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CUBANE AND INCOMPLETE CUBANE-TYPE MOLYBDENUM AND TUNGSTEN OXO/SULFIDO CLUSTERS

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I. Introduction

This review surveys the structural aspect of cubane-type compounds with $Mo_4O_{4-n}S_n$ (n = 0, 3, or 4) cores and incomplete cubane-type compounds with $Mo_3O_{4-n}S_n$ and $W_3O_{4-n}S_n$ (n = 0–4) cores (Fig. 1). Compounds with mixed-metal cubane-type cores Mo_3MS_4 (M = metals) are also included. Notes on synthetic procedures are given in Section

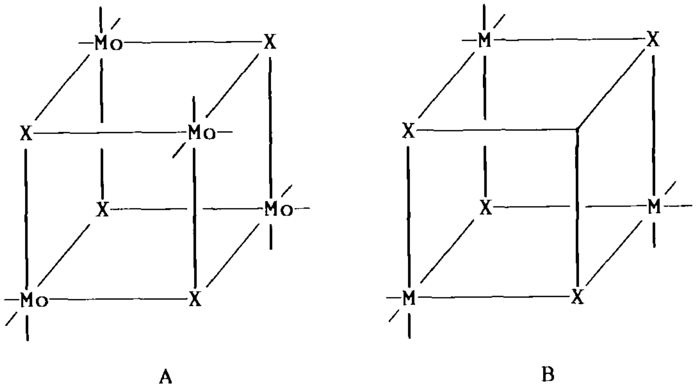

FIG. 1. Cubane-type (A) Mo_4X_4 and incomplete cubane-type (B) M_3X_4 cores. M = Mo, W; X = O, S.

VI, which, however, does not cover all of the available literature. Although the solid-state chemistry of molybdenum has been developed with, for example, infinite repeat Mo_3S_4 units, only discrete compounds with these cores are included in this review. Also, other related triangular Mo_3 and W_3 compounds such as $Mo_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3$ (*1*), $Mo_3(\mu_3\text{-}H)(\mu_3\text{-}I)(\mu\text{-}I)_3$ (*2*), $Mo_3(\mu_3\text{-}O)(\mu\text{-}S_2)_3$ (*3*) and $M_3(\mu_3\text{-}O)_2$ (M = Mo, W) (*4*) are not described here, though they are interesting. This review has been organized primarily according to the number of Mo and W metals (three or four) and secondarily according to the number of bridging sulfur atoms.

PREVIOUS REVIEWS

The first systematic review of trinuclear clusters of the early transition elements was published in 1980 by Müller *et al.* (*5*), who classified the clusters into three categories according to the number of capping ligands (μ_3-type): 0, 1, and 2. Jiang *et al.* (*6*) reported a comprehensive review of trinuclear clusters in 1985, in which they gave a more detailed classification system. Thus in addition to the number of capping ligands, the number of bridging ligands (μ_2-type) was used for classification purposes. Both reviews considered the electronic structures of the clusters. The relationship between the structures of the clusters and the number of valence electrons has also been discussed by Gubin (*7*). Reviews focusing on more specialist fields have also appeared. Thus sulfur ligands have been considered by Dance (*8*), by Müller *et al.*, (*9*, *10*), and by Zanello (*11*); Mo_3 clusters with μ_3-O and μ_3-OR (R = alkyl) have been considered by Chisholm *et al.* (*12*); and related electrochemical studies have been made by Zanello (*11*). Furthermore, Cotton has described the results of recent research on compounds with Mo—Mo bonds (*13*). Cubane-type clusters have been reviewed by Vahrenkamp (*14*), by Zanello (*11*), and by Harris (*15*). The latter in particular considers binding aspects. The binding properties of some of incomplete cubane-type molybdenum and tungsten compounds have been discussed by Cheng *et al.* (*16*). Chemical and physical properties of triangular bridged metal compounds have been reviewed by Cannon and White (*17*). A review of mixed-metal clusters has also been published (*18*). Earlier reviews by Stiefel (*19*) and by Spivack and Dori (*20*) have emphasized structural aspects of Mo compounds. A more recent review by Young (*21*) includes some description of mixed-valence compounds of both molybdenum and tungsten.

II. Incomplete Cubane-Type Clusters with $Mo_3O_{4-n}S_n$ Cores

In contrast to the situation a decade ago, many incomplete cubane-type clusters with $Mo_3O_{4-n}S_n$ cores have been prepared and the structures have been determined by X-ray structure analyses. The results obtained are summarized in Tables I–III. The formal oxidation state of molybdenum in the compounds cited here is in all cases IV. Unlike Mo(VI) and Mo(V) compounds, mononuclear oxo or dioxo compounds of the Mo(IV) state are relatively rare and all the incomplete cubane-type compounds cited here have no terminal oxo ligand. Three Mo atoms form an equilateral triangle, and three single bonds exist between each Mo. Except for the compounds **1**, **8**, and **31** (Table III), and excluding Mo—Mo bonds, each molybdenum is octahedrally coordinated.

A. INCOMPLETE CUBANE-TYPE CLUSTERS WITH Mo_3O_4 CORES

Structural parameters for the compounds with Mo_3O_4 cores are found in Table I (*22-28*). Some of the compounds are shown in Figs. 2 and 3. The Mo—Mo distance is ~2.5 Å (consistent with metal–metal bonding), and the Mo-μ_3O distance is longer than Mo-μ_2O by ~0.1 Å. The angles in Mo—μ_3O—Mo and Mo—μ_2O—Mo fall in the narrow range 75.0–76.6 and 80.6–81.5, respectively. The following tendency of Mo—L distances was observed: Mo—F < Mo—O (RCO*O*) < Mo—N (*N*CS) ≈ Mo—O (H_2*O*) < Mo—N (R_3*N*).

Compound 1 (Fig. 2) was the first to be obtained from an aqueous Mo(IV) solution. In a related study at about the same time, the two Mo_3O_4 units in compound **4** (Fig. 3) were found to be bridged by three

TABLE I

STRUCTURAL PARAMETERS FOR INCOMPLETE CUBANE-TYPE COMPOUNDS WITH Mo_3O_4 CORES[a]

Compound	Mo — Mo	Mo — μ_3O	Mo — μ_2O	Mo — L[b]	Ref.
(1) $Cs_2[Mo_3O_4(ox)_3(H_2O)_3] \cdot 4H_2O \cdot 1/2H_2C_2O_4$	2.486[1]	2.019[6]	1.921[4]	2.091[4], O(ox) 2.154[7], O(H_2O)	*22,23*
(2) $Cs_2[Mo_3O_4(ox)_3(H_2O)_3] \cdot CsCF_3SO_3 \cdot 3H_2O$	2.491[1]	2.01[1]	1.908[7]	2.102[8], O(ox) 2.15[1], O(H_2O)	*22*
(3) $[Pt(en)_2][Mo_3O_4(ox)_3(H_2O)_3] \cdot 3H_2O$	2.494[6]	2.020[3]	1.915[6]	2.094[16], O(ox) 2.164(4), O(H_2O)	*24*
(4) $Na_4[(Mo_3O_4)_2(edta)_3] \cdot 14H_2O$	2.506[13]	2.042[17]	1.918[18]	2.090[21], O 2.274[42], N	*25*
(5) $(NH_4)_5[Mo_3O_4F_9] \cdot NH_4F \cdot H_2O$	2.505	2.032	1.920	2.034, F	*26*
(6) $((CH_3)_4N)_4[Mo_3O_4(NCS)_8(H_2O)] \cdot 3H_2O$	2.518[1]	2.07[4]	1.93[4]	2.26[2], O 2.14[4], N	*27*
(7) $Na_2[Mo_3O_4(mida)_3] \cdot 7H_2O$	2.495[10]	2.043[27]	1.918[10]	2.090[22], O 2.231[6], N	*28*

[a] Note: Numbers in parentheses in the all of the tables indicate the estimated standard deviation for that particular value; brackets indicate $\sqrt{\Sigma_i(x_i - \bar{x})^2/(n - 1)}$ for several values whose unweighted arithmetic average is given, with $\bar{x}$ the mean of n values. In some cases, indicated by an asterisk, brackets are used to indicate $\sqrt{\Sigma_i(x_i - \bar{x})^2/n(n - 1)}$.

[b] The ligating atom is noted after the numeral.

edta ligands. In compound **6**, it should be noted that the thiocyanate ligand coordinates to molybdenum through the nitrogen and not the sulfur atom.

