A study of some hexanuclear mixed-metal cluster compounds containing tantalum and molybdenum

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A STUDY OF SOME HEXANUCLEAR MIXED-METAL CLUSTER COMPOUNDS
CONTAINING TANTALUM AND MOLYBDENUM

by

John Louis Meyer

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<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>EXPERIMENTAL</td>
<td>21</td>
</tr>
<tr>
<td>RESULTS AND DISCUSSION</td>
<td>30</td>
</tr>
<tr>
<td>SUGGESTIONS FOR FUTURE WORK</td>
<td>61</td>
</tr>
<tr>
<td>BIBLIOGRAPHY</td>
<td>63</td>
</tr>
<tr>
<td>APPENDIX</td>
<td>70</td>
</tr>
</tbody>
</table>
INTRODUCTION

It is well known that many of the lower halides of niobium, tantalum, molybdenum, and tungsten contain hexanuclear clusters of metal atoms. The physical and chemical characterization of compounds containing these cluster species has been the objective of several recent studies.

The purpose of this investigation was to extend the chemistry of hexanuclear metal atom clusters by preparing some new mixed-metal cluster species and subsequently comparing some of the characteristics of the heteronuclear and homonuclear metal cluster compounds.

Review of Previous Work

The chemistry of compounds containing hexanuclear transition metal clusters has already been extensively reviewed (1-12). This review has therefore been limited to compounds of tantalum and molybdenum except for developments which are still unique to hexanuclear cluster compounds of niobium or tungsten.

Syntheses

The first report of a compound which probably contained a hexanuclear tantalum cluster was by Chabrié in 1907 (13). Chabrie had reduced tantalum pentachloride with sodium amalgam at red heat under water aspirator vacuum to a substance which was partially water soluble to a green solution. This green
solution could be evaporated to yield green crystals which analyzed as TaCl$_2$$\cdot$$2$H$_2$O.

Chapin (14) reported a similar reduction of tantalum pentabromide in 1910. He found that one-seventh of the bromide present in a solution of his reduction product could be replaced by hydroxide, chloride, or iodide, and that the molecular weight of the species in propanol or water solution was 2275. The green crystalline powder was thus formulated correctly for the first time as Ta$_6$Br$_{12}$Br$_2$$\cdot$7H$_2$O, and the derivatives were formulated as Ta$_4$Br$_{12}$X$_2$$\cdot$nH$_2$O where X = Cl, I, or OH. Also in 1910 van Haagen reported the hydrogen reduction of tantalum pentabromide to Ta$_6$Br$_{14}$ (15).

In 1922 Lindner et al. (16-19) initiated a series of studies of the lower halides of tungsten, molybdenum, and tantalum. These workers reduced tantalum pentachloride with lead, aluminum, or zinc under a nitrogen atmosphere and subsequently crystallized from aqueous solution a compound formulated as H[Ta$_3$Cl$_7$$\cdot$H$_2$O]$\cdot$3H$_2$O. Ruff and Thomas (20,21) contended the compound was not one of tantalum(II) but tantalum (III), and that the correct formulation was Ta$_3$Cl$_7$$\cdot$3H$_2$O.

Körösy (22) reported reduction of tantalum pentaiodide with tantalum to a water soluble product which gave a green solution and subsequently green crystals of a lower iodide of tantalum. However, Alexander and Fairbrother (23) heated tantalum pentaiodide and tantalum together and reported no
reaction up to 500° and only thermal decomposition of the pentaiodide at temperatures of 1000°-1500°.

More recently McCarley and Kuhn (24) have reported the preparation of Ta₆X₁₂X₂ (X = Cl, Br, or I) by aluminum reduction of the corresponding tantalum pentahalide. The reactions were carried out in sealed Vycor tubes which were tilted, placed in a temperature gradient furnace, and heated to 200°/400° for X = Cl, 280°/450° for X = Br, and 300°/475° for X = I. The lower end of the tube contained all the reactants and was heated to the higher temperature.

McCarley and Boatman (25) studied the tantalum pentabromide-tantalum and tantalum pentaiodide-tantalum phase diagrams and in addition to the tetrahalides reported compounds of the stoichiometry TaBr₂.₈₃, TaBr₂.₅, TaBr₂.₃₃, and TaI₂.₃₃. The compounds TaBr₂.₅, TaBr₂.₃₃, and TaI₂.₃₃ are undoubtedly Ta₆Br₁₂Br₃, Ta₆Br₁₂Br₂, and Ta₆I₁₂I₂ respectively. All of these compounds including TaBr₂.₈₃ dissolve in water to solutions which exhibit ultraviolet, visible, and near infrared absorption spectra characteristic of Ta₆X₁₂⁺ ions.

Schäfer et al. (2,26-28) have made use of transport reactions to prepare Ta₆Cl₁₂Cl₃, Ta₆Br₁₂Br₃, and Ta₆I₁₂I₂. This group also prepared Ta₆I₁₂I₂ by reducing tantalum pentaiodide with tantalum in a temperature gradient (29). The existence of any crystalline anhydrous chloride of tantalum lower than TaCl₂.₅ has been disputed by these workers (2,26). Schäfer and Bauer (30) did acknowledge the existence of the hydrate
McCarley et al. (31) oxidized aqueous solutions of Ta$_6$Cl$_{12}^{2+}$ and Ta$_6$Br$_{12}^{2+}$ with the corresponding halogen to Ta$_6$X$_{12}^{4+}$. McCarley and Espenson (32) reported the oxidation of aqueous Ta$_6$Cl$_{12}^{2+}$ to Ta$_6$Cl$_{12}^{3+}$ by iron(III) to be essentially quantitative while a large excess of iron(III) was necessary to oxidize Ta$_6$Cl$_{12}^{3+}$ to Ta$_6$Cl$_{12}^{4+}$.

Since the original oxidations of Ta$_6$X$_{12}^{2+}$ several derivatives of the oxidized clusters have been prepared. The sulfate Ta$_6$Cl$_{12}$(SO$_4$)$_2$ precipitates when an aqueous solution of Ta$_6$Cl$_{12}^{2+}$ is acidified with sulfuric acid and oxidized with chlorine or iron(III) (31). The preparation of Ta$_6$Cl$_{12}$(SO$_4$) required an ion exchange technique (33).

Spreckelmeyer and Schäfer isolated Ta$_6$Cl$_{12}$Cl$_3$$\cdot$$7$H$_2$O (34), Ta$_6$Br$_{12}$Br$_4$$\cdot$$n$H$_2$O, and Ta$_6$Br$_{12}$Br$_3$$\cdot$$n$H$_2$O (35). Allen and Sheldon (36) had already reported Ta$_6$Cl$_{12}$Cl$_2$$\cdot$$7$H$_2$O.

Bayer and Schäfer (37) reacted Ta$_6$I$_{12}$I$_2$ with liquid iodine, pumped off the excess iodine, and isolated Ta$_6$I$_{12}I_3$.

Mackay and Schneider (38) air oxidized an ethanol solution of Ta$_6$Cl$_{12}$Cl$_2$$\cdot$$7$H$_2$O which had been saturated with anhydrous hydrogen chloride, added excess tetraethylammonium chloride, evaporated the solvent in an oxygen-free atmosphere, and reported the product to be $[(C_2H_5)_4N]_3[(Ta_6Cl_{12})Cl_6]$.

Spreckelmeyer (39) dissolved M$_6$X$_{14}$$\cdot$$8$H$_2$O in 5N ethanolic hydrogen halide, oxidized with 30 percent hydrogen peroxide, added pyridine, and isolated $(C_5H_5NH)_2[(M_6X_{12})Cl_6]$ where $M =$
Ta, Nb; X = Cl, Br; and \((C_5H_5NH)_2[(Ta_6Cl_{12})Br_6]\). These salts were said to be identical to the pyridinium salts isolated by Lindner and Feit (18).

Hughes et al. (40) have recently reported the preparation of a series of \(M_6X_{12}^{n+}\) derivatives. A methanol solution of \(Ta_6Br_{12}Br_2\) which was oxidized with bromine water, acidified with aqueous hydrogen bromide and reduced in volume yielded black crystals of \([\,(Ta_6Br_{12})Br_4(H_2O)_2\r\). Similar treatment of aqueous \(Ta_6Cl_{12}^{2+}\) resulted in red-brown \([\,(Ta_6Cl_{12})Cl_4(H_2O)_2\r\). When a methanol solution of \(Ta_6Cl_{12}^{2+}\) was so treated, the product was \(H_2[(Ta_6Cl_{12})Cl_6]nH_2O\). Aqueous solutions of \(Ta_6Cl_{12}^{2+}\) and \(Ta_6Br_{12}^{2+}\) were titrated spectrophotometrically to \(Ta_6X_{12}^{3+}\) with iron(III) or aqueous halogen, acidified with the appropriate hydrohalic acid, and partially evaporated to yield the hydrates \([\,(Ta_6X_{12})X_3(H_2O)_3\r\). These workers also prepared complexes of the general formula \([\,(C_2H_5)_4N\r][\,(Ta_6X_{12})Y_6\] where \(X, Y = \text{Cl, Br}\) by dissolving \(Ta_6X_{12}X_2\) in ethanol, oxidizing with \(Y_2\), saturating the solution with \(HY\), and adding \((C_2H_5)_4NY\). The compound \([\,(C_6H_5)_4As\r][\,(Ta_6Cl_{12})Cl_6\] was prepared similarly. In order to prepare \([\,(C_2H_5)_4N\r][\,(Ta_6Cl_{12})Cl_6\] it was necessary to start with an ethanol solution of \([\,(Ta_6Cl_{12})Cl_3(H_2O)_3\r\] and protect the solution from air oxidation until the solid complex had been obtained.

Fleming et al. (41) have also reported the preparation of dimethylsulfoxide adducts \([\,(Ta_6Cl_{12})(DMSO)_6\r](ClO_4)_2\) and
[(Ta₆Cl₁₂)Cl₃(DMSO)₃], and the only tetranegative anion of the tantalum clusters, K₄[(Ta₆Cl₁₂)Cl₆]. This complex was obtained directly by aluminum reduction of tantalum pentachloride in the presence of potassium chloride.

