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The Dimeric Complex {2,2'-[2,2-Dimethyl-1,3-propanediylbis(aminomethyl)]diphenolato-*N,N',O,O'*}copper(II) Ethanol Solvate†

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Abstract

The title complex, [Cu(C₁₉H₂₄N₂O₂)₂·2C₂H₅OH], is a centrosymmetric dimer. Each Cu atom is coordinated by two N and two O atoms from the amine–phenol ligand in a distorted square-pyramidal coordination geometry with a fifth axial bond to an O atom of the ligand coordinated by the other Cu atom. The ethanol molecule is hydrogen bonded to a phenol O atom and an amine N atom. The dihedral angle between the two CuN₂O₂ equatorial planes is 25.7 (1)°.

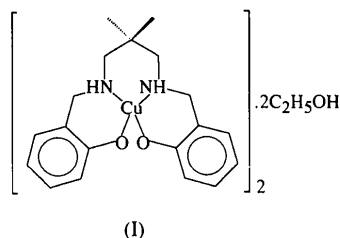
Comment

The development of the ⁶²Zn/⁶²Cu radionuclide generator increases the potential utility of copper-labelled radiopharmaceuticals imaging with positron emission tomography (PET). ⁶²Cu-PTSM [PTSM = pyruvaldehyde bis(4-methylthiosemicarbazone)], a neutral and lipophilic copper(II) complex, has been currently used as a potential copper tracer for imaging the heart and brain (Green, 1987). Besides, complexes of ⁶⁷Cu with tetradentate imine–phenol ligands have also been evaluated on their potentiality as cerebral blood-flow imaging agents (John, Bott & Green, 1994).

Tetradentate amine–phenols bear high coordinating affinity towards transition metals and are commonly used as their chelate agents. Although many crystal structures of metal complexes with N₂O₂ amine–phenols have been determined (Pillai, Barnes & Shlemper, 1993, 1994; Pillai, Barnes, John, Troutner & Shlemper, 1993; Pillai, John, Lo, Shlemper & Troutner, 1990; Pillai & Shlemper, 1994), none of the tetradentate copper(II) complex with its reduced Schiff base counterparts has been crystallographically determined so far. Here, the crystal structure of the title complex, (I), is described.

The Cu atom is coordinated by two N and two O atoms from the amine–phenol ligand in a distorted square-pyramidal coordination geometry with two phe-

nol O atoms being deprotonated. The complex exists as centrosymmetric dimers in which each Cu atom forms a fifth axial bond of length 2.291 (2) Å to an O atom of the ligand coordinated by the other Cu atom. It is well known that the hydrogen-bonding interaction of the solvent molecule with the complex in the lattice is one of the factors influencing dimeric association (Baker, Hall & Waters, 1970*a,b*; Bhadbhade & Srinivas, 1993). In the title compound, the O3···O2(*x*, *y*, 1 + *z*) and O3···N1(−*x*, 1 − *y*, 1 − *z*) distances of 2.857 (5) and 3.016 (4) Å, respectively, are clearly indicative of intermolecular hydrogen bonding between the ethanol and amine–phenol molecules.



The Cu atom is displaced 0.167 (1) Å above the plane defined by O1, O2, N1, N2. Atoms O1 and N2 are 0.273 (2) and 0.266 (2) Å, respectively, above the plane on the same side as Cu, while O2 and N1 are 0.275 (2) and 0.265 (2) Å below the plane, on the opposite side. The two bond lengths Cu—O, 1.946 (2), and Cu—N, 2.023 (3) Å, are both larger than the comparable average distances of 1.892 (5) and 1.940 (6) Å in {2,2'-[2,2-dimethyl-1,3-propanediylbis(nitrilomethylidene)]diphenolato-*N,N',O,O'*}copper(II) (Chen, Lu, Yao, Huang & Lo, 1997). The increase in these bond lengths might be attributed to steric hindrance in the dimer.

