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Structure of Tetrakis(2,6-dimethylphenyl isocyanide)rhodium(I) Tetraphenylborate Ethanol Solvate, $[Rh(C_9H_9N)_4][B(C_6H_5)_4].C_2H_6O$

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Abstract. $M_r = 992{\cdot}92$, triclinic, $P\bar{1}$, $a = 11{\cdot}615\ (3)$, $b = 23{\cdot}582\ (5)$, $c = 10{\cdot}409\ (2)$ Å, $\alpha = 91{\cdot}20\ (2)$, $\beta = 104{\cdot}19\ (2)$, $\gamma = 102{\cdot}36\ (2)°$, $U = 2691{\cdot}9$ Å^3, $Z = 2$, $D_x = 1{\cdot}224$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 0{\cdot}307$ mm^{-1}, $F(000) = 1040$, $T = 293$ K. Final $R = 0{\cdot}0554$ for 4321 observed reflections. The unit cell contains two independent monomeric square-planar cations lying across centres of inversion at 0,0,0 and $\frac{1}{2},\frac{1}{2},0$ respectively. Because of steric crowding between *ortho* methyl groups on adjacent ligands, the phenyl rings of the ligands are not coplanar with the plane of coordination. The formation of Rh—Rh bonded oligomers is thus sterically inhibited.

Introduction. Tetraisocyaniderhodium(I) cations $[Rh(CNR)_4]^+$ tend to oligomerize in solution to form dimeric and trimeric species containing weak metal–metal bonds (Singleton & Oosthuizen, 1983). The extent of the oligomerization depends on the solvent, the concentration and the bulkiness of the substituent R, with the colour of the solutions ranging from yellow or orange (monomeric) to green, blue or purple (oligomeric). Crystal structures have been reported for the purple, blue and dark-green crystals of the dimers $[Rh(CNR)_4]_2^{2+}.2X^-$ with $R = \text{Ph}$, $X = \text{BPh}_4$ (II) (Mann, Lewis, Williams, Gray & Gordon, 1978), $R = p\text{-FC}_6H_4$, $X = \text{Cl}$ (III) and $R = p\text{-NO}_2C_6H_4$, $X = \text{Cl}$ (IV) (Endres, Gottstein, Keller, Martin, Rodemer & Steiger, 1979). However, our study represents the first crystal-structure determination of the monomeric form of $[Rh(CNR)_4]^+$.

Experimental. The reaction of [Rh(1,5-cyclooctadiene)Cl]$_2$ with excess C_8H_9NC in methanol yielded, on addition of $NaBPh_4$, the title complex (I). Yellow irregular-shaped crystals suitable for X-ray examination were grown from dichloromethane/ethanol solution. Crystal: fragment, $0{\cdot}25 \times 0{\cdot}20 \times 0{\cdot}20$ mm; Philips PW1100 four-circle diffractometer, graphite-crystal-monochromatized Mo $K\alpha$ radiation; lattice parameters: 25 reflections, least-squares refinement; ω–2θ scan mode, scan width 0·90° in ω, scan speed $0{\cdot}03°\text{s}^{-1}$ in ω, 15s background at each end of the scan; 7347 reflections measured in the hemisphere $\pm h$, $\pm k$, $+l$ with $3 \leq \theta \leq 23°$, 7032 unique reflections, $R_{\text{int}} = 0{\cdot}019$; three standards measured every 60 min showed no significant deviations from mean intensities; no absorption correction applied; 4321 reflections $[F_o \geq 4\sigma(F_o)]$, index range $h \pm 12$, $k \pm 25$, l 0–11, used in analysis; structure solved by Patterson and Fourier methods and refined by least squares with *SHELX* (Sheldrick, 1978), two orientations observed for a disordered ethanol of solvation; site-occupation factors for the two orientations refined but constrained to sum to 1·0; all H-atom positions except for those in the disordered ethanol molecule located on a difference map and refined; anisotropic temperature factors used for all non-H atoms except in the disordered ethanol molecule where individual isotropic temperature factors were employed, separate common isotropic temperature factors used for the ring and methyl H atoms in each independent cation and for the H atoms in the BPh_4 anion; least-squares refinement, $\sum w(\Delta F)^2$

