 2.9260(5) Å is due to the slight bending of the Cu_2O_2 ring as Cul is located 0.044 Å from the plane, Cu1Cu2O1O2. Dihedral angles between the two CuON planes and between the aromatic planes are 4.1 and 42.2°, respectively, and donor atoms deviate by ±0.024 Å for O atoms and by ±0.019 Å for N atoms from the best plane. Coordination about Cu2 with four μ_2-bridging phenolate oxygen atoms is strictly planar as required by the symmetry. The C15–C16 and C16–C17 distances are 1.394(8) and 1.570(10) Å, respectively (table 2). This type of asymmetry in bond lengths was also observed for the mononuclear analogue, Cu(II)-*N*,*N*′-bis(2-hydroxybenzelidene)-l,3-diiminopropane, with the corresponding C–C bond distances being 1.37(1) and 1.53(1) Å, respectively [44]. The overall charge is balanced by two nitrate ions which reside on each side of the CuN_2O_2 plane. Here the nitrate ions bridge pairs of copper ions with distances Cu2–O5 2.672 Å and Cu1–O5 2.585 Å. The positioning of these ligands is responsible for the folding of the Cu2O2 planes. As a result, Cu2 is a typically tetragonally distorted Jahn Teller ion and Cu1 is a square based pyramid.

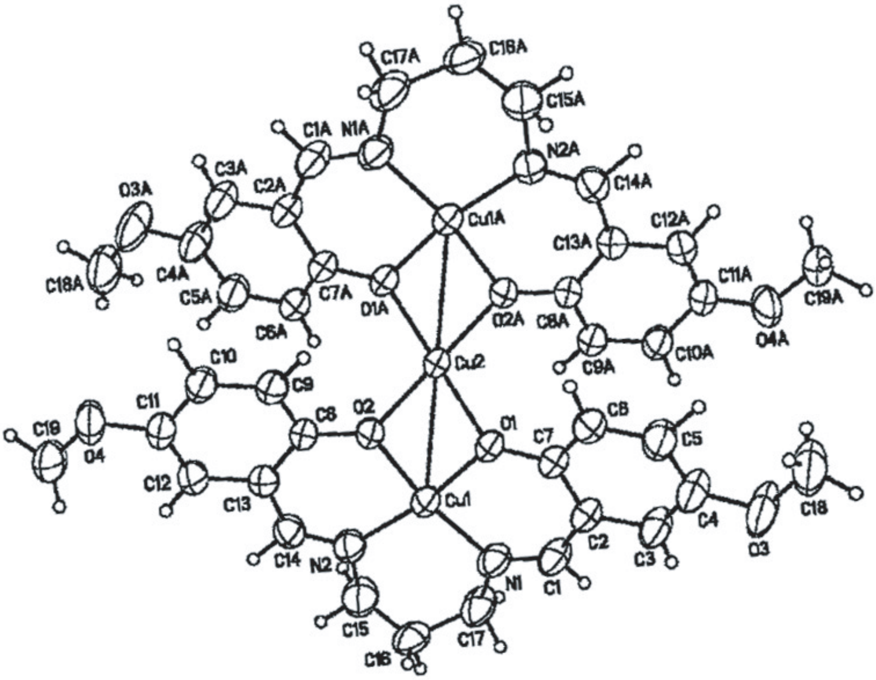

Figure 1. An ORTEP view of the complex with the atom numbering scheme.

Table 1. Crystallographic data for the complex.

