METAL-ORGANIC COMPOUNDS

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Dichlorobis[1,3-dimethylimidazole-2(3*H*)-selone-*Se*]cobalt(II)

Daniel J. Williams,[a] Timothy A. Jones,[a] Edward D. Rice,[a] Kerri J. Davis,[a] John A. Ritchie,[a] William T. Pennington[b] and George L. Schimek[b]

[a]*Department of Chemistry, Kennesaw State College, Marietta, GA 30061, USA, and* [b]*Department of Chemistry, Clemson University, Clemson, SC 29634-1905, USA. E-mail: xraylab@clemson.edu*

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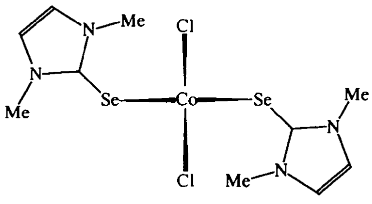
Abstract

The crystal structure of the title compound, [$CoCl_2(C_5H_8N_2Se)_2$], shows a discrete molecular structure with tetrahedral geometry around the cobalt ion. The mean Co—Cl and Co—Se distances are 2.277 (3) and 2.456 (3) Å, respectively. Bond angles around the Co atom range from 101.1 (1) to 120.0 (1)°. Ring distances and angles in the ligand compare favorably with the literature values of analogous compounds and show significant increases from values observed in the uncoordinated selone. However, the mean C—Se bond distance of 1.88 (2) Å shows no significant difference from the free ligand. Other corresponding bond distances and angles show no significant differences between the free and coordinated ligands.

Comment

The title compound, [$CoCl_2(dmise)_2$], where dmise is 1,3-dimethylimidazoleselone, is the first metal halide complex to be prepared from this new sterically hindered dialkylimidazoleselone which was reported a few years ago (Williams, Fawcett-Brown, Raye, VanDerveer, Tang & Jones, 1993). Devillanova, Verani & Sillanpaa (1981) reported the synthesis and characterization of a close analog of this compound with bis(1,3-dimethylimidazolidine-2-selone)dichlorocobalt(II), but no structures were ever reported. The imidazolidine-2-selone ligand is the same as dmise, except saturated at the carbon–carbon bond in the ring.



[$CoCl_2(dmise)_2$]

The coordination sphere around cobalt (Fig. 1) is a distorted tetrahedron approximating localized C_{2v} site symmetry, with angles ranging from 101.1 (1) to 120.0 (1)°. Large deviations from the ideal value of 109.5° are probably the result of packing restraints of the bulky dialkylimidazoleselone ligands. This speculation is based on the observance of a similar degree of distortion (101.7–121.7°) in the bond angles reported for [$CoBr_2(dmit)_2$], where dmit is the sulfur-based analog of dmise [dmit = 1,3-dimethyl-2(3*H*)-imidazolethione] (Kheddar, Protas, Le Baccon, Guglielmetti & Guerchais, 1976).

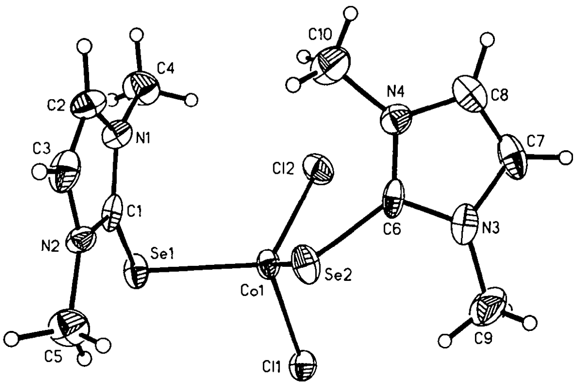


Fig. 1. View of the [$CoCl_2(dmise)_2$] molecular unit. Displacement ellipsoids are shown at the 40% probability level.

Of prime interest are the coordinated dmise ring distances and angles relative to the free ligand. The structure of dmise has been reported previously (Williams *et al.*, 1993) and one notable point is the C—Se distances which show no significant difference between the free and bonded states [1.88 (2) Å]. The other corresponding bond distances and angles show no significant changes relative to the free ligand and this lends further support to the conclusion by Williams *et al.* (1993) that there is a high degree of ring aromaticity in the free selone.

Experimental

The synthesis of dmise has been described previously (Williams *et al.*, 1993). All reagents for the synthesis of [$CoCl_2(dmise)_2$] were used as obtained commercially without further purification. In 70 ml anhydrous methanol were mixed 1.19 g (5 mmol) [$CoCl_2(H_2O)_6$] (Fisher) and 1.75 g (10 mmol) of dmise. The mixture was heated and about half of the solvent was evaporated. Blue–green crystallographic grade crystals were obtained upon cooling.

