Zr1—C7	2.577 (8)	C6—C7	1.395 (11)
Zr1—C6	2.579 (7)	C7—C8	1.401 (12)
Zr1—C8	2.584 (8)	C8—C9	1.397 (11)
Zr1—C9	2.585 (7)	C9—C10	1.392 (10)
Zr1—C3	2.587 (8)	C11—C12	1.409 (11)
Zr1—C4	2.596 (7)	C11—C15	1.409 (11)
Zr2—O2	1.960 (5)	C12—C13	1.394 (11)
Zr2—O1	1.968 (5)	C13—C14	1.404 (12)
Zr2—C14	2.563 (8)	C14—C15	1.392 (11)
Zr2—C15	2.567 (8)	C16—C20	1.399 (11)
Zr2—C16	2.571 (7)	C16—C17	1.411 (10)
Zr2—C11	2.576 (7)	C17—C18	1.385 (11)
Zr2—C20	2.583 (7)	C18—C19	1.413 (11)
Zr2—C17	2.577 (7)	C19—C20	1.384 (10)
Zr2—C13	2.582 (8)	C21—C22	1.396 (11)
Zr2—C18	2.587 (7)	C21—C25	1.395 (11)
Zr2—C19	2.586 (7)	C22—C23	1.404 (11)
Zr2—C12	2.587 (8)	C23—C24	1.402 (11)
Zr3—O2	1.976 (5)	C24—C25	1.401 (11)
Zr3—O3	1.975 (5)	C26—C27	1.392 (11)
Zr3—C22	2.554 (8)	C26—C30	1.411 (12)
Zr3—C30	2.564 (8)	C27—C28	1.406 (11)
Zr3—C29	2.569 (8)	C28—C29	1.398 (11)
Zr3—C23	2.563 (7)	C29—C30	1.385 (12)
Zr3—C25	2.566 (7)	C1*B*—C6*B*	1.343 (14)
Zr3—C24	2.569 (7)	C1*B*—C2*B*	1.347 (14)
Zr3—C27	2.584 (7)	C2*B*—C3*B*	1.356 (15)
Zr3—C21	2.587 (8)	C3*B*—C4*B*	1.370 (21)
Zr3—C28	2.588 (7)	C4*B*—C5*B*	1.381 (22)
Zr3—C26	2.596 (7)	C5*B*—C6*B*	1.360 (16)
O1—Zr1—O3	97.75 (13)	C18—C17—C16	109.1 (7)
O2—Zr2—O1	97.6 (2)	C17—C18—C19	107.2 (7)
O2—Zr3—O3	97.47 (14)	C20—C19—C18	108.1 (7)
Zr1—O1—Zr2	142.6 (2)	C19—C20—C16	109.0 (7)
Zr2—O2—Zr3	142.4 (1)	C22—C21—C25	107.3 (7)
Zr1—O3—Zr3	142.1 (2)	C21—C22—C23	108.3 (7)
C3—C2—C1	107.1 (8)	C24—C23—C22	108.1 (7)
C4—C3—C2	108.8 (8)	C25—C24—C23	107.0 (7)
C3—C4—C5	107.6 (8)	C21—C25—C24	109.2 (7)
C1—C5—C4	108.0 (8)	C27—C26—C30	107.8 (8)
C10—C6—C7	106.3 (7)	C26—C27—C28	108.1 (7)
C6—C7—C8	108.9 (8)	C29—C28—C27	107.6 (7)
C9—C8—C7	108.0 (7)	C30—C29—C28	108.6 (7)
C10—C9—C8	106.8 (7)	C29—C30—C26	108.0 (7)
C6—C10—C9	110.1 (7)	C6*B*—C1*B*—C2*B*	120.0 (10)
C12—C11—C15	107.7 (7)	C1*B*—C2*B*—C3*B*	121.9 (11)
C13—C12—C11	108.3 (8)	C2*B*—C3*B*—C4*B*	117.5 (11)
C12—C13—C14	107.5 (7)	C3*B*—C4*B*—C5*B*	121.6 (12)
C15—C14—C13	109.0 (7)	C6*B*—C5*B*—C4*B*	117.9 (12)
C14—C15—C11	107.5 (7)	C1*B*—C6*B*—C5*B*	121.1 (11)
C20—C16—C17	106.6 (7)		

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 55975 (23 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HU1023]

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Cobaltocenium Bis[(4,5-dimercapto-S^4,S^5)-1,3-dithiole-2-thionato]nickelate

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Abstract

The coordination anions of the title compound $[Co(C_5H_5)_2][Ni(dmit)_2]$ are planar with a shuttle-shaped D_{2h} configuration. The cobaltocenium cations take an eclipsed D_{5h} conformation with an average Co—C distance of 2.037 (16) Å. The crystal consists of sheets of S···S connected anionic stacks with pairs of cations between them.

