Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.068$
$wR(F^2) = 0.182$
$S = 1.117$
11 581 reflections
433 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0606P)^2 + 1.6246P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.011$ e Å^{-3}
$\Delta\rho_{min} = -0.571$ e Å^{-3}
Extinction correction: none
Scattering factors from
   International Tables for
   Crystallography (Vol. C)

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

Cu1—O2	1.915 (2)	C11—O6	1.425 (3)
Cu1—O3	1.916 (2)	C11—O8	1.476 (5)
Cu1—N2	1.925 (3)	C12—O12	1.388 (5)
Cu1—N3	1.946 (3)	C12—O10	1.399 (4)
C11—O7	1.346 (4)	C12—O11	1.411 (4)
C11—O5	1.398 (3)	C12—O9	1.436 (4)
O2—Cu1—O3	89.66 (9)	O2—Cu1—N3	170.29 (11)
O2—Cu1—N2	93.29 (10)	O3—Cu1—N3	93.47 (10)
O3—Cu1—N2	177.02 (10)	N2—Cu1—N3	83.55 (11)
C12—N1—C9—C10	−52.9 (4)	C28—N4—C25—C26	53.0 (4)
C11—O1—C10—C9	−62.9 (4)	C27—O4—C26—C25	61.9 (5)
N1—C9—C10—O1	59.2 (4)	N4—C25—C26—O4	−57.5 (5)
C10—O1—C11—C12	62.3 (4)	C26—O4—C27—C28	−62.8 (4)
C9—N1—C12—C11	52.1 (4)	O4—C27—C28—N4	59.4 (4)
O1—C11—C12—N1	−57.5 (4)	C25—N4—C28—C27	−53.9 (4)

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···O1W	0.91	2.012	2.779 (4)	140.9
N4—H4A···O3	0.91	2.186	2.840 (3)	128.2
O1W—H1W1···O2	0.94	2.282	2.933 (3)	125.9
O1W—H1W1···O3	0.94	2.110	2.972 (4)	152.3
O1W—H2W1···O6	0.94	1.911	2.852 (4)	175.5

The data collection covered over a hemisphere of reciprocal space by a combination of three sets of exposures; each set had a different φ angle (0, 88 and 180°) for the crystal and each exposure of 30 s covered 0.3° in ω. The crystal-to-detector distance was 4 cm and the detector swing angle was −35°. Crystal decay was monitored by repeating 30 initial frames at the end of data collection and analysing the duplicate reflections; it was found to be negligible.

Data collection: *SMART* (Siemens, 1996). Cell refinement: *SAINT* (Siemens, 1996). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *XP* in *SHELXTL*. Software used to prepare material for publication: *SHELXTL* and *PARST* (Nardelli, 1995).

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A neutral cobalt(II) complex of a Schiff base ligand containing mixed O$_2$S$_2$N$_2$ donors

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Abstract

In the title compound, {1,1′-[2,2′-ethylenedioxybis-(benzylidenehydrazono)]-3,3′-diphenylbis(2-thiapropane-thiolato-*S*)}cobalt(II), [Co(C$_{32}$H$_{28}$N$_4$O$_2$S$_4$)], the configuration about the cobalt(II) ion is distorted octahedral, involving two ethereal O, two β-N and two mercapto S atoms from the doubly deprotonated Schiff base ligand. The distorted octahedral configuration arises from a series of five- and six-membered chelate rings.

Comment

There is considerable interest in complexes containing sulfur donors due to their biological relevance. The

metal complexes of thiosemicarbazides and their derivatives have been tested and show striking anticancer activity (Kirschner *et al.*, 1966; Ali & Livingstone, 1974; Das & Livingstone, 1976). In another paper (Zhu *et al.*, 1999), we describe the synthesis and characterization of metal complexes *ML*, where *M* = Cu^{2+}, Ni^{2+} and Zn^{2+}, and the crystal structure of Cu*L*, where H_2L is a potential hexadentate $N_2O_2S_2$ Schiff base ligand prepared by condensation of 1,4-bis(2-formylphenyl)-1,4-dioxabutane with *S*-benzyl dithiocarbazate in a 1:2 molar ratio. As part of our studies of metal complexes containing mixed *N*,*S*-donors, we report herein the structure of $Co^{2+}L$, (I).
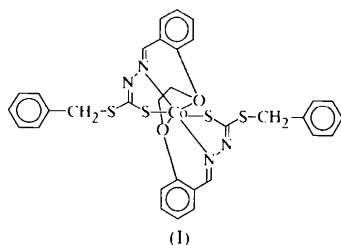
(I)

