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A New Reaction Converting the $Mo_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3$ Core to the $Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3$ Core: Structure of the $\{Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3[N(CH_2CO_2)_3]_3(H)_2\}^{3-}$ Ion

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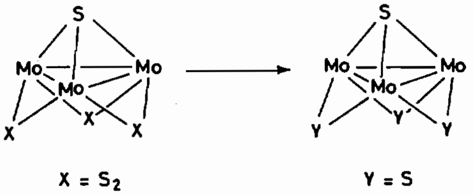
Systematic synthetic chemistry of the various equilateral triangular cluster species of molybdenum is gradually being developed [1] but there are still important lacunae in our knowledge. One phase of this chemistry deals with reactions that can be used to convert a cluster containing a certain set of bridging and/or capping non-metal atoms to a product with a different set. Of the many such interconversions that are of interest, we are concerned here with a new way of carrying out one that already has been shown to occur, namely, that represented schematically in eqn. (1). The first specific reaction used [2] is:



(1)

shown in eqn. (2), where:

$$[Mo_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3(S_2)_3]^{2-} + 12CN^- \longrightarrow$$

$$Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3(CN)_9]^{5-} + 3SCN^- + 3S_2^{2-} \qquad (2)$$

further reaction S_2^{2-} with CN^- presumably occurs. The driving force for this reaction is presumably conversion of S_2^{2-} + CN^- to S^{2-} + SCN^-. In a more recent case [3] the same starting cluster species, $[Mo_3S(S_2)_6]^{2-}$, was treated with a large excess of $Na_2(SCH_2CH_2S)$ resulting in the transformation represented in eqn. (3).

$$[Mo_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3(S_2)_3]^{2-} + 3SCH_2CH_2S^{2-} \longrightarrow$$

$$[Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3(SCH_2CH_2S)_3]^{2-} + \text{polysulfur species} \qquad (3)$$

In this case, conversion of $\mu\text{-}S_2^{2-}$ to $\mu\text{-}S^{2-}$ can be attributed to the known ability of an RS^- type anion to engage in a sulfur-atom transfer process of the type $S_2^{2-} + RS^- \rightarrow S^{2-} + RS_2^-$.

In this communication we describe a conversion of general type (1) under conditions where there is no exogenous S-atom acceptor.

Reaction of $(NH_4)_2Mo_3S_{13}\cdot 2H_2O$ [4] in DMF with a large excess of one of the chelating ligands, nitrilotriacetic acid (H_3NTA) or oxalic acid, under reflux, resulted in a color change from red to green. After about one hour the solution was allowed to cool to room temperature. Although the color of the solution is suggestive for a near-quantitative reaction, the isolation of pure products is rather tedious. Slow addition of diethyl ether yields tarry green precipitates. For the NTA-containing product, addition of $(C_4H_9)_4NCl$ prior to ether avoids oiling. Interestingly, the green powder thus obtained does not contain the $(C_4H_9)_4N^+$ cation but is contaminated with free ligand. It is purified either by Soxlet extraction with CH_2Cl_2 or by mutliple recrystallization from DMF/ether*.

We have not yet found a suitable work-up for bulk isolation of the pure oxalate-containing cluster. Again, a tarry precipitate is obtained upon ether addition, this time irrespective of addition of quaternary ammonium salts.

X-ray quality crystals for both compounds, admixed with crystals of the free ligands, were isolated in both cases by slow evaporation of ethanol/water solutions. We have completed a structure determination on the NTA-containing product** and that of the oxalate is in progress†. A perspective view of the cluster anion is shown in Fig. 1 and the more important bond lengths and angles are listed in Table I. A list of fractional coordinates and structure factors can be obtained from author F.A.C. on request. The anion has crystallographic C_{3v} symmetry and has an $Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S)_3$ core with $HNTA^{2-}$ ions occupying the outer positions through two carboxyl oxygen atoms and the nitrogen atom, just as in the recently reported $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}O)_3(HNTA)_3]^{2-}$ ion [5]. The

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*Electronic spectra, λ_{max} (ϵ), in H_2O. $(NH_4)_3[Mo_3S_4(NTA)_3(H)_2]$, 1: 610 (280); $[Mo_3S_4(C_2O_4)_3(H_2O)_3(H)_2]$, 2: 620 (210). ^{13}C NMR for 1: δ(TMS): 176.8 ppm (carboxylates) 66.2 ppm (methylenes); broad peaks at 25° and 70 °C in DMSO-d_6.

**$(NH_4)_3[Mo_3S_4(NTA)_3(H)_2]\cdot 3EtOH$: R3m (#160 on hexagonal axes), a = 16.585(4) Å, c = 14.188(4) Å; refined to R = 0.046 and R_w = 0.059.

†$[Mo_3S_4(C_2O_4)_3(H_2O)_3(H)_2]\cdot 2EtOH$. Monoclinic, $P2/c$; a = 19.403(5) Å; b = 6.555(1) Å, c = 19.512(6) Å, β = 97.38(2)°, Z = 4. The location of he two hydrogen atoms is still uncertain.

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TABLE I. Important Bond Lengths and Angles for $[Mo_3S_4(NTA)_3(H)_2]^{3-}$.

