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Bis(3,5-dimethylpyrazole-*N*^{2})(*N*-salicylideneglycinato-*O*,*N*,*O*′)copper(II)

Salam A. Warda

Department of Chemistry, Philipps-Universität Marburg, Hans-Meerwein-Straße, 35032 Marburg, Germany. E-mail: warda@ax1501.chemie.uni-marburg.de

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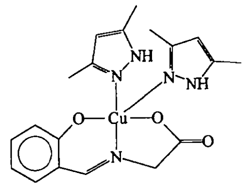
Abstract

The title compound, [Cu($C_9H_7NO_3$)($C_5H_8N_2$)$_2$], adopts a square-pyramidal Cu^{II} coordination with the tridentate *N*-salicylideneglycinato Schiff base dianion and 3,5-dimethylpyrazole ligand bound in the basal plane. The apex of the elongated pyramid is occupied by a second molecule of 3,5-dimethylpyrazole at a Cu—N distance of 2.342 (3) Å. All molecules are arranged in a single magnetic orientation.

Comment

Copper(II) complexes with tridentate Schiff base dianions of the *N*-salicylideneaminoalkanoato type (TSB^{2-}) represent a relatively simple model for studies of cooperative bonding effects, which can be investigated by electron paramagnetic resonance (EPR) spectroscopy. In these complexes, which are of the general type [Cu(TSB)(*L*)]$_n$ (Warda, 1994), three donor atoms (O, N and O) of the Schiff base and a fourth donor atom from the neutral ligand *L* (N, O or S) normally define the base of a square pyramid. For isolated (monomeric) structures, the copper coordination can be square planar or square pyramidal when a neutral donor ligand is located in the apical site (n = 1; Ueki, Ashida, Sasada & Kakudo, 1969; Warda, Friebel, Sivý, Plesch & Švajlenová, 1996). If a phenolic O atom from a neighbouring molecule is apically coordinated, dimeric structures are formed (n = 2; Warda, 1994). An instance of n = 4 is found in (4-ethylpyridine)(*N*-salicylideneglycinato)copper(II) (Warda, 1997). Polymeric structures ($n = \infty$) are generally achieved when the apical position is occupied by a carboxylic O atom from an adjacent molecule to form infinite zigzag chains (Ueki, Ashida, Sasada & Kakudo, 1967; Warda, Friebel, Sivý, Plesch & Bláhová, 1997). In this communication, we report the structure of the title compound, (I), the first structure for this class of substance with an N atom on the apical site.



(I)

The environment of the copper(II) central atom is square pyramidal, with the tridentate Schiff base TSB^{2-} dianion (*N*-salicylideneglycinato) and a monodentate ligand (3,5-dimethylpyrazole) in the basal plane. The apical Cu—N4 distance of 2.342 (3) Å, originating from an apically coordinated pyrazole ring, is comparable with the corresponding Cu—O bond length of 2.328 (2) Å in the aqua(3,5-dimethylpyrazole)(*N*-salicylideneglycinato)copper(II) complex (Warda *et al.*, 1996). In the latter case, the coordination polyhedra are arranged in such a way as to give four magnetically inequivalent Cu^{II} positions. The Cu atom of the title compound is displaced by 0.209 (1) Å from the mean plane through the basal donor atoms in the direction of the apical N4 atom; in the aqua compound, this deviation from the plane is 0.163 (1) Å.

It has been found (Warda, 1994) that EPR patterns of the title compound, (I), display only one magnetic orientation for the Cu^{II} polyhedra. This is consistent with space group $P\bar{1}$ with one moiety in the asymmetric unit. The different occupation of the apical position in these two 3,5-dimethylpyrazole-containing compounds results in the formation of two completely different structures. The 3,5-dimethylpyrazole prevents chain building *via* carboxylic O atoms because of steric crowding, but dimeric association is attained through hydrogen bonding across an inversion centre between N3—H31···O3 and N5—H51···O3. In the case of the much smaller aquo ligand, a chain structure with four magnetically inequivalent Cu^{II} positions is formed.

The existence of a second molecule of dimethylpyrazole in the formula unit was first detected by molecular analysis. In the related copper complexes with pyrazole (Kettmann, Frešová, Bláhová & Krätsmár-Šmogrović, 1993; Warda *et al.*, 1997), any second pyrazole is always non-coordinated and the apical coordination is through the O atom. This led to confusion in the interpretation of the EPR spectra of the title compound, so this single-crystal structure determination was undertaken.

