

The structure was solved by Patterson methods using *SHELXTL-Plus* (Sheldrick, 1991). The C atoms of the phenyl rings were refined as rigid groups (idealized hexagons) using the *AFIX* command in *SHELXTL-Plus*. H atoms were placed in idealized positions and included in the structure-factor calculations but were not included in the least-squares calculations.

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71682 (20 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL1054]

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Diamminebis[5-methylpyrimidine-2,4(1*H*,3*H*)-dionato(1-)-N³]copper(II) Trihydrate

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Abstract

The Cu atom in [Cu(C₅H₅N₂O₂)(NH₃)₂].3H₂O has square-planar coordination geometry. The methylpyrimidinedione ligands are *trans* with respect to each

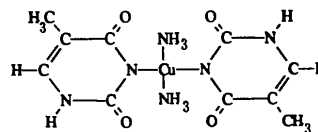
other, with Cu—N(1) and Cu—N(3) distances of 2.03 (1) and 1.99 (1) Å, respectively, while the amine Cu—N distances are 2.00 (1) and 1.96 (1) Å. Both methylpyrimidinedione ligands are essentially planar with their mean planes being inclined at 4.0°. The structure is stabilized by a network of hydrogen bonds involving amino-N and O atoms.

Comment

Reported structures of metal-ion complexes containing neutral uracil or thymine are relatively rare. Coordination of metals to either of the two heterocyclic N atoms, which are protonated at neutral pH, is unlikely; exocyclic O(2) and O(4) atoms, however, are available for complexation. Structural examples include bis(uracil)mercury(II) chloride (Carrabine & Sundaralingam, 1971) and bis(1,3-dimethyluracil)-copper(II) chloride (Cartwright, Goodgame, Johns & Skapski, 1978), with both complexes exhibiting metal binding to the O(4) atom.

At elevated pH, ring N atoms are deprotonated and thus are available for metal coordination. Complexes containing the monoanion of uracil or thymine include diamminediaquabis(uracilato)-nickel(II) (Lumme & Mutikainen, 1980) and aqua-(diethylenetriamine)(thyminato)copper(II) bromide dihydrate (Kistenmacher, Sorrell & Marzilli, 1975), with metal coordination at N(1), and triaquabis(uracilato)cadmium(II) (Mutikainen & Lumme, 1980) and bis(1-methylthyminato)mercury(II) (Kosturko, Folzer & Stewart, 1974), which exhibit metal binding at N(3).

Because of the importance of metal complexes of uracil and thymine in nucleic acid processes as well as in the development of anticancer therapies, we have synthesized several new compounds and herein report the crystal structure of the title compound (1).



(1)

There is a possible center of symmetry in the molecule at 0.2652, 0.0041, 0.8756, while the three water molecules lie independent of this center and are responsible for the non-centrosymmetric space group. The methylpyrimidinedione ligands and water molecules are hydrogen bonded with O···N and O···O distances in the range 2.74 (1)–2.90 (1) Å. It is interesting to note that the ammonia N atoms are involved in rather longer hydrogen-bonded interactions [2.91 (1)–3.46 (1) Å] with O atoms.

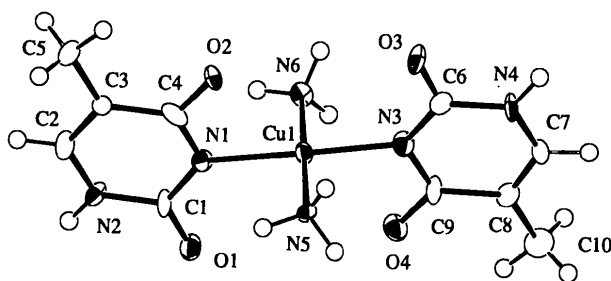


Fig. 1. Perspective view of the title compound with the crystallographic numbering scheme, plotted using ORTEPII (Johnson, 1976).