B. INCOMPLETE CUBANE-TYPE CLUSTERS WITH $Mo_3O_3S/Mo_3O_2S_2/Mo_3OS_3$ CORES

Structural parameters for the compounds with Mo_3O_3S, $Mo_3O_2S_2$, or Mo_3OS_3 cores are found in Table II (*29–34*). Structures of some of the compounds are illustrated in Figs. 4–8. Introduction of μ_3-S causes an elongation of the Mo—Mo distance of 0.1 Å, or sometimes a little more. In compound **1** (Fig. 4) one CO_2 group of each $Hnta^{2-}$ ligand is left uncoordinated, the distinction being a long (av. 1.325 Å) and a short (1.205 Å) C—O distance in each case. There are three such —COOH groups in the trimeric anionic compound. In compound 2, the coordination of the cysteinato ligand is as indicated in Fig. 5. Compound **3** has one μ_3-S, one μ_2-S, and two μ_2-O bridging ligands in the trimeric core (Fig. 6). In compound **4** (Fig. 7), two nitrogen atoms occupy the δ position (*25*) [trans to μ_3-X (X = O or S); cf. Figs. 3 and 4] and the other

TABLE II

STRUCTURAL PARAMETERS FOR INCOMPLETE CUBANE-TYPE COMPOUNDS WITH $Mo_3O_{4-n}S_n$ (n = 1–3) CORES[a]

Compound	Mo — Mo[b]	Mo — μ_3X[c]	Mo — μ_2Y[c]	Mo — L	Ref.
(1) $Ba[Mo_3O_3S(Hnta)_3] \cdot 10H_2O$	2.589[6], SO	2.360[7], S	1.917[9], O	2.097[15], O 2.264[4], N	*29,30*
(2) $K_2[Mo_3O_3S(cys)_3] \cdot 6H_2O$	2.624[9], SO	2.367[13], S	1.933[52], O	2.190[22], O 2.219[26], N 2.440[20], S	*30*
(3) $(pyH)_5[Mo_3O_2S_2(NCS)_9] \cdot 2H_2O$	2.635[0], SO 2.715(4), SS	2.320[20], S	1.945[21], O 2.257[2], S	2.135[42], N	*31*
(4) $Ba[Mo_3OS_3(ida)_3] \cdot 7H_2O$	2.612(2), SO 2.725[12], SS	2.352[14], S	1.944[8], O 2.309[15], S	2.130[27], O 2.249[14], N	*32*
(5) $[Mo_3OS_3(dtp)_4(im)]$	2.651[6], OS	2.052[37], O	2.280[12], S	2.598, S[d] 2.622, S[e] 2.232, N	*33,34*
(6) $[Mo_3(\mu_3 - O)S_3(dtp)_4(oxazole)]$	2.638[9], OS	2.027, O	2.282, S	2.590, S[d] 2.584, S[e]	*34*
(7) $[Mo_3(S,O)_{0.5}S_3(dtp)_4(SC(NH_2)_2)]$[f]	2.681[11]	2.202	2.282	2.568, S[d] 2.610, S[e] 2.633, S	*34*

[a] See footnote *a*, Table I.

[b] The μ_3X then μ_2Y atoms between the two Mo atoms follow the numeral.

[c] The μ_3X or μ_2Y atom follows the numeral.

[d] Terminal.

[e] Bridge.

[f] Disordered.

nitrogen atom resides in the γ position [trans to μ_2-X (X = O or S)], whereas all the nitrogen atoms occupy the δ position in the related compounds reported so far. Compounds **5** (Fig. 8) and **6** are rare cases in having μ_3-O alongside μ_2-S ligation, whereas all the other compounds exhibit a preference for μ_3-S occupancy on introducing sulfurs into the core. A statistical disorder of μ_3-X (X = O or S) has been reported for compound **7**.

C. INCOMPLETE CUBANE-TYPE CLUSTERS WITH Mo_3S_4 CORES

Structural parameters for the compounds with Mo_3S_4 cores are found in Table III (*34–52*). The structures of some of these compounds are illustrated in Fig. 9–13. Larger variations are observed in the Mo—Mo distances (2.731–2.830 Å) of the series of compounds as compared to

TABLE III

STRUCTURAL PARAMETERS FOR INCOMPLETE CUBANE-TYPE COMPOUNDS WITH Mo_3S_4 CORES[a]

Compound	Mo — Mo	Mo — μ_3S	Mo — μ_2S	Mo — L	Ref.
(1) $[Mo_3S_4Cp_3][Sn(CH_3)_3Cl_2]$	2.812[1]	2.314[6]	2.294[6]	2.030[7], Cp	*35*
(2) $K_5[Mo_3S_4(CN)_9] \cdot 3KCN \cdot 4H_2O$	2.775[8]	2.363[7]	2.322[10]	2.189[10], C[b] 2.220[3], C[c]	*36*
(3) $K_5[Mo_3S_4(CN)_9] \cdot 7H_2O$	2.765[7]	2.363[4]	2.312[5]	2.159[13], C[b] 2.194[17], C[d]	*37*
(4) $Ca[Mo_3S_4(ida)_3] \cdot 11.5H_2O$	2.754[11]	2.348[9]	2.294[8]	2.166[23], O 2.274[5], N	*38*
(5) $(NH_4)_3[Mo_3S_4(Hnta)_2(nta)] \cdot 3EtOH$	2.769(1)	2.344(5)	2.298(3)		*39*
(6) $[Mo_3S_4([9]aneN_3)_3](ZnCl_4)(ZnCl_3H_2O)_2 \cdot 3H_2O$	2.773[7]	2.361[10]	2.278[9]	2.27[5], N	*40*
(7) $[Mo_3S_4(H_2O)_9](pts)_4 \cdot 9H_2O$	2.732[7]	2.332[4]	2.286[6]	2.190[14], O	*41*
(8) $[(C_2H_5)_4N]_2[Mo_3S_4(SCH_2CH_2S)_3]$	2.783[12]	2.345[3]	2.293[22]	2.475[5], S[b] 2.347[8], S[d]	*42*
(9) $[Mo_3S_4(dtp)_4(H_2O)]$	2.754[18]	2.346[9]	2.281[19]	2.361(6), O 2.575[20], S	*34,43*
(10) $[Mo_3S_4(dtp)_4P(C_6H_5)_3] \cdot 0.86CH_2Cl_2$	2.744[12]	2.335[16]	2.288[15]	2.647(3), P 2.604[6], S[e] 2.588[9], S[f]	*34,44*
(11) $[Mo_3S_4(dtp)_4(PhCH_2CN)]$	2.756[9]	2.341[5]	2.282[6]	2.261(6), N 2.648[10], S[g] 2.574[17], S[h]	*34,45*
(12) $[Mo_3S_4Cl_3(dmpe)_3] \cdot PF_6 \cdot CH_3OH$	2.766(4)	2.360(9)	2.336(7)[j] 2.290(7)[k]	2.534(8), P[b] 2.605(8), P[d] 2.473(7), Cl	*46,47*
(13) $[Mo_3S_4Cl_4(PEt_3)_3(MeOH)_2]$	2.766[24]	2.355[4]	2.288[11]	2.330[5], O 2.599[6], P 2.537[6], Cl[k] 2.422[8], Cl[l]	*48*
(14) $[Mo_3S_4Cl_4(PEt_3)_4(MeOH)]$	2.790[5]	2.359[8]	2.289[23]	2.324(8), O 2.660[43], P[m] 2.600[23], P[n] 2.517[75], Cl[k] 2.452(2), Cl[l]	*48*
(15) $Cs_2[Mo_3S_4(ox)_3(H_2O)_3] \cdot 3H_2O$	2.738(5)	2.33(1)	2.28(1)	—	*46,49*
(16) $[\{Mo_3S_4(HB(pz)_3)_2\}_2(\mu - O)(\mu - pz)_2] \cdot 2THF$	2.830[24]	2.352[11]	2.292[22]	2.27[6], N 1.91[1], O	*50*
(17) $[Mo_3S_4Cl_4(PPh_3)_3(H_2O)_2] \cdot 3THF$	2.758[15]	2.345[8]	2.286[6]	2.503[3], Cl[k] 2.427[10], Cl[l] 2.621[18], P 2.273[1], O	*51*
(18) $[Mo_3S_4Cl_3(dmpe)_3]Cl \cdot 2MeOH$	2.772[6]	2.351[10]	2.309[23]	2.496[10], Cl 2.563[29], P	*51*
(19) $[Mo_3S_4(dtc)_4(dmf)] \cdot EtOH$	2.741[38]	2.336(3)(av.)	2.297(3)(av.)	2.278(7), O (DMF) 2.569(4), S[o] 2.524(3), S[p]	*52*
(20) $[Mo_3S_4(dtc)_4(py)] \cdot 2py \cdot H_2O$	2.741[36]	2.344(2)(av.)	2.289(2)(av.)	2.361(5), Py 2.593(2), S[o] 2.523(2), S[p]	*34,52*