The dimeric five-coordinate structure of the title compound is significantly different from the configuration of the palladium complexes with the analogous amine–phenol ligands. For example, both palladium(II) complexes of 2,2'-[1,3-propanediylbis(aminomethyl)]diphenolato and 2,2'-[1,4-butane-diylbis(aminomethyl)]diphenolato exhibit monomeric four-coordinate geometry rather than as dimers (Pillai, Barnes, John *et al.*, 1993; Pillai & Shlemper, 1994). Additionally, an X-ray diffraction study of a copper(II) complex with an N₂O₂-donor macrocycle, chloro(3,4:9,10-dibenzo-1,12-diaza-5,8-dioxacyclopentadecane)copper(II) perchlorate, has been reported (Adam *et al.*, 1980) in which Cu coordinates two ether O, two amine N, and one Cl atom. Despite the long Cu—O distances and the monomeric geometry of this complex, both the distortion of the N₂O₂ donor and the five-coordination are similar to those of the title compound.

Dimeric five-coordinate structures similar to that of the title compound have been observed for the

† Alternative name: bis[μ-2,2'-(4,4-dimethyl-2,6-diazaheptane-1,7-diyl)phenolato-*O,N,N',O':O*]dicopper(II) bis(ethanol) solvate.

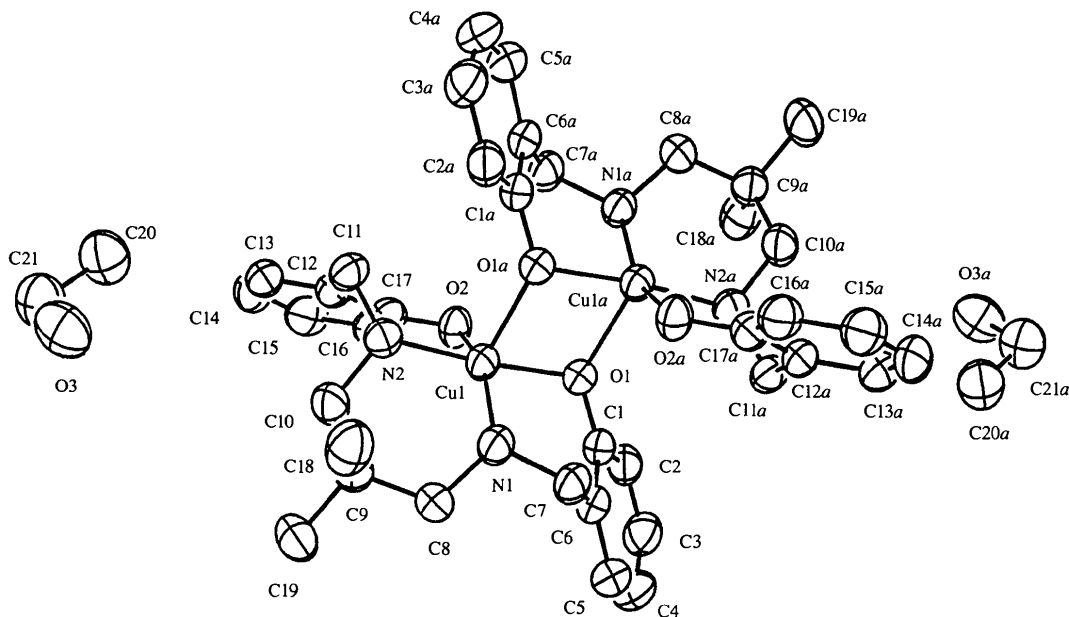


Fig. 1. A perspective view of the molecule with the atom-numbering scheme. Displacement ellipsoids are drawn at 50% probability.