Experimental

Crystal data

$[\text{Cu}(\text{C}_5\text{H}_5\text{N}_2\text{O}_2)_2(\text{NH}_3)_2] \cdot 3\text{H}_2\text{O}$

$M_r = 401.87$

Monoclinic

$P2_1$

$a = 4.965 (1) \text{ \AA}$

$b = 18.692 (4) \text{ \AA}$

$c = 9.150 (1) \text{ \AA}$

$\beta = 96.10 (2)^\circ$

$V = 844.4 (2) \text{ \AA}^3$

$Z = 2$

Data collection

Rigaku AFC-6S diffractometer

Absorption correction:

empirical (DIFABS;

Walker & Stuart, 1983)

$T_{\min} = 0.84$, $T_{\max} = 1.07$

1718 measured reflections

1537 independent reflections

1192 observed reflections

$[I > 3\sigma(I)]$

$D_x = 1.581 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71069 \text{ \AA}$

Cell parameters from 18 reflections

$\theta = 15\text{--}20^\circ$

$\mu = 1.339 \text{ mm}^{-1}$

$T = 150 \text{ K}$

Plate

$0.30 \times 0.25 \times 0.07 \text{ mm}$

Purple

$R_{\text{int}} = 0.061$

$\theta_{\text{max}} = 25^\circ$

$h = 0 \rightarrow 5$

$k = 0 \rightarrow 22$

$l = -10 \rightarrow 10$

3 standard reflections

frequency: 100 min

intensity variation: 0.61%

Extinction correction: none

Atomic scattering factors

from Cromer & Waber

(1974)

Refinement

Refinement on F^2

$R = 0.049$

$wR = 0.051$

$S = 2.28$

1192 reflections

217 parameters

H-atom parameters not

refined

$w = 1/\sigma^2(F_o)$

$(\Delta/\sigma)_{\text{max}} = 0.17$

$\Delta\rho_{\text{max}} = 0.52 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.55 \text{ e \AA}^{-3}$

Extinction correction: none

Atomic scattering factors

from Cromer & Waber

(1974)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$B_{\text{eq}} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	B_{eq}
Cu(1)	0.2658 (3)	0.0041	-0.1244 (1)	1.34 (2)
O(1)	0.674 (2)	-0.0183 (4)	0.183 (1)	1.9 (2)
O(2)	-0.009 (2)	0.1199 (5)	-0.027 (1)	2.0 (2)
O(3)	-0.141 (2)	0.0302 (4)	-0.432 (1)	1.9 (2)

O(4)	0.536 (2)	-0.1106 (5)	-0.224 (1)	2.1 (2)
O(5)	0.060 (2)	0.1742 (5)	0.623 (1)	3.0 (2)
O(6)	0.450 (3)	0.3079 (7)	0.960 (1)	6.4 (4)
O(7)	0.923 (2)	0.2555 (5)	0.863 (1)	2.6 (2)
N(1)	0.327 (2)	0.0505 (6)	0.077 (1)	1.8 (2)
N(2)	0.491 (2)	0.0641 (7)	0.324 (1)	1.6 (2)
N(3)	0.199 (2)	-0.0387 (5)	-0.324 (1)	1.7 (2)
N(4)	0.023 (2)	-0.0589 (7)	-0.567 (1)	1.8 (3)
N(5)	0.497 (2)	0.0783 (7)	-0.206 (1)	1.5 (3)
N(6)	0.038 (2)	-0.0687 (7)	-0.044 (1)	1.4 (3)
C(1)	0.507 (2)	0.0306 (7)	0.193 (1)	1.7 (3)
C(2)	0.306 (3)	0.1195 (7)	0.338 (1)	2.0 (3)
C(3)	0.136 (2)	0.1422 (7)	0.222 (1)	1.7 (3)
C(4)	0.151 (2)	0.1044 (7)	0.086 (1)	1.9 (3)
C(5)	-0.063 (3)	0.2031 (9)	0.236 (1)	2.3 (3)
C(6)	0.027 (2)	-0.0183 (7)	-0.439 (1)	1.8 (3)
C(7)	0.193 (2)	-0.1132 (7)	-0.579 (1)	1.7 (3)
C(8)	0.374 (2)	-0.1354 (6)	-0.474 (1)	1.6 (3)
C(9)	0.376 (3)	-0.0962 (7)	-0.336 (1)	2.0 (3)
C(10)	0.557 (3)	-0.1962 (8)	-0.483 (2)	2.6 (3)

