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β-(1,10-Phenanthroline)(1,3-propanediamine-*N*,*N'*-diacetato)cobalt(III) Chloride Trihydrate

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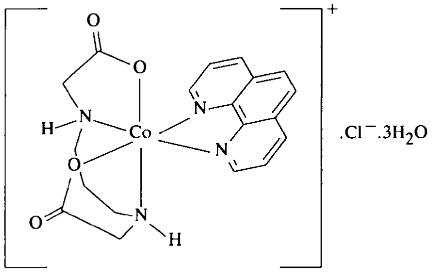
Abstract

The crystal structure of $[Co(C_7H_{12}N_2O_4)(C_{12}H_8N_2)]Cl.3H_2O$ is the first reported structure of a cobalt complex with the tetradentate 1,3-propanediamine-*N*,*N'*-diacetato ligand and it has adopted a β unsymmetrical *cis* configuration. The phenanthroline fills the two remaining coordination sites to give an approximately octahedral geometry around the Co atom.

Comment

We have prepared the title compound, (I), as part of our investigations into the photochemistry of cobalt(III)–aminocarboxylato complexes. It is surprising that the pdda ligand is featured in only two other published crystal structures, *i.e.* $Li[CrF_2(pdda)].2H_2O$ (Bianchini *et al.*, 1986) and $[Co(en)_2C_2O_4][Cr(pdda)malonato].H_2O$ (Douglas *et al.*, 1989), given the 16 reports involving only cobalt complexes of the similar ethanediamine–*N*,*N'*-diacetato (edda) ligand found in a Cambridge Structural Database (1994) search.



(I)

This preparation of the title complex was reported by Douglas & Igi in 1974. They postulated, on the basis of electronic spectroscopy, that the complex ion exists exclusively as the β geometric isomer, where one of the glycinate rings lies in the same plane as the propanediamine backbone. Our structure determination has confirmed their assessment and we have found that the complex has a Δ-*SS*/Λ-*RR* configuration, where *R* and *S* refer to the stereochemistry of the asymmetric N atoms. Of the two previously published 1,3-propanediamine-*N*,*N'*-diacetato (pdda) structures, one has a β geometry (Bianchini *et al.* 1986), while the other has all three rings coplanar with the two fluoride ligands arranged *trans* to each other (Douglas *et al.*, 1989).

Douglas & Igi (1974) noted that the trimethylene chain exerts considerable influence on the distribution of geometrical isomers with the β isomer as the sole product, which we confirmed with ion-exchange chromatography. In the case of analogous edda complexes, both symmetrical α, where both glycinate rings are perpendicular to the diamine chain, and β isomers are readily prepared (Kuroda & Watanabe, 1971). This contrast can be attributed to the large [96.32 (15)°] bite angle of the propanediamine chelate N1—Co—N2 which for the α isomer would introduce an unfavourable steric clash between an H atom in each of the glycinate rings and the H atoms *ortho* to the N atoms in the phenanthroline ligand. Such interactions are not encountered when the pdda ligand assumes a β conformation.

The Δ-*SS*/Λ-*RR* configuration allows the proton on the in-plane N atom, N2, to avoid steric interactions with the phenanthroline ligand and enables the ligand diamine hydrocarbon backbone to have a stable chair conformation. This same configuration was observed for the β-$[Co(pdda)mal]^-$ complex.

The slightly distorted octahedral geometry and the bond lengths around the Co atom are reminiscent of other β-cobalt(III)–aminocarboxylate complexes, for example, [Co(edda)(pyridine-2-carboxylato)] (Billing *et al.*, 1991) [Co(edda)(*R*-1,2-diaminopropane)]$Cl.H_2O$ (Caputo *et al.*, 1975) and $[C(NH_2)_3][Co(edda)CO_3]$ (Egan *et al.*, 1995).

A detailed analysis of bond-angle sums in the complexes K[Co(edta)] (edta is ethylenediaminetetraacetato) and [Co(edda)(*R*-1,2-diaminopropane)]$Cl.H_2O$ revealed that the ring strain is averaged over the full ring system for the edda complex, while it is concentrated in the 'in-plane' glycinate rings for the edta complex (Caputo *et al.*, 1975). This trend is followed by the title complex as evidenced by a comparison of its bond-angle sums with those of its hexadentate analogue K[Co(tmdta)] (tmdta is trimethylenediaminetetraacetato) (Marumo *et al.*, 1972). The ring strain of the tmdta complex is manifest in the pronounced distortion of the in-plane glycinate rings. The bond-angle sums, which deviate considerably from the 'ideal' values which would allow the glycine rings to be nearly planar, are an indicator of this strain. A more even distribution of ring strain is apparent within the tricyclic pdda system, where the sum of the internal angles for both glycinate rings is closer to their 'ideal' values.