Comment

Since Steimecke, Sieler, Kirmse & Hoyer (1979) first prepared $(Bu_4N)_n[Ni(dmit)_2]$ ($n = 1, 2$), a great deal of attention has been directed to $Z_x[M(dmit)_2]$ type complexes (M = Ni, Pd, Pt, Cu; $H_2dmit = H_2C_3S_5$ = 4,5-dimercapto-1,3-dithiole-2-thione; Z = various cations; $0 \le x \le 1$ or $x = 2$ because they are known to possess molecular electrical conductivity. $[M(dmit)_2]^{\delta-}$ has a planar structure with a delocalized electronic state; these anions may adhere together by means of intermolecular S···S interactions forming anionic stacks, sheets or even networks. They combine with various closed-shell counter ions or open-shell organic radicals to form conducting complexes such as superconductors $[(CH_3)_4N]_{0.5}[Ni(dmit)_2]$ (Kim, Kobayashi, Sasaki, Kato & Kobayashi, 1987) and $TTF_{0.5}[Ni(dmit)_2]$ (Bousseau, Valade, Legros, Cassoux, Garbauskas & Interrante, 1986). Metalloceniums have different tendencies to accept electrons and when they interact with $[Ni(dmit)_2]^-$ quite different compounds can be produced. The reaction of $(Bu_4N)[Ni(dmit)_2]$ and $[Fe(C_5H_5)_2]BF_4$ produces a completed charge-transfer semiconductor $[Ni(dmit)_2]$ (Fang, Li, Qu & You, 1992). However, the reaction of

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$(Bu_4N)[Ni(dmit)_2]$ with $[Fe(C_5Me_5)_2]BF_4$ results in $[Fe(C_5Me_5)_2][Ni(dmit)_2]$, which exhibits ferromagnetic interactions below 10 K (Broderick, Thompson, Godfrey, Sabat, Hoffman & Day, 1989). Here we report the structure of another new type of complex $[Co(C_5H_5)_2][Ni(dmit)_2]$. The specimen was prepared by Fang, Li, Qu & You (1992).

Two factors significantly affect the conducting ability of $Z_x[M(dmit)_2]$ type complexes. One is the electric charge δ of $[M(dmit)_2]^{\delta-}$, and the other is the degree of anionic interaction indicated by S···S distances which are shorter than the sum of the van der Waals radii, 3.70 Å (Pauling, 1960).

There are six kinds of bonds in the planar shuttle-shaped anions with average values of $a = 2.161$ (5), $b = 1.73$ (1), $c = 1.74$ (1), $d = 1.72$ (2), $e = 1.64$ (2) and $f = 1.34$ (2) Å (Fig. 1); these are very close to the respective bond distances in $[Ni(dmit)_2]^-$ (Mentzafos, Hountas & Terzis, 1988) and in $[Ni(dmit)]^{-0.29}$ (Valade, Legros, Bousseau, Cassoux, Garbauskas & Interrante, 1985). The highly delocalized electronic states of the anions is responsible for their bond parameters being very insensitive to their charges. The average Co—C(Cp) distance is 2.037 (16) Å, which is shorter than the respective value of 2.096 (8) Å in cobaltocene (Bünder & Weiss, 1975) and seemingly a little longer than that of 2.023 (6) Å in $[Co(C_5H_5)C_5H_4(COOH)]PF_6$ (Riley & Davis, 1978). Until more precise Co—C(Cp) distances of the title compound and $[Co(C_5H_5)_2]^+$ are obtained, we can only assume that the cation's charge is less than 1 and thus the anion's charge is also less than 1. The C—C distances of cobaltocenium average 1.43 (2) Å. A noticeable feature of this sandwich is its eclipsed D_{5h} configuration.