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minimized, $w = 1/\sigma^2(F)$, with the matrix blocked so that the parameters for each independent cation, the BPh_4 anion and the disordered ethanol molecule refined in separate cycles, converged to give $R = 0{\cdot}0554$ and $wR = 0{\cdot}0411$ for 4321 reflections; reductions in wR at all stages of the refinement significant at the 99·5% level (Hamilton, 1965); complex neutral-atom scattering factors used for all atoms (Cromer & Waber, 1974); in the final cycles 796 parameters varied, comprising 381 positional parameters, 402 anisotropic temperature factor components, six isotropic temperature factors, five common isotropic temperature factors, one site-occupation factor and one overall scale, $\Delta\rho \pm 0{\cdot}3$ e Å^{-3}; apart from disordered ethanol, max. shift/error in final LS cycles for non-H atoms 1·6, for H atoms 1·9 (larger values, of up to 4·4, occur in the ethanol molecule).

Discussion. The final atomic parameters are given in Table 1.* Bond lengths and angles are given in Table 2. Fig. 1 shows the two independent square-planar cations with the labelling scheme for the atoms; Fig. 2 shows the unit-cell contents. The C atoms of the BPh_4^- anion are labelled C(n1) (bonded to B) to C(n6) for each phenyl ring (n=5 to 8).

In the solid state (I) is monomeric, with the shortest Rh···Rh vector being the z axis [10·409 (2) Å] unlike the solid-state structures of (II), (III) and (IV) which are dimeric and contain weak Rh—Rh bonds of lengths 3·193 (<1) Å (II) (Mann *et al.*, 1978), 3·293 Å (III) [Cambridge Structural Database (CSD), 1983] [reported as 3·207 (2) Å (Endres *et al.*, 1979)] and 3·25 (1) Å (IV) (Endres *et al.*, 1979). As the complex cations in (I) are centrosymmetric, the central RhC_4 coordination groups are each exactly planar; however, this is not so for (II) where the staggered RhC_4 groups of the dimer show a slight tetrahedral distortion from square-planar geometry with deviations of the Rh and four C atoms from the least-squares plane through the RhC_4 group of 0·03, −0·14, 0·12, −0·14 and 0·13 Å (CSD, 1983). The eclipsed RhC_4 groups in (III) show a very slight, but not significant, pyramidal distortion from square-planar geometry with deviations of 0·05, 0·00, 0·00, −0·02 and −0·02 Å from the RhC_4 least-squares plane (CSD, 1983).

The average Rh—C bond length of 1·961 (7) Å in (I) compares well with the averages of 1·94 Å in (II) (Mann *et al.*, 1978), 1·97 Å in (III) (Endres *et al.*, 1979) and 1·95 Å (excluding the ligand *trans* to Cl) in [Rh{CN(2,4,6-*tert*-$Bu_3C_6H_2$)}$_3$Cl] (Yamamoto, Aoki &

Table 1. *Fractional atomic coordinates* (×10^4) *of non*-H *atoms and isotropic temperature factors* (Å^2 ×10^3)

The equivalent isotropic temperature factors are defined as the geometric mean of the diagonal components of the diagonalized U_{ij} matrix.

