$$t\text{-DCE}_3 \xrightarrow{k^c} c\text{-DCE} \tag{7}$$

$$t\text{-DCE}_3 \xrightarrow{k_t} t\text{-DCE} \tag{8}$$

$$A_3 \xrightarrow{k_d} A_0 \tag{9}$$

Since the intercept of Figure 1 is much larger than one, steps 3, 4, and 5 are included in order to provide a path for formation of oxetane *which does not involve singlet acetone as the chemically active species.*

Using the values of $1/a = 13.2$ and $k_{st}/ak_1 = 2.6$, a value of $k_1/k_{st} = 5$ is obtained. The same ratio is available from a Stern-Volmer analysis of the quenching of acetone fluorescence by t-DCE, which also gave a value of ~5; *i.e.*, the latter result implies that the major mode of quenching acetone fluorescence is complex formation.[11,12]

(11) L. A. Singer and G. A. Davis, *J. Am. Chem. Soc.*, **89**, 158 (1967), have described the cycloaddition reaction of fluorenone and ketenimines which *is quenched* by addition of high concentrations of ketenimine.

(12) For other recent examples of singlet quenching see L. M. Stephenson, D. G. Whitten, G. F. Vesley, and G. S. Hammond, *ibid.*, **88**, 3665 (1966); H. E. Zimmerman and J. S. Swenton, *ibid.*, **89**, 906 (1967); S. D. Andrews and A. C. Day, *Chem. Commun.*, 477 (1967).

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Received March 4, 1968

Refined Molecular Structure of the Heptamolybdate and Hexamolybdotellurate Ions[1]

Sir:

As part of a continuing program intended to provide detailed information concerning the molecular structures of the class of inorganic oxo compounds of V, Nb, Ta, Mo, and W known as the heteropoly and isopoly complexes, the methods of three-dimensional X-ray diffraction have now been applied to two polymolybdate compounds. The two new crystal structure studies have revealed the details of the structures of the heptamolybdate ion $[Mo_7O_{24}]^{6-}$ and the hexamolybdotellurate ion $[TeMo_6O_{24}]^{6-}$. The salient chemical results of these studies are reported here, but the details of the associated crystal structure analyses will be published in another place.

In 1950 Lindqvist[2] reported his study of the crystal structure of ammonium heptamolybdate (paramolybdate), $(NH_4)_6[Mo_7O_{24}]\cdot 4H_2O$, in which he determined the locations of seven independent Mo atoms in the crystal. Lindqvist did not resolve the oxygen atoms, but he proposed the most probable configuration of the whole complex ion on the basis of reasonable, assumed Mo–O distances and octahedral edge sharing. The unit-cell parameters of the crystal were originally reported by Sturdivant[3] as follows: monoclinic with a = 8.399 Å, b = 36.198 Å, c = 10.485 Å, β = 116° 0′; space group $P2_1/c$ (Z = 4). For this compound 8200 independent reflection data were collected by visual estimate of intensities on multiple-film Weissenberg patterns made with Mo $K\alpha$ radiation. In a full-matrix, least-squares analysis of these data, 176 parameters were varied, leading to a reliability factor of R = 0.096. The initial model was derived from a three-dimensional electron density synthesis, for which the Fourier phases were found from a structure-factor computation based only on the Mo atom positions as given by Lindqvist. The electron density map revealed all the atoms in the structure except hydrogen atoms, and the least-squares refinement converged rapidly in a completely straightforward way. Lindqvist's proposal for the configuration was fully confirmed. The heptamolybdate molecule ion has no symmetry that is required by the crystal symmetry, but conforms closely to the point-group symmetry 2mm (C_{2v}), which presumably is that assumed by the free ion in solution. The complex ion is shown in Figure 1 with the different types of atoms labeled. The averaged bond lengths and the maximum variation of the individual bond lengths in the crystal (which are determined with a standard error of 0.01 Å) are listed in Table I.