Cu^{II} complexes with its unreduced Schiff base counterparts, {2,2'-[1,2-ethanediylbis(nitrilomethylidene)]diphenolato-*N,N',O,O'*}copper(II). Its two adducts with chloroform (Baker, Hall & Waters, 1970*b*; Bhadbhade & Srinivas, 1993) and the one with nitrobenzene (Hall & Waters, 1960) were found to display dimers with five-coordinate Cu atoms and short fifth Cu—O bonds [2.79 (1), 2.414 (2) and 2.41 (1) Å, respectively].

It is well known that increasing the steric hindrance by elongation of the alkylene bridge will result in a change in the chelate pattern from planar to tetrahedral. The distortion of the inner coordination sphere can be recognized by the magnitude of the dihedral angle between the two planes defined by CuN_2O_2 . The dihedral angle of the title complex, 25.7 (1)°, is much larger than those of the five-coordinated dimers with a shorter alkylene backbone, {2,2'-[1,2-ethanediylbis(nitrilomethylidene)]diphenolato-*N,N',O,O'*}copper(II). On the other hand, this angle is comparable with the 24.7 (3)° of {2,2'-[1,3-propanediylbis(nitrilomethylidene)]diphenolato-*N,N',O,O'*}copper(II), but somewhat smaller than the 34.8 (2)° of {2,2'-[1,3-(2,2-dimethylpropane)diylbis(nitrilomethylidene)]diphenolato-*N,N',O,O'*}copper(II) (Chen *et al.*, 1997), both being a monomeric four-coordinated structure.

Experimental

The precursor 2,2'-[2,2-dimethyl-1,3-propanediylbis(nitrilomethylidene)]diphenolate was prepared by reaction of salicylaldehyde and 1,3-diamino-2,2-dimethylpropane (molar ratio 2:1) in ethanol solution for 2 h at 298 K. 2,2'-[2,2-Dimethyl-1,3-propanediylbis(aminomethylidene)]diphenolate was pre-

pared by mixing the precursor and NaBH_4 (molar ratio 1:2) in ethanol solution for 1 h at 333 K. The title compound was obtained by mixing copper(II) nitrate trihydrate and 2,2'-[2,2-dimethyl-1,3-propanediylbis(aminomethylidene)]diphenolate (molar ratio 2:1) in ethanol with sodium acetate (pH 8) and stirring at 298 K for 1 h. Recrystallization was from ethanol.

Crystal data

$[\text{Cu}(\text{C}_{19}\text{H}_{24}\text{N}_2\text{O}_2)]_2 \cdot 2\text{C}_2\text{H}_6\text{O}$
 $M_r = 422.0$
 Triclinic
 $P\bar{1}$
 $a = 9.951(2)$ Å
 $b = 10.877(2)$ Å
 $c = 11.156(2)$ Å
 $\alpha = 68.20(2)^\circ$
 $\beta = 66.68(2)^\circ$
 $\gamma = 88.39(2)^\circ$
 $V = 1019.5(3)$ Å³
 $Z = 2$
 $D_x = 1.375$ Mg m⁻³
 D_m not measured

Mo $K\alpha$ radiation
 $\lambda = 0.71073$ Å
 Cell parameters from 4305 reflections
 $\theta = 1.0\text{--}25.8^\circ$
 $\mu = 1.094$ mm⁻¹
 $T = 296$ K
 Columnar
 $0.35 \times 0.20 \times 0.10$ mm
 Green

Data collection

Siemens SMART-CCD diffractometer
 Full-sphere scans
 Absorption correction: empirical from equivalent data (Sheldrick, 1991)
 $T_{\min} = 0.800$, $T_{\max} = 0.896$
 8169 measured reflections
 3465 independent reflections

3017 reflections with $I > 3\sigma(I)$
 $R_{\text{int}} = 0.035$
 $\theta_{\max} = 25.6^\circ$
 $h = -11 \rightarrow 11$
 $k = -13 \rightarrow 12$
 $l = -13 \rightarrow 13$
 No standard reflections