The chemistry of the hexanuclear molybdenum clusters was studied by Lindner (16) who reduced molybdenum(V) chloride to molybdenum(II) chloride with aluminum. Hellriegel (42) and later Senderoff and Brenner (43) did the same reduction using molybdenum metal as the reducing agent. Lewis et al. (44) thermally decomposed molybdenum(III) iodide in an oxygen-free atmosphere and obtained molybdenum(II) iodide. Couch and Brenner (45) and Robinson (46) disproportionated the tribromide and trichloride of molybdenum to prepare the molybdenum(II) halides. Lindner and Helwig (19) and Durand et al. (47) prepared molybdenum(II) bromide directly from the elements at 600°-700°. Guggenberger and Sleight (48) reacted molybdenum and aqueous hydrogen bromide at 700° under 3000 atmospheres of supporting pressure and obtained orange crystals of Mo₆Br₁₂·2H₂O. Lindner et al. (49) reacted phosgene with molybdenum metal in a dry atmosphere at 600° and obtained molybdenum(II) chloride.

Matsuzaki et al. (50) followed the disproportionation and hydrogen reduction of several molybdenum halides by a thermogravimetric method. These workers found that chlorides of molybdenum from the tetrachloride down to molybdenum (2.9) chloride disproportionate to molybdenum(II) chloride at
Holste and Schäfer (51) have prepared three isomers of molybdenum(II) chloride which apparently do not contain Mo$_6$Cl$_8$ moieties. Two of these isomers give about a 2 percent yield of (Mo$_6$Cl$_8$)$_2$Cl$_4$ when tempered at 350° for 14 days while the third was about 80 percent converted to (Mo$_6$Cl$_8$)$_2$Cl$_4$ by that treatment.

Anionic and neutral complexes of hexanuclear molybdenum halides are numerous, though they are reported in the older literature as complexes of molybdenum trimers. Lindner (16, 52) prepared H(Mo$_3$Cl$_7$·H$_2$O) and H(Mo$_3$Cl$_4$Br$_3$·H$_2$O) by extracting molybdenum(II) chloride into aqueous hydrogen chloride or bromide. If cations were added to acidified solutions of the dihalides, salts such as (C$_5$H$_5$NH)(Mo$_3$Cl$_7$·H$_2$O) and (C$_5$H$_5$NH)(Mo$_3$Br$_7$) could be precipitated (17, 19).

Sheldon (53-56) prepared a series of anionic derivatives of the molybdenum clusters from hydrohalic acid solutions of the clusters. These derivatives had the general formula M$_2$(Mo$_6$X$_8$)$_2$Y$_6$ where M$^+$ = M(I)$^+$, H$_2$O$^+$, C$_5$H$_5$NH$^+$, (C$_6$H$_5$)$_3$PH$^+$, NH$_4^+$, R$_4$N$^+$; X = Cl$^-$, Br$^-$, I$^-$; Y = Cl$^-$, Br$^-$, I$^-$, OH$^-$. Sheldon arrived at the hexanuclear formulation on the basis of molecular weight data and conductivity data which showed the derivatives to be 2:1 electrolytes in nitrobenzene. Similar anionic derivatives have been prepared in a similar manner by Mackay (57), Cotton et al. (58), Clark et al. (59), and Hartley and Ware (60). Opalovskii and Samoilov (61) prepared the bromide
derivatives in iodine monobromide solvent.

Thermal decomposition of the acidic derivatives (H$_3$O)$_2$(Mo$_6$X$_8$)Y$_6$ was first observed by Rosenheim and Kohn (62) and led to a new series of derivatives of molybdenum(II) and tungsten(II) halide clusters. The derivatives thus prepared were (Mo$_6$X$_8$)Y$_4$ (M = Mo, W; X = Cl, Br, I; Y = Cl, Br, I, OH) by Sheldon (54,56), Mackay (57) and Mattes (63). Hogue and McCarley (64) have published a comprehensive report on the M = W derivatives.

Lindner et al. (49) added silver nitrate to a solution of their molybdenum(II) chloride and isolated what they formulated as Mo$_3$Cl$_4$(NO$_3$)$_2$. Durand et al. (47) used the same method to prepare Mo$_3$Br$_4$(NO$_3$)$_2$. Cotton and Curtis (65) precipitated the outer chlorides from Mo$_6$Cl$_{12}$ by adding silver perchlorate in the presence of an excess of the ligands (L) dimethylsulfoxide or dimethylformamide and obtained [(Mo$_6$Cl$_8$) L$_6$](ClO$_4$)$_4$.

Many other neutral complexes of the molybdenum clusters are known. Bis adducts of the clusters, [(Mo$_6$X$_8$)Y$_4$L$_2$] (X, Y = Cl, Br, I; L = C$_2$H$_5$N, H$_2$O, C$_2$H$_5$OH, (C$_2$H$_5$)$_3$N, (C$_6$H$_5$)$_3$PO, (C$_6$H$_5$)$_3$AsO), have been prepared by Lindner and Köhler (17) and Sheldon (54,56,66). Other bis adducts of the molybdenum chloride cluster have been prepared where L = NH$_3$ by Edwards (67) and where L = (CH$_3$)$_2$SO and HCON(CH$_3$)$_2$ by Cotton and Curtis (65). Carmichael and Edwards (68) reported that acetonitrile, propionitrile, n-butyronitrile, trimethylamine,
triethylamine, pyridine, γ-picoline, quinoline, and pyrazine all formed bis adducts with Mo₆Cl₁₂.

Adducts of the molybdenum clusters in which more than two coordination sites are occupied by neutral ligands have also been prepared. The hexakis adducts [(Mo₆Cl₈)L₆](ClO₄)₄ where L = (CH₃)₂SO or HCON(CH₃)₂ reported by Cotton and Curtis (65) have already been mentioned. Walton and Edwards (69) prepared a bis-2,5-dithiahexane adduct of the molybdenum chloride cluster but were unable to determine whether the adduct was ionic [(Mo₆Cl₈)Cl₂(DTH)₂]Cl₂ with bidentate ligands or neutral [(Mo₆Cl₈)Cl₄(DTH)₂] with unidentate ligands.

Fergusson et al. (70,71) prepared [(Mo₆Cl₈)Cl₃L₃]Cl with L = (C₆H₅)₃P and found it to be a 1:1 electrolyte. The bidentate ligands bipyridyl, o-phenanthroline and o-phenylbis(dimethylarsine) formed the 2:1 electrolytes [(Mo₆Cl₈)X₂B₂]X₂ (X = Cl, Br) and terpyridyl, a tridentate ligand, formed [(Mo₆Cl₈)Cl₃T]X, a 1:1 electrolyte.

Sheldon (55) used solutions of radioactive chloride and bromide to show that the outer halides of [(Mo₆Cl₈)X₂]²⁻ exchange rapidly but no exchange of the internal chlorides was observed. He also found that while fluoride, thiocyanate, and concentrated hydroxide solutions completely disrupt the cluster (53), hydroxide in dilute solution does exchange with internal chlorine to some extent (56,72,73). Sheldon has been able to isolate the compound [(C₂H₅)₄N]₂[(Mo₆Cl₇(OH))Cl₆] (74).
The compound \((\text{Mo}_6\text{Cl}_8)\text{Cl}_4\) decomposes above 300° in air and above 800° in vacuum (53). This cluster is unaffected by boiling lithium iodide trihydrate at 200°, disproportionates slowly in fused lithium chloride at 610°, and disproportionates rapidly in fused potassium chloride at 770° (56). Disproportionation products were molybdenum metal and hexachloro-molybdate(III). In fused lithium bromide or lithium iodide, all chlorides of the cluster exchange and \(\text{Mo}_6\text{Cl}_{12}\) is converted to \(\text{Mo}_6\text{Br}_{12}\) or \(\text{Mo}_6\text{I}_{12}\) (56).

The redox chemistry of the molybdenum and tungsten \(\text{M}_6\text{X}_8\) clusters is somewhat less extensive than the redox chemistry of the niobium and tantalum \(\text{M}_6\text{X}_{12}\) clusters. McCarley and Brown (75) oxidized tungsten(II) bromide to tungsten(III) bromide with bromine in liquid bromine. Siepmann and Schäfer (76-78) used this method to prepare \(\text{W}_6\text{Br}_{14}, \text{W}_6\text{Br}_{16}\), and \(\text{W}_6\text{Br}_{18}\) which they found to contain the \(\text{W}_6\text{Br}_8^{6+}\) cluster. These compounds could be thermally decomposed to \((\text{W}_6\text{Br}_8)\text{Br}_4\) and bromine. Siepmann et al. (79) produced the only known \(\text{M}_6\text{X}_{12}\) cluster of molybdenum or tungsten by reacting \((\text{W}_6\text{Cl}_8)\text{Cl}_4\) with liquid chlorine at 100°. The oxidation product was \((\text{W}_6\text{Cl}_{12})\text{Cl}_6\) rather than an oxidized \(\text{W}_6\text{Cl}_8\) cluster.

The only known example of tantalum or niobium in an \(\text{M}_6\text{X}_8\) type cluster is the compound \((\text{Nb}_6\text{I}_8)\text{I}_3\). This compound was first identified by Bauer et al. (29) and Simon et al. (80), and its formulation as \((\text{Nb}_6\text{I}_8)\text{I}_{6/2}\) was later confirmed through single crystal x-ray analysis by Simon et al. (81) and in an
independent x-ray study by Bateman et al. (82) on crystals prepared by Kust et al. (83). The compound was prepared by disproportionation of \( \gamma-\text{Nb}_3\text{I}_8 \) (81,82) or by niobium reduction of \( \gamma-\text{Nb}_3\text{I}_8 \) (81). It was also reported (81,84) that \((\text{Nb}_6\text{I}_8)\text{I}_3\) absorbs hydrogen above 300° at atmospheric pressure to form a compound of the limiting composition \(\text{HNb}_6\text{I}_{11}\).

The only report in the literature of a mixed-metal \(\text{M}_6\text{X}_8\) or \(\text{M}_6\text{X}_{12}\) cluster was made by Schäfer and Spreckelmeyer (85). These workers first prepared a solid solution of niobium pentabromide and tantalum pentabromide by brominating mixtures of the two metals in the 1:3 to 3:1 composition range. The pentabromides thus produced were reduced with cadmium metal, and the reaction product was extracted with water. After removal of cadmium as the sulfide, aqueous hydrogen bromide was added to crystallize the final product. Electronic absorption spectral data showed that a solution of the product was not merely a mixture of \(\text{Nb}_6\text{Br}_{12}^{2+}\) and \(\text{Ta}_6\text{Br}_{12}^{2+}\). Analytical data indicated the stoichiometry to be \([\text{Ta}_{6-x}\text{Nb}_x\text{Br}_{12}]\text{Br}_2\cdot8\text{H}_2\text{O}\) where \(x = 1.6\) to 2.4. X-ray powder patterns of this product were very similar to patterns of \(\text{Ta}_6\text{Br}_{14}\cdot8\text{H}_2\text{O}\) and \(\text{Nb}_6\text{Br}_{14}\cdot8\text{H}_2\text{O}\).