Table 2. Selected geometric parameters (\AA , $^\circ$)

Cu(1)—N(1)	2.03 (1)	Cu(1)—N(3)	1.99 (1)
Cu(1)—N(5)	2.00 (1)	Cu(1)—N(6)	1.96 (1)
O(1)—C(1)	1.24 (1)	O(2)—C(4)	1.26 (1)
O(3)—C(6)	1.24 (1)	O(4)—C(9)	1.26 (1)
N(1)—C(1)	1.36 (1)	N(1)—C(4)	1.34 (2)
N(2)—C(1)	1.36 (1)	N(2)—C(2)	1.40 (2)
N(3)—C(6)	1.34 (1)	N(3)—C(9)	1.40 (1)
N(4)—C(6)	1.39 (2)	N(4)—C(7)	1.33 (2)
C(2)—C(3)	1.35 (2)	C(3)—C(4)	1.45 (2)
C(3)—C(5)	1.52 (2)	C(7)—C(8)	1.31 (2)
C(8)—C(9)	1.46 (2)	C(8)—C(10)	1.46 (2)
N(1)—Cu(1)—N(3)	178.2 (5)	C(6)—N(4)—C(7)	122 (1)
N(1)—Cu(1)—N(5)	89.6 (4)	O(1)—C(1)—N(2)	120 (1)
N(3)—Cu(1)—N(6)	91.0 (4)	N(2)—C(2)—C(3)	121 (1)
Cu(1)—N(1)—C(1)	127.6 (9)	C(2)—C(3)—C(5)	121 (1)
C(1)—N(1)—C(4)	122 (1)	O(2)—C(4)—N(1)	118 (1)
Cu(1)—N(3)—C(6)	129.6 (9)	O(2)—C(4)—C(3)	120 (1)
C(6)—N(3)—C(9)	120 (1)	O(3)—C(6)—N(3)	123 (1)
O(1)—C(1)—N(1)	122 (1)	N(3)—C(6)—N(4)	117 (1)
N(1)—C(1)—N(2)	117 (1)	C(7)—C(8)—C(9)	114 (1)
C(2)—C(3)—C(4)	116 (1)	C(9)—C(8)—C(10)	119 (1)
C(4)—C(3)—C(5)	121 (1)	O(4)—C(9)—C(8)	122 (1)
N(1)—Cu(1)—N(5)	90.5 (4)	N(1)—C(4)—C(3)	120 (1)
N(3)—Cu(1)—N(5)	88.9 (4)	O(3)—C(6)—N(4)	119 (1)
N(5)—Cu(1)—N(6)	179.9 (5)	N(4)—C(7)—C(8)	124 (1)
Cu(1)—N(1)—C(4)	109.9 (7)	C(7)—C(8)—C(10)	125 (1)
C(1)—N(2)—C(2)	121 (1)	O(4)—C(9)—N(3)	116 (1)
Cu(1)—N(3)—C(9)	109.6 (7)	N(3)—C(9)—C(8)	120 (1)

Space groups $P2_1$ or $P2_1/m$ were determined from systematic absences ($0k0$, k odd); the former was chosen on the basis of statistical analysis of intensity distribution and confirmed by successful refinement. Lorentz-polarization and linear decay corrections were applied; allowance was made for anomalous dispersion (Ibers & Hamilton, 1974). The structure was solved by the heavy-atom method and refined by full-matrix least-squares calculations. Non-H atoms were allowed to refine with anisotropic temperature factors. H atoms were located from a difference Fourier map and included at geometrically idealized positions (C—H, N—H and O—H in the range 0.93–0.97 \AA). All calculations were performed using the TEXSAN (Molecular Structure Corporation, 1992) crystallographic software package.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71645 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: BR1046]

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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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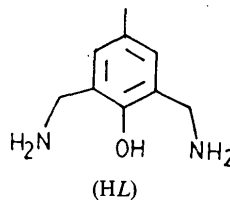
Abstract

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(C₉H₁₃N₂O₂)(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