Crystal data

[$CoCl_2(C_5H_8N_2Se)_2$]
M_r = 480.02
Mo $K\alpha$ radiation
λ = 0.71073 Å

Monoclinic
$P2_1/n$
$a = 9.510\,(2)$ Å
$b = 13.750\,(3)$ Å
$c = 13.410\,(2)$ Å
$\beta = 107.58\,(1)°$
$V = 1671.7\,(5)$ Å^3
$Z = 4$
$D_x = 1.907$ Mg m^{-3}
D_m not measured

Cell parameters from 48 reflections
$\theta = 13.07–20.52°$
$\mu = 5.692$ mm^{-1}
$T = 295$ K
Parallelepiped
0.39 × 0.34 × 0.21 mm
Blue–green

Data collection

Siemens *R3m/V* diffractometer
ω–2θ scans
Absorption correction: empirical *via* ψ scans (Sheldrick, 1991)
$T_{\min} = 0.10$, $T_{\max} = 0.31$
2463 measured reflections
2188 independent reflections

1340 reflections with $F > 6\sigma(F)$
$R_{\rm int} = 0.0581$
$\theta_{\max} = 22.5°$
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 14$
$l = -14 \rightarrow 13$
3 standard reflections every 97 reflections intensity decay: 13.0%

Refinement

Refinement on F
$R = 0.033$
$wR = 0.040$
$S = 1.16$
1340 reflections
173 parameters
H atoms placed in calculated positions; $U_{\rm H} = 0.15\,(2)$ Å^2

$w = 1/[\sigma^2(F) + 0.0005F^2]$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.38$ e Å^{-3}
$\Delta\rho_{\min} = -0.73$ e Å^{-3}
Extinction correction: none
Scattering factors from Cromer & Waber (1974)

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

Se1—Co1	2.458 (2)	Co1—Cl2	2.259 (3)
Se2—Co1	2.472 (1)	Se1—C1	1.871 (8)
Co1—Cl1	2.277 (3)	Se2—C6	1.875 (10)
Co1—Se1—C1	100.4 (3)	Se2—Co1—Cl1	112.3 (1)
Co1—Se2—C6	99.3 (2)	Se1—Co1—Cl2	120.0 (1)
Se1—Co1—Se2	101.1 (1)	Se2—Co1—Cl2	107.5 (1)
Se1—Co1—Cl1	106.3 (1)	Cl1—Co1—Cl2	109.4 (1)

Data collection was stopped at $2\theta = 45°$ due to the low percentage of observed data for high-order reflections, and due to the fact that the crystal had decayed significantly over the course of the 45° shell. A linear decay correction was applied to intensity data. The structure was solved by direct methods and refined by full-matrix least-squares techniques. All non-H atoms were refined anisotropically, and H atoms were generated with ideal geometries (C—H = 0.96 Å) and refined with a group displacement parameter as riding groups.

Data collection: *P3 Diffractometer Program* (Siemens, 1976). Cell refinement: *P3 Diffractometer Program*. Data reduction: *SHELXTL-Plus* (Sheldrick, 1991). Program(s) used to solve structure: *SHELXTL-Plus*. Program(s) used to refine structure: *SHELXTL-Plus*. Molecular graphics: *SHELXTL-Plus*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1302). Services for accessing these data are described at the back of the journal.

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π-Stacking of [Pt(2,2′-bipyridine)(ethylenediamine)]$^{2+}$ as its Hexafluorophosphate Salt

MASAKO KATO, CHIZUKO KOSUGE, SHIGENOBU YANO AND MASARU KIMURA

Department of Chemistry, Faculty of Science, Nara Women's University, Nara 630, Japan. E-mail: kato@cc.nara-wu.ac.jp

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Abstract

The crystal structure of (2,2′-bipyridine-*N,N*′)(ethylenediamine-*N,N*′)platinum(II) bis(hexafluorophosphate), $[Pt(C_2H_8N_2)(C_{10}H_8N_2)](PF_6)_2$, $[Pt(bpy)(en)](PF_6)_2$, contains π-bpy-stacked columns of platinum complex cations. The bpy ligands are stacked keeping van der Waals contacts although the crystal exhibits essentially the same $^3\pi$–π^* emission spectrum as that in dilute solution.

Comment

Square-planar platinum(II) complexes containing α-diimine ligands can form various stacking structures in the solid state which are controlled by metal–metal and/or ligand π–π interactions (Kato *et al.*, 1996). Depending on the crystal structures and thus the intermolecular interactions, crystals of the platinum complexes show characteristic emission spectra which are considerably different from those for the monomeric forms in dilute solution. The perchlorate salt of [Pt(bpy)(en)]$^{2+}$, however, exhibits almost the same $^3\pi$–π^*(bpy) emission spectrum as that in dilute solution. Thus, it was suggested that the complex had a monomeric environment in the crystal (Miskowski & Houlding, 1989).