**Structural studies**

X-ray structural studies have confirmed the existence of \(\text{M}_6\text{X}_{12}\) and \(\text{M}_6\text{X}_8\) cluster units in the lower halides of niobium, tantalum, molybdenum, and tungsten. The first such studies were by Brosset (86,87) who analyzed single crystals of
(Mo$_3$Cl$_4$)(OH)$_2$·8H$_2$O and (Mo$_3$Cl$_4$)Cl$_3$·4H$_2$O and found [(Mo$_6$Cl$_8$)X$_6$] moieties in both compounds (X represents a chlorine or an oxygen of hydroxide or water). The Mo$_6$Cl$_8$ cluster was shown to consist of an octahedron of molybdenum atoms (Mo-Mo bond lengths were 2.63 Å) with a triply bridged chlorine over each triangular face of the molybdenum octahedron (Mo-Cl bond lengths were 2.56 Å). Each of the six outer or terminal ligands, X, was radially directed from one of the six metal atoms. The terminal chlorine-molybdenum bond lengths were found to be 2.43 Å. Brosset (88) and Vaughan (89) studied the x-ray radial distribution curves of H(Mo$_3$Cl$_7$·H$_2$O)·3H$_2$O in ethanol and powdered (NH$_4$)$_2$[(Mo$_6$Cl$_8$)Cl$_6$]H$_2$O and found the results to be consistent with the presence of [(Mo$_6$Cl$_8$)Cl$_6$]$^{2-}$ ions with the interatomic distances stated above. On the basis of another single crystal study, Schäfer et al. (90) formulated molybdenum(II) chloride as [(Mo$_6$Cl$_8$)Cl$_4$/$2$Cl$_2$]. Within the Mo$_6$Cl$_8$ cluster the molybdenum-molybdenum bond lengths were 2.61 Å and the molybdenum-chlorine bond lengths were 2.47 Å. The two unshared terminal chlorines were each 2.38 Å from a molybdenum atom and the four terminal chlorines which were shared with another cluster were 2.50 Å from the nearest molybdenum.

Schäfer et al. (90) reviewed the powder data of several authors and concluded that all the dichlorides, dibromides, and diiodides of molybdenum and tungsten are isostructural.
having the \([\text{(Mo}_6\text{Cl}_8)\text{Cl}_4/2\text{Cl}_2]\) structure. Holste and Schäfer (51) have since prepared isomers of molybdenum dichloride which do not have this structure.

Guggenberger and Sleight (48) studied single crystals of Mo\(_6\text{Br}_{12}\cdot2\text{H}_2\text{O}\) and found two slightly different molybdenum-molybdenum bonded distances, 2.630 and 2.640 Å. The molybdenum-bridging bromine distances were 2.606 Å, the molybdenum-terminal bromine distances were 2.589 Å, and the molybdenum-oxygen distances were 2.191 Å. The water molecules were coordinated to molybdenum atoms in trans positions of the Mo\(_6\) octahedron.

The structure of Nb\(_6\text{I}_{11}\) was shown by Simon et al. (81) and Bateman et al. (82) to contain Nb\(_6\text{I}_8\) clusters, but these clusters were distorted from \(O_h\) symmetry to \(C_1\) symmetry. The principal feature of the distortion is a shift of two trans Nb\(_6\) atoms so that a line through these atoms is about 5° off the perpendicular to the plane of the other four Nb\(_6\) atoms. The apical trans Nb-Nb distance is 3.96 Å compared to the basal plane trans Nb-Nb distances of 4.06 and 4.08 Å. Cis Nb-Nb distances range from 2.72 to 2.94 Å. The Nb-I\(_1\) (i = inner) distances range from 2.84 to 2.90 Å, and average 2.87 Å. Three Nb-I\(_0\) (o = outer) distances were observed: 2.90, 2.93, 2.96 Å. The interatomic distances listed are from Bateman et al. (82) who suggested the observed distortion is a result of the Jahn-Teller effect. Simon et al. (81) obtained good general agreement with the structure as reported by Bateman et al.
but explained that the distortion was due at least partially to the intercluster bridging arrangement in the crystal. Simon (84) has done a neutron diffraction study on HNb$_6$I$_{11}$ and located the proton at the center of the Nb$_6$I$_8$ cluster.

Vaughan et al. (91) first ascertained the M$_6$X$_{12}$ clusters in lower halides of niobium and tantalum through diffuse x-ray scattering experiments on ethanol solutions of (M$_6$X$_{12}$)X$_2$$\cdot$7H$_2$O. These studies showed the metal-metal distances in the clusters to be 2.85 A (Nb$_6$Cl$_{12}^{2+}$), 2.88 A (Ta$_6$Cl$_{12}^{2+}$) and 2.92 A (Ta$_6$Br$_{12}^{2+}$). The cluster unit may be described as an octahedron of metal atoms with a halogen atom over each edge of the octahedron.

Burbank (92) has done a x-ray study of (Ta$_6$Cl$_{12}$)Cl$_2$$\cdot$7H$_2$O crystals and asserts that the Ta$_6$ cluster forms an elongated tetragonal bipyramid. In this structure the six terminal positions are occupied by the two terminal chlorines and four water molecules with the other three water molecules separating the cluster units into layers within the crystal. The formula would thus be [(Ta$_6$Cl$_{12}$)Cl$_2$(H$_2$O)$_4$]$\cdot$3H$_2$O.

Simon et al. (80) showed the Nb$_6$Cl$_{12}$ clusters in Nb$_6$Cl$_{14}$ are flattened, and each cluster is bridged to six other clusters. Simon then formulated Nb$_6$Cl$_{14}$ as [(Nb$_6$Cl$_{10}$)Cl$_2$/2$^{1-0}$] Cl$_2$/2$^{1-0}$Cl$_4$/2$^{0-0}$ where 'i' and 'o' denote inner or outer positions with respect to the given cluster unit. Thus all six terminal sites of the cluster are occupied. (Ta$_6$I$_{12}$)I$_2$ was found to be isostructural with (Nb$_6$Cl$_{12}$)Cl$_2$ (29).
The structure of Nb₆F₁₅ has been reported by Schäfer et al. (93a) to contain a regular octahedron of niobium atoms and the simplified intercluster bridging indicated in the formula (Nb₆F₁₂)F₆/₂°. Bauer and von Schnering (93b) report a similar structure for Ta₆Cl₁₅.

**Spectra and magnetism**

Boorman and Straughan (94) reported the spectra of M₆X₁₄ (M = Nb, Ta; X = Cl, Br) in the region 20-450 cm⁻¹. The compounds all exhibit four strong bands in this region; the positions and intensities of these bands were said to be characteristic of M₆X₁₂²⁺ ions. Mackay and Schneider (38) have reported the far infrared spectra of [(C₂H₅)₄N]₃[(Ta₆Cl₁₂)Cl₆] and a series of similar niobium cluster derivatives.

Mattes (95) reported the spectra of [M₆X₁₂]Xₙ (M = Nb, Ta; X = F, Cl, Br, I; n = 2, 3, 4). A normal coordinate analysis was done, and force constants were calculated. Fleming et al. (41) studied the far infrared spectra of several niobium cluster complexes as well as [(C₂H₅)₄N]₂[(Ta₆X₁₂)Y₆] (X, Y = Cl, Br), [(C₂H₅)₄N]₃[(Ta₆Cl₁₂)Cl₆] and the dimethylsulfoxide adducts [(Ta₆Cl₁₂)(DMSO)₆](ClO₄)₃ and [(Ta₆Cl₁₂)Cl₃(DMSO)₃]. The spectra of the [(Ta₆X₁₂)Y₆]²⁻ ions each showed six bands which could be considered as the six T₁u fundamentals expected. Not all the bands in these spectra could be definitely assigned, but exception was taken to the previous assignments of some of the bands. Meyer (96) reported the far infrared
spectra of \( K_4[(Ta_6Cl_{12})Cl_6] \) and the hydrates \( (Ta_6Cl_{12})Cl_3 \cdot 6H_2O \), \( (Ta_6Br_{12})Br_3 \cdot 6H_2O \) and \( (Ta_6Cl_{12})Br_3 \cdot nH_2O \).

The far infrared spectra of \( M_6X_8 \) clusters have been studied by several authors. Mackay (57), Clark et al. (97) and Mattes (63) investigated the spectra of the anhydrous species \( M_6X_8Y_4 \). The spectra of the hexahalo anions \( [(M_6X_8)Y_6]^2^- \) have been reported by Mackay (57), Clark et al. (97), Cotton et al. (58) and Hartley and Ware (60). Clark et al. (97) and Walton and Edwards (69) noted that the bidentate ligand adducts \( [(M_6Cl_{12})Cl_2\cdot B_2]_2Cl_2 \) gave spectra very similar to those of the hexahalo anions and the anhydrous derivatives.

Guggenberger and Sleight (48) reported the far infrared and Raman spectra of \( (Mo_6Br_8)Br_4 \cdot 2H_2O \) but made no attempt to explain their spectra. The other authors mentioned here generally assigned the results for \( M_6X_8 \) clusters according to octahedral symmetry of the clusters with two \( M-X \) modes, one \( M-M \) mode, one \( M-Y \) mode, and one \( X-M-Y \) mode infrared-allowed. There are some differences in the assignments made by the authors.

The bonding in \( M_6 \) cluster compounds has been discussed by several authors. Sheldon (53) proposed use of hybridized atomic orbitals for simple covalent metal-metal and metal-halogen bonds. Gillespie (98) used the same approach and went on to suggest a square antiprismatic bonding arrangement. Such bonding arrangement would involve nonlinear overlap of
hybridized metal atom orbitals with orbitals of halogen atoms. To account for the distorted cubic arrangement of ligands about each metal atom in the $\text{T}_6\text{X}_{12}^{2+}$ ions, Gillespie proposed three-center bonds in the face centers of the metal octahedron. Duffey (99) and Duffey et al. (100) considered the orbitals involved in metal-metal bonding to form a system which was stabilized by resonance and they were able to obtain parametric equations from a molecular orbital treatment. Cotton and Haas (101) used the LCAO-MO method to derive an analogous bonding scheme. Robin and Keubler (102) used the same method as Cotton and Haas but considered the effect of bridging halogen interactions on the ordering of the metal-metal levels. Kettle (103) noted that when both metal-metal bonds and metal-halogen bonds are considered, $\text{M}_6\text{X}_{12}^{2+}$ ($\text{M} = \text{Ta, Nb}$) and $\text{M}_6\text{X}_8^{4+}$ ($\text{M} = \text{Mo, W}$) all have 40 electrons in bonding orbitals. Schneider and Mackay (104) combined Symmetry Adapted Group Orbitals to form molecular orbitals and considered the entire $(\text{M}_6\text{X}_{12})\text{Y}_6$ system.

