usual Patterson and Fourier methods, and the non-H atoms refined anisotropically by blocked-matrix least-squares methods (*SHELX76*). The H atoms were placed in experimentally determined positions obtained from the difference maps and refined with a common isotropic thermal parameter, $U_{iso} = 0.053\ (4)\ \text{Å}^2$.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71199 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA1028]

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Structure of (η^5-Cyclopentadienyl)[1-(2-quinoxalinyl)ethene-1,2-dithiolato]cobalt(III), [(η^5-C_5H_5)Co{S_2C_2H(2-quinoxalinyl)}]

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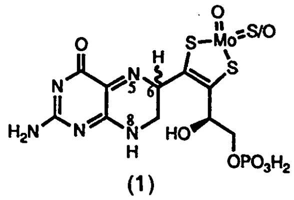
Abstract

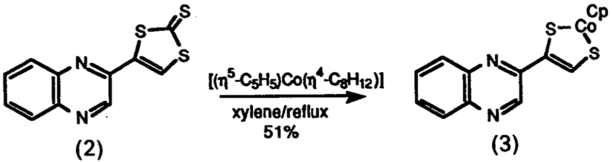
[(η^5-C_5H_5)Co{S_2C_2H(2-quinoxalinyl)}] has been prepared using a general procedure which allows for the synthesis of unsymmetrical dithiolenes; the molecular structure involves a planar cobalt–dithiolene five-membered ring which is disposed at an angle of 10.6° to the 2-quinoxalinyl group.

Comment

(Cyclopentadienyl)(ene-1,2-dithiolato)cobalt complexes have been prepared in the past; [(η^5-C_5H_5)Co{$S_2C_2(CF_3)_2$}] (Baird & White, 1966), [(η^5-C_5H_5)Co{$S_2C_2(CN)_2$}] (Churchill & Fennessey, 1968) and [(η^5-C_5H_5)Co($S_2C_6H_4$)] (Miller, Brill, Rheingold & Fultz, 1983) have been characterized by X-ray crystallography. We have extended the investigation of these systems, partly because of our interest in the synthesis of dithiolenes, which resemble the partial structure of the ligand proposed (Gardlik & Rajagopalan, 1990) for the cofactor of the oxomolybdoenzymes, Moco, (1). The title compound, (3), was prepared by the reaction of [(η^5-C_5H_5)Co(η^4-C_8H_{12})] with 4-(2-quinoxalinyl)-1,3-dithiole-2-thione, (2) (Siedle, 1976), and recrystallized from hexane.



(1)



(2) (3)

Cp = cyclopentadienyl

The atomic parameters of (3) are listed in Table 1; Table 2 lists selected bond lengths and bond angles; Fig. 1 shows an *ORTEP* (Johnson, 1965) drawing of the molecule and the numbering system used in the tables.

The dimensions of the {(η^5-C_5H_5)Co(S_2C_2)} moiety are similar to those of each of the three structurally characterized molecules of this type

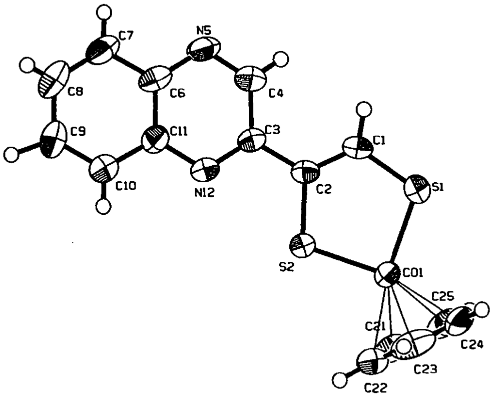


Fig. 1. *ORTEP* drawing of [(η^5-C_5H_5)Co{S_2C_2H(2-quinoxalinyl)}] showing the numbering scheme used in the tables.

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(Baird & White, 1966; Churchill & Fennessey, 1968; Miller *et al.*, 1983). The cobalt–dithiolene five-membered ring is essentially planar as is the 2-quinoxalinyl group; these two planes are mutually disposed at an angle of 10.6°.

Experimental

Crystal data

$[Co(C_{10}H_6N_2S_2)(C_5H_5)]$
$M_r = 342.32$
Monoclinic
$P2_1/c$
$a = 13.824$ (7) Å
$b = 6.178$ (8) Å
$c = 17.844$ (6) Å
$\beta = 112.26$ (3)°
$V = 1410$ (2) Å^3
$Z = 4$

$D_x = 1.612$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 20 reflections
$\theta = 4.5$- 10.1°
$\mu = 1.49$ mm^{-1}
$T = 294$ K
Tabular
0.31 × 0.24 × 0.03 mm
Black

Data collection

Rigaku AFC-6*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical (ψ scans)
$T_{\min} = 0.80$, $T_{\max} = 1.00$
4651 measured reflections
4485 independent reflections
1806 observed reflections [$I > 3\sigma(I)$]