Refinement

Refinement on F^2 $R = 0.038$ $wR = 0.048$ $S = 1.47$

3017 reflections

245 parameters

H atoms riding: see below

 $w = 1/[\sigma^2(F) + 0.001F^2]$ $(\Delta/\sigma)_{\max} = 0.003$ $\Delta\rho_{\max} = 0.31 \text{ e } \text{Å}^{-3}$ $\Delta\rho_{\min} = -0.28 \text{ e } \text{Å}^{-3}$

Extinction correc-

tion: $F^* = F[1 + 0.002\chi F^2/\sin(2\theta)]^{-1/4}$

Extinction coefficient:

 $\chi = 0.0007(4)$

Scattering factors from

SHELXTL-Plus (Sheldrick, 1991)

Absolute configuration: none

Table 1. Selected geometric parameters (Å , $^\circ$)

Cu1—O1	1.948 (2)	N1—C7	1.501 (4)
Cu1—O2	1.943 (2)	N1—C8	1.474 (5)
Cu1—N1	2.046 (3)	N2—C10	1.479 (6)
Cu1—N2	2.000 (3)	N2—C11	1.492 (4)
O1—Cu1 ⁱ	2.291 (2)	O3—O2 ⁱⁱ	2.857 (5)
O2—C17	1.343 (4)	O3—N1 ⁱⁱⁱ	3.016 (4)
O1—Cu1—O2	88.5 (1)	O2—Cu1—N2	93.9 (1)
O1—Cu1—N1	92.9 (1)	N1—Cu1—N2	87.3 (1)
O2—Cu1—N1	154.7 (1)	Cu1—O1—Cu1 ⁱ	96.4 (1)
O1—Cu1—N2	173.9 (1)		

Symmetry codes: (i) $-x, 1-y, -z$; (ii) $x, y, 1+z$; (iii) $-x, 1-y, 1-z$.

The data collection nominally covered over a full sphere of reciprocal space, by a combination of three sets of exposures; each set had a different φ angle for the crystal and each exposure covered 0.3° in ω . The crystal-to-detector distance was 5.89 cm. Coverage of the unique set is over 86% complete to at least 25.6° in θ . Crystal decay was monitored by remeasuring the first frame at the end of the data collection, and found to be negligible. H atoms were placed geometrically and refined with a riding model and with U_{iso} constrained to be 0.08 Å^2 .

Program(s) used to solve structure: SHELXTL-Plus (Sheldrick, 1991). Program(s) used to refine structure: SHELXTL-Plus. Molecular graphics: SHELXTL-Plus. Software used to prepare material for publication: SHELXTL-Plus.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AB1436). Services for accessing these data are described at the back of the journal.

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trans-[RuCl₂(dmf)₄]CF₃SO₃.CH₂Cl₂

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Abstract

The asymmetric unit of the structure of the title complex, *trans*-dichlorotetrakis(*N,N*-dimethylformamide-*O*)-ruthenium(III) trifluoromethylsulfonate dichloromethane solvate, [RuCl₂(C₃H₇NO)₄]CF₃SO₃.CH₂Cl₂, contains an ordered [RuCl₂(dmf)₄]⁺ cation, a CF₃SO₃[−] anion and a CH₂Cl₂ solvent molecule. Within the cation, the chlorine ligands adopt a mutually *trans* arrangement, with four O-bonded dmf molecules ligated equatorially to the Ru^{III} centre [Ru—Cl 2.3464(16) and 2.3376(15), and Ru—O 2.043(4), 2.045(4), 2.049(4) and 2.055(4) Å], giving a distorted octahedral stereochemistry overall.

Comment

The X-ray structure (Fig. 1) of the title compound, (I), shows a distorted octahedral arrangement around the central Ru^{III} ion, with two mutually *trans* chlorine ligands and four essentially planar O-bonded dmf ligands; Ru—Cl 2.3376(15) and 2.3464(16), and Ru—

