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An Ethanol-Solvated Copper(II) Complex of 1,3-Bis(2-hydroxybenzylimino)pentane

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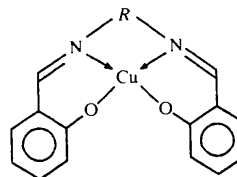
Abstract

In the title compound, {2,2'-[1,3-pentanediylo-bis(nitrilomethylidene)]diphenolato}copper(II)-ethanol (2/1), 2[Cu(C₁₉H₂₀N₂O₂)]·C₂H₆O, the Cu atom is coordinated by an N₂O₂ donor set from the imine-phenol ligand in a distorted tetrahedral coordination geometry, with the two phenol O atoms being deprotonated. There are two 'unsolvated' copper complexes and two ethanol-solvated copper complexes in the triclinic unit cell. The Cu—O and Cu—N distances are 1.891 (4)–1.897 (4) and 1.943 (5)–1.978 (5) Å, respectively. The angle between the two coordination planes defined by the ligating atoms of one complex (O11, O12, N11 and N12) and those of the other independent complex (O21, O22, N21 and N22) is 49.4 (2)°.

Comment

Radioactive copper-labelled compounds have been studied extensively because of their diagnostic and/or therapeutic potential. Thus, we have been interested in the development of suitable ligands that can form stable complexes with this metal. The chemistry of Schiff base ligands has aroused considerable attention, mainly because of preparative accessibility, diversity and struc-

tural variability. Although tetradentate imine-phenol ligands can readily form complexes with copper (John *et al.*, 1994), very few have been characterized. The solid-state structures of monomeric Cu^{II} imine-phenol complexes have been determined so far for the complexes shown schematically below: (I) (Baker *et al.*, 1970), (II) (Cheeseman *et al.*, 1966) and (III) (Yao *et al.*, 1997). We report here the synthesis and characterization of the title compound, (IV).



- (I) R = CH₂-CH₂
 (II) R = C₆H₄-C₆H₄
 (III) R = CH₂-CH₂-CH₂-CH₂
 (IV) R = CH₂-CH₂-CH(CH₂)CH₃

In the title compound, the coordination about the Cu atom forms a 6–6–6 chelate ring structure and a distorted tetrahedron with two imine N atoms and two phenol O atoms. There are two 'unsolvated' copper [Cu(C₁₉H₂₀N₂O₂)] complex molecules, *A*, and two ethanol-solvated molecules, *B*, in the centrosymmetric unit cell. The ethanol solvate is hydrogen bonded to a phenolate O atom [O50···O11 = 2.851 (8) Å] of *B*. The angle between the two coordination planes, defined by atoms O11, O12, N11 and N12, and atoms O21, O22, N21 and N22, is 49.4 (2)°.

The N—Cu1—N and O—Cu1—O angles in *B* are 92.2 (2) and 89.6 (2)°, respectively. The distortion of the coordination geometry in *A* is evident in the expansion of the N—Cu2—N angle [94.4 (2)°] and in the compression of the O—Cu2—O angle [82.4 (2)°] from 90°. Inversely, the two *trans*-O—Cu—N angles in *B*, O11—Cu1—N12 and O12—Cu1—N11, are 155.9 (2) and 156.1 (2)°, respectively, while the O—Cu—N angles in *A*, O21—Cu2—N22 and O22—Cu2—N21, are 170.1 (2) and 172.6 (2)°, respectively. As a result, the dihedral angle between the two chelate rings defined by Cu1, O11 and N11, and Cu1, O12 and N12, in *B* is 33.0 (2)°, which is much larger than the corresponding angle in *A* [8.8 (2)°].

Steric interactions of the propyl, butyl and biphenyl backbones affect the copper coordination geometry significantly in many respects (see Table 1). In the five-membered-ring system with a two-C-atom backbone [complex (I)], the Cu—N distances are short (average 1.916 Å), and the N—Cu—N angle (82.7°) and the dihedral angle (5.3°) are small. Adding a third C atom to the backbone to make a six-membered chelate ring (*A* and *B*) results in increased Cu—N lengths, N—Cu—N angles and dihedral angles. Further increasing the backbone size to give a seven-membered ring [complexes (II)

and (III)] makes it more difficult to maintain the configuration without considerable puckering of the ring. It seems that 'tuning' of the Cu—N lengths, N—Cu—N angle and dihedral angle contributes to the flexibility of the coordination of copper by tetradentate imine-phenol ligands.