	x	y	z	U_{eq}/U_{iso}
Rh(1)	0	0	0	54·3 (4)
C(1)	850 (6)	311 (3)	1824 (7)	62 (4)
N(1)	1367 (5)	498 (2)	2893 (6)	57 (3)
C(11)	1890 (6)	781 (2)	4168 (6)	52 (4)
C(12)	1092 (7)	911 (3)	4879 (7)	65 (4)
C(13)	1645 (12)	1240 (4)	6094 (9)	100 (7)
C(14)	2866 (14)	1412 (5)	6504 (10)	101 (8)
C(15)	3621 (9)	1275 (4)	5811 (11)	96 (7)
C(16)	3160 (7)	946 (3)	4611 (8)	68 (5)
C(17)	−269 (9)	715 (4)	4336 (9)	99 (7)
C(18)	3984 (9)	784 (5)	3851 (11)	110 (8)
C(2)	1565 (6)	208 (3)	−473 (6)	57 (4)
N(2)	2504 (5)	352 (2)	−691 (5)	59 (3)
C(21)	3666 (6)	613 (3)	−805 (6)	55 (4)
C(22)	4165 (7)	1169 (3)	−207 (6)	66 (5)
C(23)	5316 (8)	1428 (4)	−317 (8)	80 (6)
C(24)	5903 (7)	1137 (5)	−995 (10)	78 (6)
C(25)	5384 (7)	588 (4)	−1606 (8)	84 (6)
C(26)	4239 (6)	305 (3)	−1507 (7)	56 (4)
C(27)	3470 (12)	1495 (5)	494 (10)	108 (9)
C(28)	3630 (8)	−288 (4)	−2188 (10)	91 (6)
Rh(2)	5000	5000	0	56·7 (5)
C(3)	5704 (5)	5087 (2)	1937 (6)	56 (4)
N(3)	6085 (4)	5139 (2)	3071 (5)	58 (3)
C(31)	6488 (5)	5172 (3)	4459 (6)	54 (4)
C(32)	6551 (10)	5680 (4)	5165 (10)	79 (6)
C(33)	6889 (8)	5704 (4)	6531 (9)	84 (6)
C(34)	7177 (8)	5247 (5)	7150 (8)	81 (6)
C(35)	7120 (7)	4738 (4)	6449 (9)	80 (6)
C(36)	6786 (6)	4691 (3)	5058 (7)	64 (5)
C(37)	6188 (14)	6208 (6)	4396 (13)	135 (10)
C(38)	6743 (11)	4155 (4)	4283 (10)	101 (7)
C(4)	5934 (6)	4421 (3)	−198 (5)	60 (4)
N(4)	6526 (5)	4089 (2)	−293 (5)	65 (3)
C(41)	7310 (7)	3711 (3)	−275 (6)	64 (5)
C(42)	8481 (9)	3896 (4)	517 (8)	79 (6)
C(43)	9292 (8)	3533 (5)	615 (8)	97 (6)
C(44)	8883 (11)	3007 (5)	−80 (12)	120 (9)
C(45)	7730 (11)	2823 (4)	−897 (9)	94 (7)
C(46)	6898 (8)	3180 (3)	−1004 (7)	69 (5)
C(47)	8911 (16)	4504 (6)	1313 (13)	117 (9)
C(48)	5666 (12)	3011 (5)	−1893 (10)	107 (8)
B	8432 (6)	2471 (3)	4521 (7)	43 (4)
C(51)	9092 (5)	2222 (2)	3470 (5)	44 (4)
C(52)	8474 (6)	1875 (3)	2321 (6)	57 (4)
C(53)	9061 (8)	1644 (3)	1500 (7)	74 (5)
C(54)	10298 (8)	1758 (4)	1781 (8)	84 (6)
C(55)	10959 (7)	2100 (3)	2910 (9)	79 (5)
C(56)	10367 (6)	2323 (3)	3745 (6)	62 (4)
C(61)	7044 (5)	2531 (2)	3841 (6)	44 (3)
C(62)	6736 (6)	2770 (3)	2607 (6)	53 (4)
C(63)	5607 (7)	2895 (3)	2073 (7)	64 (5)
C(64)	4732 (6)	2768 (3)	2784 (9)	68 (5)
C(65)	4976 (7)	2539 (3)	3994 (8)	68 (5)
C(66)	6102 (6)	2423 (3)	4487 (7)	57 (4)
C(71)	8451 (6)	1997 (3)	5651 (6)	52 (4)
C(72)	7627 (6)	1461 (3)	5397 (7)	70 (5)
C(73)	7648 (8)	1034 (3)	6288 (11)	92 (7)
C(74)	8488 (12)	1126 (5)	7465 (11)	117 (9)
C(75)	9333 (9)	1644 (5)	7776 (8)	97 (7)
C(76)	9303 (7)	2066 (3)	6882 (8)	75 (6)
C(81)	9135 (5)	3132 (2)	5127 (6)	46 (4)
C(82)	9035 (6)	3365 (3)	6339 (7)	65 (5)
C(83)	9558 (8)	3940 (4)	6794 (8)	85 (6)
C(84)	10183 (8)	4309 (3)	6074 (10)	81 (6)
C(85)	10290 (6)	4102 (3)	4880 (8)	70 (5)
C(86)	9787 (6)	3530 (3)	4436 (7)	58 (4)
*S*O(1)^a	7881 (20)	6138 (10)	460 (25)	226 (12)
*S*C(1)^a	7767 (30)	6507 (18)	1256 (52)	141 (16)
*S*C(2)^a	7744 (19)	6652 (11)	2241 (25)	167 (11)
*S*O(11)^b	7563 (17)	7067 (10)	977 (22)	288 (12)
*S*C(11)^b	7859 (26)	6896 (16)	57 (30)	228 (14)
*S*C(21)^b	7301 (23)	6414 (16)	−13 (31)	222 (11)

(a,b) The site-occupation factors for the two orientations of the disordered ethanol molecule are (a) 0·41 (2) and (b) 0·59 (2). Temperature factors are U_{iso} values.