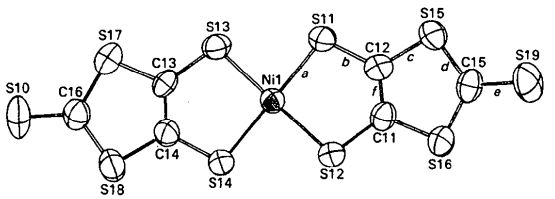

Fig. 1. Thermal ellipsoid plot of the anion.

The asymmetric unit contains four independent anions, abbreviated as $[Ni]_1$, $[Ni]_2$, $[Ni]_3$ and $[Ni]_4$. S···S distances between any two of them (less than 3.7 Å) are listed in Table 3. $[Ni]_1$ and $[Ni]_2$ are connected by five pairs of S···S intermolecular interactions; the dihedral angle between the anion planes is 75.2 (2)°. They form $\cdots[Ni]_1[Ni]_2[Ni]_1[Ni]_2\cdots$ zigzag chains or stacks along the [001] direction. $[Ni]_3$ and $[Ni]_4$ form another kind of stack with a dihedral angle of 67.9 (2)°. The two types of stacks are further connected by five S···S contacts (S10···S40, S29···S30, S20···S40 and S28···S37, S29···S45) forming two-dimensional (111) sheets. Furthermore, the neighbouring sheets are weakly connected by S27···S43, showing the character of a three-dimensional anionic network. The cyclopentadienyl rings are parallel to each other and perpendicular to the molecular planes of the anions. Cations are arranged in pairs. The Co···Co distance within a pair is 6.72 (1) Å and the shortest Co···Co distance between two nearest pairs is 9.15 (1) Å. By comparison with $[Bu_4N][Ni(dmit)_2]$ and $[Fe(C_5Me_5)_2][Ni(dmit)_2]$, the intermolecular interactions are much stronger and its electric conductivity should be considerably higher.

Experimental

Crystal data

$[Co(C_5H_5)_2][Ni(C_3S_5)_2]$	D_m = 1.89 Mg m^{-3}
M_r = 640.54	Density measured by flotation
Triclinic	Mo $K\alpha$ radiation
$P\bar{1}$	λ = 0.71069 Å
a = 19.347 (9) Å	Cell parameters from 20 reflections
b = 25.289 (7) Å	θ = 5–10°
c = 9.698 (3) Å	μ = 2.47 mm^{-1}
α = 100.60 (2)°	T = 296 K
β = 96.02 (3)°	Platelet
γ = 76.01 (3)°	0.60 × 0.40 × 0.02 mm
V = 4517 (3) Å^3	Blackish green
Z = 8	
D_x = 1.88 Mg m^{-3}	

Data collection

Rigaku AFC-5 diffractometer	6490 observed reflections [$F > 4\sigma(F)$]
$\omega/2\theta$ scans, ω-scan width (0.45+0.35tanθ)°, scan speed 8° min^{-1}	R_{int} = 0.031
	θ_{max} = 46.0°
Absorption correction: empirical	$h = 0 \rightarrow 23$
T_{min} = 0.570, T_{max} = 1.00	$k = -30 \rightarrow 30$
12675 measured reflections	$l = -12 \rightarrow 12$
12675 independent reflections	3 standard reflections
	frequency: 180 min
	intensity variation: <5.4%

Refinement

Refinement on F^2	Unit weights applied
Final R = 0.047	$(\Delta/\sigma)_{max}$ = 1.01
wR = 0.062	$\Delta\rho_{max}$ = 0.69 e Å^{-3}
S = 1.32	$\Delta\rho_{min}$ = −0.50 e Å^{-3}
6490 reflections	Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)
799 parameters	
H-atom parameters not refined	

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$B_{eq} = \frac{4}{3}\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	B_{eq}
Ni1	0.4123 (1)	0.26937 (7)	0.9632 (2)	3.73 (4)
Ni2	0.6151 (1)	0.25657 (7)	0.4984 (2)	3.61 (4)
Ni3	0.1452 (1)	0.21708 (9)	0.0276 (2)	4.45 (5)