The configuration about the cobalt(II) ion is distorted octahedral, involving two ethereal O, two β-N and two mercapto S atoms from the doubly deprotonated Schiff base ligand (Fig. 1). The bond lengths S1—C7 [1.826 (4) Å] and S4—C26 [1.817 (3) Å] are longer than the S1—C8 [1.748 (3) Å] and S4—C25 [1.756 (4) Å] bonds because of the substitution of the heavier methyl-

benzyl group at the S atoms. The angles at S1 and S4 of 103.4 (2) and 102.5 (2)°, respectively, are comparable with literature values (Fun *et al.*, 1996). The N1—C8 [1.302 (4) Å] and N4—C25 [1.285 (4) Å] distances are shorter than single bonds because of some electron delocalization. The Co—N and Co—S bond lengths [Co1—N2 2.132 (3), Co1—N3 2.112 (3), Co1—S2 2.338 (1) and Co1—S3 2.338 (1) Å] compare well with those found in a similar CoN_2S_2 Schiff base complex (Onan *et al.*, 1986). The Co—O bond lengths [Co1—O1 2.287 (3) and Co1—O2 2.320 (3) Å] agree well with those found in cobalt(II) macrocyclic polyether complexes (Streltsova & Belsky, 1991). The distorted octahedral coordination environment for such a cobalt(II) complex may arise from the steric strains among a series of five- and six-membered chelate rings.

It is interesting to compare the structure of Co*L* with that of Cu*L* (Zhu *et al.*, 1999), in which copper(II) is coordinated by two β-N and two mercapto S atoms, and is involved in a weak axial interaction with the S atom from the other molecule in the unit cell, resulting in a dimeric structure. The two ethereal molecules are left uncoordinated. The difference may arise from the fact that cobalt(II) is probably a harder ion than copper(II) since the latter has a stronger tendency to coordinate with the softer S atoms.

It should be noted that in the cobalt(III) bis(salicyldimine) complex containing mixed hexadentate $N_2O_2S_2$ donors (Chakraborty *et al.*, 1994), the average Co—N, Co—O and Co—S bond lengths [1.91 (3), 1.92 (2) and 2.21 (1) Å, respectively] are considerably shorter than
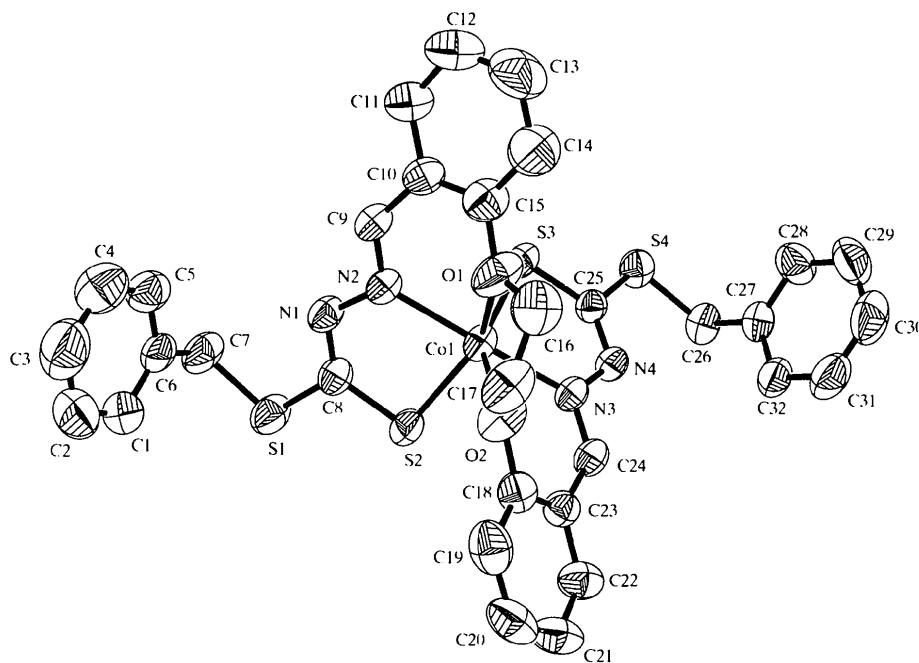

Fig. 1. The structure of the title compound, showing 50% probability displacement ellipsoids and the atom-numbering scheme.

those found in the present CoL complex, probably because the ionic radius of cobalt(III) is shorter than that of cobalt(II).

