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Structure of Bis(tetraphenylphosphonium) (Dichlorodithioferrato-*S*,*S'*)disulphidooxomolybdate(2−) Methyl Cyanide Solvate, $[P(C_6H_5)_4]_2.[FeCl_2\{MoO(S_2)\}(S)_2].C_2H_3N$

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Abstract. $M_r = 1086{\cdot}8$, triclinic, $P\bar{1}$, $a = 10{\cdot}436\,(1)$, $b = 12{\cdot}486\,(1)$, $c = 20{\cdot}277\,(2)$ Å, $\alpha = 85{\cdot}04\,(1)$, $\beta = 75{\cdot}12\,(1)$, $\gamma = 81{\cdot}38\,(1)^\circ$, $V = 2521{\cdot}6\,(4)$ Å^3, $Z = 2$, $D_x = 1{\cdot}431\,(1)$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}89$ mm^{-1}, $F(000) = 1108$, $T = 291$ K, $R = 0{\cdot}066$ for 6036 reflections. The $FeCl_2$ and $(S_2)Mo(O)$ units of the anion are linked by two μ_2-S bridges with Fe$\cdots$Mo $= 2{\cdot}746\,(1)$ Å. There is a folded central FeS_2Mo ring.

Introduction. Clusters of Fe, Mo and S atoms are of considerable current interest (Holm, 1981), especially because the iron–molybdenum cofactor of the nitrogenase enzymes (Shah & Brill, 1977; Müller & Newton, 1983) is known to contain these elements, but the structure of this entity has yet to be defined. In an attempt to produce new Fe–Mo–S clusters from a pre-formed Fe_3O unit, we studied the reaction between $[Fe_3(CH_3CO_2)_6O(H_2O)_3Cl].2H_2O$ and $[PPh_4]_2[MoS_4]$ in a 2:1 molar ratio in degassed CH_3CN solution under dinitrogen (12 h). The product, precipitated by addition of excess $[PPh_4]Cl$, was crystallographically characterized: all Fe—O bonds and the trinuclear Fe unit have been destroyed, and the title compound (I) formed.

Experimental. Crystals obtained from the reaction mixture by volume reduction; chemical analyses were satisfactory. Crystal $0{\cdot}55 \times 0{\cdot}27 \times 0{\cdot}12$ mm, sealed in a capillary, Stoe–Siemens AED diffractometer, unit-cell parameters from 2θ values of 48 reflections ($20 < 2\theta < 25^\circ$), 8852 unique reflections with $2\theta < 50^\circ$ and $h \geq 0$, 6036 with $F > 4\sigma(F)$, profile analysis (Clegg, 1981), no significant intensity variation for 3 standard reflections, semi-empirical absorption corrections based on data measured at different azimuthal angles, transmission 0·70–0·75. Multisolution direct methods, blocked-cascade refinement on F, anisotropic thermal parameters for non-H atoms, phenyl H on external C—C—C bisectors with C—H $= 0{\cdot}96$ Å, $U(\text{H}) = 1{\cdot}2U_{\text{eq}}(\text{C})$, rigid linear CH_3CN with C—C $= 1{\cdot}47$, C—N $= 1{\cdot}15$ Å and no H atoms, scattering factors from *International Tables for X-ray Crystallography* (1974), 556 parameters, $R = 0{\cdot}066$, $wR = 0{\cdot}073$, $w^{-1} = \sigma^2(F) + 0{\cdot}00077F^2$, mean $\Delta/\sigma = 0{\cdot}16$, max. $\Delta/\sigma = 0{\cdot}63$, largest peak in final difference map $= 1{\cdot}07$ e Å^{-3}, largest hole $= -0{\cdot}96$ e Å^{-3}, slope of normal probability plot $= 1{\cdot}44$. Programs: *SHELXTL* (Sheldrick, 1978), diffractometer control program by WC.

Discussion. Atomic coordinates are given in Table 1, bond lengths and angles for the anion in Table 2.* The anion structure is shown in Fig. 1. The attempt to produce an Fe–Mo cluster was unsuccessful, and the reaction is obviously complex. The corresponding bromo derivative is obtained if an excess of $[PPh_4]Br$ is added instead of $[PPh_4]Cl$ in order to precipitate the product.