Ni4	0.9030 (1)	0.28235 (8)	0.6152 (2)	3.59 (4)
Co1	0.8728 (1)	0.11673 (8)	0.9694 (2)	4.18 (5)
Co2	0.0941 (1)	0.36728 (8)	0.5812 (2)	4.19 (5)
Co3	0.6171 (1)	0.34888 (8)	0.1113 (2)	3.69 (5)
Co4	0.3568 (1)	0.13955 (8)	0.4150 (2)	4.43 (5)
S10	0.7018 (3)	0.0467 (2)	0.7443 (6)	6.9 (1)
S11	0.3575 (2)	0.2978 (2)	1.1543 (4)	5.0 (1)
S12	0.3515 (2)	0.3382 (2)	0.8665 (4)	4.5 (1)
S13	0.4691 (3)	0.1977 (2)	1.0526 (4)	5.6 (1)
S14	0.4736 (2)	0.2465 (2)	0.7795 (4)	4.6 (1)
S15	0.2371 (2)	0.3969 (2)	1.2375 (5)	5.5 (1)
S16	0.2312 (2)	0.4336 (2)	0.9718 (5)	5.4 (1)
S17	0.5905 (3)	0.1028 (2)	0.9459 (5)	6.3 (1)
S18	0.5967 (2)	0.1488 (2)	0.6979 (5)	5.3 (1)
S19	0.1239 (3)	0.4929 (2)	1.1788 (6)	7.7 (2)
S20	0.9170 (3)	0.0312 (3)	0.4061 (6)	6.9 (1)
S21	0.5977 (2)	0.3375 (2)	0.6299 (5)	4.8 (1)
S22	0.5059 (2)	0.2688 (2)	0.4149 (4)	4.3 (1)
S23	0.7237 (2)	0.2431 (2)	0.5850 (4)	4.7 (1)
S24	0.6319 (2)	0.1758 (2)	0.3666 (4)	4.3 (1)
S25	0.4605 (2)	0.4249 (2)	0.6874 (5)	5.0 (1)
S26	0.3772 (2)	0.3618 (2)	0.4915 (5)	4.8 (1)
S27	0.8482 (2)	0.1436 (2)	0.5361 (5)	5.4 (1)
S28	0.7623 (2)	0.0796 (2)	0.3469 (5)	5.3 (1)
S29	0.3016 (2)	0.4632 (2)	0.6658 (5)	5.7 (1)
S30	−0.1555 (3)	0.4384 (2)	0.1832 (6)	6.6 (1)
S31	0.1625 (2)	0.1296 (2)	0.0342 (4)	5.2 (1)
S32	0.0471 (2)	0.2254 (2)	0.1227 (4)	4.4 (1)
S33	0.1245 (2)	0.3048 (2)	0.0166 (5)	5.5 (1)
S34	0.2438 (3)	0.2073 (2)	−0.0705 (5)	6.1 (1)
S35	−0.0077 (3)	0.3967 (2)	0.0844 (5)	5.6 (1)
S36	−0.0769 (2)	0.3236 (2)	0.1839 (4)	4.5 (1)
S37	0.2772 (3)	0.0326 (2)	−0.0815 (5)	7.3 (1)
S38	0.3554 (3)	0.1032 (3)	−0.1684 (5)	7.9 (2)
S39	0.4065 (4)	−0.0186 (3)	−0.2391 (7)	11.7 (2)
S40	1.1891 (3)	0.0474 (2)	0.4673 (5)	6.1 (1)
S41	0.8313 (2)	0.3356 (2)	0.4863 (4)	5.2 (1)
S42	0.8596 (2)	0.3308 (2)	0.8079 (4)	4.1 (1)
S43	0.9430 (2)	0.2324 (2)	0.4228 (4)	4.5 (1)
S44	0.9784 (2)	0.2319 (2)	0.7462 (4)	4.04 (9)
S45	0.7112 (3)	0.4354 (2)	0.5605 (5)	6.2 (1)
S46	0.7357 (2)	0.4307 (2)	0.8565 (5)	5.1 (1)
S47	1.0651 (2)	0.1308 (2)	0.3726 (4)	4.9 (1)
S48	1.0976 (2)	0.1305 (2)	0.6693 (4)	4.7 (1)
S49	0.6136 (3)	0.5134 (2)	0.7604 (7)	8.6 (2)
C11	0.2955 (8)	0.3738 (6)	0.995 (2)	4.3 (4)
C12	0.2978 (8)	0.3573 (6)	1.118 (2)	4.1 (4)
C13	0.5287 (8)	0.1645 (6)	0.928 (2)	4.7 (4)
C14	0.5307 (8)	0.1852 (6)	0.812 (1)	4.0 (4)
C15	0.1940 (8)	0.4440 (7)	1.131 (2)	5.1 (4)
C16	0.6327 (9)	0.0966 (6)	0.795 (2)	5.0 (4)
C21	0.5069 (8)	0.3630 (6)	0.598 (1)	4.0 (4)
C22	0.4691 (7)	0.3331 (6)	0.509 (1)	3.7 (3)
C23	0.7584 (8)	0.1760 (6)	0.506 (1)	3.9 (4)
C24	0.7190 (8)	0.1469 (6)	0.417 (1)	3.8 (4)