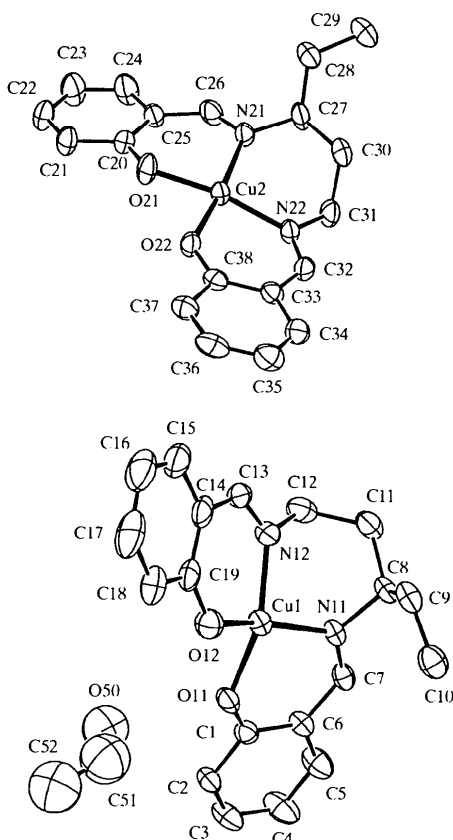


Fig. 1. Perspective view of the molecules of (IV) with the atom-numbering scheme, excluding H atoms. Displacement ellipsoids are drawn at 30% probability.

Experimental

For the preparation of the title compound, 1,3-bis(2-hydroxybenzylimino)pentane was prepared by mixing salicylaldehyde (60 mmol) and 1,3-pentanediamine (30 mmol) in 100 ml of ethanol. The reaction mixture was stirred for 6 h and then placed in a freezer for 24 h. The lower oil layer was collected by decanting the upper ethanol layer. After repeating this procedure, a yellow oil with high purity was harvested and dried *in vacuo*. Copper(II) nitrate trihydrate (3 mmol) in 95% ethanol (20 ml) and 1,3-bis(2-hydroxybenzylimino)pentane (3 mmol) in ethanol (100 ml) were mixed and heated at 333 K for 1 h. The solution was filtered and the filtrate kept in a beaker at 277 K for crystallization. Dark-blue crystals began to appear after 1–2 d, and were collected by filtration. Crystals suitable for X-ray diffraction were obtained by slow evaporation from a saturated ethanolic solution.

Crystal data

$2[\text{Cu}(\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}_2)] \cdot \text{C}_2\text{H}_6\text{O}$
 $M_r = 789.91$
 Triclinic
 $P\bar{1}$
 $a = 12.1159(16) \text{ \AA}$
 $b = 12.7354(19) \text{ \AA}$
 $c = 13.824(3) \text{ \AA}$
 $\alpha = 112.98(2)^\circ$
 $\beta = 93.55(2)^\circ$
 $\gamma = 104.94(2)^\circ$
 $V = 1865.4(5) \text{ \AA}^3$
 $Z = 2$
 $D_x = 1.406 \text{ Mg m}^{-3}$
 D_m not measured

Mo $K\alpha$ radiation
 $\lambda = 0.71073 \text{ \AA}$
 Cell parameters from 25 reflections
 $\theta = 7.02\text{--}14.49^\circ$
 $\mu = 1.19 \text{ mm}^{-1}$
 $T = 293 \text{ K}$
 Hexagonal
 $0.41 \times 0.34 \times 0.25 \text{ mm}$
 Dark blue

Data collection

Nonius CAD-4 diffractometer
 $\theta/2\theta$ scan
 Absorption correction: ψ scan (North *et al.*, 1968)
 $T_{\min} = 0.600$, $T_{\max} = 0.743$
 6878 measured reflections
 6555 independent reflections

4555 reflections with $I > 2.5\sigma(I)$
 $R_{\text{int}} = 0.014$
 $\theta_{\max} = 25^\circ$
 $h = -14 \rightarrow 13$
 $k = 0 \rightarrow 15$
 $l = -16 \rightarrow 15$
 3 standard reflections
 frequency: 60 min
 intensity decay: 1.0%

Refinement

Refinement on F
 $R = 0.051$
 $wR = 0.041$
 $S = 2.07$
 4554 reflections
 460 parameters
 Only H-atom U 's refined
 $w = 1/\sigma^2(F)$

$(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.82 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.77 \text{ e \AA}^{-3}$
 Extinction correction: none
 Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. Comparison of copper(II) coordination (\AA , $^\circ$) and the dihedral angle between chelate rings ($^\circ$) in imine-phenol complexes

	(I) ^a	(II) ^b	(III) ^c	(IV) ^d	
				A	B
Cu—O	1.906	1.90	1.898 (3)	1.891 (4)	1.894 (4)
	1.886	1.90	1.903 (3)	1.897 (4)	1.893 (4)
Cu—N	1.928	1.94	2.000 (3)	1.978 (5)	1.951 (5)
	1.904	1.96	1.941 (3)	1.950 (5)	1.943 (5)
O—Cu—O'	87.8	88.9	87.4 (1)	82.4 (2)	89.6 (2)
O—Cu—N	94.2	93.6	94.3 (1)	92.3 (2)	93.9 (2)
O—Cu—N'	176.5	154.6	144.0 (1)	170.1 (2)	155.9 (2)
O'—Cu—N	174.5	151.4	153.3 (1)	172.6 (2)	156.1 (2)
O'—Cu—N'	95.5	93.6	93.9 (1)	91.5 (2)	94.1 (2)
N—Cu—N	82.7	96.1	100.1 (1)	94.4 (2)	92.2 (2)
Dihedral angle	5.3	37.0	42.7 (1)	8.8 (2)	33.0 (2)

References: (a) Baker *et al.* (1970); (b) Cheeseman *et al.* (1966); (c) Yao *et al.* (1997); (d) this work.