TABLE III *Continued*

Compound	Mo — Mo	Mo — μ_3S	Mo — μ_2S	Mo — L	Ref.
(21) $[Mo_3S_4(dtp)_4(SC(NH_2)(NHC_3H_5))]$	2.755[10]	2.341	2.286	2.582, S[q] 2.608, S[r] 2.618, S	*34*
(22) $[Mo_3S_4(dtp)_4(py)]$	2.754[10]	2.339	2.282	2.573, S[q] 2.623, S[r] 2.360, N	*34*
(23) $[Mo_3S_4(dtp)_4(dmf)]$	2.741[38]	2.337	2.303	2.525, S[q] 2.569, S[r] 2.278, O	*34*
(24) $[Mo_3S_4(dtp)_4(PhCH_2SH)]$	2.755[11]	2.337	2.282	2.568, S[q] 2.643, S[r] 2.734, S	*34*
(25) $[Mo_3S_4(dtp)_4(oxazole)]$	2.760[8]	2.337	2.282	2.573, S[q] 2.617, S[r] 2.316, N	*34*
(26) $[Mo_3S_4(dtp)_4(CH_3CH_2CN)]$	2.754[10]	2.344	2.281	2.572, S[q] 2.633, S[r] 2.306, N	*34*
(27) $[Mo_3S_4(dtp)_3(im)_3](dtp)$	2.760[4]	2.339	2.287	2.571, S[s] 2.266, N	*34*
(28) $[Mo_3S_4(dtp)_3(\mu_2 - O_2CCH_2CH_3)(py)]$	2.731[42]	2.335	2.288	2.549, S[s] 2.372, N	*34*
(29) $[Mo_3S_4(dtp)_3(\mu_2 - O_2CH)(py)]$	2.740[37]	2.332	2.287	2.545, S[s] 2.385, N	*34*
(30) $[Mo_3S_4(dtp)_3(\mu_2 - O_2CCH_3)(py)]$	2.739[45]	2.334	2.293	2.549, S[s] 2.385, N	*34*
(31) $[Mo_3S_4(dtp)_3(bipy)](dtp)$	2.751[20]	2.337	2.275	2.589, S[s] 2.573, S	*34*

[a] See footnote *a*, Table I.

[b] Trans to μ_3S.

[c] Cis to μ_2S.

[d] Cis to μ_3S.

[e] One Pand two S ligating atoms to one Mo.

[f] Three ligating S atoms to each Mo.

[g] Bridging ligand.

[h] Nonbridging ligand.

[i] Trans to the Mo — P bond.

[j] Trans to the Mo — Cl bond.

[k] Two Cl atoms to one Mo atom.

[l] One Cl atom to each Mo atom.

[m] Two P atoms to one Mo atom.

[n] One P atom to each Mo atom.

[o] Bridging dtc.

[p] Terminal dtc.

[q] Terminal dtp.

[r] Bridging dtp.

[s] Terminal.

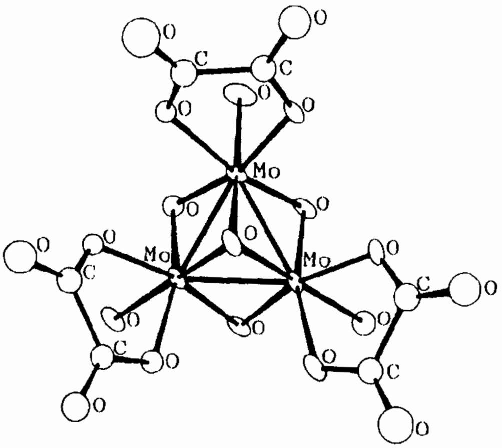

Fig. 2. Perspective view of $[Mo_3O_4(ox)_3(H_2O)_3]^{2-}$.

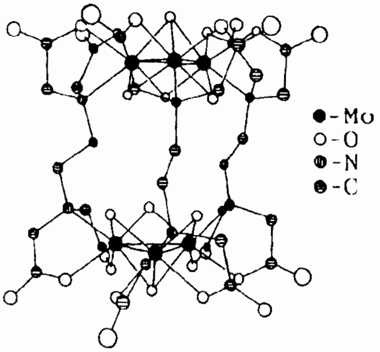

Fig. 3. Perspective view of $[(Mo_3O_4)_2(edta)_3]^{4-}$.

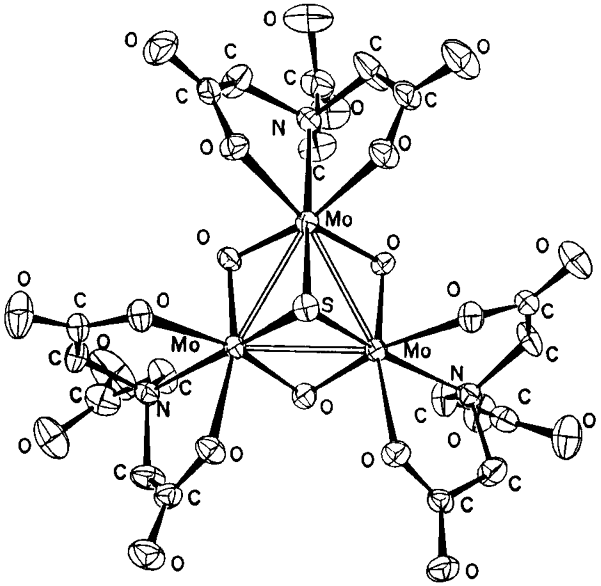

FIG. 4. Perspective view of $[Mo_3O_3S(Hnta)_3]^{2-}$.

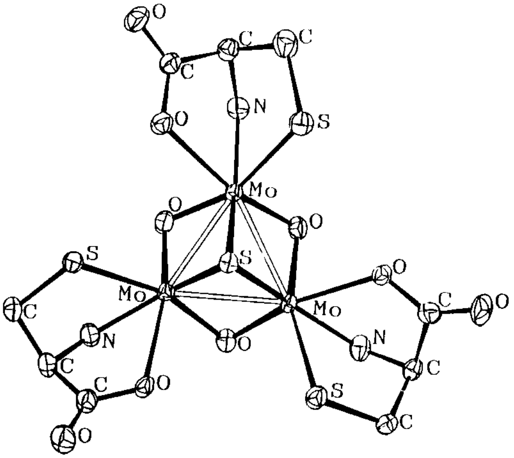

FIG. 5. Perspective view of $[Mo_3O_3S(cys)_3]^{2-}$.

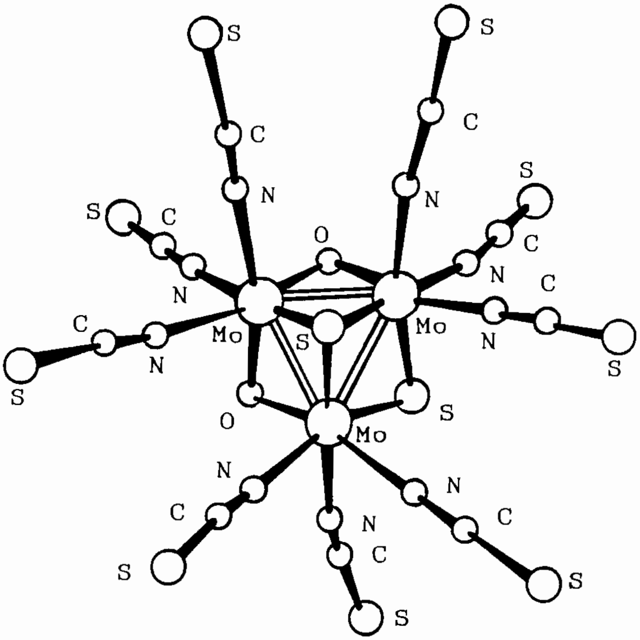

FIG. 6. Perspective view of $[Mo_3O_2S_2(NCS)_9]^{5-}$.

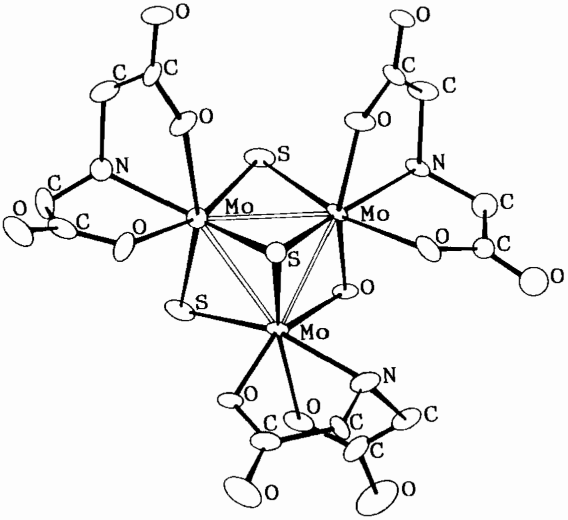

FIG. 7. Perspective view of $[Mo_3OS_3(ida)_3]^{2-}$.