C25	0.3761 (8)	0.4195 (6)	0.619 (2)	4.2 (4)
C26	0.8450 (9)	0.0821 (7)	0.426 (2)	5.4 (4)
C31	0.2404 (9)	0.1029 (7)	−0.046 (2)	5.3 (4)
C32	0.2753 (9)	0.1356 (7)	−0.088 (2)	5.7 (5)
C33	0.0065 (8)	0.2946 (6)	0.122 (1)	3.8 (3)
C34	0.0414 (8)	0.3285 (6)	0.079 (1)	4.4 (4)
C35	−0.0840 (9)	0.3887 (6)	0.150 (2)	4.7 (4)
C36	0.3483 (11)	0.0358 (8)	−0.165 (2)	7.6 (6)
C41	0.7806 (8)	0.3828 (6)	0.607 (2)	4.6 (4)
C42	0.7925 (7)	0.3812 (5)	0.747 (1)	3.7 (3)
C43	1.0106 (7)	0.1821 (6)	0.484 (1)	3.8 (4)
C44	1.0260 (8)	0.1818 (6)	0.622 (1)	3.9 (4)
C45	0.6828 (9)	0.4624 (7)	0.726 (2)	5.6 (5)
C46	1.1209 (8)	0.0985 (6)	0.500 (2)	4.5 (4)
C1*A*	0.8213 (9)	0.1694 (7)	1.129 (2)	5.4 (5)
C1*B*	0.7713 (9)	0.1484 (7)	1.030 (2)	5.1 (4)
C1*C*	0.7783 (8)	0.1623 (6)	0.896 (2)	4.6 (4)
C1*D*	0.8341 (9)	0.1933 (6)	0.917 (2)	4.8 (4)
C1*E*	0.8600 (9)	0.1976 (6)	1.061 (2)	4.5 (5)
C1*F*	0.9807 (10)	0.0833 (8)	0.980 (2)	7.1 (6)
C1*G*	0.9527 (11)	0.0753 (7)	0.840 (2)	6.9 (5)
C1*H*	0.8997 (11)	0.0456 (7)	0.832 (2)	6.8 (5)
C1*I*	0.8936 (10)	0.0336 (7)	0.967 (2)	8.2 (6)
C1*J*	0.9462 (8)	0.0589 (7)	1.0604 (4)	7.3 (5)
C2*A*	0.1995 (9)	0.3357 (7)	0.555 (2)	5.4 (4)
C2*B*	0.1799 (8)	0.3190 (7)	0.672 (2)	5.0 (4)
C2*C*	0.1240 (8)	0.2896 (6)	0.629 (2)	4.4 (4)
C2*D*	0.1106 (9)	0.2878 (7)	0.479 (2)	5.3 (4)
C2*E*	0.1582 (9)	0.3167 (7)	0.435 (2)	5.9 (5)
C2*F*	0.0822 (11)	0.4502 (7)	0.615 (2)	7.1 (6)
C2*G*	0.0586 (10)	0.4342 (8)	0.731 (2)	7.1 (6)
C2*H*	0.0024 (10)	0.4054 (7)	0.678 (2)	6.5 (5)
C2*I*	−0.0083 (11)	0.4063 (7)	0.533 (2)	6.6 (5)
C2*J*	0.0405 (11)	0.4337 (7)	0.490 (2)	7.2 (6)
C3*A*	0.5683 (9)	0.4231 (7)	0.052 (2)	5.5 (5)
C3*B*	0.5192 (9)	0.3888 (7)	0.042 (2)	5.5 (5)
C3*C*	0.5154 (9)	0.3750 (7)	0.178 (2)	6.1 (5)
C3*D*	0.5644 (10)	0.4020 (7)	0.273 (2)	6.2 (5)
C3*E*	0.5963 (10)	0.4299 (7)	0.196 (2)	6.2 (5)
C3*I*	0.6438 (9)	0.2657 (6)	0.107 (2)	5.1 (4)
C3*H*	0.6447 (8)	0.2781 (6)	−0.031 (2)	4.6 (4)
C3*G*	0.6969 (8)	0.3117 (6)	−0.023 (2)	4.7 (4)
C3*F*	0.7256 (9)	0.3214 (7)	0.120 (2)	5.2 (4)
C3*J*	0.6930 (9)	0.2933 (7)	0.200 (2)	5.7 (5)
C4*A*	0.3345 (9)	0.2233 (7)	0.458 (2)	5.8 (5)
C4*B*	0.3192 (9)	0.2017 (7)	0.574 (2)	5.2 (4)
C4*C*	0.2690 (9)	0.1673 (7)	0.527 (2)	5.3 (4)
C4*D*	0.2502 (11)	0.1684 (8)	0.380 (2)	6.3 (5)
C4*E*	0.2911 (10)	0.2037 (7)	0.338 (2)	6.3 (5)
C4*F*	0.3812 (10)	0.0640 (7)	0.290 (2)	6.5 (5)
C4*G*	0.3968 (10)	0.0589 (7)	0.434 (2)	6.1 (5)
C4*H*	0.4477 (10)	0.0907 (7)	0.494 (2)	6.5 (5)
C4*I*	0.4638 (10)	0.1170 (8)	0.387 (2)	7.0 (6)
C4*J*	0.4246 (11)	0.0999 (8)	0.263 (2)	6.9 (5)

