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A Dinuclear Copper(II) Complex [Cu₂L₂](ClO₄)₂ Derived from 2,6-Bis(aminomethyl)-4-methylphenol (HL)

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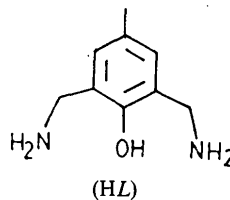
Abstract

The dinuclear copper(II) complex of 2,6-bis(aminomethyl)-4-methylphenol (HL), bis[μ-2,6-bis(aminomethyl)-4-methylphenolato-1κN,1:2κ²O,2κN']di-

copper(II) diperchlorate, [Cu₂(C₉H₁₃N₂O)₂](ClO₄)₂, has been synthesized and its structure determined. The title complex is crystallographically centrosymmetric about the midpoint of the Cu...Cu separation [3.013 (1) Å] and consists of two distorted square-pyramidal copper(II) centres bridged *via* phenoxide O atoms. Each Cu atom is coordinated (type 4 + 1) by two bridging O atoms, two secondary amine N atoms and, weakly, by one O atom of a symmetry-related perchlorate ion occupying the apical coordination site.

Comment

The chemistry of metal complexes of dinuclear chelating ligands is of considerable interest from the standpoint of correlating the magnetic, electronic, redox and catalytic properties of these compounds with their structures. Numerous studies have been reported using 2,6-diformyl-4-methylphenol as a precursor ligand for complexes with diphenolato moieties (Vigato, Tamburin & Fenton, 1990; Sorrel, 1989). Of particular interest have been the macrocyclic dinuclear complexes (Pilkington & Robson, 1970; Atkins, Blake & Schroder, 1993) derived from 2,6-diformyl-4-methylphenol and diamines. Robson and co-workers (Bell, Edwards, Hoskins, Kachab & Robson, 1989; Hoskins, Robson & Smith, 1990) have reported [2 + 2], [3 + 3] condensation reactions of 2,6-diformyl-4-methylphenol and 2,6-bis(aminomethyl)-4-methylphenol in the presence of metal salts to produce tetranickel, tetrazinc or hexacopper macrocyclic complexes. As the precursor 2,6-bis(aminomethyl)-4-methylphenol (HL) offers a wide scope of reactions, we were interested in the structure of its dicopper(II) complex, [Cu₂L₂](ClO₄)₂, in order to build a hierarchy.



An *ORTEPII* (Johnson, 1976) view of the binuclear complex with the atom-labelling scheme is shown in Fig. 1. With an inversion centre at the midpoint of the Cu...Cu^I [symmetry code: (i) -x, -y, -z] axis the asymmetric unit contains one Cu atom, one ligand and one (ClO₄)⁻ ion. The structure consists of two distorted square-pyramidal Cu^{II} centres (type 4 + 1) bridged *via* two phenoxide O atoms. The two bridging O atoms (O1 and O1ⁱ) and two secondary amine N atoms (N1 and N2ⁱ) form the approximately square base of the pyramid while the weakly

bonded O atom [Cu...O2ⁱ = 2.484 (5) Å] from a symmetry related (ClO₄)⁻ ion occupies the apical coordination site. The distortion in the CuN₂O₂ plane involves an acute angle O1—Cu—O1ⁱ of 77.8 (1)° and the Cu centre is displaced from the basal plane towards the fifth donor atom O2ⁱ by 0.087 (2) Å. The O-atom bridge angles, Cu—O1—Cuⁱ 102.2 (1)°, and the separation between the two Cu centres, 3.013 (1) Å, are comparable with the corresponding values reported for similar macrocyclic dinuclear Cu^{II} systems [103.9 (1)° and 3.088 (1) Å in C₂₆H₄₂N₄O₁₂Cl₂Cu₂ (Mandal, Thompson, Nag, Charland & Gabe, 1987*a*) and 102.8 (2)° and 2.993 (2) Å in C₂₄H₃₄N₄O₁₀Cl₂Cu₂ (Mandal, Thompson, Nag, Charland & Gabe, 1987*b*)].

