Absorption correction:
ψ scans (Sheldrick, 1990*b*)
$T_{\min} = 0.824$, $T_{\max} = 0.922$
3577 measured reflections
3311 independent reflections
2077 reflections with $F > 4\sigma(F)$
$h = -14 \rightarrow 14$
$k = 0 \rightarrow 23$
$l = 0 \rightarrow 8$
3 standard reflections every 150 reflections intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.0501$
$wR(F^2) = 0.1294$
$S = 1.027$
2867 reflections
253 parameters
H atoms riding (C—H 0.96 Å)
$w = 1/[\sigma^2(F_o^2) + (0.0515P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.336$ e Å^{-3}
$\Delta\rho_{\min} = -0.283$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Fe—C37	2.029 (5)	C3—C4	1.368 (6)
Fe—C33	2.030 (4)	C3—C11	1.405 (6)
Fe—C39	2.031 (4)	C4—C5	1.381 (7)
Fe—C34	2.033 (4)	C5—C6	1.371 (6)
Fe—C40	2.034 (4)	C6—C12	1.400 (5)
Fe—C32	2.034 (4)	C7—C8	1.360 (6)
Fe—C36	2.035 (4)	C7—C13	1.407 (5)
Fe—C35	2.038 (4)	C8—C9	1.398 (6)
Fe—C38	2.038 (4)	C9—C10	1.367 (5)
Fe—C31	2.056 (3)	C10—C14	1.415 (5)
C1—C2	1.370 (5)	C11—C12	1.401 (5)
C1—C14	1.444 (5)	C12—C13	1.470 (5)
C1—C21	1.527 (5)	C13—C14	1.416 (5)
C2—C22	1.450 (6)	C21—C31	1.513 (5)
C2—C11	1.453 (5)	C22—N23	1.138 (5)
C2—C1—C14	119.0 (3)	C12—C11—C3	119.8 (4)
C2—C1—C21	119.6 (3)	C12—C11—C2	118.6 (4)
C14—C1—C21	121.4 (3)	C3—C11—C2	121.6 (4)
C1—C2—C22	119.9 (4)	C6—C12—C11	118.0 (4)
C1—C2—C11	123.1 (4)	C6—C12—C13	122.8 (4)
C22—C2—C11	117.0 (4)	C11—C12—C13	119.2 (3)
C4—C3—C11	120.5 (5)	C7—C13—C14	118.3 (4)
C3—C4—C5	120.1 (4)	C7—C13—C12	121.6 (3)
C6—C5—C4	120.2 (4)	C14—C13—C12	120.1 (3)
C5—C6—C12	121.4 (5)	C10—C14—C13	118.4 (3)
C8—C7—C13	121.9 (4)	C10—C14—C1	121.7 (3)
C7—C8—C9	120.3 (4)	C13—C14—C1	119.9 (3)
C10—C9—C8	119.4 (4)	C31—C21—C1	111.4 (3)
C9—C10—C14	121.7 (4)	N23—C22—C2	178.3 (5)

Data were corrected for both structures for Lorentz, polarization and absorption effects. Both structures were solved by direct methods (Sheldrick, 1990*a*). Refinement on F^2 for all reflections. Weighted *R*, *wR*, and goodnesses of fit (*S*) were based on F^2. Full-matrix least-squares refinement was performed for both structures. All non-H atoms were refined anisotropically, while all H atoms were refined using a riding model.

For both compounds, data collection: *R3m/V* diffractometer control program; cell refinement: *R3m/V* diffractometer control program; data reduction: *R3m/V* diffractometer control program; program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993); molecular graphics: *SHELXTL-Plus* (Sheldrick, 1990*b*); software used to prepare material for publication: *SHELXL93*.

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: BS1011). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Dichlorobis(1,10-phenanthroline-*N*,*N*′)-cobalt(II)–Acetonitrile (1/1.5)

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Abstract

The title complex, $[CoCl_2(C_{12}H_8N_2)_2].1.5CH_3CN$, is a monomer, with the Co atom in an octahedral environment provided by two Cl^- ions and four N atoms from the two bidentate 1,10-phenanthroline molecules.

Comment

The reaction of cobalt(II) halides with neutral bidentate ligands in alcohol or acetone has been previously reported (Su & Huang, 1984). Using spectroscopic methods only, they had assigned *trans*-octahedral geometry to

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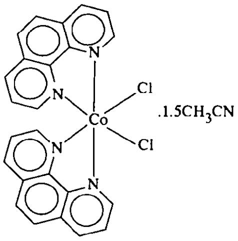
$[Co(phen)_2Cl_2]$ (phen is 1,10-phenanthroline). We found that when the reaction was carried out in acetonitrile, *cis*-$[Co(phen)_2Cl_2]$, (I), was isolated.



