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{2-[Bis(1-methyl-2-benzimidazolylmethyl)amino]ethanol}chlorocopper(II) Chloride Hydrate

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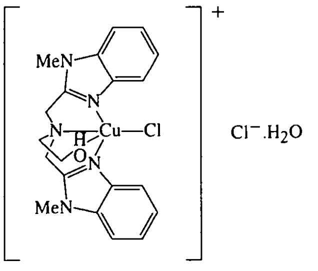
Abstract

During the multi-step synthesis of a novel and potentially binucleating ligand, the title complex, $[CuCl(C_{20}H_{23}N_5O)]Cl.H_2O$, was obtained and structurally characterized. The analysis revealed distorted five-coordinate square-pyramidal coordination geometry about Cu, with three N atoms and one Cl ion in the basal plane and the hydroxy group, which remains protonated, at the apical position [Cu—O 2.278 (2) Å].

Comment

The design, synthesis and characterization of ligands that offer coordination environments similar to those identified in metalloproteins and enzymes is an ongoing ambition of our research. The title complex, (I), displays two benzimidazole groups, a tertiary aliphatic amine and an ethyl alcohol group. Benzimidazole is an excellent model for the amino acid histidine because, in addition to structural similarities, it has a similar p*K*$_a$.



(I)

There is five-coordinate distorted square-pyramidal coordination geometry about the Cu atom, with the alcohol group in the apical position at a distance of 2.278 (2) Å from Cu. A feature of particular interest is that the alcohol group remains protonated although coordinated to the copper centre. This relatively unusual feature offers a structural model for a putative intermediate in the reduction of dioxygen for blue copper oxidases. During enzymic function a hydroperoxide is postulated to be stabilized by coordination to the Type III copper centre prior to complete reduction of the substrate. This complex represents effectively half of the Type III copper centre for the blue copper oxidases, and as such is a

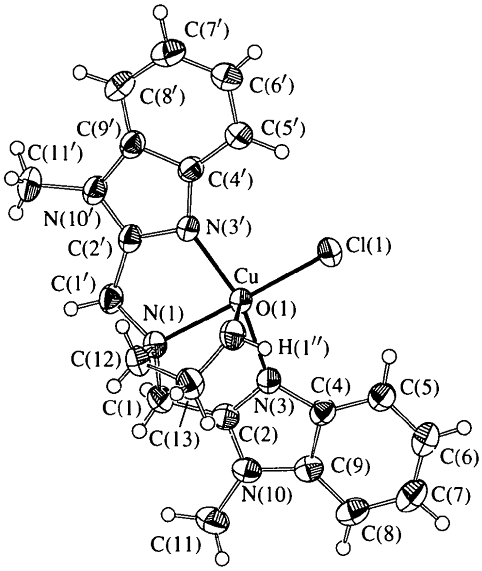


Fig. 1. A view of the cation with displacement ellipsoids drawn at the 50% probability level. H atoms are drawn as circles with arbitrary radii.

valuable structural model for that motif. Several examples of this type of coordination of alcohol groups by copper, where the Cu atom is five-coordinate and OH is a member of a chelate ring, are known, but a search of the Cambridge Crystallographic Database (Allen *et al.*, 1991) indicates that this complex has one of the shortest such Cu—O interactions yet recorded. Other examples found in structures with $R < 0.10$ are 2.383 Å in [μ-2-({2-[(*o*-hydroxo-α-methylbenzylidene)amino]-ethyl}amino)ethanol-*N*,*N*′,*O*,*O*′][μ-2-({2-[(*o*-hydroxy-α-methylbenzylidene)amino]ethyl}amino)ethanolato-*N*,*N*′,*O*,*O*′]dicopper(II) perchlorate (Cros, Laurent & Dahan, 1987), 2.410 Å in [*N*,*N*-bis(2-benzoimidazolylmethyl)ethanolamine-*N*,*N*′,*N*″,*O*]chlorocopper(II) perchlorate methanol solvate (Nishida, Takahashi & Kida, 1981) and 2.650 Å in [(*R*)-2-amino-1,1-bis(2-methoxyphenyl)-3-phenyl-1-propanol-*N*,*O*][(*R*)-1,1-bis(2-methoxyphenyl)-3-phenyl-2-salicylideneamino-1-propanolato-*N*,*O*,*O*′]copper(II) (Yanagi & Minobe, 1987). The hydroxy H atom [H(1″)] is involved in a hydrogen bond to Cl(2) at x, y, z, with O(1)···Cl(2) 2.992 (2) Å.

Experimental

The ligand, 2-[bis(1-methylbenzimidazol-2-ylmethyl)amino]-ethanol, was prepared by condensation of 1,2-diaminobenzene and iminodiacetic acid followed by methylation using adapted literature procedures (Crane & Fenton, 1990). The copper complex was prepared by reaction of the ligand with one equivalent of copper chloride in methanol. Slow evaporation gave crystals which were suitable for structure determination.