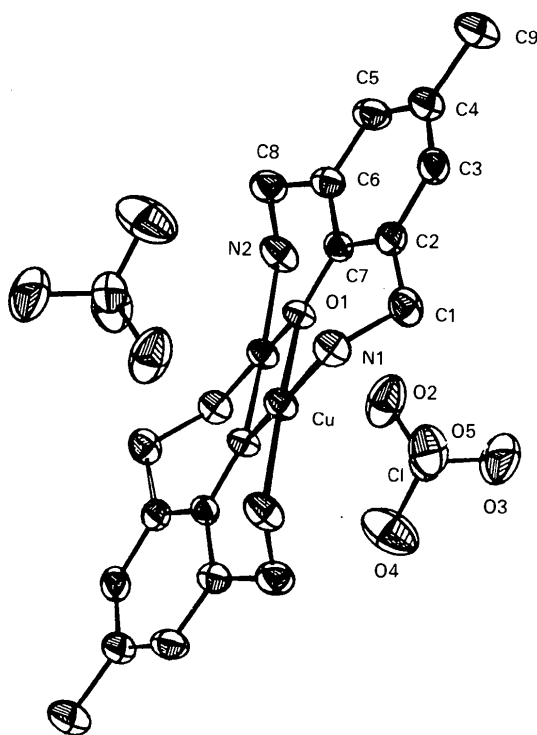


Fig. 1. ORTEP (Johnson, 1976) view of the complex giving the numbering scheme of the unique atoms.

Experimental

The title complex was synthesized by reacting an aqueous solution (10 cm³) of sodium acetate (2 g, 24.4 mmol) and [Cu(ClO₄)₂].6H₂O (1.48 g, 4 mmol) with a boiling methanol solution (150 cm³) of 2,6-bis(aminomethyl)-4-methylphenol monohydrochloride (0.81 g, 4 mmol). The solution was refluxed for 2 h and then concentrated in a rotary evaporator to ca 50 cm³. The solution was filtered and the filtrate allowed to evaporate slowly at room temperature. Deep blue crystals were collected after 24 h. Crystals suitable for X-ray diffraction were obtained by slow diffusion of diethyl ether into a methanol solution of the complex.

Crystal data

[Cu₂(C₉H₁₃N₂O₂)₂](ClO₄)₂
M_r = 656.41
 Monoclinic
*P*2₁/*a*
a = 9.301 (2) Å
b = 12.468 (4) Å
c = 10.720 (3) Å
 β = 99.48 (2)°
V = 1226.2 (6) Å³
Z = 2
D_x = 1.778 Mg m⁻³

Cu K α radiation
 λ = 1.5418 Å
 Cell parameters from 25 reflections
 θ = 10–20°
 μ = 4.43 mm⁻¹
T = 293 K
 Needle
 0.25 × 0.15 × 0.15 mm
 Deep blue

Data collection

Rigaku AFC-5R diffractometer
 $\theta/2\theta$ scans
 Absorption correction: empirical
 T_{\min} = 0.809, T_{\max} = 1.000
 1855 measured reflections
 1736 independent reflections
 1573 observed reflections
 $[I \geq 3\sigma(I)]$

*R*_{int} = 0.026
 θ_{\max} = 60°
 h = -10 → 10
 k = 0 → 14
 l = 0 → 12
 3 standard reflections monitored every 100 reflections
 intensity variation: 3%

Refinement

Refinement on *F*²
R = 0.046
wR = 0.052
S = 1.01
 1573 reflections
 203 parameters
 All H-atom parameters refined

$w = 1/[\sigma^2(F) + 0.0005F^2]$
 $(\Delta/\sigma)_{\max} = 0.58$
 $\Delta\rho_{\max} = 0.49 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.46 \text{ e \AA}^{-3}$
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Cu	-0.1098 (1)	0.0823 (1)	0.0263 (1)	0.0349 (4)
Cl	0.3297 (2)	0.0826 (1)	0.1851 (1)	0.0530 (8)
O1	0.0104 (3)	0.0460 (2)	-0.0981 (2)	0.034 (2)
O2	0.3312 (5)	0.0104 (4)	0.0839 (5)	0.083 (3)
O3	0.4598 (5)	0.1445 (5)	0.2014 (5)	0.094 (3)
O4	0.3077 (7)	0.0293 (5)	0.2938 (5)	0.111 (4)
O5	0.2089 (5)	0.1564 (3)	0.1499 (4)	0.072 (3)
N1	-0.1761 (4)	0.2148 (3)	-0.0663 (4)	0.041 (2)
N2	0.2049 (6)	-0.1070 (4)	-0.1756 (4)	0.049 (3)
C1	-0.0564 (6)	0.2728 (4)	-0.1107 (5)	0.044 (3)
C2	0.0060 (5)	0.2128 (3)	-0.2112 (4)	0.034 (2)
C3	0.0414 (5)	0.2681 (4)	-0.3146 (4)	0.042 (3)
C4	0.1098 (6)	0.2194 (4)	-0.4049 (4)	0.049 (3)
C5	0.1334 (6)	0.1110 (5)	-0.3933 (5)	0.047 (3)
C6	0.0956 (5)	0.0505 (4)	-0.2951 (4)	0.037 (3)
C7	0.0372 (5)	0.1031 (3)	-0.2000 (4)	0.032 (2)
C8	0.1103 (7)	-0.0680 (4)	-0.2935 (5)	0.054 (3)
C9	0.1570 (8)	0.2849 (6)	-0.5094 (5)	0.072 (4)