(I)

The title compound is made up of neutral $[Co(phen)_2Cl_2]$ units in which the metal ion exhibits a distorted octahedral environment. Four N atoms of two bidentate phen ligands and two Cl^- anions occupying *cis* positions form the octahedral arrangement. This geometry is related to that of the cobalt-containing 2,2′-bipyridyl complex (Krämer & Strähle, 1986) and also the 2,2′-bipyrimidine complex also containing cobalt(II) (De Munno, Nicolò & Julve, 1993). Bond distances for the title complex are in the same range (Co—Cl 2.38–2.45 and Co—N 2.14–2.17 Å) as for these complexes, whereas the Cl—Co—Cl angle is slightly larger and the N—Co—N bite angle smaller than those observed previously (Cl—Co—Cl 97.9–100.7 and N—Co—N 82.3–85.8°). $[Co(phen)_2Cl_2]$ crystallizes with 1.5 acetonitrile molecules per complex; the bipyridine complex also crystallizes with 1.5 solvent molecules, where the solvent is 1,2-dichloroethane.

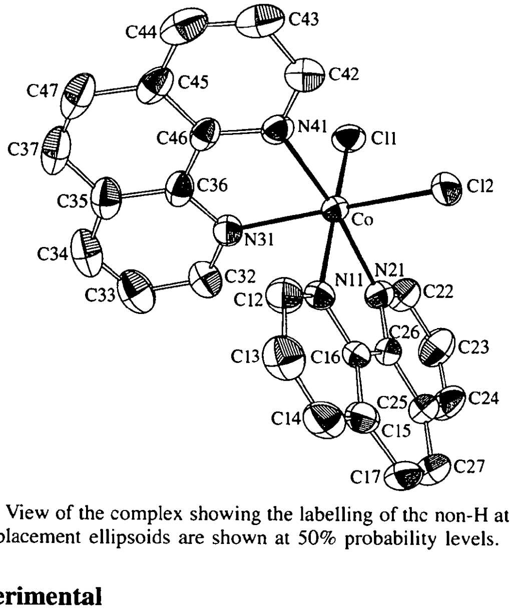


Fig. 1. View of the complex showing the labelling of the non-H atoms. Displacement ellipsoids are shown at 50% probability levels.

Experimental

The title compound was synthesized by mixing equimolar quantities of 1,10-phenanthroline and $CoCl_2$ in acetonitrile, under dry nitrogen, and then refluxing the mixture for 30 min. After a week, well developed red crystals were obtained, which were used for data collection.

Crystal data

$[CoCl_2(C_{12}H_8N_2)_2]$.-
 $1.5CH_3CN$
$M_r = 551.835$
Monoclinic
$P2_1/n$
$a = 10.969\,(2)$ Å
$b = 20.492\,(4)$ Å
$c = 11.637\,(2)$ Å
$\beta = 99.13\,(1)°$
$V = 2583\,(1)$ Å^3
$Z = 4$
$D_x = 1.419$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 29 reflections
$\theta = 12.3–17.6°$
$\mu = 0.898$ mm^{-1}
$T = 294$ K
Needle
0.46 × 0.32 × 0.16 mm
Red

Data collection

Huber four-circle diffractometer
$\theta/2\theta$ scans
Absorption correction: numerical by integration
 $T_{min} = 0.809$, $T_{max} = 0.928$
4991 measured reflections
4550 independent reflections
3279 reflections with $I > 2\sigma(I)$

$R_{int} = 0.033$
$\theta_{max} = 25°$
$h = -13 \rightarrow 12$
$k = 0 \rightarrow 24$
$l = 0 \rightarrow 13$
2 standard reflections every 50 reflections
 intensity decay: 3%

Refinement

Refinement on F
$R = 0.045$
$wR = 0.056$
$S = 1.176$
3279 reflections
308 parameters
H atoms: see below
$w = 1/\{[\sigma_{cs}(F^2) + 1.03F^2]^{1/2} - |F|\}^2$
$(\Delta/\sigma)_{max} = 0.0086$

$\Delta\rho_{max} = 0.75\,(7)$ e Å^{-3}
$\Delta\rho_{min} = -0.30\,(7)$ e Å^{-3}
Extinction correction: type 1 Lorentzian isotropic (Becker & Coppens, 1974)
Extinction coefficient: $1\,(1) \times 10^3$
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

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

Co—N41	2.155 (3)	Co—N31	2.167 (3)
Co—N21	2.157 (3)	Co—Cl1	2.416 (1)
Co—N11	2.164 (3)	Co—Cl2	2.423 (1)
N11—Co—N41	97.2 (1)	N11—Co—N21	76.7 (1)
N31—Co—N41	76.7 (1)	Cl1—Co—Cl2	101.65 (4)