Table 2. *Selected bond lengths* (Å) *and angles* (°)

Ni1—S11	2.151 (5)	S15—C15	1.722 (17)
Ni1—S12	2.163 (5)	S16—C11	1.744 (14)
Ni1—S13	2.159 (5)	S16—C15	1.724 (18)
Ni1—S14	2.156 (5)	S17—C13	1.745 (15)
Co1—C1*A*	2.021 (15)	S17—C16	1.715 (18)
Co1—C1*B*	2.039 (16)	S18—C14	1.747 (14)
Co1—C1*C*	2.047 (15)	S18—C16	1.730 (17)
Co1—C1*D*	2.035 (16)	S19—C15	1.642 (15)
Co1—C1*E*	2.041 (15)	C11—C12	1.328 (23)
Co1—C1*F*	2.053 (18)	C13—C14	1.335 (23)
Co1—C1*G*	2.049 (19)	C1*A*—C1*B*	1.416 (24)
Co1—C1*H*	2.020 (17)	C1*A*—C1*E*	1.428 (28)
Co1—C1*I*	2.038 (18)	C1*B*—C1*C*	1.434 (25)
Co1—C1*J*	2.036 (19)	C1*C*—C1*D*	1.457 (25)
S10—C16	1.647 (15)	C1*D*—C1*E*	1.424 (23)
S11—C12	1.730 (14)	C1*F*—C1*G*	1.404 (27)
S12—C11	1.712 (15)	C1*F*—C1*J*	1.388 (33)
S13—C13	1.715 (16)	C1*G*—C1*H*	1.399 (33)
S14—C14	1.733 (14)	C1*H*—C1*I*	1.418 (32)
S15—C12	1.738 (15)	C1*I*—C1*J*	1.473 (29)
S11—Ni1—S12	92.9 (2)	S16—C11—C12	116 (2)
S11—Ni1—S13	87.8 (2)	S13—C13—S17	123 (2)
S11—Ni1—S14	174.4 (3)	S13—C13—C14	121 (2)
S12—Ni1—S13	176.7 (2)	S17—C13—C14	116 (1)
S12—Ni1—S14	86.3 (2)	S14—C14—S18	121.6 (9)
S13—Ni1—S14	93.3 (2)	S14—C14—C13	122 (2)
C1*A*—Co1—C1*B*	40.8 (7)	S18—C14—C13	116 (2)
C1*A*—Co1—C1*E*	41.1 (8)	C12—S15—C15	96.6 (8)
C1*A*—Co1—C1*G*	160.4 (8)	C11—S16—C15	97.1 (8)
C1*B*—Co1—C1*C*	41.1 (7)	C13—S17—C16	97.1 (8)
C1*B*—Co1—C1*F*	160.4 (7)	C14—S18—C16	96.6 (8)
C1*C*—Co1—C1*D*	41.8 (7)	S15—C15—S16	113.3 (8)
C1*C*—Co1—C1*J*	162.4 (9)	S15—C15—S19	122 (2)
C1*D*—Co1—C1*E*	40.9 (6)	S16—C15—S19	124 (2)
C1*D*—Co1—C1*I*	162.6 (7)	S10—C16—S17	125 (2)
C1*E*—Co1—C1*H*	161.5 (8)	S10—C16—S18	122 (2)
C1*F*—Co1—C1*J*	39.7 (9)	S17—C16—S18	113.7 (8)
C1*G*—Co1—C1*H*	40.2 (8)	C1*B*—C1*A*—C1*E*	109 (2)
C1*I*—Co1—C1*J*	42.4 (8)	C1*A*—C1*B*—C1*C*	108 (2)
Ni1—S11—C12	102.1 (6)	C1*B*—C1*C*—C1*D*	106 (1)
Ni1—S12—C11	102.0 (6)	C1*C*—C1*D*—C1*E*	109 (2)
Ni1—S13—C13	102.2 (6)	C1*A*—C1*E*—C1*D*	107 (2)
Ni1—S14—C14	101.4 (6)	C1*G*—C1*F*—C1*J*	110 (2)

