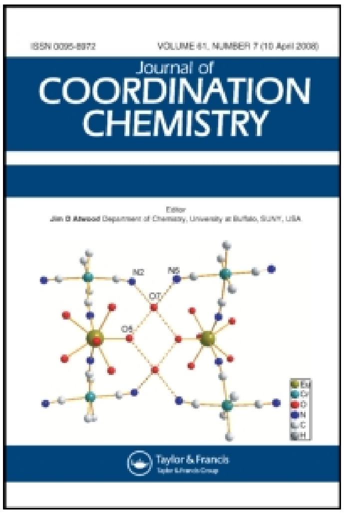

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Synthesis, structure, and properties of a tetranuclear copper(II) tridentate Schiff-base complex with a pseudo-double-cubane core

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A tetranuclear copper(II) complex, $[Cu_4(L)_4]\cdot(NMP)$, with a tridentate Schiff-base ligand has been synthesized and its crystal structure, spectroscopic properties studied (H_2L = salicylidene-2-aminobenzoic alcohol, NMP = *N*-methylpyrrole). The complex crystallizes in the monoclinic, space group C2/c, with $a = 21.461(5)$, $b = 12.231(3)$, $c = 19.898(5)$ Å, $\beta = 96.402(4)^\circ$, $V = 5190(2)$ Å^3, $Z = 4$, and $R_1 = 0.0589$. The complex is centrosymmetric and the structure can be visualized as a pseudo-double cubane, where both the cubes share a common face and in each cube one of the Cu(II) corners is missing. The four copper atoms are located at the corners of a pseudo-double-cubane core and each copper(II) has square-pyramidal coordination.

Keywords: Tetranuclear complex; Copper(II) complex; Crystal structure; Schiff-base ligand; Double-cubane core

1. Introduction

Polynuclear metal complexes including four identical μ_3-O bridges arising either from OH [1] or OMe [2, 3] or O-alkoxo [4, 5] moieties have attracted intense interest due to their interesting magnetic properties [6, 7]. Utilization of a polydentate, Schiff-base ligand, which can function in both bridging and chelating capacities, represents a promising route to the synthesis of polynuclear complexes. Here a novel tetranuclear copper(II) complex with a tridentate Schiff-base ligand derived from salicylidene-2-aminobenzoic alcohol is reported. The structure of this complex can be visualized as a pseudo-double cubane similar to a previously reported polynuclear copper(II) complex [8–10].

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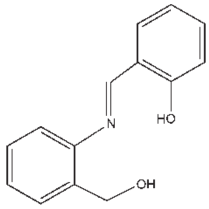
2. Experimental

2.1. *Synthesis*

Salicylidene-2-aminobenzoic alcohol (H_2L) was prepared by the condensation of salicylaldehyde and 2-aminobenzoic alcohol in ethanol. To an ethanol solution ($50\,cm^3$) of H_2L (1.15 g, 5 mmol) was added *N*-methylpyrrole (0.40 g, 5 mmol) with stirring at room temperature for 15 min. Then $CuCl_2 \cdot 2H_2O$ (0.85 g, 5 mmol) was added. The resulting green solid was further stirred for 1 h and filtered. The solid was recrystallized from *N*,*N′*-dimethylformamide (DMF) to give black crystals suitable for X-ray diffraction.



2.2. *Physical measurements*

Elemental analyses (C, N and H) were carried out with a Variuo EL elemental analyzer. Anal. Calcd for $C_{61}H_{51}Cu_4N_5O_8$ (%): C, 59.22; N, 5.66; H, 4.13. Found: C, 58.99; N, 5.78; H, 4.11. The IR spectrum was recorded on a Nicolet AVATAR 360 FT-IR spectrophotometer as KBr pellets. An electronic spectrum was recorded on a Shimadzu 240 spectrophotometer.

