

Aqua(5,6-dimethyl-1,10-phenanthroline-*N,N'*)(glycolato-*O,O'*)copper(II) nitrate

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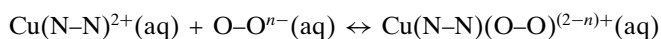
Received 8 September 1999

Accepted 28 March 2000

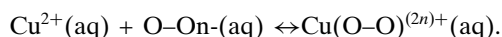
The title compound, $[\text{Cu}(\text{C}_2\text{H}_3\text{O}_3)(\text{C}_{14}\text{H}_{12}\text{N}_2)(\text{H}_2\text{O})]\text{NO}_3$, is the first example of a mixed copper glycolate compound with a diimine ligand. The copper(II) compound lies in a slightly distorted square-pyramidal coordination environment with one water molecule coordinated in the apical position. The glycolate ligand binds to the Cu atom as a chelate through a carboxylate and the α -OH O atom which, together with the N atoms of the substituted phenanthroline, constitute the base of the pyramid.

Comment

Solution–equilibrium studies performed on a wide variety of ternary copper chelates in which one ligand is a good π -acceptor like 2,2'-bipyridine or 1,10-phenanthroline and the other is an oxygen donor have always shown that, contrary to what is expected on a statistical basis, the stability constant for the reaction



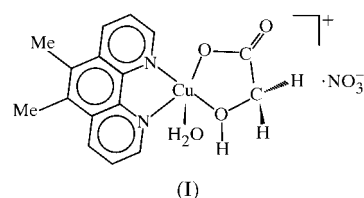
is always larger than for the reaction:



This behavior has been explained by Sigel *et al.* (1973) based on the hard and soft acids and bases principle. Since a π -acceptor ligand will withdraw electron density from a bound copper ion, $\text{Cu}(\text{N}-\text{N})^{2+}$ will be a harder acid than simple aqueous Cu^{2+} and consequently hard bases such as oxygen donors will prefer the former over the latter.

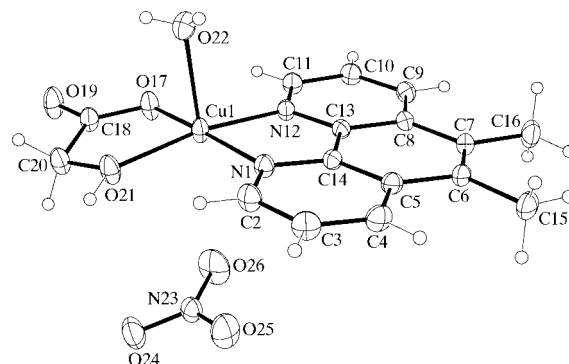
To be able to evaluate the effect of the variations in π -accepting properties of differently substituted phenanthrolines, of which ternary complexes have low solubility, we have studied the variation in Cu–O stretching frequencies of a series of these complexes in the solid state (Gasque, Medina *et al.*, 1999), finding a very good correlation between them and the $\text{p}K_a$ values of the substituted phenanthrolines. It has been previously accepted (Drago & Joerg, 1996) that the π -acceptor ability of a ligand increases as its σ basicity, or $\text{p}K_a$, decreases.

Furthermore, for these spectroscopic studies to be valid, isostructurality of all the complexes must be proven. With this objective, we have crystallized and determined the structure of a series of $\text{Cu}(x\text{-phen})(\text{O}-\text{O})$ complexes (Solans *et al.*, 1987; Gasque, Moreno-Esparza *et al.*, 1999; Gasque *et al.*, 1999*a,b*), where $x\text{-phen}$ is a substituted phenanthroline and $\text{O}-\text{O}$ is malonate or salicylaldehyde. In this paper, the $\text{O}-\text{O}$ ligand is an α -hydroxyacid anion. Since we have also performed a systematic study of the IR spectra of metal glycolates (Medina *et al.*, 2000*a*), comparison of the Cu–O frequencies for the title complex, (I), shows that they are indeed shifted to higher values, as expected.



The glycolate anion is known to form both monomeric and polymeric complexes. The Mn and Zn complexes are discrete six-coordinate pseudo-octahedral molecules having the formula $\text{cis-MG}_2(\text{H}_2\text{O})_2$ (G = glycolate, M = Mn, Zn; Fischinger & Webb, 1969; Lis, 1980), while the Cu and Co complexes constitute a bidimensional sheet-coordination polymer in which each metal atom is octahedrally coordinated to glycolate ligands in a *trans* configuration, and carbonyl O atoms from adjacent units complete the coordination octahedron (Prout *et al.*, 1968; Medina *et al.*, 2000*b*).

In (I), each Cu^{II} atom is at the center of a distorted octahedron, defined by the α -OH and the carboxy O atoms from the glycolate ligand, both N atoms from the phenanthroline ligand and two *trans*-O atoms, one from a water molecule and the other from the nitrate moiety. The plane defined by the four donor atoms from the two chelating ligands has an r.m.s. deviation of 0.0573 Å [distances: N1 0.0549 (9), N12 –0.0588 (10), O17 0.0597 (10) and O21 –0.0558 (9) Å]. Atom Cu1 is 0.1593 Å above the least-squares plane. Indicative of a typical Jahn–Teller distortion, distances from the Cu atom to the two axial O atoms are elongated and very different from each other. While O22(W) is 2.2681 (18) Å from the metal


Figure 1

A view of the title compound with displacement ellipsoids shown at the 40% probability level.