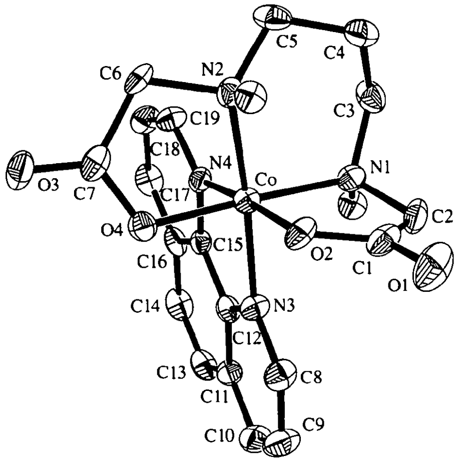


Fig. 1. A view of the $[Co(pdda)phen]^+$ complex cation. Displacement ellipsoids are drawn at the 50% probability level.

Experimental

The title complex was prepared by the oxidation of Co^{II} in the presence of equimolar quantities of H_2pdda and phenanthroline, according to the method of Douglas & Igi (1974). The compound was isolated as the chloride salt following ion-exchange chromatography (SP-Sephadex C25). Recrystallization from hot dilute HCl with slow cooling produced single crystals suitable for the X-ray study.

Crystal data

$[Co(C_7H_{12}N_2O_4)(C_{12}H_8N_2)]$-
$Cl.3H_2O$
$M_r = 516.82$
Monoclinic
$P2_1/c$
$a = 8.715\ (6)$ Å
$b = 10.229\ (5)$ Å
$c = 25.007\ (12)$ Å
$\beta = 96.17\ (4)°$
$V = 2216\ (2)$ Å^3
$Z = 4$
$D_x = 1.549$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 4.86–16.17°$
$\mu = 0.944$ mm^{-1}
$T = 293\ (2)$ K
Block
0.63 × 0.40 × 0.25 mm
Red

Data collection

Siemens $P4$ four-circle diffractometer
ω scans
Absorption correction: empirical ψ scan (*XPREP* in *SHELXTL*; Sheldrick, 1994)
$T_{min} = 0.578$, $T_{max} = 0.790$
5618 measured reflections
3829 independent reflections

2457 reflections with $I > 2\sigma(I)$
$R_{int} = 0.029$
$\theta_{max} = 24.99°$
$h = -10 \rightarrow 3$
$k = 0 \rightarrow 12$
$l = -29 \rightarrow 29$
3 standard reflections every 97 reflections intensity decay: 38.55%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.103$
$S = 1.026$
3829 reflections
307 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o^2) + (0.0653P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.935$ e Å^{-3}
$\Delta\rho_{min} = -0.707$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Co—O2	1.909 (3)	Co—N2	1.972 (3)
Co—O4	1.910 (3)	Co—N3	1.974 (3)
Co—N1	1.961 (4)	Co—N4	1.996 (4)
O2—Co—O4	90.43 (13)	N1—Co—N3	89.71 (15)
O2—Co—N1	86.54 (15)	N2—Co—N3	172.79 (15)
O4—Co—N1	176.87 (13)	O2—Co—N4	174.37 (14)
O2—Co—N2	85.78 (14)	O4—Co—N4	90.60 (14)
O4—Co—N2	84.22 (14)	N1—Co—N4	92.34 (15)
N1—Co—N2	96.32 (15)	N2—Co—N4	99.83 (15)
O2—Co—N3	90.64 (14)	N3—Co—N4	83.84 (14)
O4—Co—N3	89.56 (15)		

The title structure was solved by direct methods and refined by a full-matrix least-squares procedure on F^2 with anisotropic displacement parameters for all non-H atoms. All H atoms were placed at calculated positions except those of the water molecules which were located on the electron-density difference map. The interatomic distances of those H atoms were restrained to sensible values. An absorption correction was applied using ψ scans and assuming an ellipsoidal crystal shape. An abnormally large decay in the check reflections was noted and the intensities adjusted to compensate for this.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1994). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1171). Services for accessing these data are described at the back of the journal.

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

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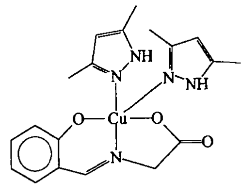
Abstract

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 coordi-