Allen and Sheldon (36) made the first attempt to interpret the electronic spectra of these cluster compounds. They reported data on aqueous $\text{M}_6\text{X}_{12}^{2+}$ and assigned all the absorptions to metal-metal transitions according to the MO scheme reported by Cotton and Haas (101). Robin and Kuebler (102) reported the spectra of $\text{T}_6\text{X}_{12}^{2+}$ ($\text{X} = \text{Cl, Br}$) and mistook (104,105) the spectra of $\text{T}_6\text{X}_{12}^{3+}$ for those of $\text{T}_6\text{X}_{12}^{4+}$. The
electronic spectra of some $\text{Nb}_6\text{Cl}_{12}^{2+}$ derivatives were reported by Field and Kepert (106). These authors asserted that their data ruled out the assignments of Allen and Sheldon and were more consistent with the work of Robin and Kuebler. Fleming and McCarley (105) reported the spectra of several $\text{Nb}_6\text{X}_{12}^{n+}$ and $\text{Ta}_6\text{Cl}_{12}^{n+}$ derivatives and also disagreed with the assignments of Allen and Sheldon. These authors assigned the bands according to the MO scheme of Cotton and Haas but designated several of the bands as arising from charge transfer. Fleming and McCarley also pointed out that the spectral and magnetic data of Field and Kepert indicate the presence of significant amounts of $\text{Nb}_6\text{Cl}_{12}^{3+}$ in the solutions measured as $\text{Nb}_6\text{Cl}_{12}^{2+}$. Schneider and Mackay (104) reported the absorption spectra of several $\text{Nb}_6\text{Cl}_{12}^{n+}$ derivatives but their data for $[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_6]^{4-}$ have been found to agree with that for a $\text{Nb}_6\text{Cl}_{12}^{3+}$ derivative (105,107). Speckelmeyer (107) has tabulated data of his own and other authors on the electronic spectra of many $\text{M}_6\text{X}_{12}^{n+}$ species ($\text{M} = \text{Ta, Nb}; \text{X} = \text{Cl, Br}; n = 2, 3, 4$), $\text{Ta}_6\text{I}_{12}^{2+}$ and $\text{Nb}_6\text{F}_{12}^{3+}$.

van Bronswyk (108) has questioned the assignment as charge transfer bands some absorptions in the ultraviolet spectra of $\text{Nb}_6\text{Cl}_{12}^{n+}$. His question arises from a photolysis experiment in which no enhancement of inner chloride exchange was observed when solutions of $\text{Nb}_6\text{Cl}_{12}^{n+}$ were appropriately irradiated.

Schäfer et al. (109) have measured the electronic spectra
of several cluster compounds including \((\text{Ta}_6\text{I}_{12})\text{I}_2\), \((\text{Ta}_6\text{Cl}_{12})\text{Cl}_3\), \((\text{Ta}_6\text{Br}_{12})\text{Br}_2\), \((\text{Ta}_6\text{Br}_{12})\text{Br}_3\), \((\text{Ta}_6\text{Cl}_{12})\text{Cl}_2\cdot8\text{H}_2\text{O}\), \((\text{Ta}_6\text{Br}_{12})\text{Br}_2\cdot8\text{H}_2\text{O}\), \((\text{Nb}_6\text{I}_8)\text{I}_3\), \((\text{Mo}_6\text{Cl}_{18})\text{Cl}_4\) and \((\text{Mo}_6\text{Br}_8)\text{Br}_4\).

Of these compounds only those containing \(\text{M}_6\text{X}_{12}\) cluster units had absorption maxima at wavelengths longer than 500 nm. The electronic spectra of molybdenum dihalides and derivatives of the dihalides have been investigated by Sheldon (53,54,55), Edwards (67), Carmichael and Edwards (68) and Fergusson et al. (71). The hexahalo anions, neutral adducts, and anhydrous dihalides were studied, and all show one or more charge transfer bands in the region 300-360 nm.

The compounds \((\text{M}_6\text{X}_8)\text{Y}_4\) (\(\text{M} = \text{Mo}, \text{W}; \text{X}, \text{Y} = \text{Cl}, \text{Br}, \text{I})\) were found to be diamagnetic by Schäfer and Schnering (2), Sheldon (54,56), Schäfer and Siepmann (78), Tjabbes (110) and Klemm and Steinberg (111). Sheldon (54,74) and Edwards (67) determined that derivatives such as \(\text{H}_2[(\text{Mo}_6\text{Cl}_{18})\text{X}_6]\cdot\text{nH}_2\text{O}\) (\(\text{X} = \text{Cl}, \text{Br}, \text{I}\)), \(\text{R}_2[(\text{Mo}_6\text{Cl}_{18})\text{Cl}_6]\) and \((\text{Mo}_6\text{Cl}_{18})\text{Cl}_4\cdot4\text{NH}_3\) were also diamagnetic.

McCarley et al. (112) and Schneider and Mackay (113) have examined the magnetic properties of some \(\text{Nb}_6\text{Cl}_{12}\) derivatives and found that the 2+ and 4+ clusters are diamagnetic while the 3+ derivatives are paramagnetic. Schäfer (26,80) reported that \((\text{Nb}_6\text{Cl}_{12})\text{Cl}_2\) is diamagnetic and \((\text{Ta}_6\text{Cl}_{12})\text{Cl}_3\) is paramagnetic with a moment corresponding to one unpaired electron per cluster unit. Schäfer (28) also reported that \((\text{Ta}_6\text{Br}_{12})\)
Br$_3$ is paramagnetic.

Converse and McCarley (114) have published on a comprehensive study of the magnetic properties of $M_6X_{12}^{n+}$ derivatives and found the $2^+$ and $4^+$ clusters to be diamagnetic while the $3^+$ clusters are paramagnetic with moments corresponding to one unpaired electron per cluster unit. These workers went on to derive values of the temperature independent paramagnetism of a variety of derivatives of $M_6X_{12}$ clusters.

Schäfer et al. (81) found (Nb$_6$I$_8$I)$_3$ to be paramagnetic with a complicated temperature dependence of the susceptibility which could be interpreted in terms of a doublet-quartet transition. Simon (84) determined that (HNb$_6$I$_8$I)$_3$ is diamagnetic.
EXPERIMENTAL

Equipment

The synthesis of starting materials for this work was done in evacuated glass systems. All air sensitive products and reactants were handled and stored in a dry box which contained an argon atmosphere maintained at a dew point of ca. -60°.

Materials

Melting grade tantalum powder was purchased from Fansteel Metallurgical Corporation or tantalum sheet was obtained from laboratory stock. Aluminum round of 99.999 percent nominal purity and molybdenum sheet were obtained from laboratory stock. For the synthesis of high purity aluminum trichloride, electronic grade (99.99 percent) hydrogen chloride was purchased from Air Products and Chemicals, Inc. All other chemicals used were of reagent grade and used as obtained.

Synthesis

Chlorides of tantalum, molybdenum, and aluminum

Tantalum pentachloride and molybdenum pentachloride were prepared as described for tantalum pentachloride by Kuhn (115) with one modification. Each reaction was scaled up to yield about two hundred grams of the metal pentachloride.

High purity aluminum chloride was obtained by passing electronic grade (99.99 percent) hydrogen chloride over
turnings of high purity aluminum (99.999 percent) at 300°.

Bis(tetraethylammonium)hexachloro(dodeca-μ-chloro-dimolybdenumtetratantalum) \([(C_2H_5)_4N]_2[(Ta_4Mo_2Cl_{12})Cl_6]\]^1

Tantalum pentachloride and molybdenum pentachloride in equimolar amounts and enough aluminum to reduce the tantalum (V) to tantalum(2.33) and the molybdenum(V) to molybdenum(II) were placed in a Pyrex tube (40 mm. inner diameter, 4 inches long with an access port of 9 mm. inner diameter and 4 inches long). After aluminum trichloride and sodium chloride in nearly equimolar amounts were added to serve as a solvent, the tube was evacuated and sealed off. In a typical reaction 15 grams of tantalum pentachloride (0.042 moles), 11.4 grams of molybdenum pentachloride (0.042 moles), 1.7 grams of aluminum (0.063 moles), 12.0 grams of aluminum trichloride (0.090 moles), and 6.1 grams of sodium chloride (0.105 moles) were sealed in the tube.

The sealed tube was wrapped with aluminum foil, then wrapped with a heating tape, and finally wrapped in asbestos tape. A thermocouple was inserted into the wrapping inside the heating tape. Thus wrapped, the heating tape was plugged into a Variac, the tube was clamped to a shaker and shaken gently for three days at 320°. At this time the tube was opened, and its contents were crushed with a mortar and pestle.

^1Hereafter the anion will be referred to as the 4-2 complex (as in Ta₄Mo₂).
The crushed product was added bit by bit to 600-800 ml. of water and stirred for four hours in order to dissolve the NaAlCl₄, AlCl₃ and Ta₆Cl₁₄. The resulting mixture was centrifuged; the collected solids were extracted with water a second time for two hours, and the solids were again centrifuged from the solution. An overnight extraction of the solids with 500 ml. of absolute ethanol yielded a very dark opaque solution which was centrifuged, filtered, and diluted with water to make the solvent about 25 percent water by volume. The ethanol-water solution was passed through a cation exchange column (Dowex 50W-X8, 50-100 mesh, acid form) and transferred to a round bottom flask. An ethanol solution of an excess of tetraethylammonium chloride was added; the solution was thoroughly flushed with argon, cooled in an ice bath, and saturated with anhydrous hydrogen chloride. About six hours later 2.2 grams of fine dark green (black?) crystals were collected on a glass frit, washed with absolute ethanol, ethyl ether, and air dried. These crystals were soluble in acetonitrile and no changes were observed in the electronic spectrum of the solution when a portion of the solution was treated with chlorine or zinc.