The interactions between C9 and S3($-x$+2, $-y$, $-z$+1) [3.749 (4) Å] and between C24 and S2($-x$+$\frac{3}{2}$, $-y$+$\frac{1}{2}$, $-z$+1) [3.676 (3) Å] help the molecules to form a linear chain along the b axis. The benzyl rings are twisted by 66.3 (1)° with respect to each other. The C1–C6 and C10–C15 rings are perpendicular to each other [dihedral angle 88.5 (2)°], and rings C18–C23 and C27–C32 make a dihedral angle of 82.1 (1)° with one another.

Experimental

The title compound was synthesized by refluxing a minor excess of Co(OAc)$_2$·4H$_2$O with the Schiff base ligand H$_2$L {L = 1,1'-[2,2'-ethylenedioxybis(benzylidenehydrazono)]-3,3'-diphenylbis(2-thiapropanethiolate)} in dimethyl sulfoxide for 3 h. Water was then added to precipitate the product. Single crystals suitable for X-ray diffraction were obtained from a CH$_2$Cl$_2$ solution carefully layered with 2-propanol.

Crystal data

[Co(C32H28N4O2S4)]
M_r = 687.75
Monoclinic
$C2/c$
a = 15.578 (1) Å
b = 22.428 (1) Å
c = 19.406 (1) Å
β = 108.83 (1)°
V = 6417.2 (2) Å^3
Z = 8
D_x = 1.424 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 6074 reflections
θ = 2.76–33.22°
μ = 0.831 mm^{-1}
T = 293 (2) K
Prism
0.36 × 0.10 × 0.10 mm
Dark brown

Data collection

Seimens SMART CCD area-detector diffractometer
ω scans
Absorption correction: empirical (SADABS; Sheldrick, 1996a)
T_{min} = 0.794, T_{max} = 0.943
20 537 measured reflections
7339 independent reflections

3973 reflections with $I > 2\sigma(I)$
R_{int} = 0.066
θ_{max} = 27.5°
h = $-19 \rightarrow 19$
k = $0 \rightarrow 29$
l = $0 \rightarrow 25$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.059
$wR(F^2)$ = 0.087
S = 1.145
7332 reflections
388 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0228P)^2 + 4.7561P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = -0.001
$\Delta\rho_{max}$ = 0.281 e Å^{-3}
$\Delta\rho_{min}$ = -0.238 e Å^{-3}
Extinction correction: none
Scattering factors from International Tables for Crystallography (Vol. C)

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

Co1—N3	2.112 (3)	Co1—S2	2.338 (1)
Co1—N2	2.132 (3)	Co1—S3	2.338 (1)
Co1—O1	2.287 (3)	S2—C8	1.724 (3)
Co1—O2	2.320 (3)	S3—C25	1.731 (3)
N3—Co1—N2	171.1 (1)	O2—Co1—S2	88.8 (9)
N3—Co1—O1	110.1 (1)	N3—Co1—S3	82.6 (1)
N2—Co1—O1	76.5 (1)	N2—Co1—S3	91.1 (1)
N3—Co1—O2	76.8 (1)	O1—Co1—S3	95.0 (1)
N2—Co1—O2	111.6 (1)	O2—Co1—S3	146.6 (1)
O1—Co1—O2	68.5 (1)	S2—Co1—S3	119.4 (1)
N3—Co1—S2	95.8 (1)	C8—S1—C7	103.4 (2)
N2—Co1—S2	81.9 (1)	C8—S2—Co1	95.86 (1)
O1—Co1—S2	139.5 (1)	C25—S3—Co1	95.4 (1)

The data collection covered over a hemisphere of reciprocal space by a combination of three sets of exposures. Each set had a different φ angle (0, 88 and 180°) for the crystal and each exposure of 10 s covered 0.3° in ω. The crystal-to-detector distance was 4 cm and the detector swing angle was -35°. Coverage of the unique set is over 99% complete. Crystal decay was monitored by repeating 30 initial frames at the end of data collection and analysing the duplicate reflections; it was found to be negligible.

Data collection: SMART (Siemens, 1996a). Cell refinement: SAINT (Siemens, 1996b). Data reduction: SAINT. Program(s) used to solve structure: SHELXTL (Sheldrick, 1996b). Program(s) used to refine structure: SHELXTL. Molecular graphics: SHELXTL. Software used to prepare material for publication: SHELXTL and PARST (Nardelli, 1995).

