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The Structure of μ_3-Thio-μ_3-tris(disulfido)chlorato-*cyclo*-tris[(diethyl dioxodithiophosphato-*S,S'*)molybdenum](3*Mo–Mo*), $C_{12}H_{30}ClMo_3O_6P_3S_{13}$

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Abstract. $M_r = 1103{\cdot}34$, triclinic, $P\bar{1}$, $a = 11{\cdot}570$ (2), $b = 13{\cdot}093$ (1), $c = 14{\cdot}399$ (2) Å, $\alpha = 102{\cdot}62$ (1), $\beta = 102{\cdot}15$ (1), $\gamma = 111{\cdot}87$ (1)°, $V = 1870$ (1) Å^3, $Z = 2$, $D_x = 1{\cdot}960$ g cm^{-3}, graphite-monochromatized Mo $K\alpha$, $\lambda = 0{\cdot}71073$ Å, $\mu = 18{\cdot}935$ cm^{-1}, $F(000) = 1092$, $T = 295$ K, final $R = 0{\cdot}055$ for 4113 reflections. In the thio-capped trinuclear Mo cluster, some of the skeleton atoms are in a distorted pseudocubane configuration with three S atoms capped by a Cl atom. The S–Cl bonding is covalent.

Introduction. In the course of studying the behavior of middle-valence Mo atoms in an EtOH–HCl medium, a series of stable trinuclear Mo clusters was synthesized and investigated by X-ray crystallography, including $(C_5H_7S_2)_3[Mo_3(\mu_3\text{-}S)_2(\mu\text{-}Cl)_3Cl_6]$ and $(C_5H_7S_2)_3[Mo_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3Cl_7]$ (Huang Jinling, Shang Maoyu, Huang Jianquan & Lu Jiaxi, 1982; Huang Jinling, Shang Maoyu, Liu Shixiong & Lu Jiaxi, 1982). It seemed interesting to pursue further study on this kind of compound in connection with its chemical behavior, such as ligand replacement reactions. In this respect, we were able to obtain a new trinuclear cluster with the $[S_2P(OEt)_2]^-$ radical as its terminal ligand.

Experimental. Straw-yellow long parallelepipeds, produced by K_2MoOCl_5 and P_2S_5 in EtOH saturated with HCl gas; $0{\cdot}15 \times 0{\cdot}19 \times 0{\cdot}37$ mm. Enraf–Nonius CAD-4 diffractometer, 25 reflections for measuring lattice parameters, $2 \le 2\theta \le 46°$, h 0–12, k −12–12, l −14–14; 5193 data, all unique, 4113 with $I \ge 3\sigma(I)$; Enraf–Nonius crystallographic computing package (Frenz, 1980), PDP 11/70 computer. Lp correction, absorption ignored; heavy-atom method, anisotropic full-matrix refinement on F, H not determined; final $R = 0{\cdot}055$, $R_w = 0{\cdot}061$, $w = 1$; atomic scattering factors from *International Tables for X-ray Crystallography* (1974).*

Discussion. Table 1 gives the atomic coordinates and Table 2 the interatomic distances and angles. Figs. 1 and 2 show the structure and the packing of the cluster, respectively.

In the cluster three Mo atoms form an equilateral-triangle configuration with an average Mo–Mo bond length of 2·725 (3) Å. One μ_3-S atom [S(1)] binds the three Mo atoms together to form a monocapped cluster core. Each pair of Mo atoms is bridged further by an S_2^{2-} ligand in such a manner that one of the S atoms [S(3), S(5), S(7)] lies basically on the plane formed by the three Mo atoms and the other [S(2), S(4), S(6)] is situated on the side opposite to the μ_3-S atom. The cluster unit $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3]$ has been reported in several cases, *e.g.* $(NH_4)_2[Mo_3S_{13}]$ (Müller, Pohl, Dartmann, Cohen, Bennet & Kirchner, 1979), $Mo_3S_7Cl_4$ (Marcoll, Rabenau, Mootz & Wunderlich, 1974) and $\{Mo_3S_7[S_2P(Et)_2]_3\}$ $[S_2P(Et)_2]$ (Keck, Kuchen, Mathow, Meyer, Mootz & Wunderlich, 1981). Nevertheless, the title structure differs sharply from these because of the presence of an additional Cl atom bridging the three out-of-plane S atoms, with an average