Crystal data

$[CuCl(C_{20}H_{23}N_5O)]Cl.H_2O$
$M_r = 501.90$
Monoclinic
$P2_1/c$
$a = 8.336\ (2)$ Å
$b = 15.044\ (4)$ Å
$c = 17.454\ (6)$ Å
$\beta = 99.46\ (2)^\circ$
$V = 2159\ (1)$ Å^3
$Z = 4$
$D_x = 1.544$ Mg m^{-3}
$D_m = 1.54\ (1)$ Mg m^{-3}
D_m measured by flotation in CCl_3CH_3–$CHBr_2CH_3$

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 6 reflections
$\theta = 19.24$–22.16°
$\mu = 1.29$ mm^{-1}
$T = 293$ K
Prism
0.42 × 0.42 × 0.27 mm
Blue–green

Data collection

CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: by integration from crystal shape
$T_{\min} = 0.640$, $T_{\max} = 0.687$
6289 measured reflections
6289 independent reflections

5902 observed reflections $[F^2 > 0]$
$\theta_{\max} = 30.0^\circ$
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 21$
$l = -24 \rightarrow 24$
6 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.056$
$wR(F^2) = 0.104$
$S = 1.798$
5902 reflections
367 parameters
All H-atom parameters refined
Weighting scheme based on measured e.s.d.'s

$(\Delta/\sigma)_{\max} = 0.383$
$\Delta\rho_{\max} = 0.667$ e Å^{-3}
$\Delta\rho_{\min} = -0.508$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Tables 2.2B and 2.3.1)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Cu	0.54780 (3)	0.62181 (2)	0.45713 (2)	0.0315 (1)
Cl(1)	0.76579 (8)	0.54412 (5)	0.43435 (4)	0.0491 (3)
Cl(2)	0.95721 (8)	0.82912 (6)	0.49576 (6)	0.0681 (5)
N(1)	0.3354 (2)	0.6894 (1)	0.4784 (1)	0.0331 (9)
C(1)	0.3255 (3)	0.6847 (2)	0.5624 (2)	0.039 (1)
C(2)	0.4904 (3)	0.6642 (2)	0.6059 (1)	0.035 (1)
N(3)	0.6089 (2)	0.6360 (1)	0.5702 (1)	0.036 (1)
C(4)	0.7451 (3)	0.6255 (2)	0.6283 (1)	0.036 (1)
C(5)	0.9032 (3)	0.5994 (2)	0.6245 (2)	0.043 (1)
C(6)	1.0103 (4)	0.5958 (2)	0.6936 (2)	0.049 (1)
C(7)	0.9639 (4)	0.6171 (2)	0.7643 (2)	0.051 (2)
C(8)	0.8073 (4)	0.6434 (2)	0.7686 (2)	0.046 (1)
C(9)	0.6997 (3)	0.6475 (2)	0.6993 (1)	0.038 (1)
N(10)	0.5368 (3)	0.6719 (1)	0.6829 (1)	0.037 (1)
C(11)	0.4369 (4)	0.6963 (2)	0.7407 (2)	0.050 (2)
C(1′)	0.1930 (3)	0.6471 (2)	0.4289 (2)	0.038 (1)
C(2′)	0.2505 (3)	0.6197 (2)	0.3562 (1)	0.035 (1)
N(3′)	0.4062 (2)	0.5990 (1)	0.3574 (1)	0.0337 (9)
C(4′)	0.4208 (3)	0.5772 (2)	0.2816 (1)	0.034 (1)
C(5′)	0.5545 (3)	0.5536 (2)	0.2484 (2)	0.042 (1)
C(6′)	0.5300 (4)	0.5382 (2)	0.1695 (2)	0.049 (2)
C(7′)	0.3773 (4)	0.5474 (2)	0.1242 (2)	0.051 (2)
C(8′)	0.2427 (4)	0.5711 (2)	0.1555 (2)	0.045 (1)
C(9′)	0.2679 (3)	0.5861 (2)	0.2353 (1)	0.036 (1)
N(10′)	0.1625 (2)	0.6134 (1)	0.2847 (1)	0.037 (1)
C(11′)	−0.0112 (3)	0.6315 (3)	0.2605 (2)	0.054 (2)
C(12)	0.3531 (3)	0.7829 (2)	0.4522 (2)	0.040 (1)
C(13)	0.5226 (3)	0.8180 (2)	0.4722 (2)	0.043 (1)
O(1)	0.6226 (2)	0.7634 (1)	0.4330 (1)	0.042 (1)
O(2)	0.1686 (4)	0.9923 (2)	0.4346 (2)	0.070 (2)