$R_{\rm int} = 0.018$
$\theta_{\max} = 30°$
$h = 0 \rightarrow 19$
$k = 0 \rightarrow 8$
$l = -24 \rightarrow 22$
3 standard reflections monitored every 150 reflections
intensity variation: −3.14%

Refinement

Refinement on F
Final $R = 0.043$
$wR = 0.043$
$S = 1.33$
1806 reflections
225 parameters
All H-atom parameters refined

$w = 4F_o^2/\sigma^2(F_o^2)$
$(\Delta/\sigma)_{\max} = 0.01$
$\Delta\rho_{\max} = 0.47$ e Å^{-3}
$\Delta\rho_{\min} = -0.31$ e Å^{-3}
Atomic scattering factors from Cromer & Waber (1974)

Table 1. *Positional and thermal parameters* (Å^2) *with e.s.d.'s in parentheses*

$$B_{\rm eq} = (8\pi^2/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
Co(1)	0.98911 (5)	0.1682 (1)	0.87044 (4)	3.07 (2)
S(1)	1.0721 (1)	0.4535 (2)	0.9179 (1)	5.05 (7)
S(2)	1.1238 (1)	0.0247 (2)	0.86490 (8)	3.85 (5)
N(5)	1.5071 (3)	0.2516 (8)	0.9421 (3)	4.5 (2)
N(12)	1.3334 (3)	−0.0172 (7)	0.8622 (2)	3.5 (2)
C(1)	1.1960 (4)	0.406 (1)	0.9240 (3)	4.2 (2)
C(2)	1.2212 (3)	0.2148 (8)	0.8998 (3)	3.1 (2)
C(3)	1.3247 (3)	0.1598 (9)	0.9002 (3)	3.1 (2)
C(4)	1.4135 (4)	0.294 (1)	0.9400 (3)	4.3 (2)
C(6)	1.5164 (4)	0.071 (1)	0.9019 (3)	3.9 (2)
C(7)	1.6147 (4)	0.013 (1)	0.9010 (4)	5.0 (3)
C(8)	1.6253 (5)	−0.171 (1)	0.8639 (5)	6.0 (3)
C(9)	1.5405 (4)	−0.307 (1)	0.8247 (4)	5.3 (3)
C(10)	1.4448 (4)	−0.254 (1)	0.8248 (4)	4.4 (2)
C(11)	1.4307 (4)	−0.0657 (9)	0.8631 (3)	3.5 (2)
C(21)	0.8979 (4)	−0.064 (1)	0.8919 (4)	4.4 (3)
C(22)	0.8831 (4)	−0.065 (1)	0.8112 (4)	4.7 (3)
C(23)	0.8474 (4)	0.135 (1)	0.7790 (4)	5.6 (3)
C(24)	0.8383 (5)	0.264 (1)	0.8399 (7)	7.0 (4)
C(25)	0.8711 (4)	0.137 (1)	0.9108 (4)	5.4 (3)

Table 2. *Selected bond lengths* (Å) *and bond angles* (°) *with e.s.d.'s in parentheses*

Co(1)—S(1)	2.099 (3)	C(2)—C(3)	1.468 (6)
Co(1)—S(2)	2.098 (2)	C(3)—C(4)	1.428 (7)
Co(1)—C(21)	2.038 (6)	C(6)—C(7)	1.411 (7)
Co(1)—C(22)	2.040 (6)	C(6)—C(11)	1.404 (7)
Co(1)—C(23)	2.030 (5)	C(7)—C(8)	1.35 (1)
Co(1)—C(24)	2.033 (6)	C(8)—C(9)	1.395 (9)
Co(1)—C(25)	2.026 (5)	C(9)—C(10)	1.364 (7)
S(1)—C(1)	1.700 (6)	C(10)—C(11)	1.399 (7)
S(2)—C(2)	1.716 (5)	C(21)—C(22)	1.376 (8)
N(5)—C(4)	1.306 (7)	C(21)—C(25)	1.372 (9)
N(5)—C(6)	1.360 (7)	C(22)—C(23)	1.371 (9)
N(12)—C(3)	1.317 (6)	C(23)—C(24)	1.39 (1)
N(12)—C(11)	1.372 (6)	C(24)—C(25)	1.41 (1)
C(1)—C(2)	1.350 (7)		
S(1)—Co(1)—S(2)	90.82 (8)	S(2)—C(2)—C(1)	117.0 (4)
S(2)—C(2)—C(3)	118.2 (4)	C(1)—C(2)—C(3)	124.7 (5)
N(12)—C(3)—C(2)	118.0 (4)	N(12)—C(3)—C(4)	120.6 (4)
C(2)—C(3)—C(4)	121.4 (5)	N(5)—C(4)—C(3)	123.6 (5)
N(5)—C(6)—C(7)	119.8 (5)	N(5)—C(6)—C(11)	121.5 (5)
C(7)—C(6)—C(11)	118.7 (6)	C(6)—C(7)—C(8)	120.0 (6)
C(7)—C(8)—C(9)	121.7 (6)	C(8)—C(9)—C(10)	119.0 (6)
C(9)—C(10)—C(11)	121.0 (6)	N(12)—C(11)—C(6)	121.0 (5)
N(12)—C(11)—C(10)	119.5 (5)	C(6)—C(11)—C(10)	119.5 (5)
C(22)—C(21)—C(25)	108.3 (6)	Co(1)—S(1)—C(1)	105.4 (2)
Co(1)—S(2)—C(2)	106.4 (2)	C(21)—C(22)—C(23)	108.7 (6)
C(4)—N(5)—C(6)	116.1 (5)	C(3)—N(12)—C(11)	117.1 (4)
S(1)—C(1)—C(2)	120.3 (4)	C(22)—C(23)—C(24)	108.2 (6)