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39088 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0108-2701/84/050759-03$01.50

Table 1. *Atomic coordinates* ($\times 10^5$ *for* Mo; $\times 10^4$ *for* Cl, S, P, O; $\times 10^3$ *for* C) *and equivalent isotropic temperature factors*

$$B_{eq} = \tfrac{1}{3}\sum_i\sum_j B_{ij}a^*_i a^*_j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}(Å^2)
Mo(1)	−168 (9)	32386 (7)	26166 (7)	2·88
Mo(2)	−12671 (9)	19005 (7)	6443 (7)	2·88
Mo(3)	−19368 (9)	10370 (7)	21119 (7)	2·93
Cl(1)	−3754 (3)	3194 (3)	1644 (3)	5·31
S(1)	119 (3)	1521 (2)	1839 (2)	3·16
S(2)	−1178 (3)	3766 (2)	1364 (2)	3·55
S(3)	573 (3)	3885 (2)	1207 (2)	3·83
S(4)	−1955 (3)	2748 (2)	3113 (2)	3·45
S(5)	−637 (3)	2302 (2)	3879 (2)	3·67
S(6)	−3437 (3)	1172 (2)	771 (2)	3·56
S(7)	−2904 (3)	−124 (2)	305 (2)	3·86
S(8)	2369 (3)	3850 (3)	3442 (2)	4·13
S(9)	722 (3)	5259 (2)	3847 (2)	4·05
S(10)	−207 (3)	1119 (2)	−486 (2)	3·87
S(11)	−2318 (3)	2066 (2)	−1022 (2)	4·12
S(12)	−1564 (3)	−627 (2)	2457 (3)	4·32
S(13)	−3964 (3)	−47 (3)	2564 (3)	4·66
P(1)	2510 (3)	5349 (3)	4287 (3)	4·07
P(2)	−1352 (3)	1285 (2)	−1633 (2)	3·77
P(3)	−3276 (3)	−1200 (3)	2727 (3)	4·28
O(1)	3096 (10)	5583 (7)	5429 (7)	5·70
O(2)	3610 (9)	6458 (8)	4248 (8)	6·30
O(3)	−572 (8)	1924 (6)	−2263 (6)	4·73
O(4)	−2263 (8)	120 (6)	−2501 (6)	4·59
O(5)	−3144 (9)	−1396 (8)	3767 (7)	5·75
O(6)	−4252 (9)	−2475 (7)	2078 (7)	5·36
C(1)	275 (1)	469 (1)	592 (1)	6·03
C(2)	388 (1)	443 (1)	626 (1)	7·50
C(3)	344 (2)	694 (1)	343 (1)	7·63
C(4)	355 (2)	814 (1)	392 (1)	9·87
C(5)	49 (2)	313 (1)	−177 (1)	7·13
C(6)	126 (2)	340 (1)	−245 (1)	7·63
C(7)	−326 (1)	−86 (1)	−232 (1)	5·36
C(8)	−416 (2)	−175 (1)	−333 (1)	7·55
C(9)	−229 (2)	−48 (1)	472 (1)	7·34
C(10)	−151 (2)	−97 (1)	529 (1)	9·35
C(11)	−478 (2)	−287 (1)	97 (1)	7·71
C(12)	−591 (2)	−412 (2)	67 (1)	10·9

Table 2. *Bond distances* (Å) *and angles* (°)

Mo(1)–Mo(2)	2·727 (1)	Mo(3)–S(4)	2·394 (2)
Mo(1)–Mo(3)	2·722 (1)	Mo(3)–S(5)	2·484 (2)
Mo(1)–S(1)	2·360 (2)	Mo(3)–S(6)	2·396 (2)
Mo(1)–S(2)	2·397 (2)	Mo(3)–S(7)	2·472 (2)
Mo(1)–S(3)	2·491 (2)	Mo(3)–S(12)	2·502 (2)
Mo(1)–S(4)	2·399 (2)	Mo(3)–S(13)	2·550 (2)
Mo(1)–S(5)	2·489 (2)	S(2)–S(3)	2·038 (2)
Mo(1)–S(8)	2·496 (2)	S(2)–Cl(1)	2·930 (3)
Mo(1)–S(9)	2·549 (2)	S(4)–S(5)	2·030 (2)
Mo(2)–Mo(3)	2·725 (1)	S(4)–Cl(1)	2·956 (3)
Mo(2)–S(1)	2·362 (2)	S(6)–S(7)	2·041 (2)
Mo(2)–S(2)	2·390 (2)	S(6)–Cl(1)	2·862 (2)
Mo(2)–S(3)	2·485 (2)	S(8)–P(1)	1·998 (2)
Mo(2)–S(6)	2·394 (2)	S(9)–P(1)	1·983 (3)
Mo(2)–S(7)	2·482 (2)	S(10)–P(2)	1·996 (2)
Mo(2)–S(10)	2·499 (2)	S(11)–P(2)	1·985 (3)
Mo(2)–S(11)	2·545 (2)	S(12)–P(3)	1·996 (3)
Mo(3)–S(1)	2·365 (2)	S(13)–P(3)	1·984 (3)