The compound consists of two $[PPh_4]^+$ cations, a $[(S_2)Mo(O)(\mu_2\text{-}S)_2FeCl_2]^{2-}$ anion and a CH_3CN solvent molecule; there are no particularly short contacts between the various ions and solvent molecules. The structure of the same salt as dimethylformamide (DMF) solvate has recently been reported by Müller, Sarkar, Bögge, Jostes, Trautwein & Lauer (1983); the preparative route was completely different. The anions in the two structures show no significant differences. In both cases a non-crystallographic mirror plane runs through the Mo, O, Fe and Cl atoms [r.m.s. deviation $= 0{\cdot}013\,(1)$ Å]. The S_2FeCl_2 unit resembles closely those in $[S_2Mo(\mu_2\text{-}S)_2FeCl_2]^{2-}$ (Tieckelmann, Silvis, Kent, Huynh, Waszczak, Teo & Averill, 1980; Müller, Tölle & Bögge, 1980) and $[Mo\{(\mu_2\text{-}S)_2FeCl_2\}_2]^{2-}$ (Coucouvanis, Baenziger, Simhon, Stremple, Swenson,

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* Tables of structure factors, anisotropic thermal parameters, H-atom parameters and cation geometry have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39130 (42 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* ($Å^2 \times 10^3$)

$U = \frac{1}{3}$(trace of the orthogonalized U_{ij} matrix).

	x	*y*	*z*	*U*
Mo	1881 (1)	1977 (1)	2926 (1)	47 (1)
Fe	1310 (1)	3936 (1)	2265 (1)	43 (1)
S(1)	−123 (2)	3089 (2)	3087 (1)	54 (1)
S(2)	3356 (2)	3077 (1)	2253 (1)	56 (1)
S(3)	1357 (3)	1300 (2)	4084 (1)	80 (1)
S(4)	3388 (3)	1344 (2)	3627 (1)	88 (1)
O	1788 (5)	966 (4)	2459 (2)	72 (2)
Cl(1)	1149 (2)	5681 (1)	2529 (1)	57 (1)
Cl(2)	855 (2)	3902 (2)	1235 (1)	59 (1)
P(1)	6775 (2)	6733 (1)	4234 (1)	40 (1)
P(2)	7617 (2)	12055 (1)	−107 (1)	42 (1)
C(111)	7857 (6)	7725 (5)	3847 (3)	44 (2)
C(112)	7841 (8)	8207 (6)	3210 (4)	67 (3)
C(113)	8618 (8)	9019 (6)	2947 (4)	74 (3)
C(114)	9399 (7)	9357 (6)	3324 (4)	73 (3)
C(115)	9418 (7)	8896 (6)	3945 (4)	66 (3)
C(116)	8660 (6)	8072 (5)	4218 (4)	55 (3)
C(121)	7534 (5)	5783 (5)	4786 (3)	37 (2)
C(122)	7598 (6)	6083 (5)	5414 (3)	47 (2)
C(123)	8188 (6)	5357 (5)	5829 (3)	49 (3)
C(124)	8706 (6)	4318 (6)	5626 (4)	52 (3)
C(125)	8660 (7)	4022 (6)	4996 (4)	56 (3)
C(126)	8080 (6)	4748 (5)	4576 (3)	49 (3)
C(131)	6432 (6)	6033 (5)	3575 (3)	43 (2)
C(132)	5167 (6)	5779 (5)	3615 (3)	49 (2)
C(133)	4966 (7)	5162 (6)	3126 (4)	64 (3)
C(134)	6033 (8)	4779 (6)	2606 (4)	60 (3)
C(135)	7292 (7)	5028 (6)	2563 (3)	54 (3)
C(136)	7495 (6)	5640 (5)	3036 (3)	51 (3)
C(141)	5250 (6)	7420 (5)	4746 (3)	42 (2)
C(142)	4564 (6)	6919 (6)	5328 (4)	57 (3)
C(143)	3402 (7)	7445 (7)	5743 (4)	71 (3)
C(144)	2936 (8)	8461 (7)	5554 (5)	96 (4)
C(145)	3556 (10)	8950 (7)	4947 (6)	129 (5)
C(146)	4771 (9)	8442 (7)	4557 (5)	95 (4)
C(211)	6361 (6)	13082 (5)	−301 (3)	47 (2)
C(212)	6621 (6)	13617 (5)	−937 (3)	53 (3)
C(213)	5618 (7)	14297 (6)	−1147 (4)	65 (3)
C(214)	4351 (7)	14435 (6)	−723 (4)	64 (3)
C(215)	4072 (7)	13916 (6)	−82 (4)	64 (3)
C(216)	5085 (6)	13241 (5)	138 (4)	53 (3)
C(221)	7507 (6)	11869 (5)	789 (3)	45 (2)
C(222)	6511 (7)	11323 (6)	1197 (4)	64 (3)
C(223)	6369 (8)	11191 (7)	1897 (4)	71 (3)
C(224)	7232 (9)	11597 (6)	2181 (4)	80 (4)
C(225)	8223 (9)	12134 (7)	1792 (4)	86 (4)
C(226)	8363 (8)	12279 (6)	1095 (4)	66 (3)
C(231)	9238 (6)	12383 (5)	−554 (3)	44 (2)
C(232)	10173 (7)	11644 (6)	−965 (3)	58 (3)
C(233)	11429 (7)	11902 (6)	−1268 (3)	61 (3)
C(234)	11792 (7)	12873 (6)	−1194 (4)	68 (3)
C(235)	10858 (7)	13634 (7)	−811 (4)	76 (4)
C(236)	9591 (7)	13389 (6)	−501 (4)	63 (3)
C(241)	7352 (6)	10811 (5)	−396 (3)	46 (2)
C(242)	7954 (7)	9839 (5)	−164 (4)	63 (3)
C(243)	7845 (8)	8870 (6)	−419 (4)	72 (3)
C(244)	7113 (7)	8874 (6)	−888 (4)	64 (3)
C(245)	6505 (7)	9843 (6)	−1121 (4)	60 (3)
C(246)	6612 (6)	10813 (6)	−863 (4)	56 (3)
N(3)	5315 (7)	8298 (7)	2281 (4)	139 (5)
C(31)	4221	8273	2579	92 (5)
C(32)	2823	8242	2960	145 (6)