S11—C12—S15	122 (1)	C1F—C1G—C1H	108 (2)
S11—C12—C11	121 (2)	C1G—C1H—C1I	110 (2)
S15—C12—C11	117 (2)	C1H—C1I—C1J	106 (2)
S12—C11—S16	122 (1)	C1F—C1J—C1I	109 (2)
S12—C11—C12	123 (2)		

Table 3. *Contact distances* (<3.7 Å) *between anions*

S11···S22	3.65 (1)	S27···S43	3.60 (1)
S11···S26	3.40 (1)	S29···S45	3.62 (1)
S15···S26	3.53 (1)	S30···S46	3.62 (1)
S16···S29	3.66 (1)	S31···S48	3.63 (1)
S18···S24	3.57 (1)	S32···S43	3.66 (1)
S10···S40	3.32 (1)	S32···S47	3.64 (1)
S28···S37	3.64 (1)	S36···S41	3.51 (1)
S29···S30	3.53 (1)	S36···S43	3.49 (1)
S20···S40	3.62 (1)		

Data collection: *AFD* (Rigaku Corporation, 1985*a*). Cell refinement: *AFD*. Data reduction: *RCRYSTAN* (Rigaku Corporation, 1985*b*). Program(s) used to solve and refine structure: *SDP* (Frenz, 1978). Computer: VAX 11/785. Refinement was by the full-matrix least-squares method. H atoms were located and included in the structure-factor calculations but their positions were not refined.

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, complete bond distances and angles, and least-squares-planes data, as well as packing diagrams have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71004 (25 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: LI1014]

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Structure of Tricarbonyltris(diphenylphosphine)molybdenum(0) Hexane Solvate: *fac*-$[Mo(CO)_3(PPh_2H)_3]\cdot 0.25C_6H_{14}$

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Abstract

The two independent molecules in the asymmetric unit confirm a *fac*-octahedral metal geometry with bond distances Mo—P (mean) 2.502 (4) and Mo—C (mean) 1.964 (12) Å.

Comment

Two other *fac*-$Mo(CO)_3$(triphosphine) structures have been reported: $Mo(CO)_3(Ph_2P.NEt.PPh.NEt.PPh_2)$ with Mo—P (mean) 2.476 and Mo—C

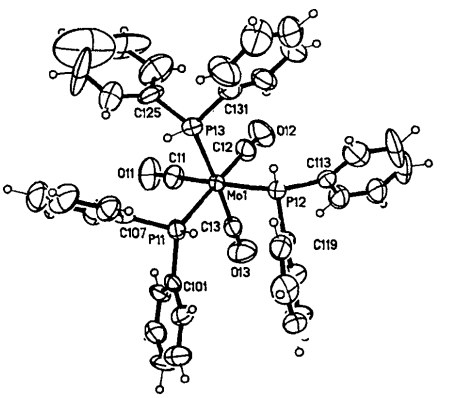

Fig. 1. Perspective view of the title compound (molecule 1) showing the atomic numbering. The H atoms are represented by spheres of arbitrary size. Non-H atoms are represented with 50% probability ellipsoids for thermal motion.