Bond Lengths (Å)			
Mo–Mo	2.769(1)	C(2)–O(1)	1.292(12)
Mo–S(1)	2.344(5)	C(2)–O(2)	1.24(2)
Mo–S(2)	2.298(3)	C(2)–C(1)	1.48(2)
Mo–O(1)	2.098(7)	N(1)–C(1)	1.544(14)
Mo–N(1)	2.266(5)	N(1)–C(3)	1.51(2)
		C(4)–C(3)	1.513(13)
		C(4)–O(3)	1.186(8)
		C(4)–O(4)	1.33(2)
Bond Angles (deg.)			
Mo–Mo–Mo	60	O(1)–Mo–O(1)	77.2(4)
S(1)–Mo–S(2)	105.4(1)	O(1)–Mo–N(1)	76.5(3)
S(1)–Mo–O(1)	87.1(2)	Mo–S(1)–Mo	72.4(2)
S(1)–Mo–N(1)	159.0(3)	Mo–S(2)–Mo	74.1(1)
S(2)–Mo–S(2)	96.5(1)		
S(2)–Mo–O(1)	162.7(3)		
S(2)–Mo–O(1)′	91.4(3)		
S(2)–Mo–N(1)	88.3(2)		

observed diamagnetism in the NMR spectrum is suggestive for a 6 e^- cluster, *i.e.* no net reduction or oxidation occurred during the reaction. For the purpose of charge balance one of the nitrilotriacetic acid ligands is assumed to be present in the trianionic form.

We should like to draw particular attention to the fact that in this work it has been possible to carry out a transformation of type (1) without employing any reagent specifically intended to abstract sulfur atoms from the μ-S_2^{2-} ions to generate μ-S^{2-} ions. There is no precipitate of elemental sulfur and it is our hypothesis that the other three S_2^{2-} ions initially present may serve to bind the liberated sulfur atoms thus forming S_3^{2-} or other related species. We are attempting to obtain direct evidence on this point.

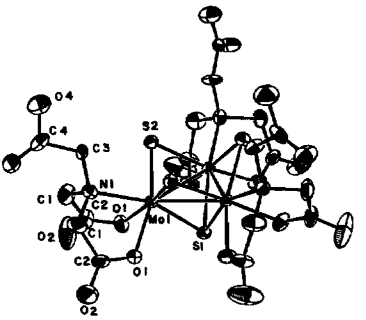

Fig. 1. An ORTEP view of the cluster cation, giving the atom labelling scheme. All atoms are represented by their ellipsoids of thermal vibration at the 40% probability level.

Finally, the present structure affords interesting comparisons with those of related compounds in which there are variations in the μ_3-X and μ_2-X groups. Data are given in Table II. The change from μ_3-O to μ_3-S, while retaining three μ_2-O groups lengthens the Mo–Mo bonds by about 0.10 Å, while the additional change of three μ_2-O groups to μ_2-S groups causes another increase, of about 0.19 Å. We do not yet have an $Mo_3(\mu_3\text{-}O)(\mu_2\text{-}S)_3$ containing species available for structural study. When μ_2-S groups are replaced by μ_2-S_2 groups, there is a small contraction, *ca.* 0.03 Å. The various Mo–X and Mo–Y distances are about the same in all cases. Despite the variations in Mo–Mo distances, we would assign a formal Mo–Mo bond order of unity in all these isoelectronic species.

Acknowledgement

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TABLE II. Bond Lengths in Some Compounds Containing $Mo_3(\mu_3\text{-}X)(\mu_2\text{-}Y)_3$ Cores.

Cluster Species	Mo–Mo (Å)	Mo–μ_3-X (Å)	Mo–μ_2-Y (Å)	Ref.
$\{Mo_3(\mu_3\text{-}O)(\mu_2\text{-}O)_3(C_2O_4)_3(H_2O)_3\}^{2-}$	2.486(1)	2.019(6)	1.921(7)	10
$\{Mo_3(\mu_3\text{-}S)(\mu_2\text{-}O)_3[N(CH_2CO_2)_3H]_3\}^{2-}$	2.589	2.360	1.197	9
$\{Mo_3(\mu_3\text{-}S)(\mu_2S)_3[N(CH_2CO_2)_3]_3(H)_2\}^{3-}$	2.769(1)	2.344(5)	2.298(3)	[a]
$\{Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S)_3(CN)_9\}^{5-}$	2.765(7)	2.363(4)	2.312(5)	11
$\{Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S)_3(SCH_2CH_2S)_3\}^{2-}$	2.78	2.35	*ca.* 2.30	4
$\{Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_2)_3(S_2)_3\}^{2-}$	2.722	2.353	2.487[b,d] 2.419[c,d]	5
$\{Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_2)_3(Et_2PS_2)_3\}^{P}$	2.737	2.379	2.490[b] 2.403[c]	12
$\{Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_2)_3Cl_2Cl_{4/2}\}$	2.745	2.36	2.49[b] 2.41[c]	13

[a] This work. [b] Upper S atom of μ_2-S_2. [c] Lower S atom of μ_2-S_2. [d] The upper and lower S atoms are mislabeled in ref. 5.

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