

trile molecule (N1, C30, C31) was refined isotropically; H atoms isotropic but not refined. All calculations were performed on a MicroVAX 3100 using *SDP* (B. A. Frenz & Associates, Inc., 1985).

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 55449 (34 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: PA1021]

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Structure of Carbonylbis(diphenyldithiophosphinato)(triphenylphosphine)ruthenium Diethyl Ether Solvate, $[\text{Ru}(\text{CO})(\text{S}_2\text{PPh}_2)_2(\text{PPh}_3)] \cdot 0.25\text{Et}_2\text{O}$

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Abstract

Ruthenium is six coordinate; the principal distortion from octahedral geometry at the metal centre arises from the narrow bite angle of the chelating dithio ligand. The Ru–S distances vary by more than 0.11 Å; the bond *trans* to CO [2.5407 (11) Å] is significantly longer than that *trans* to PPh₃ [2.5205 (11) Å] and both are much longer than the other two mutually *trans* Ru–S distances [2.4295 (11), 2.4363 (10) Å]. These observations concur with the expected order of decreasing *trans* influence, CO > PPh₃ ≫ Ph₂PS₂[−].

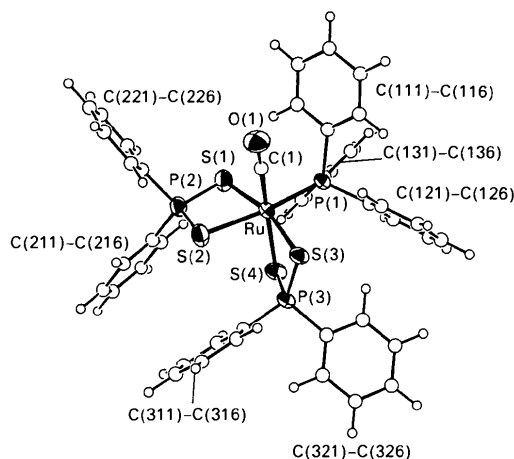
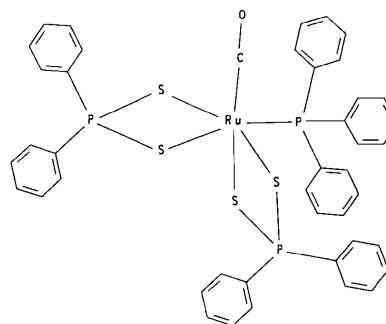


Fig. 1. View of the molecule showing the labelling of the non-H atoms. Thermal ellipsoids are drawn at the 30% probability level.

Comment

The proton-decoupled ³¹P NMR spectra of the complexes $[\text{Ru}(\text{S}_2\text{PR}_2)_2(\text{PPh}_3)(\text{CO})]$, $R = \text{Me}, \text{Ph}$ (Cole-Hamilton & Stephenson, 1974), OEt (McQueen, Schröder, Stephenson & Yellowlees, unpublished), show firstly that there are two magnetically inequivalent environments for the ³¹P nuclei of the dithiolate ligands and secondly that only one of these nuclei exhibits a ³ J_{PP} coupling to the coordinated PPh₃. Fig. 1 shows an Ru atom coordinated by two bidentate dithiolates in addition to the CO and PPh₃ ligands. We have used close analogues of the title compound in the preparation of tetracyanoethylene (tcne) complexes; in one there is an interesting intramolecular interaction between bound tcne and a phenyl ring in one S₂PPh₂[−] ligand and another has intermolecular stacking of bound tcne ligands (Blake, McQueen, Schröder, Stephenson & Yellowlees, 1988).