H atoms were located by calculations based on geometric considerations. H-atom positions were fixed in the refinement.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *NRCVAX* (Gabe *et al.*, 1989). Program(s) used to solve structure: *NRCVAX*. Program(s) used to refine structure: *NRCVAX*.

Molecular graphics: ORTEPII (Johnson, 1976). Software used to prepare material for publication: NRCVAX.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1071). Services for accessing these data are described at the back of the journal.

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A Copper(II) Complex of a Structurally Reinforced Chiral 14-Membered Aza-Macrocycle

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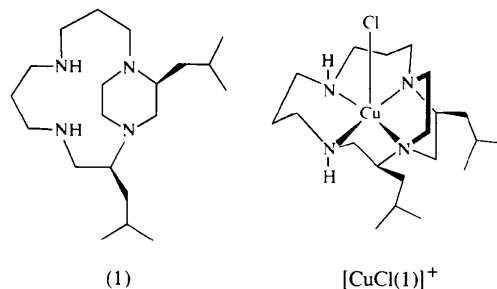
Abstract

The structure of a copper(II) complex cation of a reinforced chiral 14-membered aza-macrocycle, namely, chloro[(2*S*,13*S*)-2,13-diisobutyl-1,4,8,12-tetraazabicyclo[10.2.2]tetradecane-κ⁴N]copper(II), which crystallizes as a perchlorate hydrate, [CuCl(C₂₀H₄₂N₄)]ClO₄·H₂O, has been determined. The copper(II) cation lies in the macrocyclic cavity coordinated in a square-pyramidal

manner by the four N atoms of the aza-macrocycle, with the chloride anion in an apical position.

Comment

The syntheses of structurally reinforced macrocyclic polyamines and their metal complexes have been studied recently in areas such as molecular recognition and bio-inorganic chemistry (Mitewa & Bontchev, 1994). Although numerous structurally reinforced macrocyclic polyamines have been analyzed in many studies, carbon-backbone functionalized versions are less common (Aston *et al.*, 1994). Recently, we synthesized novel chiral and structurally reinforced 15-, 18- and 20-membered-ring polyamines, and their copper(II) complexes (Seki *et al.*, 1996; Yoshiki *et al.*, 1996). This paper describes the crystal structure of a copper(II) complex of a new chiral and structurally reinforced 14-membered polyamine, (2*S*,13*S*)-2,13-diisobutyl-1,4,8,12-tetraazabicyclo[10.2.2]tetradecane, (1).



A view of the complex is shown in Fig. 1. The copper complex cation is five-coordinate, bound to four N atoms of the macrocycle and to a chloride anion. The coordination geometry around the copper cation is best described as square pyramidal with the apical position being occupied by the chloride anion. The four N atoms of the macrocyclic ligand are approximately planar (within 0.0979 Å), with the copper(II) cation located in the direction of the chloride ligand, 0.310 Å from the N₄ plane. Both six-membered chelate rings in the complex (Cu1, N9, C10, C11, C12, N13 and Cu1, N13, C14, C15, C16, N3) have pseudo-chair forms. The absolute configurations of the N9 and N13 atoms are *R* and *S*, respectively, while the piperazine ring (C1, C2, N3, C4, C5, N6) is in a boat form. The Cu—N bond lengths are in the range 1.998 (7)–2.05 (1) Å, comparable to the strain-free *M*—N length (2.03 Å) for [Cu(1,4,8,11-tetraazacyclotetradecane)] (Hancock, 1989), and the average *M*—N lengths of 2.03 (2), 2.030 (7) and 2.033 (8) Å for [Cu₂(1,4,7,10,13,16,19,22,25,28-decaazacyclotriacontane)HCl₂]³⁺ or [Cu₂([30]-aneN₁₀)-HCl₂]³⁺ (Bencini *et al.*, 1987), [Cu{(2*R*,5*R*,8*R*,11*R*)-1,4,7,10-tetraphenyl-2,5,8,11-tetraethyl-1,4,7,10-tetraazacyclododecane}Cl]⁺ or [Cu(tecyclen)Cl]⁺ (Sakurai *et al.*, 1982), and [Cu(1,3,6,9,11,14-hexaazatricyclo-