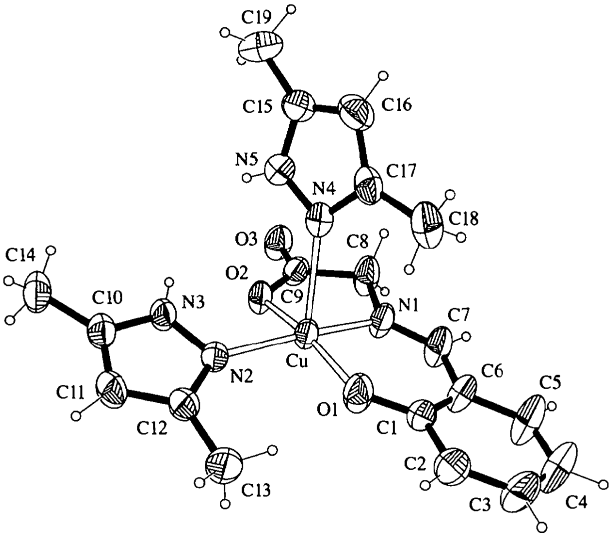


Fig. 1. The asymmetric unit of the title compound with the atom-numbering scheme. Ellipsoids are drawn at the 50% probability level.

Experimental

The title compound was synthesized from aqua(*N*-salicylideneglycinato)copper(II) hemihydrate (Ueki *et al.*, 1967; Warda, 1994) and 3,5-dimethylpyrazole in ethanol.

Crystal data

$[Cu(C_9H_7NO_3)(C_5H_8N_2)_2]$
$M_r = 432.96$
Triclinic
$P\bar{1}$
$a = 8.9206\,(19)$ Å
$b = 10.484\,(2)$ Å
$c = 10.8614\,(17)$ Å
$\alpha = 93.046\,(14)°$
$\beta = 93.663\,(15)°$
$\gamma = 99.182\,(16)°$
$V = 998.7\,(3)$ Å^3
$Z = 2$
$D_x = 1.440$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å
Cell parameters from 25 reflections
$\theta = 34.47–38.07°$
$\mu = 1.796$ mm^{-1}
$T = 293\,(2)$ K
Prism
$0.250 \times 0.150 \times 0.125$ mm
Dark green

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
3128 measured reflections
2950 independent reflections
2901 reflections with $I > 2\sigma(I)$
$R_{int} = 0.031$

$\theta_{max} = 59.95°$
$h = -10 \rightarrow 9$
$k = -11 \rightarrow 11$
$l = 0 \rightarrow 12$
3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.128$
$S = 1.083$
2950 reflections
258 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0753P)^2 + 1.1666P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.685$ e Å^{-3}
$\Delta\rho_{min} = -0.577$ e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.0050 (7)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Cu—O1	1.909 (2)	Cu—N2	2.009 (3)
Cu—N1	1.948 (3)	Cu—N4	2.342 (3)
Cu—O2	2.004 (2)		
O1—Cu—N1	91.86 (11)	O2—Cu—N2	88.55 (9)
O1—Cu—O2	164.41 (11)	O1—Cu—N4	106.30 (11)
N1—Cu—O2	82.28 (10)	N1—Cu—N4	88.96 (11)
O1—Cu—N2	94.82 (10)	O2—Cu—N4	88.10 (9)
N1—Cu—N2	167.52 (12)	N2—Cu—N4	99.22 (10)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H31···O3^{i}	0.91	2.13	2.905 (4)	142.7
N5—H51···O3^{i}	0.94	1.86	2.790 (4)	167.7

Symmetry code: (i) $1 - x, 1 - y, -z$.

The H atoms of the N—H groups (H31 and H51) were found in the difference syntheses and refined using a riding model with U_{iso} equal to $1.2U_{eq}$ of their N atoms: this factor was also used for C—H. CH and CH_2 groups were calculated with suitable geometry using *SHELXL*97 (Sheldrick, 1997) and refined with a riding model. The methyl groups were handled as rigid groups with U_{iso} equal to $1.5U_{eq}$ of the attached C atom. The residual electron density and the deepest hole of 0.69 and 0.58 e Å^{-3}, respectively, are near the Cu atom at distances of 1.14 and 0.88 Å, respectively.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1992). Cell refinement: *CAD*-4 *EXPRESS*. Data reduction: *XCAD*-4 (Harms, 1997). Program(s) used to solve structure: *SHELXS*96 (Sheldrick, 1990). Molecular graphics: *XP* in *SHELXTL* (Siemens, 1996). Software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1209). Services for accessing these data are described at the back of the journal.