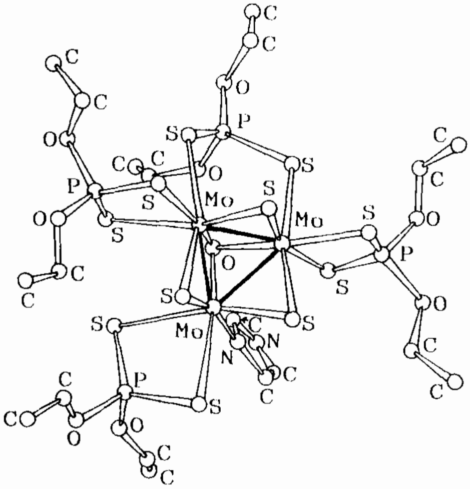

FIG. 8. Perspective view of $[Mo_3OS_3(dtp)_4(im)]$.

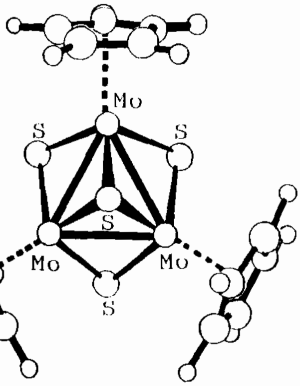

FIG. 9. Perspective view of $[Mo_3S_4Cp_3]^+$.

those having an Mo_3O_4 core (2.486–2.518 Å). However, this may be due to a greater variety of the ligands used in the Mo_3S_4 compounds. The cyclopentadienyl complex **1** (Table III) was the first compound reported to have an Mo_3S_4 core. The cation (Fig. 9) of compound **1** consists of three $Mo(h^5\text{-}C_5H_5)$ centers positioned at the vertices of an equilateral triangle. In the cyano compounds **2** and **3**, the Mo—C bonds trans to μ_3-S are slightly shorter than those of Mo—C (cis to μ_3-S). The coordination modes of **4** and **5** are the same of those of **7** (Table I) and **1** (Table II). Each molybdenum in **6** (Fig. 10) has three ligating nitrogen atoms. Water molecules only are coordinated to the Mo_3S_4 core in **7** (Fig. 11). Each molybdenum atom in compound **8** (Fig. 12) is five coordinated, again ignoring the Mo—Mo bonds, and the mean planes defined by each ligand are nearly perpendicular to the equilateral triangle of Mo(IV) atoms. It is interesting that there are three terminal and one bridging $S_2P(OEt)_2$ ligands in **9** (Fig. 13), **10**, and **11**. This ligand has been used extensively and to good effect by the group in Fuzho, China. There are two kinds of Mo—μ_2S and Mo—P distances, respectively, in **12**. Structure **14** can be derived from that of **13** by replacing one of the methanol ligands with a PEt_3 and changing the coordination environment at Mo(2). In compound **16**, two incorporating Mo_3S_4 clusters are bridged by an oxygen atom (with the Mo—O—Mo angle close to 135°) and two bridging bidentate pyrazole $BH(pz)_3^-$ anions. The latter is potentially a tridentate anion. Compound **16** has the longest Mo—Mo distance. The molecular structure of **17** has an idealized C_s symmetry. Other compounds (**18–31**) in this series are examples containing either the dtc or dtp ligands.

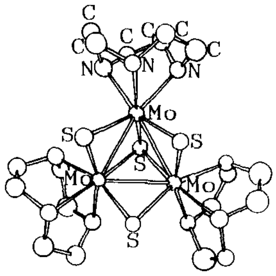

FIG. 10. Perspective view of $[Mo_3S_4([9]aneN_3)_3]^{4+}$.

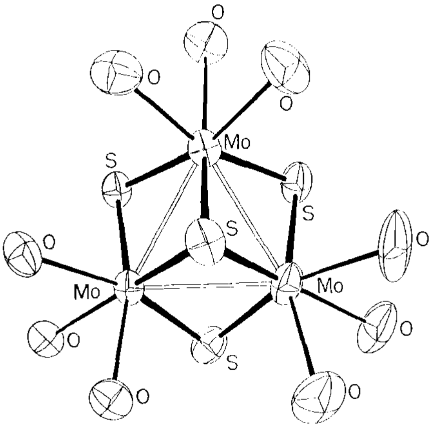

FIG. 11. Perspective view of $[Mo_3S_4(H_2O)_9]^{4+}$.

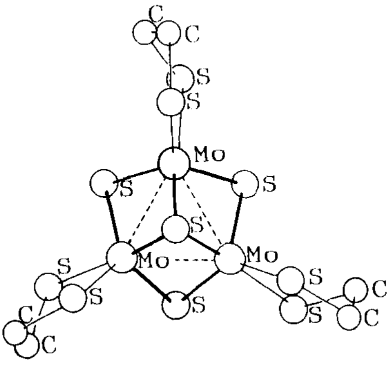

FIG. 12. Perspective view of $[Mo_3S_4(SCH_2CH_2S)_3]^{2-}$.

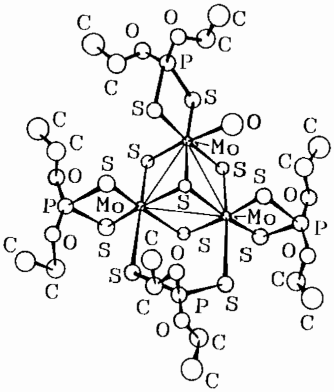

FIG. 13. Perspective view of $[Mo_3S_4(dtp)_4(H_2O)]$.

III. Cubane-Type Clusters with $Mo_4O_{4-n}S_n$ Cores

Although the series is incomplete, cubane-type clusters with $Mo_4O_{4-n}S_n$ ($n = 0, 3$, or 4) cores have been prepared and structures have been determined by X-ray crystallography. The results are summarized in Tables IV (*53–57*) and V (*58–71*). Contrary to the case of incomplete cubane-type clusters, wherein only the IV oxidation state of molybdenum appears, the oxidation state of molybdenum varies from VI to III. The total oxidation number of each Mo_4 cluster is indicated in the tables.

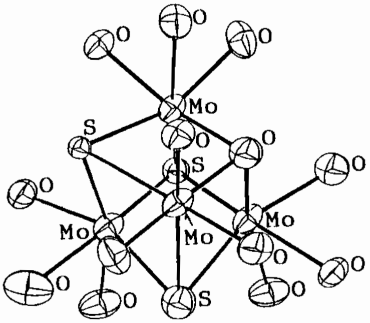

FIG. 14. Perspective view of $[Mo_4OS_3(H_2O)_{12}]^{5+}$.

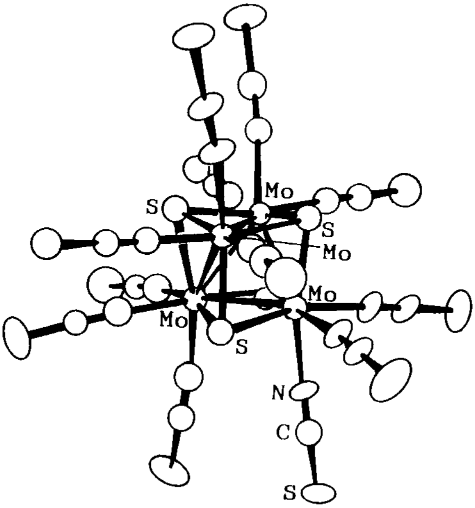

FIG. 15. Perspective view of $[Mo_4S_4(NCS)_{12}]^{6-}$.

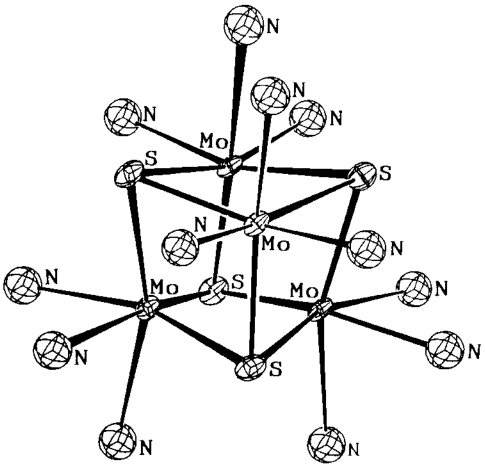

FIG. 16. Perspective view of $[Mo_4S_4(NH_3)_{12}]^{4+}$.