Chemical formula	$C_{38}H_{40}Cu_3N_6O_{14}$
Formula weight	994.38
Space group	$P2_1/n$
Unit cell dimensions (Å, °)	
a	10.6305(5)
b	13.0719(7)
c	14.6336(8)
β	102.549(1)
Volume (Å^3)	1984.9(2)
Z	2
Radiation	Mo-Kα ($\lambda = 0.71073$ Å)
T (K)	293(2)
ρ_{calcd} (Mg m^{-3})	1.665
μ (mm^{-1})	1.670
Data collected	11877
Unique data	4661
R factor (gt)	0.0523
R factor (all)	0.0841

3.3. *Spectroscopic properties*

Electronic spectra of the complex recorded in CH_3CN solution shows bands at 218 (16,260 cm^{-1} M^{-1}), 232 (17,720 cm^{-1} M^{-1}), and 238 nm (17,830 cm^{-1} M^{-1}) due to

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

Cu1–Cu2	2.9260(5)	Cu1–O1	1.952(3)
Cu1–O2	1.949(2)	Cu1–N1	1.969(3)
Cu1–N2	1.972(3)	Cu2–O1	1.968(2)
Cu2–O2	1.938(3)	Cu2–Cu1A	2.9260(5)
Cu2–O1A	1.968(2)	Cu2–O2A	1.938(3)
N1–C1	1.288(5)	N1–C17	1.479(5)
N2–C14	1.298(5)	N2–C15	1.488(5)
C15–C16	1.394(8)	C16–C17	1.570(10)
Cu2–Cu1–O1	41.92(7)	Cu2–Cu1–O2	41.02(8)
O1–Cu1–O2	76.17(11)	Cu2–Cu1–N1	129.49(10)
O1–Cu1–N1	92.87(12)	O2–Cu1–N1	169.00(13)
Cu2–Cu1–N2	128.55(10)	O1–Cu1–N2	167.27(12)
O2–Cu1–N2	91.73(12)	N1–Cu1–N2	99.11(14)
Cu1–Cu2–O1	41.52(8)	Cu1–Cu2–O2	41.31(7)
O1–Cu2–O2	76.07(11)	Cu1–Cu2–Cu1A	180.00(2)
O1–Cu2–Cu1A	138.48(8)	O2–Cu2–Cu1A	138.69(7)
Cu1–Cu2–O1A	138.48(8)	O1–Cu2–O1A	180.00(18)
O2–Cu2–O1A	103.93(11)	Cu1A–Cu2–O1A	41.52(8)
Cu1–Cu2–O2A	138.69(7)	O1–Cu2–O2A	103.93(11)
O2–Cu2–O2A	180.0(2)	Cu1A–Cu2–O2A	41.31(7)
O1A–Cu2–O2A	76.07(11)	Cu1–O1–Cu2	96.57(11)
Cu1–O1–C7	127.8(2)	Cu2–O1–C7	135.0(2)
Cu1–O2–Cu2	97.67(11)	Cu1–O2–C8	128.9(2)
Cu2–O2–C8	133.1(2)	Cu1–N1–C17	120.5(3)
Cu1–N2–C14	124.3(3)	Cu1–N2–C15	119.6(3)

benzene rings. Absorption at 394 nm (14,260 $\mathrm{cm^{-1}\,M^{-1}}$) is associated with charge transfer from the filled d-orbitals of Cu(II) to antibonding π^* orbitals of phenolic residues [44]. The band at 585 nm (408 $\mathrm{cm^{-1}\,M^{-1}}$) is the characteristic d–d transition for copper(II) [45].

IR spectra (KBr disc) show characteristic absorptions of the Schiff base and NO_3^-. Absorption due to the coordinated Schiff base link is at 1,605 $\mathrm{cm^{-1}}$, shifted from 1,650 $\mathrm{cm^{-1}}$ for the free ligand. Strong absorption at 1,385 $\mathrm{cm^{-1}}$ indicates the existence of non-coordinated ionic nitrate [46].

The magnetic moment (μ) of **1** at 300 K is 1.627 BM per Cu_3 unit. This indicates that only one unpaired electron is associated with a strong antiferromagnetic interaction ($S = 1/2$) per Cu_3 unit. This may be due to the fact that there are no inter-trimer contacts within 4 Å between copper atoms. As a result, it can be assumed that the principal coupling interaction is intramolecular.

Supplementary material

Crystallographic data (excluding structure factors) for the structure in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC 134231. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, CB2 IEZ, UK (Fax: +44 1223 336033, E-mail: deposit@ccdc.cam.ac.uk).

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