Mo(2)–Mo(1)–Mo(3)	60·02 (2)	Mo(1)–S(2)–Mo(2)	69·45 (5)
S(2)–Mo(1)–S(3)	49·22 (6)	S(3)–S(2)–Cl(1)	169·68 (9)
S(4)–Mo(1)–S(5)	49·05 (6)	Mo(1)–S(3)–Mo(2)	66·45 (5)
S(8)–Mo(1)–S(9)	77·58 (6)	Mo(1)–S(4)–Mo(3)	69·19 (5)
Mo(1)–Mo(2)–Mo(3)	59·84 (2)	S(5)–S(4)–Cl(1)	168·58 (10)
S(2)–Mo(2)–S(3)	49·37 (6)	Mo(1)–S(5)–Mo(3)	66·36 (5)
S(6)–Mo(2)–S(7)	49·47 (6)	Mo(2)–S(6)–Mo(3)	69·35 (5)
S(10)–Mo(2)–S(11)	77·55 (6)	S(7)–S(6)–Cl(1)	170·66 (5)
Mo(1)–Mo(3)–Mo(2)	60·09 (2)	Mo(2)–S(7)–Mo(3)	66·75 (4)
S(4)–Mo(3)–S(5)	49·14 (6)	S(8)–P(1)–S(9)	105·13 (11)
S(6)–Mo(3)–S(7)	49·56 (6)	S(10)–P(2)–S(11)	105·02 (11)
S(12)–Mo(3)–S(13)	77·51 (6)	S(12)–P(2)–S(13)	105·25 (11)
Mo(1)–S(1)–Mo(2)	70·54 (5)	S(2)–Cl(1)–S(4)	66·63 (6)
Mo(1)–S(1)–Mo(3)	70·34 (5)	S(2)–Cl(1)–S(6)	67·19 (6)
Mo(2)–S(1)–Mo(3)	70·40 (5)	S(4)–Cl(1)–S(6)	67·52 (6)

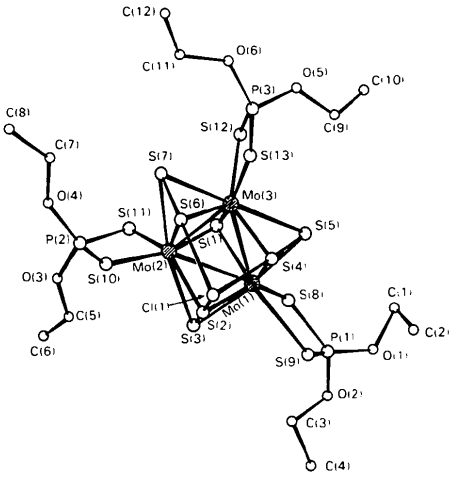

Fig. 1. Structure of the cluster with atom numbering.

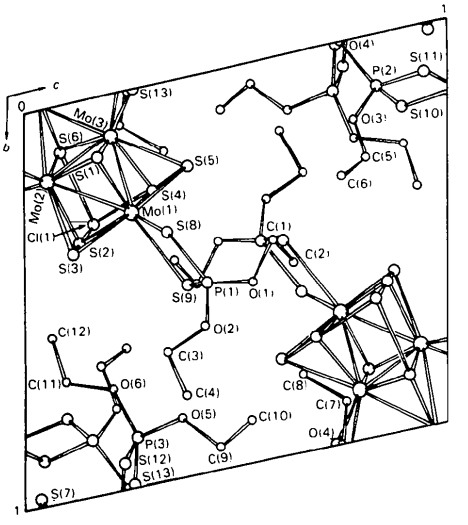

Fig. 2. Packing of the cluster.