**Anal:** Calcd. for \([(C₂H₅)₄N]₂[(Ta₄Mo₂Cl₁₂)Cl₆]\) with observed values in parentheses: Ta, 39.9 (38.3); Mo, 10.6 (10.5); C, 10.6 (10.8); H, 2.22 (2.25); Cl, 35.2 (33.7).
Bis(tetra-n-butylammonium)hexachloro(dodeca-μ-chloro-molybdenumpentatantalum) \[ \text{[(n-C}_4\text{H}_9\text{N)}_4\text{N]}_2[(\text{Ta}_5\text{MoCl}_{12})\text{Cl}_6]}^2 \]

The general procedure for this compound was the same as for the preceding compound, but the proportion of the pentahalides in the starting mixture was altered to maximize the yield of 5-1 cluster over 4-2 cluster. In one specific reaction 25 grams of tantalum pentachloride (0.07 moles), 1.9 grams of molybdenum pentachloride (0.007 moles), 1.78 grams of aluminum (0.066 moles), 14.4 grams of aluminum trichloride (0.108 moles), and 4.3 grams of sodium chloride (0.074 moles) were sealed into the reaction tube and shaken for 3.5 days at 320°. The product was extracted with 600 ml. of water for six hours, with 600 ml. of water overnight, and then with 500 ml. of absolute ethanol for seven hours. The solution was centrifuged, made 20 percent water by volume, and passed through Dowex 50W-X8 cation exchange resin (50-100 mesh, acid form). Excess tetra-n-butylammonium chloride was added to the solution which was then cooled in an ice bath, flushed with argon, saturated with anhydrous hydrogen chloride, and allowed to stand overnight. A few crystals were filtered away from the mother solution. Then the solution was oxidized with chlorine and heated in air for four hours. At that time 0.6 grams of

\[ \text{2Hereafter the anion will be referred to as the 5-1-2 complex as in Ta}_5\text{Mo}_1 \text{ cluster complex with a charge of 2-}. \]
very dark fine crystals were collected on a glass frit and recrystallized from hydrogen chloride saturated ethanol. The final yield was 0.5 grams of dark red needle-shaped crystals which seemed to be contaminated with about 10 mole percent 4-2 cluster (from spectral data).

**Anal:** Calcd. for \([(n-C_4H_9)_4N]_2[(Ta_5MoCl_{12})Cl_6]\) with observed values in parentheses: Ta, 42.2 (41.1); Mo, 4.5 (5.0); C, 18.0 (18.2); H, 3.78 (3.56).

**Tris(tetraethylammonium)hexachloro(dodeca-\(\mu\)-chloro-molybdenum-pentatantalum) \([ (C_2H_5)_4N]_3[(Ta_5MoCl_{12})Cl_6] \)**

This compound can easily be obtained by reducing an acetonitrile solution of the 5-1-2 compound with zinc. Conversely, the 5-1-3 compound can be oxidized with chlorine in acetonitrile solution to obtain the 5-1-2 compound. What follows is a description of a single experiment which afforded exceptionally pure 5-1 cluster, largely in the reduced form.

The products of three previous preparations which had yielded mixtures of about 70-80 percent 5-1 clusters and 20-30 percent 4-2 cluster were combined in one acetonitrile solution. Metallic zinc was added, and the solution was allowed to stand for a week at room temperature. Some turbidity had appeared, but filtration restored the clarity of the solution. One gram of tetraethylammonium chloride in acetonitrile was

\[3\text{Hereafter the anion will be referred to as the 5-1-3 complex as in } Ta_5Mo_1 \text{ cluster complex with a charge of } 3^-\].
added every few days until ten grams had been added. More turbidity appeared, and the solution was filtered through a glass frit under aspirator vacuum. This filtration step lowered the temperature of the effluent solution sufficiently to cause crystallization of very pure \([\text{[(C}_2\text{H}_5)_4\text{N]}_3\text{[(Ta}_5\text{MoCl}_4\text{]}_2\text{]}\text{Cl}_6\)]. A second crop of crystals was collected by evaporation of the mother solution under aspirator vacuum. An electronic spectrum showed this second crop of crystals to be contaminated with about 10 percent 4-2 cluster. The first crop of crystals was analyzed.

**Anal.:** Calcd. for \([\text{[(C}_2\text{H}_5)_4\text{N]}_3\text{[(Ta}_5\text{MoCl}_4\text{]}_2\text{]}\text{Cl}_6\)] with observed values in parentheses: Ta, 44.6 (44.1); Mo, 4.73 (4.77); Cl, 31.4 (31.5); C, 14.2 (13.7); H, 2.98 (2.87).

**Analytical Procedures**

Carbon and hydrogen analyses were done by J. J. Richard of the Ames Laboratory Analytical Service Group, Iowa State University of Science and Technology, Ames, Iowa. Molybdenum analyses were done by M. J. Tschetter or L. T. Sadanaga of the same group. Some tantalum analyses were done by M. J. Tschetter.

When tantalum was not determined by the service group, a total metal oxide determination, coupled with a molybdenum determination by the service group, facilitated calculation of the tantalum content of the compound in question. Total metal
oxide was determined by the "H-tube" method of Schäfer and Dohmann (ll6). In this method a sample is oxidized with nitric acid in a manner that allows simultaneous quantitative collection of silver chloride and metal oxide. This method was therefore also used for some chlorine analyses. Other chlorine determinations were done by hydrolyzing a sample in hot aqueous ammonia or hot dilute potassium hydroxide, oxidizing with 30 percent hydrogen peroxide, acidifying with nitric acid, and titrating potentiometrically with standard silver nitrate.

Physical Measurements

Magnetic susceptibilities

Magnetic susceptibilities were determined by the Faraday method on a balance constructed by J. G. Converse (117).

Far infrared spectra

Far infrared spectra were measured by C. C. Hill of the Ames Laboratory Spectrochemistry Group, Iowa State University of Science and Technology, Ames, Iowa. Samples were submitted as solids and measured as Nujol mulls. All far infrared spectra were obtained with polyethylene windows on a Beckman IR-11 spectrophotometer in the region 40-600 cm⁻¹.

Electronic spectra

All electronic spectra were measured on acetonitrile solutions made up by dissolving weighed amounts of a sample in
acetonitrile and diluting to volume in a volumetric flask. The solutions were contained in 10 mm. fused quartz cells for measurement and measured with a Cary Model 14 recording spectrophotometer using a solvent reference. A baseline was recorded for each spectrum so accurate absorbance values could be determined.

Data processing

The electronic spectra of these compounds were rather complex, so the spectra were resolved into Gaussian components. A computer program was developed for this purpose by the Ames Laboratory Computer Services Group, Iowa State University of Science and Technology, Ames, Iowa. This program used components peaks defined by Equation 1 (118) to fit experimental spectra.

\[
\epsilon = \epsilon_0 \exp \left( -\frac{(\nu - \nu_0)^2}{\theta^2} \right)
\]

(1)

where:  
\( \epsilon = \) extinction coefficient in \( \lambda \) mole\(^{-1}\)cm\(^{-1}\),  
\( \epsilon_0 = \) extinction coefficient at the absorption maximum,  
\( \nu = \) wavenumber in cm\(^{-1}\),  
\( \nu_0 = \) wavenumber at the absorption maximum,  
\( \theta = \delta/\sqrt{\ln 2} \)  
\( \delta = \) absorption half-width at half-height.

A least squares procedure was used to obtain a best fit of calculated Gaussian components to the observed spectra. Input data consisted of observed wavelength and absorbance values, the number of components into which the given region
of the spectrum was to be resolved, and estimated \( \nu_0 \), \( \varepsilon_0 \), and \( \theta \) values for each Gaussian component. Up to one hundred observed wavelength-absorbance couples could be read into the computer. The maximum number of components into which the given region of the spectrum could be resolved was five. The computer varied the \( \nu_0 \), \( \varepsilon_0 \), and \( \theta \) parameters two at a time, iterating until a variation of 0.1 percent in each did not improve the fit of the sum of the calculated components to the observed spectrum.

The computer output was the calculated \( \nu_0 \), \( \varepsilon_0 \), and \( \theta \) values for each component and a graphical representation of the fit of the sum of the calculated components to the observed spectrum. A listing of the computer program is given in the Appendix.
RESULTS AND DISCUSSION

Synthesis

This work represents the first preparation of mixed-metal $M_6X_{12}$ or $M_6X_8$ clusters containing metals from different groups. The basic preparative reactions are described by Equations 2 and 3.

\[
5\text{TaCl}_5 + 5\text{MoCl}_5 + 5\text{Al} \xrightarrow{320^\circ, 3\text{ days}} 5\text{AlCl}_3 + \text{Ta}_5\text{MoCl}_{15} \quad (2)
\]

\[
12\text{TaCl}_5 + 6\text{MoCl}_5 + 14\text{Al} \xrightarrow{320^\circ, 3\text{ days}} 14\text{AlCl}_3 + 3\text{Ta}_4\text{Mo}_2\text{Cl}_{16} \quad (3)
\]

Schäfer and Spreckelmeyer (83) prepared a tantalum-niobium mixed-metal cluster by reducing a solid solution of the two metal pentabromides. The reduction of an intimate mixture of pentahalides such as the solid solution used by Schäfer and Spreckelmeyer was done here by dissolving tantalum pentachloride and molybdenum pentachloride in a suitable solvent and reducing them in solution. When the reaction was run without a solvent, no mixed-metal cluster was observed in the products.

The solvent system sodium chloride-aluminum trichloride was selected because of its wide liquid range with a low vapor pressure and variable acidity over the temperature range desired. Empirically, an acidic solvent of about 60 mole
percent aluminum trichloride seemed to favor preparation of 5-1 clusters while less acidic or neutral solvents favored preparation of the 4-2 cluster. Best results for 4-2 preparations were obtained with solvents containing 50 to 53 mole percent aluminum trichloride.

Another attractive feature of this solvent system was that it did not add any component to the total reaction mass that was deemed likely to interfere in subsequent treatments of the reaction mass.

Aluminum was chosen as the reducing agent partly because it goes to aluminum trichloride upon reaction and thus also avoids further complication of an already complex product mass. Aluminum was also known to reduce tantalum(V) chloride to the Ta$_6$Cl$_{12}^{2+}$ cluster and molybdenum(V) chloride to the Mo$_6$Cl$_{18}^{4+}$ cluster.

Some preliminary reactions for the reduction of tantalum pentachloride alone showed that the tantalum cluster begins forming at an appreciable rate at about 325°. Molybdenum pentachloride was reduced somewhat more readily at the same temperature, but only about a 15 percent yield of molybdenum dichloride was obtained in three days at 320°.

A temperature of 310° was selected for the first attempt to prepare a mixed-metal cluster. It was thought that this temperature would minimize the production of tantalum or molybdenum clusters while perhaps producing significant amounts of the desired product. Mixed-metal clusters were indeed
prepared, but these were accompanied by surprising amounts of tantalum cluster. Tantalum cluster was apparently produced more readily at these temperatures if some molybdenum pentachloride was originally present. No molybdenum cluster was ever observed in the products except when molybdenum pentachloride was originally present in large excess. Some tantalum cluster has been observed in every product.