Experimental

Crystal data

$[\text{Ru}(\text{C}_{12}\text{H}_{10}\text{PS}_2)_2(\text{C}_{18}\text{H}_{15}\text{P})-$
 $(\text{CO})] \cdot 0.25\text{C}_4\text{H}_{10}\text{O}$
 $M_r = 908.5$

$D_x = 1.398 \text{ Mg m}^{-3}$
Mo $K\alpha$ radiation
 $\lambda = 0.71073 \text{ \AA}$

Triclinic

$P\bar{1}$
 $a = 11.072$ (3) Å
 $b = 13.873$ (5) Å
 $c = 14.310$ (4) Å
 $\alpha = 92.38$ (3)°
 $\beta = 98.583$ (24)°
 $\gamma = 95.95$ (3)°
 $V = 2158$ Å³
 $Z = 2$

Cell parameters from 25

reflections
 $\theta = 14.5\text{--}15^\circ$
 $\mu = 0.684$ mm⁻¹
 $T = 298$ K
 Tablet
 $0.66 \times 0.55 \times 0.21$ mm
 Dark orange

Data collection

Enraf-Nonius CAD-4 four-circle diffractometer
 ω -2 θ scans
 Absorption correction: none
 5623 measured reflections
 4972 observed reflections
 $[F > 4.0\sigma(F)]$

$R_{\text{int}} = 0.016$
 $\theta_{\text{max}} = 22.5^\circ$
 $h = -11 \rightarrow 11$
 $k = -14 \rightarrow 14$
 $l = 0 \rightarrow 15$
 2 standard reflections
 frequency: 60 min
 intensity variation: $< \pm 3\%$

Refinement

Refinement on F^2
 Final $R = 0.0378$
 $wR = 0.0622$
 $S = 1.723$
 4972 reflections
 397 parameters
 $w = 1/[\sigma^2(F) + 0.001F^2]$

$(\Delta/\sigma)_{\text{max}} = 0.03$
 $\Delta\rho_{\text{max}} = 0.62$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.45$ e Å⁻³
 Extinction correction: none
 Atomic scattering factors
 inlaid except for Ru
 (Cromer & Mann, 1968)

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (Å²)

$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Ru	0.18344 (3)	0.232500 (20)	0.210120 (20)	0.03222 (23)
P(1)	0.30091 (9)	0.14084 (7)	0.12902 (7)	0.0346 (6)
S(1)	0.27713 (10)	0.18669 (8)	0.36404 (7)	0.0508 (7)
S(4)	0.34060 (9)	0.38056 (7)	0.21597 (8)	0.0453 (6)
S(3)	0.08967 (9)	0.31855 (7)	0.07801 (7)	0.0386 (6)
P(3)	0.20735 (9)	0.43439 (7)	0.13122 (7)	0.0374 (6)
P(2)	0.16125 (10)	0.26776 (8)	0.41988 (7)	0.0428 (6)
S(2)	0.05669 (10)	0.31907 (8)	0.31203 (7)	0.0516 (7)
O(1)	-0.0179 (3)	0.07116 (24)	0.19062 (25)	0.0675 (22)
C(1)	0.0608 (4)	0.1327 (3)	0.1973 (3)	0.0431 (24)
C(111)	0.2417 (3)	0.01249 (14)	0.11860 (18)	0.0435 (24)
C(112)	0.1940 (3)	-0.03856 (14)	0.03276 (18)	0.057 (3)
C(113)	0.1453 (3)	-0.13553 (14)	0.03172 (18)	0.072 (3)
C(114)	0.1444 (3)	-0.18147 (14)	0.11654 (18)	0.075 (4)
C(115)	0.1921 (3)	-0.13042 (14)	0.20240 (18)	0.084 (4)
C(116)	0.2408 (3)	-0.03346 (14)	0.20343 (18)	0.068 (3)
C(121)	0.31300 (24)	0.17143 (20)	0.00811 (14)	0.0447 (24)
C(122)	0.20478 (24)	0.16777 (20)	-0.05651 (14)	0.052 (3)
C(123)	0.20944 (32)	0.19336 (20)	-0.14927 (14)	0.074 (4)
C(124)	0.32228 (24)	0.22260 (20)	-0.17738 (14)	0.087 (4)
C(125)	0.43050 (24)	0.22626 (20)	-0.11275 (14)	0.087 (4)
C(126)	0.42582 (24)	0.20069 (20)	-0.02001 (14)	0.061 (3)
C(131)	0.46041 (17)	0.13207 (19)	0.18124 (19)	0.0419 (23)
C(132)	0.52381 (17)	0.20117 (19)	0.24960 (19)	0.0468 (25)
C(133)	0.64730 (17)	0.19550 (10)	0.28439 (19)	0.063 (3)
C(134)	0.70739 (17)	0.12075 (19)	0.25083 (19)	0.071 (3)
C(135)	0.64400 (17)	0.05166 (19)	0.18248 (19)	0.078 (4)
C(136)	0.52051 (17)	0.05733 (19)	0.14768 (19)	0.062 (3)
C(211)	0.2402 (3)	0.36468 (23)	0.49999 (24)	0.056 (3)
C(212)	0.1717 (3)	0.43314 (23)	0.53465 (24)	0.098 (5)
C(213)	0.2303 (3)	0.50965 (23)	0.59686 (24)	0.130 (6)
C(214)	0.3574 (3)	0.51767 (23)	0.62440 (24)	0.115 (6)
C(215)	0.4259 (3)	0.44918 (23)	0.58972 (24)	0.164 (8)
C(216)	0.3673 (3)	0.37269 (23)	0.52752 (24)	0.117 (6)

