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Two Heteroleptic Cobalt(III) Cyclopentadienyl/Dithiolene Complexes

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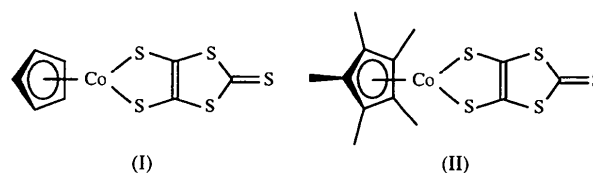
Abstract

The crystal structure determinations of (η^5 -cyclopentadienyl)(4,5-dimercapto-1,3-dithiole-2-thionato)cobalt(III), [Co(C₅H₅)(C₃S₅)], and (4,5-dimercapto-1,3-dithiole-2-thionato)(η^5 -pentamethylcyclopentadienyl)cobalt(III), [Co(C₁₀H₁₅)(C₃S₅)], show that Cp* substitution does not significantly modify the geometric features of these complexes, which are characterized by a perpendicular arrangement of the planar Cp or Cp* and (CoS₂C₂) moieties.

Comment

In the course of our work on electroactive materials built from heteroleptic cyclopentadienyl/dithiolene complexes with Ti, Nb and Mo (Fourmigué & Coulon, 1994; Fourmigué, Lenoir, Coulon, Guyon & Amaudrut, 1995; Guyon, Fourmigué, Audebert & Amaudrut, 1995; Guyon, Lenoir, Fourmigué, Larsen & Amaudrut, 1990), we have been interested in the corresponding Co complexes of general formula CpCo(dithiolene), where Cp is the cyclopentadienyl ligand. The structures of such Co^{III} complexes with various dithiolenes have been reported, *e.g.* S₂C₂(CN)₂ (Churchill & Fennessey, 1968), S₂C₂(CF₃)₂ (Baird & White, 1966), S₂C₆H₄ (Miller, Brill, Rheingold & Fultz, 1983); complexes with nitrogen-containing dithiolenes have also been reported (Werner, Xiaolan & Nurnberg, 1992; Armstrong *et al.*, 1993). More recently, sulfur-rich dithiolene ligands such as dmit²⁻ or dddt²⁻ (where dmit²⁻ is 4,5-dimercapto-1,3-dithiole-2-thionate and dddt²⁻ is 5,6-dihydro-1,4-dithiine-2,3-dithiolate) have been used (Ushijima *et al.*, 1990, 1991) and the electrochemical properties of the complexes investigated. These latter ligands have been shown to be particularly versatile in homoleptic paramagnetic complexes as, for example, in Ni(dmit)₂⁻, since they promote a solid-state organization with strong intermolecular S··S interactions, a prerequisite for the setting of collective electronic properties such as conductivity, superconductivity and magnetism (Canadell, Ravy, Pouget & Brossard, 1990).

In this paper, the crystal structures of CpCo(dmit), (I), and Cp*Co(dmit), (II), are reported. The geometry of the cyclopentadienyl complex, (I), is compared with that of previously reported complexes as well as with the Cp* analogue, (II), for which no crystal structure with any dithiolene ligand has been reported previously.



In both compounds, the Co(S₂C₂) moiety is nearly planar and perpendicular to the Cp [88.4(2)°] and the Cp* [87.8(2)°] moieties. The dimensions of the [(η -C₅H₅)Co(S₂C₂)] moiety in (I) are similar to those of each of the five structurally characterized molecules of this type. With the Cp* ligand, a slight elongation of the Co—S bonds was observed, which might be attributable to the more electron-rich character of the Cp* ligand when compared with the Cp ligand.

In the solid state, short S··S contacts are identified in (I) [S4··S1¹ 3.608(3), S2··S1¹ 3.655(3) and S4··S3¹ 3.733(3) Å; symmetry code: (i) $x - 1, y, z$], thus linking the parallel dmit moieties of neighbouring molecules obtained by translation along the *a* axis. These short

contacts in (I) are attributable to the combined effects of van der Waals (Ellern *et al.*, 1994) and π - π interactions (Hunter & Sanders, 1990), while in (II), the larger Cp* ligand prevents such a compact packing and S...S contacts appear to be larger than the sum of the van der Waals radii (3.7 Å) [S2...S3ⁱⁱ 3.807 (5), S4...S1ⁱⁱ 3.869 (5) Å; symmetry code: (ii) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$].