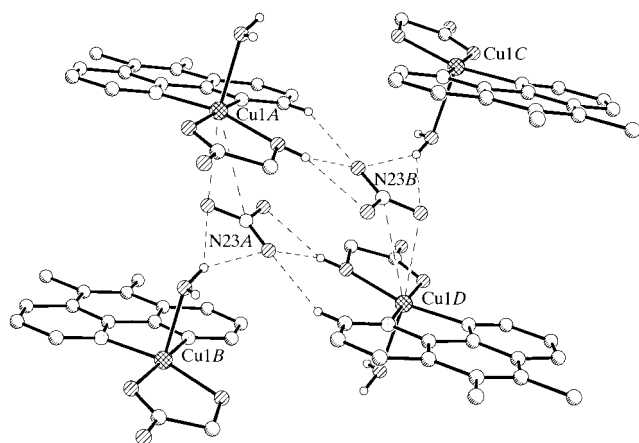


Figure 2

A representative of the complete coordination around the Cu atom and the hydrogen bonding in the title compound.

center, O26(NO₃) is 2.932 (3) Å from Cu1, with an O—Cu—O angle of 170.12 (16)°.

The free rotation of the coordinated water molecule is hindered by a rather strong hydrogen bond to the free carbonyl group of a neighboring cation, with an H22A···O19ⁱ separation of 2.00 Å and an O22—H22A···O19ⁱ angle of 172° [symmetry code: (i) $-x, -y, -z + 1$]. Additional hydrogen bonding stabilizes the overall packing, as shown in Fig. 2, involving the three O atoms of the nitrate ions, the OH group of the glycolate (O21) and the water molecule (O22). Separations range from 2.00 to 2.33 Å (Table 2).

Experimental

5,6-Dimethyl-1,10-phenanthroline (0.5 mmol) was dissolved in methanol and added to a methanolic solution of Cu(NO₃)₂ (0.5 mmol). To this mixture an aqueous solution of glycolic acid (0.5 mmol) neutralized with NaHCO₃ (0.5 mmol) was added. The resulting deep-blue solution was left standing until crystals formed, which were then filtered and vacuum dried.

Crystal data

[Cu(C₂H₃O₃)(C₁₄H₁₂N₂)(H₂O)]NO₃
M_r = 426.87
 Triclinic, *P* $\bar{1}$
a = 7.0373 (7) Å
b = 10.0928 (11) Å
c = 13.1649 (13) Å
 α = 103.225 (8)°
 β = 105.450 (12)°
 γ = 103.760 (9)°
V = 831.68 (15) Å³

Z = 2
D_x = 1.705 Mg m⁻³
 Mo *K* α radiation
 Cell parameters from 35 reflections
 θ = 4.57–12.51°
 μ = 1.361 mm⁻¹
T = 293 (2) K
 Needle, blue
 0.7 × 0.3 × 0.2 mm

Data collection

Siemens *P4* diffractometer
 2 θ / ω scans
 Absorption correction: ψ scan
 (XSCANS; Fait, 1991)
T_{min} = 0.614, *T_{max}* = 0.762
 4927 measured reflections
 3969 independent reflections
 3406 reflections with *I* > 2 σ (*I*)

R_{int} = 0.019
 θ_{\max} = 28°
h = -1 → 9
k = -12 → 12
l = -17 → 17
 3 standard reflections every 97 reflections
 intensity decay: 7.20%

Refinement

Refinement on *F*²
R[*F*² > 2 σ (*F*²)] = 0.034
wR(*F*²) = 0.092
S = 1.054
 3969 reflections
 245 parameters
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0419P)^2 + 0.3303P]$
 where $P = (F_o^2 + 2F_c^2)/3$

(Δ/σ)_{max} < 0.001
 $\Delta\rho_{\max} = 0.38 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.36 \text{ e \AA}^{-3}$
 Extinction correction: SHELXL97
 (Sheldrick, 1997)
 Extinction coefficient: 0.0109 (14)

Table 1

Selected geometric parameters (Å, °).

Cu1—O17	1.9144 (15)	Cu1—N12	2.0044 (16)
Cu1—N1	1.9913 (17)	Cu1—O22	2.2681 (18)
Cu1—O21	1.9918 (15)	Cu1—O26	2.932 (3)
O17—Cu1—N1	172.93 (7)	O17—Cu1—O22	93.45 (7)
O17—Cu1—O21	83.09 (6)	N1—Cu1—O22	92.64 (7)
N1—Cu1—O21	99.98 (6)	O21—Cu1—O22	94.83 (7)
O17—Cu1—N12	93.32 (7)	N12—Cu1—O22	97.65 (7)
N1—Cu1—N12	82.30 (7)	O22—Cu1—O26	170.12 (16)
O21—Cu1—N12	167.20 (7)		

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O21—H21···O24 ⁱ	0.86	2.00	2.795 (2)	154
O21—H21···O25 ⁱ	0.86	2.27	3.030 (2)	146
O21—H21···N23 ⁱ	0.86	2.48	3.344 (2)	176
O22—H22A···O19 ⁱⁱ	0.88	2.00	2.747 (3)	172
O22—H22B···O24 ⁱⁱⁱ	0.88	2.24	3.052 (3)	154
O22—H22B···O26 ⁱⁱⁱ	0.88	2.33	3.103 (3)	147
O22—H22B···N23 ⁱⁱⁱ	0.88	2.61	3.469 (3)	166

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

H atoms on the water molecule (O22) were located in a difference Fourier map and were then constrained to ride on the O atom. The remaining H atoms were placed in idealized positions and refined with a riding model.

Data collection: XSCANS (Fait, 1991); cell refinement: XSCANS; data reduction: XSCANS; program(s) used to solve structure: SHELXTL (Sheldrick, 1995); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL; software used to prepare material for publication: SHELXL97.

The authors acknowledge Patricia Altúzar for her collaboration in the refinement of the crystal structure.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1111). Services for accessing these data are described at the back of the journal.

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