C(221)	0.07286 (24)	0.19495 (19)	0.49183 (18)	0.048 (3)
C(222)	0.13346 (24)	0.14627 (19)	0.56501 (18)	0.065 (3)
C(223)	0.06612 (24)	0.08375 (19)	0.61698 (18)	0.088 (4)
C(224)	-0.06184 (24)	0.06994 (19)	0.59578 (18)	0.096 (5)
C(225)	-0.12241 (24)	0.11861 (19)	0.52258 (18)	0.093 (5)
C(226)	-0.05509 (24)	0.18113 (19)	0.47063 (18)	0.067 (3)
C(311)	0.13541 (23)	0.52035 (18)	0.19555 (18)	0.0424 (23)
C(312)	0.01383 (23)	0.53596 (18)	0.16450 (18)	0.059 (3)
C(313)	-0.04271 (23)	0.60158 (28)	0.21521 (18)	0.079 (4)
C(314)	0.02232 (23)	0.65157 (18)	0.29698 (18)	0.078 (4)
C(315)	0.14389 (23)	0.63596 (18)	0.32803 (18)	0.086 (4)
C(316)	0.20044 (23)	0.57034 (18)	0.27733 (18)	0.069 (3)
C(321)	0.2631 (3)	0.49929 (18)	0.03758 (18)	0.0443 (24)
C(322)	0.2408 (3)	0.59480 (18)	0.02160 (18)	0.070 (3)
C(323)	0.2833 (3)	0.64095 (18)	-0.05391 (18)	0.089 (4)
C(324)	0.3482 (3)	0.59157 (18)	-0.11344 (18)	0.083 (4)
C(325)	0.3705 (3)	0.49604 (18)	-0.09746 (18)	0.089 (4)
C(326)	0.3279 (3)	0.44990 (18)	-0.02195 (18)	0.074 (4)
C(3)*	0.4618 (11)	-0.1145 (9)	0.4265 (9)	0.0800
C(2)*	0.4882 (10)	0.0225 (8)	0.5460 (7)	0.0800
O(2)*	0.5177 (15)	0.1547 (12)	0.6413 (13)	0.0800

*These atoms have s.o.f.'s of 0.47, 0.53 and 0.22 respectively.