A. CUBANE-TYPE CLUSTERS WITH Mo_4O_4/Mo_4OS_3 CORES

Structural parameters for the compounds with Mo_4O_4 or Mo_4OS_3 cores are found in Table IV. No compounds with Mo_4O_3S or $Mo_4O_2S_2$ cores have been reported. Compared to the incomplete cubane-type compounds described above, only limited numbers of cubane-type compounds with oxo bridge(s) are known. Each molybdenum in compounds **1** and **2** has two terminal oxo ligands. X-Ray photoelectron spectroscopy (XPS) spectra show the oxidation states of the Mo, Rh, and Ir atoms to be VI, III, and III, respectively. The dimension of the cube in **3** may be compared with the corresponding distances for **1** and **2** in Table V. The Mo_4 units of **4** and **5** have crystallographic C_{3v} and approximate C_{3v} symmetry, respectively: the Mo_4 unit is a triangular pyramid and slant-edge lengths are shorter than basal-edge lengths, though an oxo ligand bridges the basal three molybdenum atoms. Compound **4** has three terminal and three bridging dtp ligands and **5** has four terminal and two bridging dtp ligands. The structure of the aqua complex of Mo_4OS_3, **6**, (Fig. 14) has been determined recently. Two groups of Mo—Mo distances are observed: the difference is large in compound **3** and small in compounds **4** and **5**.

B. CUBANE-TYPE CLUSTERS WITH Mo_4S_4 CORES

Structural parameters for the compounds with Mo_4S_4 cores are listed in Table V. In compounds **1**, **2**, and **3**, which have Mo_4 (+20) cores, the two Mo_2S_2 units are separated by more than 3.6 Å. The Mo_4 unit of compound **4** (Fig. 15) is a triangular pyramid, with slant-edge lengths of

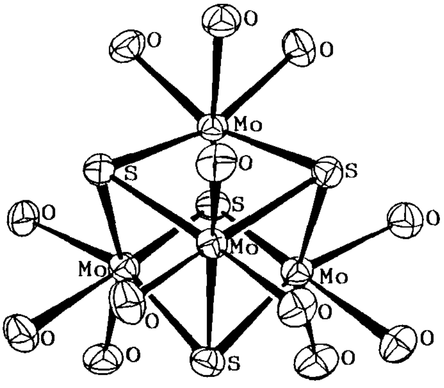

FIG. 17. Perspective view of $[Mo_4S_4(H_2O)_{12}]^{5+}$.

TABLE IV

STRUCTURAL PARAMETERS FOR CUBANE-TYPE COMPLEXES WITH $Mo_4O_{4-n}S_n$ CORES (n = 0 or 3)[a]

Compound	Mo — Mo	Mo — μ_3O	Mo — μ_3S	Mo — L	Ref.
(1) $[Mo_4O_4(O)_8(ORhC_5Me_5)_4] \cdot 2H_2O$, $Mo_4(+24)$	2.359(2)	1.967(8)[b] 2.340[2][c]	—	1.705[11], O_t 1.901(8), O (Rh) 3.225[7], Rh	*53*
(2) $[Mo_4O_4(O)_8(OIrC_5Me_5)_4]$, Mo_4 (+24)	2.343(5)	1.96(2)[b] 2.35[3][c]	—	1.71[1], O_t 1.89(2), O (Ir) 3.257(1), Ir	*53*
(3) $[Mo_4O_4(O)_4(OOPMe_2)_2(OSPMe_2)_2]$, $Mo_4(+20)$	2.635[d] 3.42[d]	1.976[b] 2.384[c]	—	1.636, O_t 2.081, O 2.490, S	*54*
(4) $[Mo_4OS_3(dtp)_6] \cdot 3CH_3CN$, $Mo_4(+14)$	2.831(1)[e] 2.700(1)[e]	2.036(5)	2.356[30]	2.556[19], S	*55*
(5) $[Mo_4OS_3(dtp)_6]$, $Mo_4(+14)$	2.817[5][e] 2.726[46][e]	2.005[11]	2.344[24]	2.562[29], S	*56*
(6) $[Mo_4OS_3(H_2O)_{12}](pts)_5 \cdot 14H_2O$, $Mo_4(+13)$	2.737[13]	1.96[7]	2.361[18]	2.184[15], O	*57*

[a] See footnote *a*, Table I.

[b] Cis to O_t.

[c] Trans to O_t.

[d] Two short and four long distances.

[e] Three long and three short distances.

2.791(1) Å and basal-edge lengths of 2.869(1) Å. The six Mo—Mo distances can be divided into two sets in the Mo_4 (+14) compounds: three long and three short for **4** and two short and four long for **5**, **6**, **11**, and **14**, though the difference between the sets is not so large as is found for the Mo_4 (+20) compounds. Four terminal and two bridging $S_2CN(C_2H_5)_2$ ligands exist in **5**. Likewise, the presence of four terminal and two bridging S_2PEt_2 ligands can be seen in **6**. The Mo—Mo distances of the Mo_4 (+12) compounds fall in a narrow range, as seen in compounds **8** (Fig. 16), **9**, **13**, and **16**. The range of the Mo—Mo distance in **7** (Fig. 17) is smaller than that of compound **12**, but is a little larger than those of Mo_4 (+12) compounds. As far as compound **10** is concerned, the situation is complicated: if the charge of the nitrogen oxide is estimated (*72*) to be −1 from the observed ν(NO) = 1450 cm^{-1}, the oxidation number of Mo_4 is calculated to be +12; however, the observed Mo—Mo distance indicates that the oxidation number of Mo_4 is +20. If the +1 charge of NO is assigned to NO from the Mo—N—O linearity, the charge of Mo_4 is calculated to be +4, which is unlikely. The two sets of compounds, $[Mo_4S_4(edta)_2]^{2-/3-/4-}$ [**11**, **12** (Fig. 18), and **13**, respectively] and $[Mo_4S_4(C_5H_4Pr^i)_4]^{0/+1/+2}$ (**14**, **15**, and **16**, respectively), are the only cases so

TABLE V

STRUCTURAL PARAMETERS FOR CUBANE-TYPE COMPLEXES WITH Mo_4S_4 CORES[a]

Compound	Mo—Mo	Mo—μ_3S	Mo—L	Ref.
(1) $[Mo_4S_4(NC_6H_4CH_3)_4(dtp)_4]$, $Mo_4(+20)$	2.862[1][b] 3.69[4][b]	2.366[5][c] 2.704[12][c]	1.723[19], N[d] 2.552[13], S	*58*
(2) $[Mo_4S_4(O)_2(NC_6H_5)_2(dtp)_4]$, $Mo_4(+20)$	2.844[2][b] 3.85[4][b]	2.359[7][c] 2.843[55][c]	1.71[2], N 1.68[2], O 2.532[9], S	*59*
(3) $[Mo_4S_4(NC_6H_4CH_3)_4(S_2CN(i-C_4H_9)_2)_4]$, $Mo_4(+20)$	2.881[3][b] 3.66[4][b]	2.382[15][c] 2.687[25][c]	1.72[1], N 2.524[24], S	*60*
(4) $(NH_4)_6[Mo_4S_4(NCS)_{12}] \cdot 10H_2O$, $Mo_4(+14)$	2.791(1)[e] 2.869(1)[e]	—	—	*61*
(5) $[Mo_4S_4(Et_2dtc)_6] \cdot 2CHCl_3$, $Mo_4(+14)$	2.732(5)[b] 2.861[6][b]	2.35[2]	2.52[3], S	*62, 63*
(6) $[Mo_4S_4(S_2PEt_2)_6]$, $Mo_4(+14)$	2.786[1][b] 2.879[1][b]	2.354[12]	2.575[12], S	*64*
(7) $[Mo_4S_4(H_2O)_{12}](pts)_5 \cdot 14H_2O$, $Mo_4(+13)$	2.802[18]	2.349[4]	2.188[11], O	*57*
(8) $[Mo_4S_4(NH_3)_{12}]Cl_4 \cdot 7H_2O$, $Mo_4(+12)$	2.797[7]	2.370[5]	2.336[15], N	*65*
(9) $K_8[Mo_4S_4(CN)_{12}] \cdot 4H_2O$, $Mo_4(+12)$	2.854[1]	2.381[1]	2.190[1], C	*66*
(10) $K_8[Mo_4S_4(NO)_4(CN)_8] \cdot 4H_2O$, $Mo_4(+12$ or $+20)$	2.99[3][b] 3.67[4][b]	2.76[2] 2.35[2]	2.21[2], CN 1.76[2], NO[f]	*67*
(11) $Na_2[Mo_4S_4(edta)_2] \cdot 6.5H_2O$, $Mo_4(+14)$	2.761[28][b] 2.860[14][b]	2.355[24]	2.273[14], N 2.095[11], O	*68*
(12) $Ca_{1.5}[Mo_4S_4(edta)_2] \cdot 13H_2O$, $Mo_4(+13)$	2.780[19][g] 2.863[25][g]	2.356[6]	2.289[8], N 2.141[9], O	*69*
(13) $Mg_2[Mo_4S_4(edta)_2] \cdot 22H_2O$, Mo4(+12)	2.783[11] —	2.355[4]	2.279[3], N 2.179[16], O	*68*
(14) $[Mo_4S_4(C_5H_4Pr^i)_4](I_3^{-1})_2$, $Mo_4(+14)$	2.805[21][g] 2.885[19][g]	2.343[2]	2.331[6], Cp	*70*
(15) $[Mo_4S_4(C_5H_4Pr^i)_4]BF_4$, $Mo_4(+13)$	2.894[8]	2.343[3]	2.348[6], Cp	*70*
(16) $[Mo_4S_4(C_5H_4Pr^i)_4]$, $Mo_4(+12)$	2.904[7]	2.344[2]	2.356[1], Cp	*70*
(17) $[(H_2O)_9Mo_3S_4MoS_4Mo_3(H_2O)_9](pts)_8 \cdot 18H_2O$	2.770[4][h] 3.046[18][h]	2.334[13][i] 2.452[9][i]	2.178[18], O	*71*