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* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, selected non-bonded contact distances and least-squares-planes' calculations have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39285 (36 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

Rh(1)–C(1)	1·957 (6)	Rh(2)–C(3)	1·969 (6)
Rh(1)–C(2)	1·963 (7)	Rh(2)–C(4)	1·953 (8)
N(1)–C(1)	1·154 (8)	N(3)–C(3)	1·148 (8)
N(2)–C(2)	1·150 (9)	N(4)–C(4)	1·164 (10)
N(1)–C(11)	1·405 (8)	N(3)–C(31)	1·400 (8)
N(2)–C(21)	1·393 (8)	N(4)–C(41)	1·402 (11)
C(11)–C(12)	1·395 (12)	C(31)–C(32)	1·371 (12)
C(12)–C(13)	1·400 (11)	C(32)–C(33)	1·375 (13)
C(13)–C(14)	1·344 (19)	C(33)–C(34)	1·330 (15)
C(14)–C(15)	1·348 (20)	C(34)–C(35)	1·371 (14)
C(15)–C(16)	1·379 (12)	C(35)–C(36)	1·400 (11)
C(16)–C(11)	1·398 (10)	C(36)–C(31)	1·373 (10)
C(12)–C(17)	1·507 (12)	C(32)–C(37)	1·572 (17)
C(16)–C(18)	1·484 (16)	C(36)–C(38)	1·472 (13)
C(21) C(22)	1·381 (9)	C(41)–C(42)	1·379 (11)
C(22)–C(23)	1·379 (12)	C(42)–C(43)	1·391 (16)
C(23)–C(24)	1·360 (15)	C(43)–C(44)	1·353 (15)
C(24)–C(25)	1·374 (13)	C(44)–C(45)	1·372 (15)
C(25)–C(26)	1·385 (10)	C(45)–C(46)	1·396 (15)
C(26)–C(21)	1·388 (10)	C(46)–C(41)	1·379 (9)
C(22)–C(27)	1·519 (16)	C(42)–C(47)	1·558 (16)
C(26)–C(28)	1·498 (10)	C(46)–C(48)	1·468 (13)
B–C(51)	1·646 (10)	B–C(71)	1·640 (9)
B–C(61)	1·632 (9)	B–C(81)	1·629 (8)
C(51)–C(52)	1·379 (7)	C(71)–C(72)	1·388 (9)
C(52)–C(53)	1·385 (12)	C(72)–C(73)	1·383 (13)
C(53)–C(54)	1·359 (13)	C(73)–C(74)	1·346 (14)
C(54)–C(55)	1·369 (10)	C(74)–C(75)	1·369 (15)
C(55)–C(56)	1·390 (12)	C(75)–C(76)	1·377 (13)
C(56)–C(51)	1·403 (9)	C(76)–C(71)	1·395 (9)
C(61)–C(62)	1·409 (9)	C(81)–C(82)	1·406 (10)
C(62)–C(63)	1·389 (10)	C(82)–C(83)	1·383 (11)
C(63)–C(64)	1·385 (12)	C(83)–C(84)	1·368 (13)
C(64)–C(65)	1·370 (12)	C(84)–C(85)	1·369 (14)
C(65)–C(66)	1·370 (10)	C(85)–C(86)	1·371 (10)
C(66)–C(61)	1·400 (10)	C(86)–C(81)	1·401 (9)

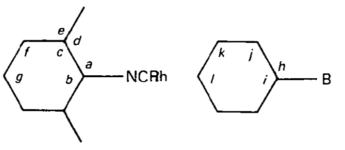
C–H bond lengths

	Mean	Minimum	Maximum
(i) Complex cations			
H–C(ring)	0·94 (9)	0·77 (7)	1·13 (5)
H–C(methyl)	0·89 (10)	0·66 (15)	1·04 (7)
(ii) BPh_4 anion			
H–C(ring)	0·96 (6)	0·84 (6)	1·10 (6)