Further attempts to coreduce the pentachlorides of tantalum and molybdenum showed that yields of all the clusters concerned fell off sharply if the reaction was carried out at temperatures less than 300° or for times shorter than three days. On the other hand, reaction temperatures greater than about 320° and reaction times of longer than three days did not improve the yields significantly. The highest temperature tested was 375°; the longest reaction time tried was ten days. The best yield of mixed-metal cluster ever obtained was about 30 percent of the theoretical yield. A more typical yield was about 15 percent of the theoretical yield.

Reaction time and temperature seemed to have little effect in determining which mixed-metal cluster predominated in the reaction product. The most effective variable in the reaction in this regard was the tantalum:molybdenum ratio in the starting mixture. Best results in preparing the 5-1 cluster were obtained with tantalum:molybdenum ratios of 8:1 to 10:1. When ratios higher than 10:1 were used, it was difficult to separate the relatively small amount of mixed-metal
cluster from the relatively large amount of tantalum cluster produced. Ratios of less than 8:1 resulted in greater contamination of the 5-1 cluster by the 4-2 cluster. When the 4-2 cluster was the desired product, a tantalum:molybdenum ratio of 1:1 gave the best results. Molybdenum cluster was observed as a product only when the tantalum:molybdenum ratio was lowered to 1:3 and even then some tantalum cluster was also prepared.

When the coreduction reaction had been completed, the reduction mass contained sodium chloride or aluminum trichloride, sodium tetrachloroaluminate and tantalum chloride cluster as well as the desired products, any partially reduced tantalum or molybdenum chlorides, and any unreacted aluminum metal. As previously mentioned, some molybdenum dichloride might also have been present but it never presented any special separation problems.

Most of the contaminating components were leached out easily with water. The reduction mass first had to be crushed to pass through a 20 mesh screen or the larger lumps remained dry in their cores while being stirred in water for several hours. The first water extraction of a finely crushed reduction mass removed most of the sodium chloride and aluminum trichloride, hydrolyzed any higher tantalum or molybdenum halides present, and removed some of the tantalum cluster. A second water extraction served to complete the removal of all the soluble components except some of the tantalum cluster
which was slow to dissolve. These first two water extractions were completed in six to ten hours of stirring in water.

Water extraction could be continued to remove all the tantalum cluster present, but that required several days of constant stirring of the solid fraction in water. The mixed-metal clusters were insoluble in water, but such prolonged stirring in water decreased their ultimate yield, probably through slow hydrolysis.

Extended water extractions could be avoided if an ion exchange step was included to remove the residual tantalum cluster. After the first two water extractions, the solid fraction was extracted with absolute ethanol for ten to twelve hours. This treatment dissolved the remaining tantalum cluster and most of the mixed-metal clusters. The ethanol solution was then made 20 to 25 percent water before the ion exchange step to avoid dehydrating the resin so severely that the ion-exchange process never occurred. When the ethanol-water solution was passed through Dowex 50W-X8 cation exchange resin (acid form), a dark ring of tantalum cluster was retained, while the mixed-metal clusters were passed through the column. The mixed-metal clusters apparently exist as molecular species in these solutions, since a solution will also pass through an anion exchange column without loss of the cluster.

Since the spectral data for compounds comparable to these mixed-metal clusters pertain mostly to anionic moieties, the mixed-metal clusters were isolated in anionic form. Isolation
of the cluster species as complex anions also provided for some fractionation of the mixture of mixed-metal clusters which was almost always obtained from the initial reaction.

The anation of the mixture of mixed-metal clusters was done under nonoxidizing conditions so the subsequent fractionation would be of \([\text{(Ta}_4\text{Mo}_2\text{Cl}_{12})\text{Cl}_6]^{2-}\) and \([\text{(Ta}_5\text{MoCl}_{12})\text{Cl}_6]^{3-}\) and not two ions of the same charge. Under these conditions the 4-2 derivative was apparently the less soluble component of the mixture and partially crystallized out of the solution in the presence of excess tetraalkylammonium cation. Normally, very little of the 5-1-3 derivative crystallized until the volume of the solution was reduced by about 30 percent. When the volume of the solution was reduced, more of the 4-2 derivative crystallized along with the 5-1 derivative. For this reason, the 4-2 cluster derivatives could usually be isolated in higher purity than the 5-1 derivatives.

The highest purity 5-1 derivative prepared in this work was the 5-1-3 compound obtained from a long term fractionation procedure. Several impure samples containing about 70 percent 5-1 cluster were combined, dissolved in acetonitrile, and reduced with zinc at room temperature for about a week. The solution had then become quite turbid and was centrifuged to remove the turbidity. The experiment planned was to add small amounts of tetraethylammonium chloride to the solution periodically and collect fractions of recrystallized complexes as the cation concentration increased. More turbidity appeared
every few days and was removed by centrifuging the solution. When a few crystals finally appeared about six weeks into the experiment, a vacuum filtration was employed to collect the crystals. Not much product was filtered off, but several hundred milligrams of crystals appeared on the bottom of the filter flask. The spectrum of an acetonitrile solution of this compound showed no evidence for the presence of any 4-2 complex.

Apparently, the turbidity which formed slowly throughout the procedure was due predominantly to disruption of the 4-2 cluster with only slight loss of 5-1-3 cluster. When the temperature of the solution was lowered by the aspirator vacuum the solubility of the 5-1-3 derivative was exceeded while the amount of 4-2 cluster present had been so reduced that the limit of its solubility was not reached. Evaporation had reduced the original volume of the solution by about 30 percent.

In an attempt to take advantage of the apparently greater stability of the 5-1-3 cluster toward solvolysis over the similar stability of the 4-2 cluster, another acetonitrile solution of a mixture of mixed-metal clusters was refluxed for 12 hours in the presence of metallic zinc. This treatment resulted in the disruption of both clusters. Subsequent trials have not uncovered any set of conditions or a time duration which would make this method useful as a routine purification procedure.

The complexes were usually isolated as tetraethylammonium
salts. Several trial fractionations using other cations showed no noticeable dependence of the success of the fractionation on the identity of the cation. Other cations tried were tetra-n-butylammonium, triethylammonium, diethylammonium, n-propylammonium, and tetramethylammonium.

One cesium salt was isolated after two successive recrystallizations of the tetra-n-butylammonium salt of the 5-1-2 cluster from ethanol saturated with anhydrous hydrogen chloride by adding excess cesium chloride. This derivative was prepared solely for the purpose of obtaining a far infrared spectrum, and was not independently analyzed.

The electronic spectrum of the \([\text{Ta}_6\text{Cl}_{12}\text{Cl}_6]^{4-}\) ion is discussed later in this section. No salt of this ion was isolated. A solution of the ion was obtained by sealing an acetonitrile solution of \([\text{C}_2\text{H}_5\text{NH}]_2[\text{Ta}_6\text{Cl}_{12}\text{Cl}_6]\) (40) and a few granules of metallic zinc into a special spectrophotometer cell and heating the cell gently for about two hours before measuring the spectrum. The spectrum obtained showed no trace of derivatives of an oxidized tantalum cluster.

It should be noted in this discussion that routine preliminary determination of the purity of a compound was done by examining its electronic spectrum and not by elemental analysis. Early in this work, the tantalum:molybdenum ratios and the chlorine:metal ratios of the reaction products established the products as mixtures of \(\text{Ta}_5\text{MoCl}_{12}^{7+}\) and \(\text{Ta}_4\text{Mo}_2\text{Cl}_{12}^{4+}\) derivatives. Qualitative electronic spectra were then determined
for the individual components of the mixture by examining the spectra of several different mixtures. Once the qualitative spectrum of each species was known, elemental analyses were carried out only on the highest purity compounds isolated.

Electronic Spectra and Magnetic Data

Electronic spectra

The determination of the electronic structure of $\text{M}_{6}\text{X}_{12}$ cluster derivatives through the study of the electronic spectra of the clusters has been the object of several previous studies (102, 104, 105, 106, 108, 113). It was hoped that substitution of one or more of the metal atoms in the $\text{M}_{6}\text{X}_{12}$ cluster core would alter the electronic spectra of the cluster derivatives in such a way as to facilitate the definite assignment of at least some of the observed bands in the spectra. To this end, spectra of the ions $[(\text{Ta}_5\text{MoCl}_{12})\text{Cl}_6]^{2-}$ and $[(\text{Ta}_4\text{Mo}_2\text{Cl}_{12})\text{Cl}_6]^{2-}$ were measured in acetonitrile solution over the energy range 6.5 to 45 kK and analyzed as described in the experimental section. The spectrum of the $[(\text{Ta}_6\text{Cl}_{12})\text{Cl}_6]^{4-}$ ion was also measured and analyzed.

Before discussing the spectra, it should be ascertained whether the spectra are indeed of the ions mentioned or of some dissociated species where solvent has substituted for terminal halide on the cluster. Schneider and Mackay (38, 113) studied the conductance of $[(\text{C}_2\text{H}_5)_4\text{N}]_n[\text{(Nb}_6\text{Cl}_{12})\text{Cl}_6]$ ($n = 2, 3, 4$) in nitromethane solution and found the compounds to be n:1
electrolytes. These authors also found (113) that the infra-red spectra of those compounds in nitromethane solution agreed very well with the data on the solids, further indicating no dissociation of the terminal halogens. Fleming and McCarley (105) compared the electronic reflectance spectra of compounds containing the $[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_6]^{2,3,4-}$ ions to the spectra of these compounds in several solvents and found good agreement between the acetonitrile solution spectra and the reflectance spectra of the 3- and 2- ions. These data are also in good agreement with the nitromethane solution data for the 3- ion as obtained by Schneider and Mackay (113). The data of Fleming and McCarley (105) do indicate that the $[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_6]^{4-}$ ion may be dissociated to some extent in acetonitrile. Finally, in this work it was observed that the mixed metal cluster complexes could be recrystallized from acetonitrile without lowering the chlorine:metal ratio. Considering all of the above observations, it is unlikely that the mixed-metal cluster anions are significantly dissociated in acetonitrile solution, but the stability of the $[(\text{Ta}_6\text{Cl}_{12})\text{Cl}_6]^{4-}$ ion with respect to dissociation in acetonitrile is questionable.