Table 2. *Selected geometric parameters (Å, °)*

Cu—Cl(1)	2.251 (1)	Cu—N(3′)	1.966 (2)
Cu—N(1)	2.127 (2)	Cu—O(1)	2.278 (2)
Cu—N(3)	1.967 (2)		
Cl(1)—Cu—N(1)	177.24 (6)	N(1)—Cu—N(3′)	80.91 (8)
Cl(1)—Cu—N(3)	98.63 (6)	N(1)—Cu—O(1)	81.14 (7)
Cl(1)—Cu—N(3′)	97.93 (6)	N(3)—Cu—N(3′)	157.81 (9)
Cl(1)—Cu—O(1)	101.52 (5)	N(3)—Cu—O(1)	92.89 (8)
N(1)—Cu—N(3)	81.88 (8)	N(3′)—Cu—O(1)	98.18 (7)

The structure was solved by using Patterson and Fourier techniques. The position of the second water molecule H atom could not be located from a difference map. It was omitted from all calculations.

Data reduction: *Xtal DIFDAT*, *ADDREF*, *ABSORB* and *SORTRF* (Hall, Flack & Stewart, 1992). Program(s) used to solve structure: *Xtal*. Program(s) used to refine structure: *Xtal CRYLSQ*. Molecular graphics: *Xtal*. Software used to prepare material for publication: *Xtal CIFIO*.

We thank Associate Professor A. H. White and Dr B. W. Skelton of the University of Western Australia who collected the data.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: SK1011). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Biologically Active Gold Complex: Trichloro[(2-pyridyl)methanol-*N*]gold(III)

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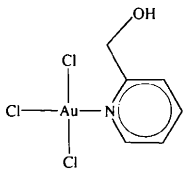
Abstract

The crystal structure of the title complex, $[AuCl_3(C_6H_7NO)]$, has been determined by X-ray diffraction. The coordination geometry around the Au^{III} atom is square planar. The bond lengths and angles in the complex agree with the literature values.

Comment

Interest in gold compounds has been growing in recent years as some possess anti-arthritic and anti-tumour properties (Ni Dhubhghaill & Sadler, 1993; Sadler & Sue, 1994). Most studies, however, have centered on the activity of gold(I) compounds and very little is known about gold(III) compounds. In the course of our studies of the activity of gold(III) complexes, we have determined the structure of the title complex, $AuCl_3Hpm$, by X-ray diffraction.



$AuCl_3Hpm$

The Au atom in $AuCl_3Hpm$ shows the usual square-planar coordination geometry, and is coordinated by three Cl atoms and the N atom of the pyridine ring. The Au atom is also essentially coplanar with the pyridine ring, the angle between the coordination plane and the pyridine ring being 73.0 (3)°. The O atom deviates from the pyridine ring plane by 0.76 (2) Å. Bond lengths and angles around the Au atom and in the rest of the molecule are in agreement with values from the literature (Holowczak, Stanel & Wong, 1985; Hollis & Lippard, 1983; Timkovich & Tulinsky, 1977).

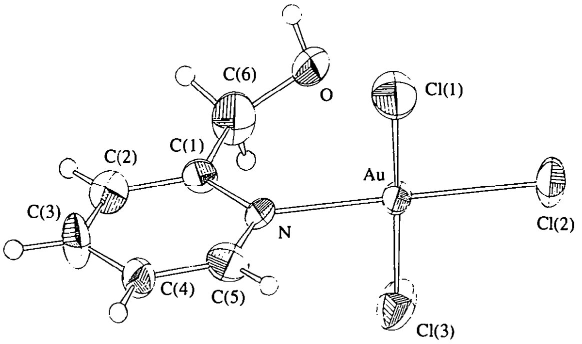


Fig. 1. *ORTEPII* (Johnson, 1976) drawing of $AuCl_3Hpm$. Displacement ellipsoids are shown at the 50% probability level for non-H atoms and H atoms are represented by small spheres of arbitrary radii.

Experimental

The compound was prepared as described in the literature (Dar *et al.*, 1992) and was recrystallized from ethyl ether.

Crystal data

$[AuCl_3(C_6H_7NO)]$
$M_r = 412.43$
Monoclinic
$P2_1/n$
$a = 7.826$ (2) Å
$b = 14.606$ (4) Å
$c = 8.830$ (3) Å
$\beta = 96.58$ (2)°
$V = 1002.7$ (5) Å^3
$Z = 4$
$D_x = 2.727$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 17$–$23°$
$\mu = 15.4$ mm^{-1}
$T = 298$ K
Prism
0.5 × 0.4 × 0.4 mm
Yellow

Data collection

Nonius CAD-4 diffractometer

$R_{\rm int} = 0.0405$
$\theta_{\rm max} = 26.9°$