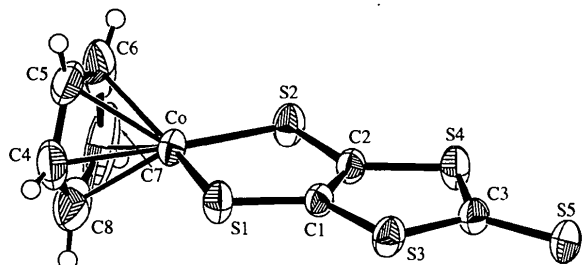


Fig. 1. Molecular structure of (I) with displacement ellipsoids drawn at the 50% probability level.

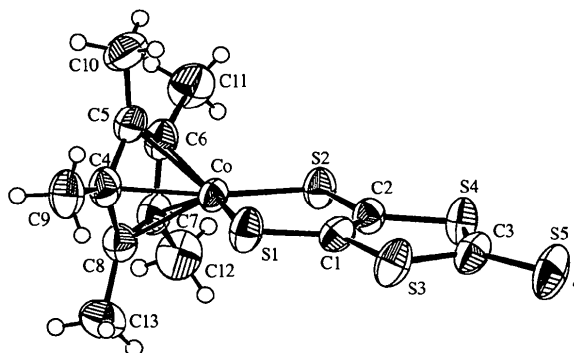


Fig. 2. Molecular structure of (II) with displacement ellipsoids drawn at the 50% probability level.

Experimental

Compounds (I) and (II) were prepared as described previously (Ushijima *et al.*, 1990). Single crystals of (I) and (II) were obtained by recrystallization from toluene and ethyl acetate, respectively.

Compound (I)

Crystal data

[Co(C₅H₅)(C₃S₅)]

$M_r = 320.35$

Monoclinic

$P2_1/n$

$a = 5.9564$ (8) Å

$b = 7.8830$ (3) Å

$c = 23.2930$ (3) Å

$\beta = 97.180$ (10)°

$V = 1085.1$ (5) Å³

$Z = 4$

$D_x = 1.961$ Mg m⁻³

D_m not measured

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 25 reflections

$\theta = 8.3$ – 15.5 °

$\mu = 2.494$ mm⁻¹

$T = 293$ (2) K

Plate

$0.180 \times 0.150 \times 0.045$ mm

Black

Data collection

Enraf–Nonius CAD-4 diffractometer

ω - 2θ scans

Absorption correction:

ψ scan (SHELXTL/PC;

Sheldrick, 1995)

$T_{\min} = 0.722, T_{\max} = 0.894$

2338 measured reflections

2126 independent reflections

1484 reflections with

$I > 2\sigma(I)$

$R_{\text{int}} = 0.187$

$\theta_{\max} = 25.97$ °

$h = 0 \rightarrow 7$

$k = 0 \rightarrow 9$

$l = -28 \rightarrow 28$

3 standard reflections

frequency: 60 min

intensity decay: none

Refinement

Refinement on F^2

$R(F) = 0.032$

$wR(F^2) = 0.073$

$S = 1.106$

2126 reflections

127 parameters

H-atom parameters

constrained; see below

$w = 1/[\sigma^2(F_o^2) + (0.0396P)^2 + 0.852P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.511$ e Å⁻³

$\Delta\rho_{\min} = -0.476$ e Å⁻³

Extinction correction: none

Scattering factors from

International Tables for Crystallography (Vol. C)

Compound (II)

Crystal data

[Co(C₁₀H₁₅)(C₃S₅)]

$M_r = 390.525$

Monoclinic

$P2_1/n$

$a = 12.140$ (2) Å

$b = 11.488$ (2) Å

$c = 12.698$ (3) Å

$\beta = 110.91$ (2)°

$V = 1654.3$ (6) Å³

$Z = 4$

$D_x = 1.568$ Mg m⁻³

D_m not measured

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 2000 reflections

$\theta = 2$ – 24 °

$\mu = 1.65$ mm⁻¹

$T = 293$ K

Plate

$0.39 \times 0.28 \times 0.03$ mm

Black

Data collection

Stoe IPDS diffractometer

Rotation scans, $\Delta\varphi = 3$ °

Absorption correction:

numerical (FACEIT; Stoe & Cie, 1995)