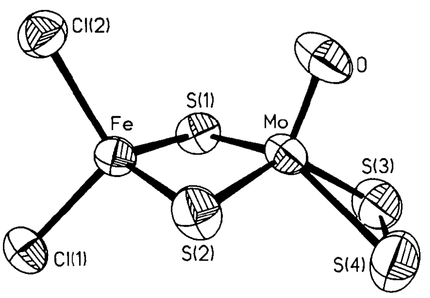

Fig. 1. Structure of the anion, showing the atom labelling and 50% probability ellipsoids.

Table 2. *Bond lengths* (Å) *and angles* (°) *for the anion*

Mo–Fe	2·746 (1)	Mo–S(1)	2·294 (2)
Mo–S(2)	2·312 (2)	Mo–S(3)	2·381 (2)
Mo–S(4)	2·388 (3)	Mo–O	1·671 (5)
Fe–S(1)	2·241 (2)	Fe–S(2)	2·237 (2)
Fe–Cl(1)	2·260 (2)	Fe–Cl(2)	2·262 (2)
S(3)–S(4)	2·091 (3)		
Fe–Mo–S(1)	51·9 (1)	Fe–Mo–S(2)	51·6 (1)
S(1)–Mo–S(2)	102·3 (1)	Fe–Mo–S(3)	134·6 (1)
S(1)–Mo–S(3)	91·7 (1)	S(2)–Mo–S(3)	136·8 (1)
Fe–Mo–S(4)	133·3 (1)	S(1)–Mo–S(4)	134·4 (1)
S(2)–Mo–S(4)	92·0 (1)	S(3)–Mo–S(4)	52·0 (1)
Fe–Mo–O	109·8 (2)	S(1)–Mo–O	107·2 (2)
S(2)–Mo–O	108·2 (2)	S(3)–Mo–O	106·1 (2)
S(4)–Mo–O	109·0 (2)	Mo–Fe–S(1)	53·6 (1)
Mo–Fe–S(2)	54·1 (1)	S(1)–Fe–S(2)	106·5 (1)
Mo–Fe–Cl(1)	133·7 (1)	S(1)–Fe–Cl(1)	108·8 (1)
S(2)–Fe–Cl(1)	110·2 (1)	Mo–Fe–Cl(2)	117·4 (1)
S(1)–Fe–Cl(2)	111·5 (1)	S(2)–Fe–Cl(2)	110·9 (1)
Cl(1)–Fe–Cl(2)	108·9 (1)	Mo–S(1)–Fe	74·5 (1)
Mo–S(2)–Fe	74·2 (1)	Mo–S(3)–S(4)	64·2 (1)
Mo–S(4)–S(3)	63·8 (1)		

Simopoulos, Kostikas, Petrouleas & Papaefthymiou, 1980). The $(S_2)MoO(S)_2$ fragment is similar to that in various $[(S_2)MoO(\mu_2\text{-}S)_2MoO(S_2)]^{2-}$ salts (Clegg, Mohan, Müller, Neumann, Rittner & Sheldrick, 1980; Clegg, Sheldrick, Garner & Christou, 1980).