Selected angles

C(1)–Rh(1)–C(2)	88·6 (3)	C(3)–Rh(2)–C(4)	90·8 (3)
Rh(1)–C(1)–N(1)	178·9 (6)	Rh(2)–C(3)–N(3)	178·2 (6)
Rh(1)–C(2)–N(2)	176·3 (5)	Rh(2)–C(4)–N(4)	177·7 (5)
C(1)–N(1)–C(11)	172·0 (7)	C(3)–N(3)–C(31)	176·2 (6)
C(2)–N(2)–C(21)	169·9 (6)	C(4)–N(4)–C(41)	174·1 (5)
C(51)–B–C(61)	113·7 (5)	C(61)–B–C(71)	111·1 (5)
C(51)–B–C(71)	104·0 (5)	C(61)–B–C(81)	103·4 (5)
C(51)–B–C(81)	111·7 (5)	C(71)–B–C(81)	113·3 (5)

Mean bond angles



(*a*)	118·2 (13)	(*d*)	121·5 (11)	(*g*)	122·6 (11)	(*j*)	123·1 (8)
(*b*)	123·7 (9)	(*e*)	121·5 (12)	(*h*)	122·7 (16)	(*k*)	119·9 (11)
(*c*)	117·0 (14)	(*f*)	119·9 (10)	(*i*)	114·4 (3)	(*l*)	119·7 (12)

Yamazaki, 1979), and also with the range of 1·97 to 1·99 Å in $[Rh\{CN(p\text{-}MeC_6H_4)\}_4I]_2^{2+}$ (Olmstead & Balch, 1978) and the average of 1·97 Å in $[Rh_3(CNCH_2C_6H_5)_{12}I_2]^{3+}$ (Balch & Olmstead, 1979) [bond lengths taken from CSD (1983)], where the nominal oxidation states of the Rh atoms in the last two complexes are 2 and $\frac{5}{3}$ respectively. The geometries of the isocyanide ligands show no unusual features and are in good agreement with those reported previously.

The C_6 rings of the isocyanide ligands in the complex cations of (I) are not coplanar with the coordination planes. The dihedral angles between the planes of the rings and the associated coordination plane lie in the range 19·3 (14) to 45·6 (5)°. The deviations from coplanarity can be ascribed to steric interactions between the *ortho* methyl groups on the rings of adjacent ligands with C(Me)···C(Me) distances in the range 3·74 (1) to 4·43 (1) Å. These compare with the van der Waals radius of a methyl group of *ca* 2·0 Å (Pauling, 1960). The presence of bulky methyl groups inhibits the formation of a dimer similar to (II) and (III), although association is still possible and has been

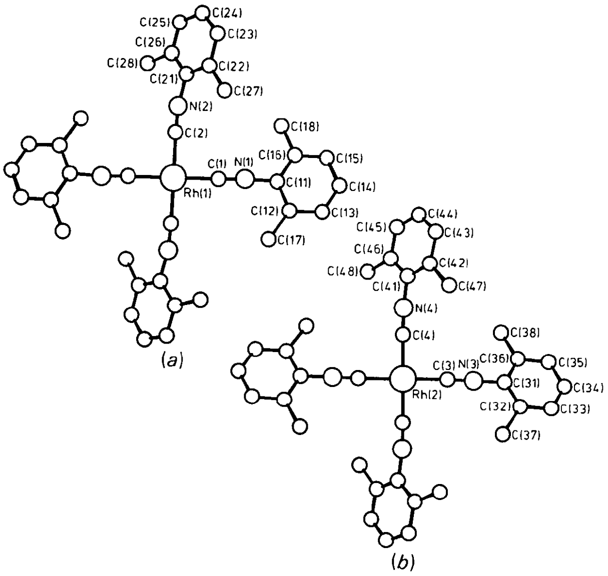


Fig. 1. Perspective views of (*a*) cation (1) and (*b*) cation (2), showing the atom-labelling scheme.