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Chloro(di-2-pyridyl-κN-amine)(propionato-κ²O,O′)copper(II) monohydrate

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Abstract

In the title compound, $[CuCl(C_3H_5O_2)(C_{10}H_9N_3)]\cdot H_2O$, the CuN_2O_2Cl chromophore involves a distorted square-based pyramidal structure, with nearly symmetrically bonded bidentate di-2-pyridylamine and propionate groups in the basal plane, and a Cl atom at the apex. The Cu atom is displaced from the basal plane towards the apical Cl atom by 0.304 (1) Å.

Comment

Di-2-pyridylamine (dpyam) and similar ligands (rigid or semi-rigid) are well known for their stabilizing effect on the five-coordination state of copper(II) (Harrison & Hathaway, 1980). The five-coordination copper(II) complexes usually show a stereochemistry ranging from a slightly distorted trigonal-bipyramidal to a distorted square-pyramidal arrangement (Greiner *et al.*, 1994; Harrison *et al.*, 1981; Nagle *et al.*, 1990). A structural pathway from a regular trigonal-bipyramidal [τ = 1.0; $\tau = (\beta - \alpha)/60$, where α and β are basal angles (Addison *et al.*, 1984)] to a regular square-based pyramidal (τ = 0.0) stereochemistry has been suggested for these complexes (Hathaway, 1984, 1987; Murphy *et al.*, 1998). The inherent flexibility of the copper(II) coordination sphere and the dpyam ligand along with the non-stereospecific nature of the rather large spherical halide ion led to our interest in these complexes. Herewith we report the structure of the title compound, (I), a five-

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coordination complex where a chloride ion is present along with the dpyam ligand.

(I)
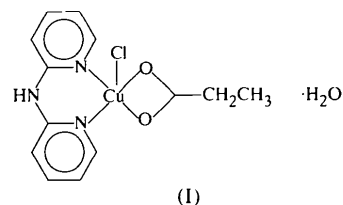
The asymmetric unit of (I) consists of a neutral $[Cu(dpyam)(O_2CCH_2CH_3)Cl]$ unit and an uncoordinated water molecule. The copper(II) ion involves a distorted square-based pyramidal CuN_2O_2Cl chromophore. The dpyam ligand bonds symmetrically in the plane with Cu—N distances of 1.970 (2) and 1.972 (2) Å, and a bite angle of 93.95 (6)°, which is in the range normally observed for the coordinated dpyam ligand (Ray & Hathaway, 1978). The propionate group also bonds nearly symmetrically in the plane, with C—O distances of 2.012 (2) and 2.049 (1) Å, and an O1—Cu1—O2 bite angle of 64.14 (6)°. A chloride anion then occupies the apical position of the CuN_2O_2Cl chromophore, with a longer Cu—Cl distance of 2.489 (1) Å. The ligand atoms which are involved in the coordination (N1, N2, O1 and O2) are coplanar and the Cu atom lies 0.304 (1) Å above this plane, towards the apical Cl atom, giving identical *trans* in-plane N—Cu—O angles of 156.84 (7)°. A zero τ value $\{[(N1—Cu1—O2) - (N2—Cu1—O1)]/60\}$ indicates that (I) is consistent with a nearly regular square-based pyramidal stereochemistry (Addison *et al.*, 1984; Murphy *et al.*, 1998). The N1—Cu1—N2 and O1—Cu1—O2 planes make a dihedral angle of 23.24 (7)°.

There are no unusual bond lengths or angles in the dpyam ligand. The pyridine rings are planar and they form a dihedral angle of 2.37 (7)°. Atoms O1, O2, C11 and C12 of the propionate group are essentially coplanar, and the dihedral angle between this plane and the mean plane through the dpyam ligand is 16.6 (1)°; the
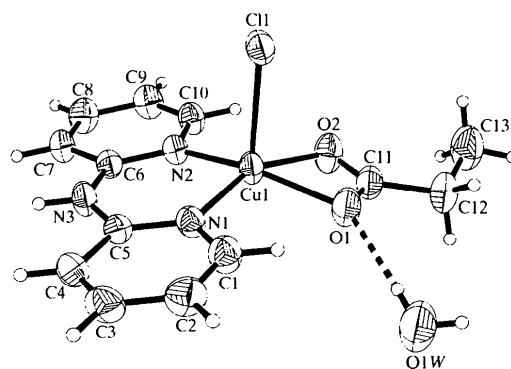
Fig. 1. The structure of (I) showing 50% probability displacement ellipsoids and the atom-numbering scheme.