Table 2. Selected geometric parameters (Å, °)

Cu...Cu	3.013 (1)	Cu—O1	1.929 (3)
Cu—N1	1.972 (4)	Cu—N2	1.976 (5)
Cl—O2	1.411 (4)	Cl—O3	1.422 (5)

Cl—O4	1.386 (5)	Cl—O5	1.453 (4)
N1—C1	1.471 (6)	N2—C8	1.497 (8)
O1—C7	1.360 (5)	C1—C2	1.505 (7)
C2—C3	1.390 (6)	C3—C4	1.384 (7)
C2—C7	1.399 (6)	C4—C5	1.371 (8)
C5—C6	1.387 (7)	C6—C7	1.396 (6)
C6—C8	1.484 (7)	C4—C9	1.510 (7)
N1—Cu—O1	91.0 (1)	O3—Cl—O2	108.9 (3)
O4—Cl—O2	111.2 (4)	O4—Cl—O3	113.4 (3)
O5—Cl—O2	108.0 (3)	O5—Cl—O3	107.1 (3)
O5—Cl—O4	107.9 (3)	Cu—O1—Cu	102.2 (1)
C7—O1—Cu	129.5 (3)	C1—N1—Cu	112.6 (3)
Cu—N2—C8	110.7 (4)	C2—C1—N1	112.9 (4)
C3—C2—C1	119.6 (4)	C7—C2—C1	121.6 (4)
C7—C2—C3	118.8 (4)	C4—C3—C2	122.4 (5)
C5—C4—C3	117.1 (4)	C9—C4—C3	120.4 (5)
C9—C4—C5	122.6 (5)	C6—C5—C4	123.2 (5)
C7—C6—C5	118.5 (4)	C8—C6—C5	121.1 (5)
C8—C6—C7	120.4 (4)	C2—C7—O1	121.2 (4)
C6—C7—O1	119.0 (4)	C6—C7—C2	119.8 (4)
C6—C8—N2	112.0 (4)		

The structure was solved and refined using *SHELX76* (Sheldrick, 1976). The metal-atom position was deduced from a Patterson synthesis and remaining non-H atoms were located by successive ΔF syntheses. Refinement was by full-matrix least squares. H atoms (except the methyl H atoms) were located from the difference Fourier map and refined isotropically. Molecular geometry calculations were performed using *PARST* (Nardelli, 1982).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, including H-atom geometry, have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71655 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HE1005]

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Tetrapotassium μ -Carbonato- μ -oxo-bis[nitriilotriacetatoiron(III)] Dimethanol Dihydrate

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Abstract

The structure of a μ -carbonato- μ -oxo-diiron(III) complex with the tetradentate tripodal ligand nitriilotriacetate (nta), [Fe₂(nta)₂(CO₃)O]⁴⁻, has been determined by single-crystal X-ray diffraction for the potassium salt, K₄[Fe₂(C₆H₆NO₆)₂(CO₃)O].2CH₃-OH.2H₂O. The binuclear complex has crystallographic twofold symmetry and the coordination geometry around the Fe atoms is distorted octahedral. The Fe—O—Fe bridge angle is 121.1 (2)° and the Fe...Fe interatomic distance is 3.188 (1) Å. The Fe₂(CO₃)O core is not planar; the dihedral angle between the Fe₂O and CO₃ planes is 33.8 (5)°.

Comment

The Fe^{III}-nta solution, prepared by mixing an iron(III) solution and nitriilotriacetic acid, H₃nta, exhibits unique reactivity. The repeated intraperitoneal injection of the Fe^{III}-nta solution to rats and rabbits induces an iron overload similar to human hemochromatosis (Awai, Narasaki, Yamanoi & Seno, 1979). The Fe^{III}-nta solution is nephrotoxic and renal carcinoma is also induced (Okada & Midorikawa, 1982). In animals treated with the above solution, the products of lipid peroxidation increase (Goddard, Basford & Sweeney, 1986). Nishida, Yoshizawa & Akamatsu (1991) succeeded in isolating the Fe^{III} complex with the nta ligand, [Fe₂O(acetato)(nta)₂]³⁻, and concluded that the unique reactivity of the Fe^{III}-nta solution described