The H atoms were found from the difference Fourier map and then refined isotropically. Anomalous-dispersion effects were included in $F_{\rm calc}$ (Ibers & Hamilton, 1964). Computer programs used: *TEXSAN* (Molecular Structure Corporation, 1985), *DIRDIF* (Beurskens, 1984) and *ORTEP* (Johnson, 1965).

We thank the University of Manchester and UMIST for the purchase of the Rigaku AFC-6*S* diffractometer.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, complete geometry and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71229 (37 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: MU1042]

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The *Pbca* Polymorph of Dichloro(η^4-1,5-cyclooctadiene)palladium(II)

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Abstract

The Pd—C bond length range is 2.189 (2)–2.221 (2) Å, the Pd—Cl lengths are 2.3065 (6) and 2.3072 (6) Å, and the Cl—Pd—Cl angle is 91.84 (2)°. The cyclooctadiene ring is in the twist-boat conformation, with C=C bond lengths of 1.382 (3) and 1.385 (3) Å.

Comment

The published structure of (1,5-cod)$PdCl_2$ (cod = cyclooctadiene) has space group $P2_12_12_1$, and the crystals obtained from CH_2Cl_2 are described as both needles and octahedra (Rettig, Wing & Wiger, 1981) or only as 'un cristal allongé suivant l'axe *c*...' (the 6.876 Å axis) (Benchekroun, Herpin, Julia & Saussine, 1977). Our crystallizations from CH_2Cl_2 yielded needles, octahedra and prisms with rhombic cross sections. In order to clarify the uncertainty, we measured the unit-cell dimensions of all three morphological types. We found the needles to have space group $P2_12_12_1$, with dimensions $a = 6.874$ (2), $b = 12.293$ (1), $c = 10.972$ (2) Å at 296 K, in good agreement with the published structure. We found that the rhombic prism and the octahedron are both a second polymorph, of space group *Pbca*, identical to that described by Howells (1973). A rhombic prism yielded unit-cell dimensions $a = 11.8266$ (9), $b = 11.9875$ (12), $c = 13.0812$ (9) Å at 295 K. We have carried out a full structure determination using a flattened octahedron.

The determination reported here represents an increase in precision over the $P2_12_12_1$ form by a factor of 2–3, and the agreement between the two molecular structures is good, including the conformation of the cod ring. The root-mean-square deviation between the two sets of eight endocyclic torsion angles is 6.8°, and the largest individual deviation is only 10°, for C2—C3—C4—C5. All four Pd—C bond distances of the *Pbca* form agree with those of the $P2_12_12_1$ form within experimental error. While the $P2_12_12_1$ form exhibited a difference in Pd—Cl distances of marginal significance, our determination has equal Pd—Cl distances.

The Cl—Pd—Cl angle is slightly larger in the *Pbca* form; 91.84 (2) *versus* 90.31 (5)°. This angle has a value of 94.02 (5)° in dichloro(norbornadiene)palladium(II) (Baenziger, Richards & Doyle, 1965), 91.11 (3)° in dichloro[(1,2,5,6-η)-cyclooctatetraene]palladium(II) (Baenziger, Goebel, Berg & Doyle, 1978), 91.9° in dichloro(1,4-cyclooctadiene)palladium(II) (Rettig *et al.*, 1981) and 90.1° in dichloro(1,5-cyclononadiene)palladium(II) (Rettig *et al.*, 1981).

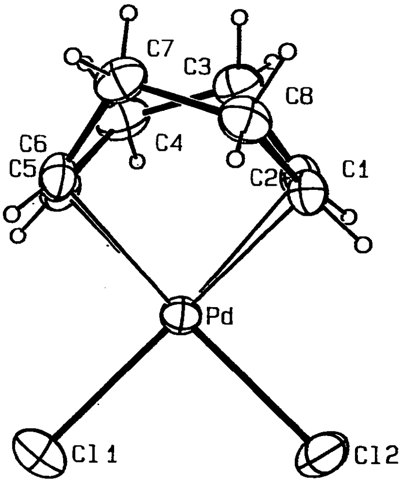

Fig. 1. *ORTEP* (Johnson, 1976) drawing of the title compound, with thermal ellipsoids drawn at the 40% probability level.

Experimental

Crystal data

[$PdCl_2(C_8H_{12})$]
$M_r = 285.5$

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å