Table 2. Bond lengths (Å) and angles (°)

Ru—P(1)	2.3078 (10)	P(1)—C(131)	1.830 (3)
Ru—S(1)	2.4295 (11)	S(1)—P(2)	2.0199 (15)
Ru—S(2)	2.5205 (11)	S(4)—P(3)	1.9937 (14)
Ru—S(3)	2.4363 (10)	S(3)—P(3)	2.0070 (14)
Ru—S(4)	2.5407 (11)	P(3)—C(311)	1.797 (3)
Ru—C(1)	1.819 (4)	P(3)—C(321)	1.794 (3)
C(1)—O(1)	1.145 (5)	P(2)—S(2)	1.9894 (15)
P(1)—C(111)	1.825 (3)	P(2)—C(211)	1.793 (4)
P(1)—C(121)	1.819 (3)	P(2)—C(221)	1.795 (3)
P(1)—Ru—S(1)	93.46 (4)	S(4)—P(3)—C(321)	112.70 (10)
P(1)—Ru—S(4)	91.02 (4)	S(3)—P(3)—C(311)	112.22 (10)
P(1)—Ru—S(3)	98.46 (4)	S(3)—P(3)—C(321)	110.45 (10)
P(1)—Ru—S(2)	173.79 (4)	C(311)—P(3)—C(321)	105.57 (13)
P(1)—Ru—C(1)	90.80 (13)	S(1)—P(2)—S(2)	106.98 (7)
S(1)—Ru—S(4)	91.79 (4)	S(1)—P(2)—C(211)	112.76 (12)
S(1)—Ru—S(3)	165.16 (4)	S(1)—P(2)—C(221)	109.69 (10)
S(1)—Ru—S(2)	81.21 (4)	S(2)—P(2)—C(211)	110.94 (12)
S(1)—Ru—C(1)	93.59 (13)	S(2)—P(2)—C(221)	112.51 (10)
S(4)—Ru—S(3)	79.25 (3)	C(211)—P(2)—C(221)	104.05 (15)
S(4)—Ru—S(2)	92.33 (4)	Ru—S(2)—P(2)	84.98 (5)
S(4)—Ru—C(1)	174.20 (13)	Ru—C(1)—O(1)	178.2 (4)
S(3)—Ru—S(2)	87.30 (4)	P(1)—C(111)—C(112)	123.85 (20)
S(3)—Ru—C(1)	95.03 (13)	P(1)—C(111)—C(116)	116.10 (19)
S(2)—Ru—C(1)	86.36 (13)	P(1)—C(121)—C(122)	118.04 (19)
Ru—P(1)—C(111)	111.74 (9)	P(1)—C(121)—C(126)	121.93 (19)
Ru—P(1)—C(121)	116.76 (9)	P(1)—C(131)—C(132)	121.30 (19)
Ru—P(1)—C(131)	118.69 (9)	P(1)—C(131)—C(136)	118.62 (19)
C(111)—P(1)—C(121)	104.37 (12)	P(2)—C(211)—C(212)	118.5 (3)
C(111)—P(1)—C(131)	99.79 (12)	P(2)—C(211)—C(216)	121.4 (3)
C(121)—P(1)—C(131)	103.28 (12)	P(2)—C(221)—C(222)	119.38 (20)
Ru—S(1)—P(2)	86.79 (5)	P(2)—C(221)—C(226)	120.45 (20)
Ru—S(4)—P(3)	84.10 (5)	P(3)—C(311)—C(312)	119.95 (19)
Ru—S(3)—P(3)	86.63 (5)	P(3)—C(311)—C(316)	120.04 (19)
S(4)—P(3)—S(3)	105.06 (6)	P(3)—C(321)—C(322)	122.36 (21)
S(4)—P(3)—C(311)	110.99 (10)	P(3)—C(321)—C(326)	117.61 (20)

An ω -scan width of $(0.8+0.4\tan\theta)^\circ$ was used for data collection. The structure was solved using *SHELX76* (Sheldrick, 1976) from a Patterson synthesis which revealed the position of the metal atom; the other non-H atoms were located by iterative cycles of least-squares refinement and ΔF synthesis. Refinement was by full-matrix least squares using *SHELX76* (Sheldrick, 1976). The H atoms were refined in rigid groups with the phenyl-ring H atoms at calculated positions and the solvent H atoms omitted. A poorly defined partially occupied diethyl ether molecule also occurs in the lattice. Fig. 1 was produced using an interactive version of *ORTEPII* (Mallinson & Muir, 1985). Molecular geometry calculations were performed using *CALC* (Gould & Taylor, 1985).