S—Cl distance of 2·90 (3) Å to complete a distorted pseudocubane-cluster skeleton configuration. The compound is insoluble in water while it dissolves readily in common organic solvents, showing that the S—Cl bonding is prevalently covalent in character.

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The Structure of Bis(tetraethylammonium) Bis(μ-acetato-*O*,*O*')-tri-μ-chloro-pentachloro-μ_3-oxo-*cyclo*-trimolybdate(3*Mo*–*Mo*), $2C_8H_{20}N^+.C_4H_6Cl_8Mo_3O_5^{2-}$

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Abstract. $M_r = 966{\cdot}04$, orthorhombic, $Pna2_1$, $a = 17{\cdot}815$ (1), $b = 16{\cdot}629$ (2), $c = 12{\cdot}003$ (1) Å, $V = 3556$ (1) Å^3, $Z = 4$, $D_m = 1{\cdot}80$, $D_x = 1{\cdot}804$ g cm^{-3}, graphite-monochromatized Mo $K\alpha$, $\lambda = 0{\cdot}71073$ Å, $\mu = 16{\cdot}564$ cm^{-1}, $F(000) = 1928$, $T = 295$ K, final $R = 0{\cdot}048$ for 2584 reflections. In the mono-oxo-capped trinuclear Mo cluster anion, the three Mo atoms [Mo(1), Mo(2), Mo(3)], the μ_3-O atom [O(1)] and three μ-Cl atoms [Cl(1), Cl(2), Cl(3)] form an apex-deficient cubane-like configuration. The symmetry of the anion is C_s.

Introduction. The title crystal was one of the trinuclear Mo clusters (Huang Jinling, Shang Maoyu, Huang Jianquan & Lu Jiaxi, 1982; Shang Maoyu, Huang Jinling & Lu Jiaxi, 1984) synthesized for a systematic study of middle-valence Mo clusters to get a better understanding of possible structure configurations as well as the metal–metal bonding characters.

Experimental. Black octahedron-like crystals produced by $MoCl_3.3H_2O$, Ac_2O and Et_4NI in EtOH saturated with HCl gas; D_m by flotation in xylene/bromoform: $0{\cdot}19 \times 0{\cdot}30 \times 0{\cdot}33$ mm, Enraf–Nonius CAD-4 diffractometer, 25 reflections for measuring lattice parameters, $2 \le 2\theta \le 50°$, h 0–21, k 0–20, l 0–14, 3661 data, all independent, 2584 with $I \ge 3\sigma(I)$, Enraf–Nonius crystallographic computing package (Frenz, 1980), PDP 11/70 computer; Lp correction, empirical absorption correction based on ψ scans of 9 Bragg reflections, transmission factors 0·8979–0·9991; heavy-atom method, full-matrix refinement on F, Mo, Cl anisotropic, O, N, C isotropic, H not determined; final $R = 0{\cdot}048$ for observed reflections, $R_w = 0{\cdot}051$, $w = 1$; max. $\Delta/\sigma = 0{\cdot}52$, $\Delta\rho$ excursions $\pm 0{\cdot}7$ e Å^{-3}; atomic scattering factors from *International Tables for X-ray Crystallography* (1974).*

Discussion. Table 1 gives the atomic coordinates and Table 2 the interatomic distances and angles. Figs. 1 and 2 show the structure and packing of the cluster, respectively.

Three independent Mo atoms form a triangular configuration with an average side length of 2·60 (1) Å corresponding to a Mo–Mo bond order of one (Müller, Josters & Cotton, 1980). One μ_3-O atom [O(1)] and three μ-Cl atoms [Cl(1), Cl(2), Cl(3)] bind the three Mo atoms together to form an apex-deficient cubane-like

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39089 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

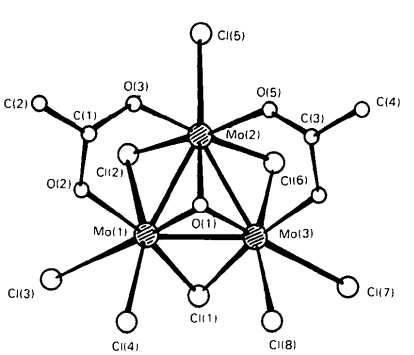

Fig. 1. Structure of the cluster with atom numbering.

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