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[a] See footnote *a*, Table I.

[b] Two short and four long distances.

[c] Eight short and four long distances.

[d] Mo≡N (triple bond).

[e] Three short and three long distances.

[f] The angles Mo—N—O = 166.3(5)° and 178.2(6)°.

[g] Four short and two long distances.

[h] Three short and three long distances per half of the core.

[i] Nine short and three long distances per half of the core.

far reported to form a set of consecutive oxidation numbers of molybdenum. The mean Mo—Mo distance in the former decreases as the oxidation number of Mo_4 decreases, whereas that in the latter increases. Data on the double-cubane-type compound, **17** (Fig. 19) are also included in the table.

IV. Incomplete Cubane-Type $W_3O_{4-n}S_n$ Cores

As seen in Table VI, the incomplete cubane-type compounds with $W_3O_{4-n}S_n$ cores are not as well known as is the case for the corresponding molybdenum analogs. The oxidation state of tungsten in the table is in all cases IV. A particularly important finding is that the dimensions of the tungsten compounds are nearly the same as those of the molybdenum analogs.

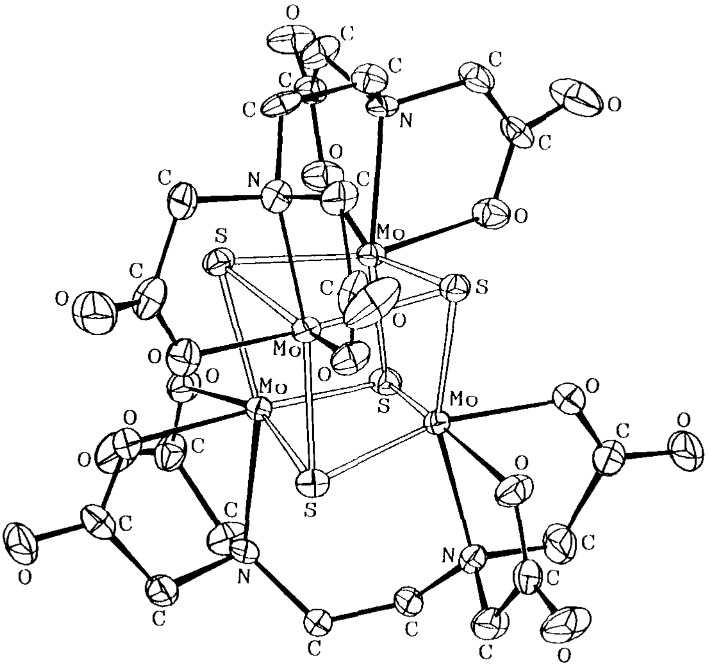

FIG. 18. Perspective view of $[Mo_4S_4(edta)_2]^{3-}$.

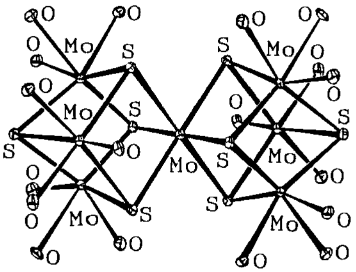

FIG. 19. Perspective view of $[(H_2O)_9Mo_3S_4MoS_4Mo_3(H_2O)_9]^{8+}$.

A. INCOMPLETE CUBANE-TYPE CLUSTERS WITH $W_3O_4/W_3O_3S/W_3O_2S_2/W_3OS_3$ CORES

Structural parameters for the compounds with W_3O_4, W_3O_3S, $W_3O_2S_2$, and W_3OS_3 cores are found in Table VI (*73–78*). The W—W distance of compounds incorporating the W_3O_4 cluster appears slightly longer than the corresponding distance in the molybdenum analogs. Compound 1 was the first compound having a W_3O_4 core for which the structure was determined. The structure of **2** (Fig. 20) can be compared with compound **6** in Table III. Compounds **4** (Fig. 21), **5, 6,** and **7** have a μ_3-S group. No μ_3-O trimeric compounds of tungsten with μ_2-S ligands have been reported, in contrast to the reported cases with Mo_3OS_3 cores.

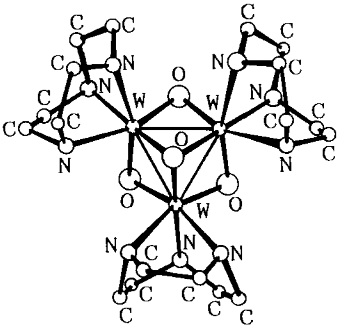

FIG. 20. Perspective view of $[W_3O_4([9]aneN_3)_3]^{4+}$.

TABLE VI

STRUCTURAL PARAMETERS FOR INCOMPLETE CUBANE-TYPE COMPLEXES WITH $W_3O_{4-n}S_n$ CORES ($n = 0 - 3$)[a]

Compound	W—W[b]	W—μ_3X[c]	W—μ_2Y[c]	W—L	Ref.
(1) $(NH_4)_5[W_3O_4F_9] \cdot NH_4F \cdot H_2O$	2.514[1]	2.07[1]	1.95[3]	2.03[4], F	*73*
(2) $[W_3O_4([9]aneN_3)_3][ZnBr_4]_2$	2.528[12]	2.10[4]	1.92[3]	2.22[4], N	*74*
(3) $(NH_4)_2((C_2H_5)_4N)_3[W_3O_4(NCS)_9] \cdot nH_2O$	2.534	2.039	1.911	2.110, N	*74a*
(4) $[W_3O_3S(NCS)_9]^{5-}$	2.612(6), SO	2.34(2), S	1.98(2), S	—	75
(5) $K_2[W_3O_3S(Hnta)_3] \cdot 9H_2O$	2.596(2), SO	2.380(8), S	1.949[3], S	2.096[32], O 2.236(20), N	*76*
(6) $Ba[W_3O_2S_2(Hnta)_3] \cdot 9H_2O$	2.612[7], SO 2.684(2), SS	2.375[8]	2.005[30], O 2.275[16], S	2.274[12], N 2.093[21], O	77
(7) $K_2[W_3OS_3(Hnta)_3] \cdot KCl \cdot 7H_2O$	2.620(1), SO 2.724[6], SS	2.344[8]	1.952[6], O 2.315[5], S	2.089[24], O 2.273[20], N	*78*

[a] See footnote *a*, Table I.

[b] The μ_3X then the μ_2Y atoms between the two W atoms follow the numeral.

[c] The μ_3X or μ_2Y atom follows the numeral.

B. INCOMPLETE CUBANE-TYPE CLUSTERS WITH W_3S_4 CORES

Structural parameters for the compounds with W_3S_4 are found in Table VII (*47, 79–84*). Compound 1 (Fig. 22) was the first to be prepared having a sulfur bridge in the triangle W_3 core. Compounds **2** (Fig. 23) and **3** can be compared with the corresponding molybdenum compounds, **7** and **12,** in Table III, respectively. In the case of compound **6,** each tungsten atom is coordinated by two μ_2-S, a μ_3-S, and a dtp. There are some differences among the W—W bond lengths and the W—μ_3S—W and W—μ_2S—W angles; these may be due to the effect of the acetate bridging ligand. Structure **7** is similar to structure **6.**

V. Cubane-Type Mixed-Metal Clusters with Mo_3MS_4 Cores

There are three kinds of cubane-type cores in this series of complexes (Fig. 24). There are the single cubane-type, Mo_3MS_4, the double cubane-type, $Mo_3S_4MMS_4Mo_3$, and the sandwich cubane-type, $Mo_3S_4MS_4Mo_3$. Structural parameters are collected in Table VIII (*34, 85–92*). Formal charges of the cores are noted after each compound in the table.