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55371 (36 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA1009]

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Tetraethylammonium Tetrachlorocuprate(II), [N(C₂H₅)₄]₂[CuCl₄]

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Abstract

The structure has been determined by single-crystal X-ray diffraction at 120 K. There are two independent copper sites, one at 4 and the other very close to the fourfold axis with positional disorder. The structures of the [CuCl₄]²⁻ ions have a *D*_{2d} type distortion from tetrahedral symmetry with the larger Cl—Cu—Cl bond angles 122.3 (1)–128.1 (5)°.

Comment

The [CuCl₄]²⁻ ion in the solid state adopts various geometries from planar through tetrahedral to trigo-

nal bipyramidal (Smith, 1976). Several spectroscopic studies have been carried out to establish the relationships between the geometry and the electronic reflectance spectra (Lamotte-Brasseur, 1974; Battaglia, Bonamartini Corradi, Marcotrigiano, Menabue & Pellacani, 1979), paramagnetic susceptibilities (Lamotte-Brasseur & Van den Bossche, 1974) and X-ray absorption spectra (Sano, Komorita & Yamatera, 1992). An X-ray structure analysis of the title compound by Lamotte-Brasseur (1973) was not completed, possibly because of difficulties in modelling the positional disorder of the Cu(2) atom.

The flattening of the [CuCl₄]²⁻ ion from a regular tetrahedron can be measured by taking the average of the two larger Cl—Cu—Cl angles, θ (Willett, Haugen, Lebsack & Morrey, 1974), or by the dihedral angle between the two Cl—Cu—Cl planes (Battaglia *et al.*, 1979). As speculated by Lamotte-Brasseur & Van den Bossche (1974), the *D*_{2d} type distortion of the [CuCl₄]²⁻ ion in this [N(C₂H₅)₄]₂[CuCl₄] salt [$\theta = 124.7 (5)^\circ$] is smaller than in [N(CH₃)₄]₂[CuCl₄] [$\theta = 129.3 (3)^\circ$; Morosin & Lingafelter, 1961; Clay, Murray-Rust & Murray-Rust, 1975], [NH(CH₃)₃]₂[CuCl₄] [$\theta = 132.9 (1)^\circ$; Williams, Brown & Taylor, 1992], [NH₂(CH₃)₂]₂[CuCl₄] [$\theta = 135.8 (2)^\circ$; Willett & Larsen, 1971], [NH(C₂H₅)₃]₂[CuCl₄] [$\theta = 134.8 (2)^\circ$; Lamotte-Brasseur, Dideberg & Dupont, 1973] and [N(CH₃)₃(CH₂C₆H₅)₂]₂[CuCl₄] [$\theta = 132.5 (1)^\circ$; Bonamico, Dessy & Vaciago, 1967].

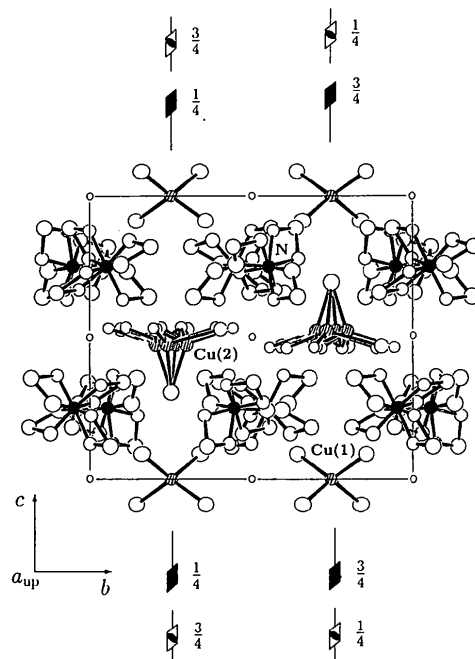


Fig. 1. Projection of the crystal structure along *a*. Black and hatched spheres represent N and Cu atoms respectively.