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A Stable Sulfonato–Cobalt(III) Complex: Δ-[Co{OS(O)$_2$CH$_2$CH$_2$NH$_2$-*N*,*O*}(en)$_2$](ClO$_4$)$_2$

Mayumi Murata,[a] Masaaki Kojima,[a] Masakazu Kita,[b] Setsuo Kashino[a] and Yuzo Yoshikawa[a]

[a]*Department of Chemistry, Faculty of Science, Okayama University, Tsushima, Okayama 700, Japan, and* [b]*Department of Chemistry, Naruto University of Education, Takashima, Naruto 772, Japan. E-mail: mayumi@cc.okayama-u.ac.jp*

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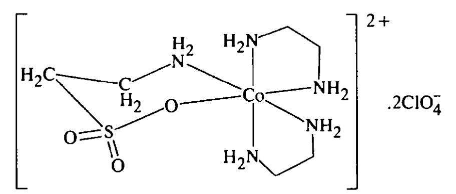
Abstract

A stable sulfonato complex, (2-aminoethanesulfonato-*N*,*O*)bis(ethylenediamine-*N*,*N'*)cobalt(III) perchlorate, [Co(C$_2$H$_6$NO$_3$S)(C$_2$H$_8$N$_2$)$_2$](ClO$_4$)$_2$, was prepared by oxidation of [Co{OS(O)CH$_2$CH$_2$NH$_2$-*N*,*O*}(en)$_2$]$^{2+}$ (en = NH$_2$CH$_2$CH$_2$NH$_2$) in acid media. This sulfonato complex was resolved by SP-Sephadex column chromatography and the absolute configuration of the slower eluted $(-)_{589}$-isomer was determined by X-ray analysis to be Δ.

Comment

Generally, monodentate sulfonato–cobalt(III) complexes are aquated easily and the coordinating ability of a monodentate sulfonate ligand is usually weak. For example, the half-life of aquation of [Co{OS(O)$_2$CH$_3$}(NH$_3$)$_5$]$^{2+}$ is *ca* 58 min at 298 K (Jackson, Jurisson & O'Leary, 1993). In the present work, we considered that a cobalt(III) complex involving the 2-aminoethanesulfonate *N*,*O*-chelate may be stable enough to be isolated. Accordingly, we actually prepared the first stable sulfonato–cobalt(III) complex (Murata *et al.*, 1996). This sulfonato complex was resolved by SP-Sephadex column chromatography, and the slower eluted complex, $(-)_{589}$-[Co{OS(O)$_2$CH$_2$CH$_2$NH$_2$-*N*,*O*}(en)$_2$]$^{2+}$, was assigned the Δ configuration on the basis of the circular dichroism (CD) sign at *ca* 535 nm in the first spin-allowed *d–d* band region. We carried out the X-ray analysis of the title complex, (I), in order to confirm this assignment.



(I)

A perspective view of the complex cation obtained from the eluate containing the slower eluted isomer, $(-)_{589}$-Δ-[Co{OS(O)$_2$CH$_2$CH$_2$NH$_2$-*N*,*O*}(en)$_2$]$^{2+}$, is shown in Fig. 1. The coordination geometry around the Co atom is approximately octahedral. The sulfonate ligand coordinates to the Co atom with *N*,*O*-chelation. The S—O1 [1.482 (2) Å] bond length is longer than both S—O2 [1.446 (2) Å] and S—O3 [1.439 (2) Å]. The sulfonate O atom in the complex does not induce a significant *trans* influence. To our knowledge, this is the first example of a stable sulfonato–cobalt(III) complex.

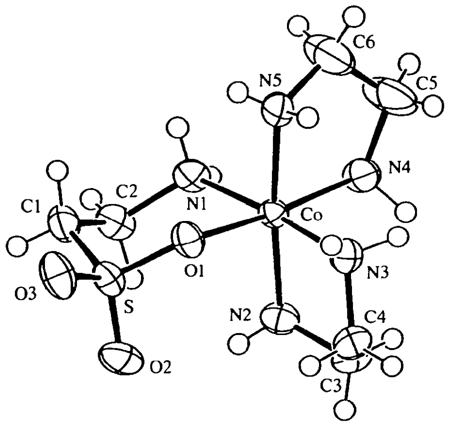


Fig. 1. An *ORTEP*II (Johnson, 1976) drawing for the complex cation, $(-)_{589}$-Δ-[Co{OS(O)$_2$CH$_2$CH$_2$NH$_2$}(en)$_2$]$^{2+}$, with displacement ellipsoids at the 50% probability level. H atoms are represented by circles (representing B = 1.0 Å^2).

Experimental

[Caution: perchlorate salts of metal complexes can be explosive and should be handled with care.] A mixture of 30% H$_2$O$_2$ (10 g, 88 mmol) and 60% HClO$_4$ (10 g) was added dropwise to a dimethyl sulfoxide solution (15 ml) of [Co{OS(O)CH$_2$CH$_2$NH$_2$-*N*,*O*}(en)$_2$](ClO$_4$)$_2$ (1 g, 2 mmol) (Mäcke, Houlding & Adamson, 1980) with stirring and at a