2.3. *Crystal structure determination*

A single crystal with approximate dimensions of $0.18 \times 0.11 \times 0.07\,mm^3$ was placed on a Bruker Smart-1000 CCD diffractometer. Intensity data were collected with graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å) at 298(2) K. A total of 13 318 reflections were collected, 4553 of which were independent ($R_{int} = 0.0673$) and used for the structure determination.The structure was solved by the direct method and refined by full-matrix least-squares on F^2 with anisotropic thermal parameters for all non-hydrogen atoms. The final refinements converged at $R_1 = 0.0589$, $wR_2 = 0.1373$ with $\omega = 1/[\sigma^2\ (F_o^2) + (0.0787P)^2 + 0.0000P]$, where $P = (F_o^2 + 2F_c^2)/3$. All hydrogen atoms were located geometrically and refined isotropically.

2.4. *Crystal data*

$C_{61}H_{51}Cu_4N_5O_8$, $M = 1236.23$, monoclinic, space group C2/c, $a = 21.461(5)$, $b = 12.231(3)$, $c = 19.898(5)$ Å, $\beta = 96.402(4)°$, $V = 5190(2)$ Å^3, $Z = 4$, $D_x = 1.582\,mg/m^3$, $F(000) = 2528$, μ(Mo-K_α) $= 1.681\,mm^{-1}$, $S = 1.003$, $(\Delta\rho)max = 0.737$, $(\Delta\rho)min = -1.233\,e$ Å^{-3}.

3. Results and discussion

3.1. *Crystal structure*

The molecular structure of the complex is illustrated in figure 1(a) with the atom numbering scheme. Selected bond distances and angles are given in table 1. The complex is made up of tetranuclear [$Cu_4(L)_4$] species and one *N*-methylpyrrole (NMP) molecule. The complex is centrosymmetric and the structure can be visualized

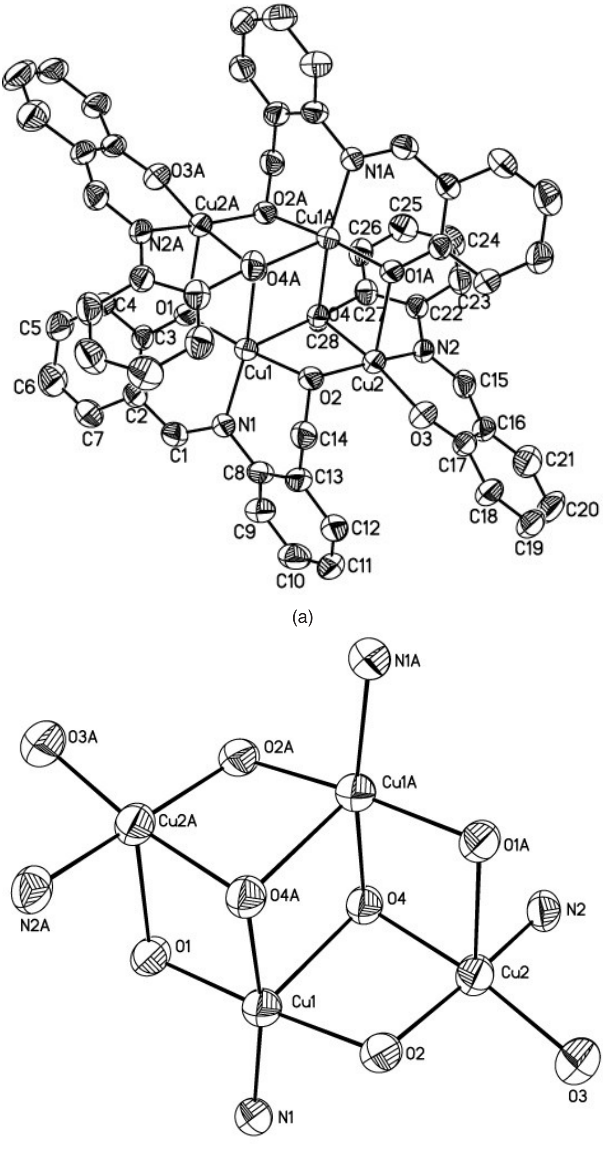


Figure 1. (a) An ORTEP view of the title complex with the atom numbering scheme and (b) its core structure.