The $Fe(\mu_2\text{-}S)_2Mo$ unit in complexes containing it is usually planar or very nearly so (Coucouvanis, 1981). However, in (1) a significant folding is observed, with a dihedral angle between the FeS_2 and MoS_2 planes of 161·0 (2)°. Since this folding is also observed in the DMF solvate (dihedral angle = 158·5°), it is clearly an inherent property of the anion, and not a fortuitous product of crystal packing forces. The folding, together with the very acute Fe—S—Mo angles, permits a short Fe···Mo approach of 2·746 (1) Å, consistent with a considerable and direct metal–metal interaction.

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Copper(I)–Olefin Complexes. Structure of 1-Chloro-2-(1-2-η-cyclohexene)-μ-[hydrotri(1-pyrazolyl)borato-N:N',N'']-dicopper(I), $C_{15}H_{20}BClCu_2N_6$

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Abstract. $M_r = 457\cdot71$, triclinic, $P\bar{1}$, $a = 9\cdot951$ (3), $b = 11\cdot737$ (3), $c = 9\cdot130$ (2) Å, $\alpha = 100\cdot51$ (2), $\beta = 115\cdot80$ (2), $\gamma = 79\cdot15$ (2)°, $V = 936\cdot8$ (9) Å^3, $Z = 2$, $D_x = 1\cdot623$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å (graphite monochromator), $\mu = 25\cdot078$ cm^{-1}, $F(000) = 464$, $T = 173$ K, final $R = 0\cdot026$, $R_w = 0\cdot027$ for 3582 reflections. The material was prepared from cuprous chloride and potassium hydrotri(1-pyrazolyl)borate in a dichloromethane–cyclohexene mixture. The geometry about one of the Cu^I ions, which is coordinated to two pyrazole N atoms and a cyclohexene molecule, is trigonal planar, whereas the geometry about the second Cu^I ion, which is coordinated to a pyrazole N atom and a Cl^- ion, is linear.

Introduction. Cu^I adducts with ethylene and other monoolefins have been of interest for many years (Jardine, 1975; Herberhold, 1974; Quinn & Tsai, 1969). These complexes generally lose olefin readily in the absence of excess olefin and have been only poorly characterized in most cases. Our interest in Cu^I–monoolefin coordination chemistry arises from the proposal that Cu^I ion may play a critical role in the binding of the plant hormone ethylene to its receptor site (Beyer & Blomstrom, 1980). We reported recently the synthesis, spectroscopy and structures of a series of Cu^I–monoolefin complexes that show binding of olefins, particularly ethylene, characteristic of the native systems and demonstrate that Cu^I–olefin chemistry is consistent with the proposed role of copper at the ethylene receptor site (Thompson, Harlow & Whitney, 1983). In this contribution, we present the crystallographic results on the cyclohexene complex $Cu(HBpz_3)(C_6H_{10}).CuCl$, where $HBpz_3$ is hydrotri(1-pyrazolyl)borate. This structural study was undertaken because a structure could not be assigned unambiguously to this complex on the basis of analytical and spectroscopic results alone (Thompson, Harlow & Whitney, 1983).

Experimental. Crystals grown from a dichloromethane–cyclohexene solution at 233 K as previously described (Thompson, Harlow & Whitney, 1983). Crystal 0·26 × 0·27 × 0·40 mm, encapsulated in a glass capillary under a nitrogen atmosphere. Syntex $P\bar{3}$ diffractometer, $T = 173$ K, ω-scan technique, scan width 1°, scan velocity 4·0–10·0° min^{-1}, ratio of total background time to scan time unity. Lattice parameters refined on the basis of 50 computer-centered reflections from diverse regions of reciprocal space. Empirical absorption correction, transmission factors 0·833–1·00. $4° < 2\theta < 55°$ ($-12 \leq h \leq 12$; $0 \leq k \leq 14$; $-10 \leq l \leq 10$). Three standard reflections collected after every 200 reflections: no significant variation. Total number of reflections: 4299; unique data used in refinement: 3582 [$F_o^2 > 2\sigma(F_o)^2$]; number of unobserved reflections: 717. Data processed by using counting statistics and a p value of 0·02 to derive standard deviations (Corfield, Doedens & Ibers, 1967). Number of variables: 306. All crystallographic calculations performed on a Digital Equipment Corporation VAX 11/780 computer using a system of programs developed by Dr J. C. Calabrese, Central Research and Development Department, E. I. du Pont de Nemours and Company, Wilmington, Delaware. Cu atom located by direct methods. Positions of remaining non-hydrogen atoms obtained by the usual combination of structure factor and Fourier synthesis calculations

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