$T_{\min} = 0.591, T_{\max} = 0.940$

10 261 measured reflections

2641 independent reflections

1725 reflections with

$F > 3\sigma(F)$

$R_{\text{int}} = 0.076$

$\theta_{\max} = 24.27$ °

$h = -13 \rightarrow 13$

$k = -13 \rightarrow 13$

$l = -14 \rightarrow 14$

Refinement

Refinement on F

$R = 0.05$

$wR = 0.055$

$S = 1.193$

1725 reflections

172 parameters

H-atom parameters

constrained; see below

$(\Delta/\sigma)_{\max} = 0.004$

$\Delta\rho_{\max} = 0.809$ e Å⁻³

$\Delta\rho_{\min} = -1.45$ e Å⁻³

Extinction correction: none

Scattering factors from

International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (\AA , $^\circ$) for (I) and (II)

	(I)	(II)
Co—S1	2.1233 (11)	2.138 (2)
Co—S2	2.1266 (11)	2.135 (2)
S1—C1	1.705 (3)	1.713 (6)
S2—C2	1.702 (4)	1.725 (7)
S3—C1	1.733 (3)	1.741 (7)
S4—C2	1.738 (4)	1.739 (6)
S3—C3	1.714 (4)	1.719 (6)
S4—C3	1.728 (4)	1.725 (8)
S5—C3	1.661 (4)	1.657 (7)
C1—C2	1.377 (5)	1.352 (9)
Mean Co—C†	2.028 (12)	2.050 (7)
S1—Co—S2	93.20 (4)	93.65 (7)
C1—S1—Co1	103.14 (13)	102.3 (2)
C2—S2—Co2	103.30 (12)	102.3 (2)

† Estimated errors on averaged Co—C distances are calculated as $\sigma = [\sum(d_i - d_{\text{mean}})^2 / (n - 1)]^{1/2}$, $n = 5$.

Data for (II) were collected with an area detector (Stoe IPDS) with a crystal-to-plate distance of 80 mm ($\theta_{\text{max}} = 24.27^\circ$), an exposure time of 5 min per plate, with φ varying from 0 to 200° by increments $\Delta\varphi = 3^\circ$; the duration of measurement was 10 h. With respect to the ψ -scan absorption correction for (I), discrepancies between the resulting $T_{\text{max}}/T_{\text{min}}$ values and those expected from the μ value and crystal size might be attributable to the very thin shape of the crystal, which makes an accurate determination of the smallest crystal dimension difficult. H atoms were introduced at calculated positions, included in structure-factor calculations and not refined (riding model). In the final electron-density map of (II), the strongest negative density peak was found to be -1.45 e \AA^{-3} in the vicinity (1 \AA) of the Co atom. Two C atoms (C6 and C7) of the Cp ring in (I) exhibit strongly anisotropic displacement parameters ($U_3/U_1 = 12$), but attempts to introduce a disorder model for the Cp ring were unsuccessful.

Data collection: CAD-4 EXPRESS (Enraf-Nonius, 1994) for (I); EXPOSE (Stoe & Cie, 1995) for (II). Cell refinement: CAD-4 EXPRESS for (I); SELECT (Stoe & Cie, 1995) for (II). Data reduction: XCAD-4 (Harms, 1993) for (I); INTEGRATE (Stoe & Cie, 1995) for (II). Program(s) used to solve structures: SHELXS86 (Sheldrick, 1990) for (I); Xtal3.2 (Hall, Flack & Stewart, 1992) for (II). Program(s) used to refine structures: SHELXL93 (Sheldrick, 1993) for (I); Xtal3.2 for (II). For both compounds, molecular graphics: ORTEPII (Johnson, 1976). Software used to prepare material for publication: SHELXL93 for (I); Xtal3.2 for (II).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AB1475). Services for accessing these data are described at the back of the journal.

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Bis(2,2'-bipyridine-*N,N'*)(tricyanomethanido-*N*)copper(II) Tricyanomethanide

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Abstract

The crystal structure of $[\text{Cu}\{\text{C}(\text{CN})_3\}(\text{C}_{10}\text{H}_8\text{N}_2)_2][\text{C}(\text{CN})_3]$ is formed by discrete $[\text{Cu}(\text{bipy})_2\{\text{C}(\text{CN})_3\}]^+$ cations and $[\text{C}(\text{CN})_3]^-$ anions (bipy is 2,2'-bipyridine). The coordination polyhedron of Cu^{II} is a distorted trigonal bipyramid with a $\{\text{CuN}_5\}$ chromophore.