Table 1. Selected bond distances (Å) and angles (°).

Cu(1)–O(1)	1.907(5)	Cu(2)–O(3)	1.885(5)
Cu(1)–O(2)	1.915(4)	Cu(2)–O(4)	1.946(5)
Cu(1)–N(1)	1.992(5)	Cu(2)–N(2)	1.986(6)
Cu(1)–O(4A)	2.051(4)	Cu(2)–O(2)	1.989(5)
Cu(1)–O(4)	2.231(4)	Cu(2)–O(1A)	2.301(4)
Cu(1)–Cu(2)	3.0500(13)	Cu (2)–Cu(1A)	3.1360(13)
Cu(1)–Cu(1A)	3.2921(16)	Cu (2)–Cu(2A)	5.2379(19)
O(1)–Cu(1)–O(2)	174.30(18)	O(3)–Cu(2)–O(4)	172.62(2)
O(1)–Cu(1)–N(1)	92.6(2)	O(3)–Cu(2)–N(2)	94.3(2)
O(2)–Cu(1)–N(1)	93.0 (2)	O(4)–Cu(2)–N(2)	90.5(2)
O(1)–Cu(1)–O(4A)	83.76(18)	O(3)–Cu(2)–O(2)	90.9 (2)
O(2)–Cu(1)–O(4A)	90.54(18)	O(4)–Cu(2)–O(2)	83.45(18)
N(1)–Cu(1)–O(4A)	167.7(2)	N(2)–Cu(2)–O(2)	169.3(2)
O(1)–Cu(1)–O(4)	100.71(19)	O(3)–Cu(2)–O(1A)	108.72(19)
O(2)–Cu(1)–O(4)	77.94(18)	O(4)–Cu(2)–O(1A)	76.52(17)
N(1)–Cu(1)–O(4)	112.63(19)	N(2)–Cu(2)–O(1A)	93.2(2)
O(4A)–Cu(1)–O(4)	79.60(18)	O(2)–Cu(2)–O(1A)	94.04(18)

Symmetry operator: $-x+1/2$, $-y+3/2$, $-z$.

as a pseudo-double cubane, where both cubes share a common face and in each cube one of the Cu(II) corners is missing. The deprotonated Schiff-base ligand binds to copper atoms as a dianionic tridentate ligand. The four copper atoms are located at the four corners of a pseudo-double-cubane core and bridged by two μ-alkoxo, two μ-phenoxo, and two μ_3-alkoxo bridges (figure 1(b)). The Cu1–Cu1A and Cu2–Cu25 distances are 3.2921(16), 5.2379(19) Å, respectively. The neighboring Cu1–Cu2 and Cu1–Cu2A distances are 3.0500(13) and 3.1360(13) Å, close to those in other tetranuclear copper(II) complexes with double-cubane cores [8–11]. Each Cu(II) ion exhibits square-pyramidal coordination. The basal plane of Cu1 is comprised of N1, O1 (μ-phenoxo), O2 (μ-alkoxo), and O4A (μ_3-alkoxo) atoms and the apical position is occupied by O4 (μ_3-alkoxo) atom. However, the basal plane of Cu2 is formed by N2, O2 (μ-alkoxo), O3, and O4 (μ_3-alkoxo) atoms and the apical position is occupied by O1A (μ-phenoxo) atom. Two copper atoms deviate slightly from the least square basal planes by 0.0841 and 0.0976 Å, respectively. The dihedral angles between these two basal planes are 86.1°.

3.2. *IR and electronic spectrum*

The IR spectrum of the complex shows a strong absorption at 1620 $\mathrm{cm^{-1}}$ due to ν(CH=N) band, which is shifted towards lower frequency compared to that of the free Schiff base ligand [12]. The electronic spectrum of the complex in DMF shows a d–d band at $\lambda_{\max}$ value of 610 nm, together with three more intense bands with $\lambda_{\max}$ values of 266, 296 and 410 nm, which are assigned to L^{2-} $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ and the ligand to metal charge-transfer transition, respectively [10, 13, 14].

Supplementary material

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

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