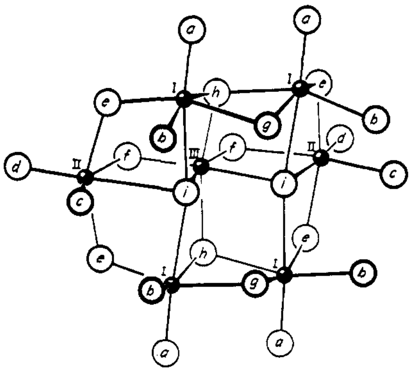

Figure 1. Oblique view of the heptamolybdate molecule ion $[Mo_7O_{24}]^{6-}$. Atoms are labeled according to the ideal 2mm symmetry (a horizontal mirror plane contains Mo_{II}, Mo_{III}, O_c, O_d, O_f and O_i; a vertical mirror plane contains Mo_{III}, O_g, and O_h, and a twofold axis lies at their intersection).

Table I. Bond Lengths in the Heptamolybdate Complex Ion $[Mo_7O_{24}]^{6-}$, Averaged over the Ideal Molecular Symmetry 2mm (see Figure 1)

Bonded atoms	No. of bonds in molecule	Max var in crystal, Å	Av bond length, Å
Mo_I–O_a	4	0.015	1.710
O_b	4	0.028	1.728
O_e	4	0.027	1.966
O_g	4	0.034	1.945
O_h	4	0.012	2.179
Mo_{II}–O_c	2	0.008	1.716
O_d	2	0.012	1.741
O_e	4	0.018	1.915
O_f	2	0.078	2.415
O_i	2	0.010	2.155
Mo_{III}–O_f	2	0.007	1.754
O_h	2	0.012	1.903
O_i	2	0.006	2.264
Mo_I–Mo_I	2	0.015	3.257
Mo_I–Mo_{II}	4	0.031	3.206
Mo_I–Mo_{III}	4	0.029	3.405
Mo_{II}–Mo_{III}	2	0.048	3.434

In 1948 a brief note[4] was published describing the results of a preliminary study of the hexamolybdotellurate complex ion as contained in the orthorhombic

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(1) Publication approved by the Director, U. S. Geological Survey.

(2) I. Lindqvist, *Arkiv Kemi*, **2**, 325 (1950).

(3) J. H. Sturdivant, *J. Am. Chem. Soc.*, **59**, 630 (1937).

(4) H. T. Evans, Jr., *ibid.*, **70**, 1291 (1948).

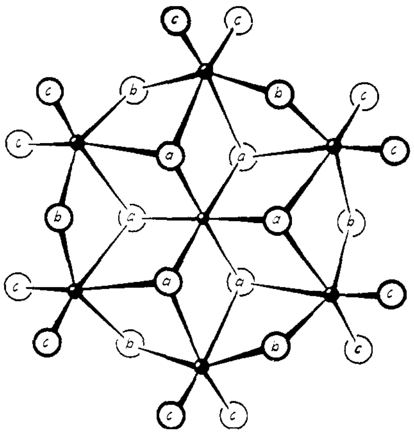

Figure 2. The hexamolybdotellurate complex ion $[TeMo_6O_{24}]^{6-}$, viewed along the trigonal axis through Te at the center. Atoms are labeled according to the ideal $\bar{3}m2$ symmetry (mirror planes viewed on edge pass through O_b–O_a–Te–O_a–O_b, and twofold axes pass through Mo–Te–Mo).

crystals $(NH_4)_6[TeMo_6O_{24}]\cdot 7H_2O$ and $K_6[TeMo_6O_{24}]\cdot 7H_2O$. Again only the heavy metal atoms were located directly and were found to be consistent with a flat structure containing seven octahedra, first proposed by Anderson.[5] A complete resolution has now been obtained of this complex ion as it occurs in the monoclinic compound $(NH_4)_6[TeMo_6O_{24}]\cdot Te(OH)_6\cdot 7H_2O$, in which it forms a crystal complex with telluric acid. The unit cell of the crystal conforms to the space group A2/a (or Aa) and has a = 21.353 Å, b = 9.950 Å, c = 18.757 Å, and β = 115° 37′; 5050 independent reflection data were collected for this crystal by visual estimate of intensities on multiple-film Weissenberg patterns made with Mo Kα radiation. The location of the Te atoms on symmetry centers in the space group A2/a made the structure analysis a trivial matter. A total of 114 parameters were varied in the full-matrix, least-squares analysis, and the final reliability factor is R = 0.100. The configuration of the hexamolybdotellurate ion previously proposed was fully confirmed, and individual bond lengths were determined with a standard error of 0.01 Å. The symmetry of the hexamolybdotellurate molecule ion conforms closely to $\bar{3}m$ (D_{3d}), which presumably represents the true symmetry of the free ion in solution. The complex ion is shown in Figure 2 as seen along the trigonal axis. The bond lengths averaged over the ideal symmetry are given in Table II.