The resolved electronic spectra of the three mixed-metal cluster derivatives and the $[(\text{Ta}_6\text{Cl}_{12})\text{Cl}_6]^{4-}$ ion are shown in Figures 1-4. The data are compared in Figure 5 and summarized in Table 1. Spectral data for three homonuclear cluster compounds of tantalum and niobium have been included in Figure 5 to facilitate additional comparisons.
Figure 1. The electronic spectrum of the $[(Ta_6Cl_{12})Cl_6]^{4-}$ ion in acetonitrile solution. The crosses represent the observed spectrum, the lower solid curves represent the individual Gaussian components and the upper solid curve is the calculated spectrum.
Figure 2. The electronic spectrum of $(\text{Et}_4\text{N})_2[\text{Ta}_4\text{Mo}_2\text{Cl}_{12}]\text{Cl}_6$ in acetonitrile. The crosses represent the observed spectrum, the lower solid curves represent the individual Gaussian components and the upper solid curve is the calculated spectrum.
Figure 3. The electronic spectrum of \((\text{Et}_4\text{N})_3[\text{Ta}_5\text{MoCl}_{12}\text{Cl}_6]\) in acetonitrile. The crosses represent the observed spectrum, the lower solid curves represent the individual Gaussian components and the upper solid curve is the calculated spectrum.
Figure 4. The electronic spectrum of (Et₄N)₂[(Ta₅MoCl₁₂)Cl₆] in acetonitrile. The crosses represent the observed spectrum, the lower solid curves represent the individual Gaussian components and the upper solid curve is the calculated spectrum.
Figure 5. The electronic spectra of some $M_6X_{12}^{n+}$ cluster derivatives

A. $Nb_6Cl_{12}Cl_6^{3-}$ in acetonitrile, data from reference (105)

B. $Ta_6Cl_{12}^{3+}$ in ethanol, data from reference (105)

C. $Ta_5MoCl_{12}Cl_6^{2-}$ in acetonitrile

D. $Ta_4Mo_2Cl_{12}Cl_6^{2-}$ in acetonitrile

E. $Ta_5MoCl_{12}Cl_6^{3-}$ in acetonitrile

F. $Ta_6Cl_{12}Cl_6^{4-}$ in acetonitrile

G. $Nb_6Cl_{12}Cl_6^{4-}$ in acetonitrile, data from reference (105)
Table 1. Electronic absorption data

<table>
<thead>
<tr>
<th></th>
<th>[((\text{Ta}<em>6\text{Cl}</em>{12})\text{Cl}_6)]^{4-}</th>
<th>[((\text{Ta}<em>5\text{MoCl}</em>{12})\text{Cl}_6)]^{3-}</th>
<th>[((\text{Ta}<em>5\text{MoCl}</em>{12})\text{Cl}_6)]^{2-}</th>
<th>[((\text{Ta}_4\text{Mo}<em>2\text{Cl}</em>{12})\text{Cl}_6)]^{2-}</th>
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<tbody>
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<td>$v_b$</td>
<td>$\epsilon_c$ $\delta_b$</td>
<td>$v_b$ $\epsilon_c$ $\delta_b$</td>
<td>$v_b$ $\epsilon_c$ $\delta_b$</td>
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<td>8.84 0.15 0.79</td>
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<tr>
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<td>9.67 0.22 0.72</td>
<td>10.30 1.29 0.52</td>
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</tr>
<tr>
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<td>13.69 0.76 1.30</td>
<td>11.24 0.59 0.45</td>
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<tr>
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<td>17.0 0.64 1.20</td>
<td>13.56 1.30 1.21</td>
<td></td>
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<tr>
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<td>3.01 1.07 24.8 2.88 1.64</td>
<td>21.1 2.20 2.06</td>
<td>17.4 1.57 2.36</td>
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<td>---- ----</td>
<td>20.1 0.59 1.00</td>
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<td>30.0</td>
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<td>27.1 13.16 2.68</td>
<td>23.1 5.12 1.61</td>
<td></td>
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<tr>
<td>35.5</td>
<td>5.61 4.28 35.9 8.73 3.78</td>
<td>35.0 8.23 2.90</td>
<td>26.4 7.46 1.76</td>
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</tr>
<tr>
<td>42.9</td>
<td>18.9 3.33 41.7 27.01 3.14</td>
<td>40.8 44.45 2.82</td>
<td>28.6 2.01 0.76</td>
<td></td>
</tr>
<tr>
<td>46.9</td>
<td>---- ---- 46.9 30.61 1.88</td>
<td>29.9 4.50 2.91</td>
<td>32.8 6.42 1.64</td>
<td></td>
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<td>43.2 35.42 3.80</td>
<td>39.2 17.61 4.48</td>
<td>43.2 35.42 3.80</td>
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<tr>
<td>43.2</td>
<td>46.9 30.61 1.88</td>
<td>46.9 30.61 1.88</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$Absorptions are resolved Gaussian components. Spectra were obtained on acetonitrile solutions of tetraethylammonium salts.

$^b$In units of kiloKaysers (1 kK = 1000 cm$^{-1}$).

$^c$In units of liter mole$^{-1}$cm$^{-1}$ (x 10$^{-3}$).
Figure 1 shows the resolved spectrum of the \([\text{Ta}_6\text{Cl}_{12}]^{4-}\) ion in acetonitrile solution. The fit of the observed spectrum by the calculated spectrum is less satisfactory for this ion than for any of the others as can be seen from a cursory examination of Figures 1 to 4. From a visual inspection of Figure 1, it seems that the small absorption band at 27.9 kK should not have been included in the calculated spectrum. When attempts were made to fit the observed spectrum with a calculated spectrum not including this band, the results were always clearly less satisfactory. It is possible, however, that the poor fit of the spectrum without the 27.9 kK band resulted from deviations from the assumed Gaussian shape of the bands included and not because another band was needed to fit the data.

The same criterion for including an absorption in the calculated spectrum was used in the spectrum of the 4-2 complex shown in Figure 2. In order to get a reasonably good fit of the observed spectrum, a total of fifteen absorption bands had to be used in the computations even though the existence of a few of the bands was otherwise questionable. No significance can be afforded the highest energy band. It was included in the computations as an end absorption and the data do not extend to wavelengths including this band.

The spectra are all shown in Figure 5 together with the spectra of some related cluster compounds. The spectra of all these compounds should indeed be comparable. Considering
first the Ta$_6$Cl$_{12}^{n+}$ and Nb$_6$Cl$_{12}^{n+}$ derivatives, structural data indicate that the metal atom clusters in K$_4$[(Nb$_6$Cl$_{12}$)Cl$_6$] (119), (Ta$_6$Cl$_{12}$)Cl$_3$ (93b) and H$_2$[(Ta$_6$Cl$_{12}$)Cl$_6$]$^1$ all are nearly perfect octahedra with $O_h$ symmetry. Also, Fleming and McCarley (105) have reported that the spectra of tantalum and niobium clusters in solution are qualitatively independent of the solvent so even if solvation of the anions occurs, significant distortion of the metal octahedra does not occur or has no gross effect on the spectra. The magnetic data for tantalum and niobium cluster compounds discussed in the previous work section also indicate that the electronic structures of those clusters are similar.

Fleming (120) has already noted that the tantalum cluster bands generally appear at energies from 2 to 8 kK higher than the niobium cluster bands. Such a shift is in good agreement with the shifts found in comparing the spectra of hexahalo complexes of 4d$^n$ and 5d$^n$ metals (121, p. 154).

When comparing the spectra of the mixed-metal clusters to the spectra of the homonuclear clusters, it is important to note that the substitution of one molybdenum atom for one tantalum atom (or niobium atom, if the compound existed) results in an increase of the positive charge of the cluster by one unit. The new cluster is then "isoelectronic" with the parent

cluster if only metal-metal bonding electrons are considered. That is to say that \( \text{Ta}_6\text{Cl}_{12}\text{Cl}_6^{4^-} \), \( \text{Ta}_5\text{MoCl}_{12}\text{Cl}_6^{3^-} \) and \( \text{Ta}_4\text{Mo}_2\text{Cl}_{12}\text{Cl}_6^{2^-} \) should all have sixteen metal-metal bonding electrons.

For the "isoelectronic" compounds in Figure 5, dashed lines connect the bands which are thought to be analogous. There are no dashed lines to any bands in the spectrum of the 4-2 compound for reasons to be discussed later. All analogies between bands of tantalum and niobium clusters are those drawn by Fleming and McCarley (105).

The dashed lines emphasize a few discrepancies in the spectra presented. Fleming and McCarley (105) did not carry out Gaussian analyses of their spectra of tantalum cluster derivatives and could easily have missed a comparatively weak band at 16-20 kK. The existence of such a band in the spectrum of \( \text{Ta}_6\text{Cl}_{12}^{3+} \) (spectrum B) is strongly suggested by presence of such a band in the spectra of \( \text{Nb}_6\text{Cl}_{12}\text{Cl}_6^{3^-} \) and \( \text{Ta}_5\text{MoCl}_{12}\text{Cl}_6^{2^-} \), spectra A and C respectively.

Spectra E, F, and G are the spectra of \( \text{Ta}_5\text{MoCl}_{12}\text{Cl}_6^{3^-} \), \( \text{Ta}_6\text{Cl}_{12}\text{Cl}_6^{4^-} \), and \( \text{Nb}_6\text{Cl}_{12}\text{Cl}_6^{4^-} \) respectively. The spectra of the tantalum and tantalum-molybdenum clusters show two more absorptions in the energy range presented than the spectrum of the niobium cluster; the 43 kK absorption of the niobium cluster undoubtedly corresponds to absorptions in the other spectra which occur at higher energies than were investigated. In order to bring about a one:one correspondence of these
spectra, the niobium cluster spectrum would have to contain additional bands at about 9 kK and at about 22 kK. These bands would correspond to the 10.4 kK and 27.8 kK bands in the 5-1-3 spectrum, and the 11.5 kK and 27.9 kK bands in the $\text{Ta}_6\text{Cl}_{12}\text{Cl}_6^{4-}$ spectrum. The two bands concerned are obvious in the 5-1-3 spectrum (see Figure 3) but considerably less obvious in the $\text{Ta}_6\text{Cl}_{12}\text{Cl}_6^{4-}$ spectrum (see Figure 1). They were included in the Gaussian analysis of the $\text{Ta}_6\text{Cl}_{12}\text{Cl}_6^{4-}$ spectrum because a reasonable fit of the observed spectrum could not be obtained without them.

Not much can be said about the spectrum of the 4-2 derivative (Figure 2). It is quite possible that the sample used to obtain this spectrum was actually a mixture of two compounds containing the cis and trans isomers of the $\text{Ta}_4\text{Mo}_2$ cluster core. The fact that fourteen absorptions appear in the electronic spectrum compared to nine bands in the spectra of the "isoelectronic" 5-1-3 and $\text{Ta}_6\text{Cl}_{12}\text{Cl}_6^{4-}$ ions lends some support to this contention. Also, the change from a $\text{Ta}_6$ cluster core to a $\text{Ta}_5\text{Mo}$ cluster core did not result in any profound changes in the spectrum of the cluster. Extrapolation of that result to the dissubstituted cluster is tenuous, but it seems reasonable that both isomers may be present. Unfortunately, the infrared spectra to be discussed shortly are of no help in resolving the dilemma.