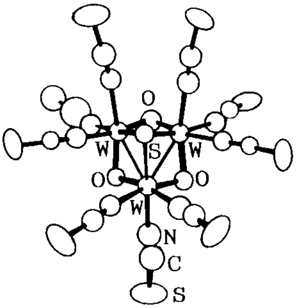

FIG. 21. Perspective view of $[W_3O_3S(NCS)_9]^{5-}$.

Compounds **1** (Fig. 25) to **7** are of the single cubane-type, and compound **8** (Fig. 26) is of the double cubane-type. Compounds **9** and **10** (Fig. 27) are of the sandwich cubane-type, wherein a tin or mercury atom is bonded to two incomplete cubane-type Mo_3S_4 corese, and are common to both cubes that are generated.

Although no distinct differences are found for the Mo—Mo distances in the mixed-metal clusters except for **5**, short (**1**, **2**, **3**, and **8**), and long (**6**, **7**, **9**, and **10**) Mo—M distances are observed. The first group has transition elements M in the cores, whereas the second group has nontransition elements M in the cores. The Mo—Cu distances in **3** and **8** are slightly longer than those of Mo—Fe and Mo—Ni in **1** and **2**, respectively.

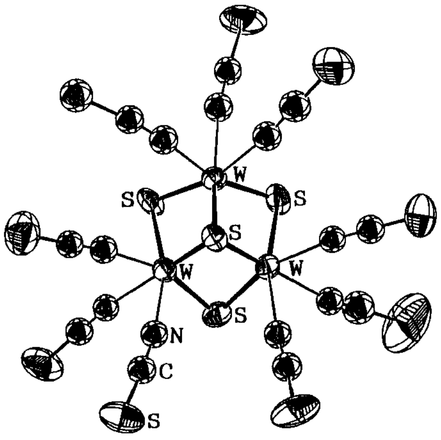

FIG. 22. Perspective view of $[W_3S_4(NCS)_9]^{5-}$.

TABLE VII

STRUCTURAL PARAMETERS FOR INCOMPLETE CUBANE-TYPE COMPLEXES WITH W_3S_4 CORES[a]

	Compound W—W	W—μ_3S	W—μ_2S	W—L	Ref.
(1) $(bpyH)_5[W_3S_4(NCS)_9] \cdot 3H_2O$	2.767[4]	2.363[12]	2.310[7]	2.153[32], N	*79*
(2) $[W_3S_4(H_2O)_9](pts)_4 \cdot 7H_2O$	2.723[15]	2.351[3]	2.283[5]	2.176[17], O	*80*
(3) $[W_3S_4Cl_3(dmpe)_3]PF_6 \cdot H_2O$	2.755(1)	2.382(5)	2.308[14][b]	2.595(3), P[b] 2.520(4), P[c] 2.488(4), C1	*47, 81*
(4) $[W_3S_4Cl_3(depe)_3][PF_6]$	2.776[3]	2.368[15]	2.305[17]	2.468[7], C1 2.617[6], P[b] 2.528[6], P[c]	*47*
(5) $[W_3S_4H_3(dmpe)_3][BPh_4]$	2.751[4]	2.354[2]	2.335[9]	2.516[6], P[b] 2.476[9], P[c]	*47*
(6) $[W_3S_4(dtp)_3(\mu_2 - O_2CCH_3)(py)] \cdot (0.5HCON(CH_3)_2)$	2.6835(5)[d] 2.748[7]	2.353[2]	2.306[11]	2.541[24], S 2.209[0], O 2.329(6), N	*82*
(7) $[W_3S_4(dtp)_3(\mu_2\text{-}O_2CCH_3)(py)]$	2.6728(6)[d] 2.745[7]	2.343[3]	2.298[6]	2.538[26], S 2.174[33], O 2.390[8], N	*83*
(8) $[(NH_4)_3(HSO_3)][W_3S_4(S_4)_3(H_2O)_3]$	2.784(1)	—	2.283[30]	2.503[51], S 2.335(7), O	*84*

[a] See footnote *a*, Table I.

[b] Trans to μ_2S.

[c] Trans to μ_3S.

[d] Bridging CH_3CO_2 between two W atoms.

VI. Note on Preparation of Clusters

Preparation of the clusters described above is treated briefly here, although a thorough coverage of the literature is not intended.

A. COMPOUNDS WITH Mo_3O_4 CORES

The Mo(IV) aqua ion was first reported by Souchay *et al.* as a monomeric species in 1966 (*93*), and the $Mo_3O_4^{4+}$ core structure has been confirmed by single-crystal X-ray structure analyses, as described in this review, ^{95}Mo NMR (*94*), EXAFS structure analysis (*95*), and ^{18}O-labeling experiments (*96*), after the appearance of many contradictory reports (*97*). Information on the reduction products of the Mo(IV) aqua ion is also available (*98*), Richens and Sykes have summarized the preparation of the different aqua ions of molybdenum in oxidation states II to V (*99*).

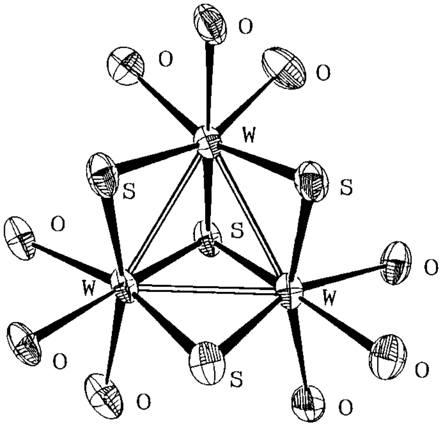

FIG. 23. Perspective view of $[W_3S_4(H_2O)_9]^{4+}$.

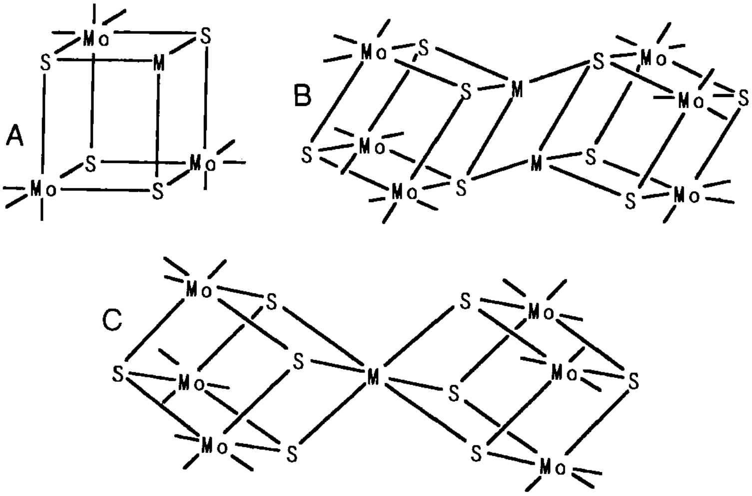

FIG. 24. Mixed-metal cubane-type cores. (A) Single cubane-type. (B) Double cubane-type. (C) Sandwich cubane-type.

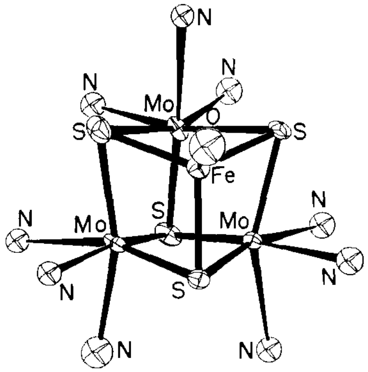

FIG. 25. Perspective view of $[Mo_3FeS_4(NH_3)_9(H_2O)]^{4+}$.

B. COMPOUNDS WITH $Mo_3O_{4-n}S_n$ (n = 1–4) CORES

Two methods are useful for the preparation of compounds with Mo_3O_3S: (1) reduction of $Mo_2O_3S^{2+}$ with $NaBH_4$ (*30*) and (2) reduction of $Mo_2O_3S^{2+}$ with $[MoCl_6]^{3-}$ (*100*). Compounds **1** and **2** in Table II were prepared from the aqua ion $Mo_3O_3S(aq)^{4+}$ and the corresponding ligands.