Table II. Bond Lengths in the Hexamolybdotellurate Complex Ion $[TeMo_6O_{24}]^{6-}$, Averaged over the Ideal Molecular Symmetry $\bar{3}m$ (see Figure 2)

Bonded atoms	No. of bonds in molecule	Max var in crystal, Å	Av bond length, Å
Te–O_a	6	0.005	1.938
Mo–O_a	12	0.032	2.299
Mo–O_b	12	0.046	1.943
Mo–O_c	12	0.029	1.714
Te–Mo	6	0.016	3.299
Mo–Mo	6	0.040	3.299

In the crystal, the complex ion is joined to the telluric acid molecule only through hydrogen bonds. The telluric acid molecule $Te(OH)_6$ is a nearly regular octahedron, with an average Te–OH bond length of 1.910 Å.

Recently Perloff[6] completed a very precise crystal structure analysis of the triclinic compound $Na_3[H_6CrMo_6O_{24}]\cdot 8H_2O$, using counter-measured, three-dimensional data taken with Mo Kα radiation. He found that the hexahydrogen hexamolybdochromate(III) molecule ion has the same configuration as the hexamolybdotellurate ion. Furthermore, the corresponding averaged Mo–O bond lengths in the two complex ions are in agreement within 0.007 Å, although the central Cr–O bond length (1.975 Å) was found to be slightly longer than the Te–O bond.

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(5) J. S. Anderson, *Nature*, 140, 850 (1937).

(6) A. Perloff, Doctoral Dissertation, Georgetown University, Washington, D. C., 1966.

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Received January 22, 1968

Transition Metal Bonding through a Donor–Acceptor Interaction. $(C_5H_5)_2MoH_2\cdot Mo(CO)_5$ and Related Derivatives[1]

Sir:

We wish to report the synthesis and spectroscopic studies of a series of compounds containing metal-to-metal bonds formed through a donor–acceptor interaction.

The cyclopentadienyl hydrides Cp_2MoH_2 (Cp = C_5H_5) and Cp_2WH_2[2] have previously been shown to possess donor properties through a nonbonding electron pair on the metal atom to acceptor moieties such as the proton,[2] the boron halides,[3] and some group III alkyls.[4] We have now demonstrated that this donor property can also lead to strong interactions with transition metals that, in their complexes, exhibit *acceptor* power. The cyclopentadienyl hydrides can function as ligand, L, in complexes of the general formula $LM(CO)_5$ (M = Cr, Mo, W), which adducts are formed by displacement of tetrahydrofuran (THF) from the intermediate $(THF)M(CO)_5$.

To a solution of $(THF)M(CO)_5$ (M = Cr, Mo, or W)[5] is added 3 mmoles of $Cp_2M'H_2$ (M′ = Mo or W) in 20 ml of THF. After stirring at 50° for 15 min, the solvent is slowly stripped off and volatile residues are removed by sublimation under high vacuum at 50° for 10 hr. The remainder is dissolved in ether–hexane (1:1) and filtered, and the new compounds crystallize slowly at 0°, yield 25–40% based on $Cp_2M'H_2$.

Anal. Calcd for $C_{15}H_{12}Mo_2O_5$: C, 38.82; H, 2.61; Mo, 41.34; O, 17.24. Found: C, 38.93; H, 2.72; Mo, 41.46; O, 17.15.[6]

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(1) Research supported by U. S. Public Health Service Grant GM-14336.

(2) M. L. H. Green, J. A. McCleverty, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 4854 (1961).

(3) M. P. Johnson and D. F. Shriver, *J. Am. Chem. Soc.*, 88, 301 (1966).

(4) H. Brunner, P. C. Wailes, and H. D. Kaesz, *Inorg. Nucl. Chem. Letters*, 1, 125 (1965).

(5) Prepared by mercury lamp irradiation of 10 mmoles of $M(CO)_6$ in 70 ml of boiling THF until about 80% of the calculated volume of CO is evolved; see similar preparations of $LM(CO)_5$: W. Stohmeier, *Angew. Chem.*, 76, 873 (1964), and references cited therein such as D. P. Tate, J. M. Augl, and W. R. Knipple, *Inorg. Chem.*, 1, 434 (1962).