The crystals contained acetonitrile molecules disordered over three sites. The three molecules were constrained to be linear and to be identical (Pawley, 1971), with isotropic displacement parameters. The sum of the occupation factors was 1.7, however, molecule 2 is close to a symmetry-related molecule and so cannot have an occupation factor of greater than 0.5. Furthermore, molecule 3 is close to molecules 1 and 2 so that the sum of the occupations for 1 and 3 cannot be greater than 1.0. The occupations were constrained so that oc(1) + oc(3) = 1 and oc(2) = 0.5, giving 1.5 solvent molecules per complex. H atoms of phenanthroline were placed in calculated positions, with C—H = 0.95 Å and U_{iso} 20% larger than U_{eq} of the parent atom. H atoms of acetonitrile were not included.

Data collection: *MAD* (Allibon, 1995). Cell refinement: *MAD*. Data reduction: *KRYSTAL* (Hazell, 1995). Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994) and *KRYSTAL*. Program(s) used to refine structure: modified *ORFLS* (Busing, Martin & Levy, 1962) and *KRYSTAL*. Molecular graphics: *ORTEP*III (Burnett & Johnson, 1996) and *KRYSTAL*. Software used to prepare material for publication: *KRYSTAL*.

AH is indebted to the Carlsberg Foundation and to the Danish Science Research Council for the diffractometer.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: AB1462). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1997). C**53**, 725–726

Bis(propionato-*O*)[5,10,15,20-tetra(*p*-chlorophenyl)porphyrinato-κ^4N]tin(IV) Dichloromethane Solvate

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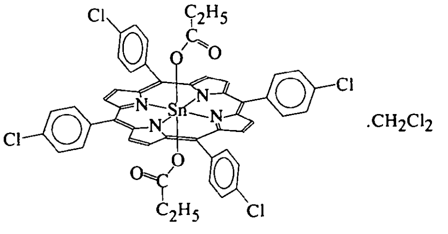
Abstract

As part of experiments directed towards the preparation of porphyrin derivatives of the main group elements, the title compound, $[Sn(C_{44}H_{24}Cl_4N_4)(C_3H_5O_2)_2].CH_2Cl_2$, crystallized as deep red crystals from dichloromethane.

Comment

The molecular structure of the title compound, (I), is shown in Fig. 1. The Sn atom lies on a centre of symmetry leading to a very symmetric structure. The geometry around the Sn atom is an almost regular octahedron, with Sn—N distances of 2.077 (4) and 2.091 (4) Å, and an Sn—O distance of 2.093 (4) Å. All angles around the Sn atom are close to 90°. The porphyrin ring system shows only minor deviations from planarity (mean deviation 0.024 Å) and bond distances are similar to those found in the closely related [Sn(TPP)(OAc)$_2$] (Liu, Lin, Chen & Wang, 1996) and [Sb(TPP){OCH(CH$_3$)$_2$}] structures (Barbour, Belcher, Brothers, Rickard & Ware, 1992).



(I)

As in [Sn(TPP)(OAc)$_2$], the interaction between the Sn atom and the carboxylic acid group is unidentate, the second O atom being 3.363 (5) Å from the Sn atom. There are no significant intermolecular interactions. The dichloromethane solvent lies on a twofold axis and in addition shows disorder of the Cl atom which has been modelled as two half-weighted atoms.

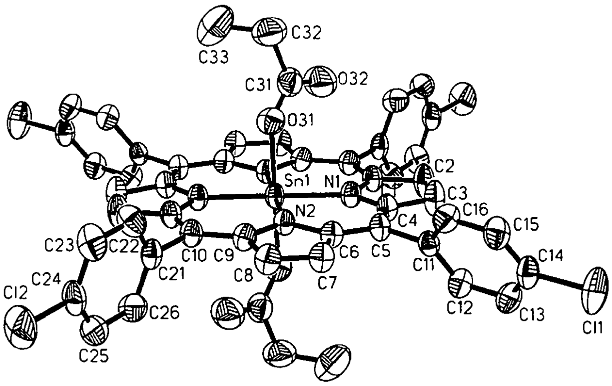


Fig. 1. The structure of [Sn(TpClTPP)(OOCEt)$_2$]. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity.

Experimental

SnCl$_4$ (2 ml, 17.1 mmol) and H$_2$TpClPP (1.2 g, 1.6 mmol) were refluxed in chlorobenzene for 30 min. The solvent was removed under reduced pressure and the resulting crude solid chromatographed on basic alumina with dichloromethane as solvent. A single red band was removed, propionic acid (1 ml)