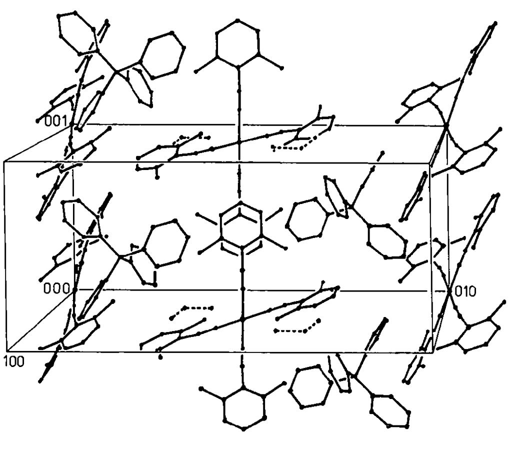


Fig. 2. The unit cell viewed perpendicular to the *bc* plane. Only one orientation of the disordered EtOH molecule is shown using broken lines.

observed in solution and in the solid state for $[Rh\{CN(2,6\text{-}Me_2C_6H_3)\}_4]^+$ cations with various anions (Baumann, Keller, Nöthe, Rupp & Uhlmann, 1976). The conformations of the aryl rings with respect to the coordination plane are in general agreement with the conformation predicted on the basis of calculated 'fan angles' for $2,6\text{-}Me_2C_6H_3NC$ ligands (Yamamoto *et al.*, 1979).

The geometry of the BPh_4 anion is as expected and shows no unusual features. The disordered ethanol molecule is very poorly defined and no significance can be placed on the observed geometry of this molecule.

Intensity data were collected at the National Physical Research Laboratory, CSIR.

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Structures of Bis(1,5-dithiacyclooctan-3-ol-*O*,*S*,*S'*)nickel(II) Diperchlorate Dimethanol, $[Ni(C_6H_{12}OS_2)_2](ClO_4)_2.2CH_4O$, and Bis(1,5-dithiacyclooctan-3-ol-*O*,*S*,*S'*)iron(II) Diperchlorate, $[Fe(C_6H_{12}OS_2)_2](ClO_4)_2$

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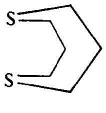
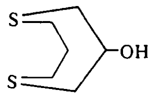
Abstract. $[Ni(C_6H_{12}OS_2)_2](ClO_4)_2.2CH_3OH$: $M_r = 650{\cdot}28$, $P2_1/c$, $a = 10{\cdot}734\,(2)$, $b = 11{\cdot}853\,(3)$, $c = 10{\cdot}392\,(2)$ Å, $\beta = 103{\cdot}62\,(2)°$, $V = 1285{\cdot}0\,(5)$ Å^3, $Z = 2$, D_m(298 K) decomp., D_x(140 K) = $1{\cdot}68$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 13{\cdot}3$ cm^{-1}, $F(000) = 676$, $T = 140$ K, $R = 0{\cdot}037$, 1960 unique observed reflections, recrystallization from methanol. The complex is centrosymmetric with Ni–S of 2·398 (1) and 2·396 (1) Å, Ni–O of 2·046 (3) Å. A molecule of methanol present in the lattice is hydrogen-bonded to the hydroxyl group of the ligand and to an oxygen atom of an uncoordinated perchlorate ion. $[Fe(C_6H_{12}OS_2)_2](ClO_4)_2$: $M_r = 583{\cdot}33$, $P2_1/c$, $a = 7{\cdot}990\,(2)$, $b = 8{\cdot}573\,(2)$, $c = 15{\cdot}681\,(3)$ Å, $\beta = 95{\cdot}50\,(2)°$, $V = 1069{\cdot}2\,(4)$ Å^3, $Z = 2$, D_m(298 K) decomp., D_x(140 K) = $1{\cdot}81$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 13{\cdot}8$ cm^{-1}, $F(000) = 600$, $T = 140$ K, $R = 0{\cdot}046$, 1601 unique observed reflections, recrystallization from methanol. The complex resembles the nickel species except that the thioether–metal bonds are much longer: Fe–S 2·565 (1) and 2·514 (1) Å, Fe–O 2·062 (3) Å.

Introduction. The coordination mode of 1,5-dithiacyclooctane in transition-metal complexes varies considerably. Either one or two sulfurs can coordinate to the metal, and thus bidentate (Hirschon & Musker, 1980), bridging (Hill & Hope, 1974) or monodentate (Olmstead, Williams & Musker, 1982) modes are observed. Substitution of a hydroxyl group in the 3-position of the ring



1,5-dithiacyclooctane



1,5-dithiacyclooctan-3-ol

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