Some preparative methods of the sulfur-bridged incomplete cubane-type aqua ion $Mo_3S_4(aq)^{4+}$ have been reported: (1) reduction of $[Mo_2O_2S_2(cys)_2]^{2-}$ with $NaBH_4$ (*38*), (2) reaction of $Mo(CO)_6$ with Na_2S (*49*), and (3) electrolysis of $[Mo_2O_2S_2(cys)_2]^{2-}$ (*100*).

Compound **9** in Table III is prepared from $MoCl_3 \cdot 3H_2O$, P_2O_5, and H_2S (*34*).

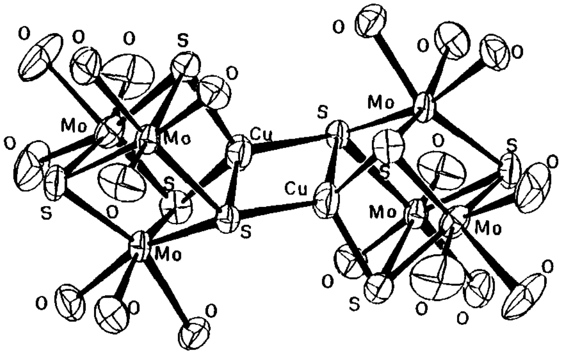

FIG. 26. Perspective view of $[(H_2O)_9Mo_3S_4CuCuS_4Mo_3(H_2O)_9]^{8+}$.

TABLE VIII

CUBANE-TYPE MIXED-METAL CLUSTERS WITH Mo_3MS_4 CORES[a]

	Compound Mo—Mo	Mo—M	M—μ_3S	Mo—L	M—L	Ref.
(1) $[Mo_3FeS_4(NH_3)_9(H_2O)]Cl_4$ (4+)	2.794[18]	2.683[10]	2.249[7]	2.269[34], N	2.039[0], O	*85*
(2) $[Mo_3NiS_4(H_2O)_{10}](pts)_4 \cdot 7H_2O$ (4+)	2.755[10]	2.641[9]	2.204[5]	2.21[1], O	1.97(1), O	*86*
(3) $[Mo_3CuS_4(dtp)_3(CH_3COO)(I)(dmf)]$ (5+)	2.770(2) 2.749(2) 2.679(2)[b]	2.849[39]	2.294[15]	2.538[29], S 2.214(13), O[c] 2.182[1], O[d]	2.454, I	*87*
(4) $[Mo_3CuS_4(dtp)_3(CH_3COO)(I)(H_2O)]$ (5+)	2.741[43]	—	—	2.527, S[e] 2.295,O	—	*34*
(5) $[Mo_3WS_4(Et_2PS_2)_6]$[f] (6+)	2.752(1)[g] 2.961(1)	—	2.357[18]	2.576[13], S	—	*88*
(6) $[Mo_3SbS_4(dtp)_4(Cl_3)(EtOH)]EtOH$[h] (7+)	2.735[12]	3.822[9]	2.775[36]	2.560[21], S[i] 2.576[9], S[j] 2.243(20), O	2.775[36], Cl	*89*
(7) $[Mo_3SbS_4(dtp)_4(Cl_3)(oxazole)]$[h] (7+)	2.741[12]	3.825[19]	2.780[27]	2.553[37], S[h] 2.551(6), S[j] 2.271(12), N	2.383[18], Cl	*89*
(8) $[(H_2O)_9Mo_3S_4CuCuS_4Mo_3(H_2O)_9](pts)_8 \cdot 20H_2O$[k] (8+)	2.730[8]	2.886[93]	2.30[13]	2.178[22], O	—	*90*
(9) $[(H_2O)_9Mo_3S_4SnS_4Mo_3(H_2O)_9](pts)_8 \cdot 26H_2O$ (8+)	2.689[7]	3.712[37]	2.626[28]	2.177[21], O	—	*91*
(10) $[(H_2O)_9Mo_3S_4HgS_4Mo_3(H_2O)_9](pts)_8 \cdot 20H_2O$ (8+)	2.713[9]	3.833[93]	2.84[12]	2.172[27], O	—	*92*

[a] M represents metals; see footnote *a*, Table I.

[b] Acetato bridge between two Mo atoms.

[c] O atom of dmf.

[d] O atom of CH_3COO.

[e] Terminal.

[f] Three Mo atoms and one W atom are statistically disordered; three bridging and three terminal $Et_2PS_2^-$ exist.

[g] A bridging $Et_2PS_2^-$ exists between metals.

[h] Three terminal and a bridging dtp ligand exist.

[i] S atoms of the terminal dtp ligands.

[j] S atoms of the bridging dtp ligands.

[k] Cu—Cu′ = 2.424(3) Å.

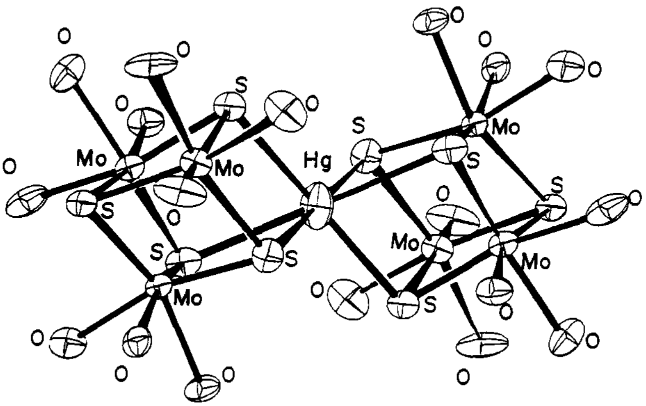

FIG. 27. Perspective view of $[(H_2O)_9Mo_3S_4HgS_4Mo_3(H_2O)_9]^{8+}$.

C. Compounds with Mo_4S_4 Cores

Compounds **11, 12,** and **13** in Table V were prepared by the reduction of $[Mo_2O_2S_2(edta)_2]^{2-}$ with $NaBH_4$ (*101*). Compounds **14, 15,** and **16** were prepared from $[Mo_2(\mu\text{-}Cl)_4(\eta\text{-}C_5H_4Pr^i)_2]$.

D. Compounds with W_3S_4 Cores

Compound **1** in Table VII was prepared by the reduction of $(NH_4)_2WS_4$ with $NaBH_4$. Compounds **3** and **4** in Table VII were prepared from WCl_4, NaHS, and the corresponding ligand, respectively. Compound **8** in Table VII was prepared from tungsten metal, sulfur, bromine, and $(NH_4)_2S_2$. Reaction of **8** with concentrated HCl and HBr gave $W_3S_4(aq)^{4+}$ by the elimination of the $S_4{}^{2-}$ ligand.

E. Compounds with Mo_3MS_4 Cores

Compounds **1, 2, 8, 9,** and **10** in Table VIII were obtained by the reaction of the aqua ion $Mo_3S_4(aq)^{4+}$ in dilute HCl with corresponding metals. Compound **5** in Table VIII was prepared by the reaction of $Mo_3S_4(Et_2PS_2)_4$ with $W(CO)_3(CH_3CN)_3$. Compounds **3, 4, 6,** and **7** in Table VIII were prepared from $[Mo_3S_4(dtp)_4L]$ (L = H_2O or C_3H_3ON) and CuI (for **3** and **4**) or $SbCl_3$ (for **6** and **7**).

Abbreviations

ox	oxalate anion (2 −), $C_2O_4^{2-}$
nta	nitrilotriacetate anion (3 −), $N(CH_2CO_2)_3^{3-}$
edta	ethylenediaminetatraactate anion (4 −), $(O_2C)_2N(CH_2)_2N(CO_2)_2^{4-}$
ida	iminodiacetate anion (2 −), $NH\ (CO_2)_2^{2-}$
cys	L-cysteine anion (2 −), $SCH_2CH(NH_2)CO_2^{2-}$
mida	methyliminodiacetate anion (2 −), $NCH_3\ (CO_2)_2^{2-}$
pts	*para*-toluensulfonate anion (1 −), $CH_3C_6H_4SO_3^-$
[9]aneN_3	1,4,7-triazacyclononane, $\{NH(CH_2CH_2)\}_3$
dtc	diethyl dithiocarbamate anion (1 −), $Et_2NCS_2^-$
dtp	diethyl dithiophospahte anion (1 −), $S_2P(OEt)_2^-$
dmf	dimethylformamide, $HCON(CH_3)_2$
Him	imidazole, $C_3H_4N_2$
oxazole	C_3H_3NO
HB(pz)$_3$	tris (pyrazoborate)(1 −), $BH(C_3H_3N_2)_3^-$
Hpz	pyrazole, $C_3H_4N_2$
dmpe	1,2-bis (dimethylphosphine) ethane, $Me_2PCH_2CH_2PMe_2$
depe	1,2-bis (diethylphosphine) ethane, $Et_2PCH_2CH_2PEt_2$

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