As previously stated, it had been hoped that the electronic spectra of these compounds would provide some new
information about the electronic structure of $M_6X_{12}^{n+}$ clusters. The spectra of the Ta$_5$Mo cluster species have so far served only to substantiate the identity of the compounds. There is presently insufficient data available on the Ta$_4$Mo$_2$ compound to justify drawing any conclusions from the electronic spectra.

Magnetic properties

The compounds described previously as "isoelectronic" should have similar magnetic properties. As discussed in the Introduction, derivatives of Ta$_6$Cl$_{12}^{2+}$ and Ta$_6$Cl$_{12}^{4+}$ are diamagnetic while derivatives of Ta$_6$Cl$_{12}^{3+}$ have magnetic moments corresponding to one unpaired electron per cluster unit. Tables 2 and 3 summarize the magnetic data obtained on the mixed-metal cluster compounds and some comparable data on homonuclear cluster compounds. Detailed ($\chi$ vs T) data on the mixed-metal compounds are given in the Appendix.

From the observed magnetic moments of the mixed-metal clusters (Table 2), it is apparent that the two clusters which were expected to be diamagnetic (Ta$_5$MoCl$_{18}^{3-}$ and Ta$_4$Mo$_2$Cl$_{18}^{2-}$) contain magnetically significant amounts of paramagnetic material. Comparison of the observed and calculated moments of the 5-1-2 complex indicates the presence of some diamagnetic impurity in what was expected to be a paramagnetic compound. First thoughts about these discrepancies in the magnetic behavior of the mixed-metal cluster compounds were that the major contaminant of each compound was one of the other mixed-
Table 2. Magnetic moments (B.M.)

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\mu_{\text{obs.}})</th>
<th>(\mu_{\text{calc.}})</th>
<th>(\tilde{g}) (epr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\text{Et}_4\text{N})_3\text{Ta}<em>6\text{Cl}</em>{18})^a</td>
<td>1.67</td>
<td>1.66</td>
<td>1.922</td>
</tr>
<tr>
<td>((\text{Bu}_4\text{N})_2\text{Ta}<em>5\text{MoCl}</em>{18})</td>
<td>1.47</td>
<td>1.69</td>
<td>1.958^b</td>
</tr>
<tr>
<td>((\text{Et}_4\text{N})_3\text{Ta}<em>5\text{MoCl}</em>{18})</td>
<td>0.76</td>
<td>--</td>
<td>[1.942]^b</td>
</tr>
<tr>
<td>((\text{Et}_4\text{N})_2\text{Ta}_4\text{Mo}<em>2\text{Cl}</em>{18})</td>
<td>0.42</td>
<td>--</td>
<td>[1.985]^b</td>
</tr>
</tbody>
</table>

^a Data from reference (114).

^b Measured by W. E. Antholine of this laboratory on powdered samples. Brackets indicate that the listed \(\tilde{g}\) value is for paramagnetic impurities. Data taken at room temperature.

Table 3. Magnetic susceptibilities (cgsu) at room temperature

<table>
<thead>
<tr>
<th>Compound</th>
<th>(10^6 \chi_M)</th>
<th>(10^6 \chi_D)</th>
<th>(10^6 \chi_{\text{TIP}})^a</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\text{Et}_4\text{N})_3\text{Ta}<em>5\text{MoCl}</em>{18})</td>
<td>-550</td>
<td>-1066</td>
<td>516</td>
</tr>
<tr>
<td>((\text{Bu}_4\text{N})_2\text{Ta}<em>5\text{MoCl}</em>{18})</td>
<td>-510</td>
<td>-1136</td>
<td>626</td>
</tr>
<tr>
<td>((\text{Et}_4\text{N})_2\text{Ta}_4\text{Mo}<em>2\text{Cl}</em>{18})</td>
<td>-410</td>
<td>-958</td>
<td>548</td>
</tr>
<tr>
<td>((\text{Et}_4\text{N})_3\text{Ta}<em>6\text{Cl}</em>{18})^b</td>
<td>-557</td>
<td>-1054</td>
<td>497</td>
</tr>
<tr>
<td>((\text{Et}_4\text{N})_2\text{Ta}<em>6\text{Cl}</em>{18})^b</td>
<td>-433</td>
<td>-934</td>
<td>501</td>
</tr>
<tr>
<td>((\text{Et}_4\text{N})_3\text{Nb}<em>6\text{Cl}</em>{18})^b</td>
<td>-372</td>
<td>-1024</td>
<td>652</td>
</tr>
</tbody>
</table>

^a \(\chi_{\text{TIP}}\) calculated from \(\chi_M = \chi_D + \chi_{\text{TIP}}\).

^b Data from reference (114).
metal cluster compounds. The epr data (Table 2) have refuted this theory, at least for the 5-1-3 and 4-2 complexes.

The epr spectrum of the 5-1-2 complex shows one well formed apparently symmetrical resonance from which a $g$ value of 1.958 was calculated. This value leads to a calculated moment of 1.69 B.M. compared to the measured value of 1.47 B.M. According to Equation 4, the major impurity in the 5-1-2

$$x = \frac{\mu_a^2}{\mu_p^2} \frac{M_p}{M_a}$$

where $x =$ weight fraction of paramagnetic component of mixture of one paramagnetic component and one diamagnetic component.

$\mu_a =$ apparent magnetic moment of the mixture.

$\mu_p =$ magnetic moment of paramagnetic component.

$M_a =$ apparent molecular weight of mixture.

$M_p =$ molecular weight of paramagnetic component.

sample was the 4-2 complex. The sample would have had to contain about twenty five weight percent of this impurity. It is believed that such an amount of the 4-2 complex in the sample would have manifested itself in the electronic spectrum of the sample, and the spectrum of this particular sample of the 5-1-2 complex did show some evidence for the presence of the 4-2 complex.

The derivation of Equation 4 is given in the Appendix.
The 5-1-3 complex was expected to be diamagnetic, but a magnetic moment of 0.76 B.M. was observed. An epr spectrum of the sample showed a resonance from which a $g$ value of 1.942 was calculated. Therefore the major magnetic contaminant is probably not the 5-1-2 complex for which a $g$ value of 1.958 was determined.

It is interesting to note that if the molecular weights of the 5-1-3 complex (2030) and a paramagnetic impurity were equal and if the moment of the impurity were 1.7 B.M. twenty weight percent of the impurity would cause a moment of 0.76 B.M. for the sample. If the molecular weight of the impurity were less than 2030, the weight percent of impurity required to account for a moment of 0.76 B.M. would also be less. A complicating factor in the interpretation of these data is that the analytical data on this compound are quite good for $(\text{Et}_4\text{N})_3\text{Ta}_5\text{MoCl}_{18}$. Any impurity of ten to twenty weight percent should be readily evident from the elemental analyses. Also the electronic spectrum of this sample corresponds very well with the spectra of the "isoelectronic" species Ta$_6$Cl$_{18}^-$ and Nb$_6$Cl$_{18}^4$-. The bands in the spectrum of the 5-1-3 complex are quite intense however, and the spectrum of an impurity could have been completely masked.

The purity of the 4-2 complex as calculated from magnetic data, is the highest of any of the compounds prepared. The observed moment of 0.42 B.M. corresponds to contamination of about six weight percent by a compound of similar molecular
weight and a moment of 1.7 B.M. The observed $\bar{g}$ value of 1.985 indicates that the contaminant is none of the aforementioned compounds or contaminants.

The magnetic susceptibilities of the mixed-metal cluster compounds are listed in Table 3 along with similar data for some homonuclear metal cluster compounds. The data show that the $X_{\text{TP}}$ of these mixed-metal clusters is essentially the same as for the homonuclear metal clusters.

Far Infrared Spectra

The far infrared spectra of these mixed-metal cluster compounds are less informative than had been expected. The total reducible representation of the $[(\text{Ta}_5\text{MoCl}_{12})\text{Cl}_6]^{n-}$ ion in $C_{4v}$ symmetry is given by Equation 5 in terms of the irreducible representations it contains. Only $A_1$ and $E$ modes are infrared active in $C_{4v}$ symmetry; one $A_1$ and two $E$ modes arise from translations and rotations of the ion. This leaves thirteen $A_1$ and seventeen $E$ modes, for a total of thirty bands which should appear in the spectrum. As can be seen from the data in Table 4, a total of eleven bands appeared in the spectrum of $[(n-C_4H_9)_4N]_2[(\text{Ta}_5\text{MoCl}_{12})\text{Cl}_6]$ and in the spectrum of the corresponding cesium salt. Only seven bands appeared in the spectrum of the 5-1-3 complex.
Table 4. Far infrared spectra (cm\(^{-1}\))\(^a\)

<table>
<thead>
<tr>
<th>Band no.</th>
<th>Cs(^+) Ta(<em>6)Cl(</em>{18})(^{-})</th>
<th>Cs(^+) Ta(<em>5)MoCl(</em>{18})(^{-})</th>
<th>n-Bu(_4)N(^+) Ta(_4)Mo(<em>2)Cl(</em>{18})(^{-})</th>
<th>Et(_4)N(^+) Ta(<em>6)Cl(</em>{18})(^{-})</th>
<th>Et(_4)N(^+) Ta(<em>5)MoCl(</em>{18})(^{-})</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>---</td>
<td>348sh</td>
<td>350sh</td>
<td>348vs, vb</td>
<td>352sh</td>
</tr>
<tr>
<td>B</td>
<td>332 vs(F)</td>
<td>335vs</td>
<td>336vs</td>
<td>324vs</td>
<td>326vs</td>
</tr>
<tr>
<td>C</td>
<td>290 s(P)</td>
<td>296m</td>
<td>300s</td>
<td>303s</td>
<td>290vs</td>
</tr>
<tr>
<td>D</td>
<td>---</td>
<td>282w</td>
<td>286w</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>E</td>
<td>253 vs(F)</td>
<td>254vs</td>
<td>261vs</td>
<td>260vs</td>
<td>243vs</td>
</tr>
<tr>
<td>G</td>
<td>---</td>
<td>200w</td>
<td>202m</td>
<td>202s</td>
<td>197m</td>
</tr>
<tr>
<td>H</td>
<td>165 m(F)</td>
<td>187m</td>
<td>187s</td>
<td>185w</td>
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</tr>
<tr>
<td>I</td>
<td>153 w</td>
<td>162w</td>
<td>163w</td>
<td>---</td>
<td>153w</td>
</tr>
<tr>
<td>J</td>
<td>141 s(F)</td>
<td>142m</td>
<td>138m</td>
<td>144m</td>
<td>141m</td>
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<tr>
<td></td>
<td>118 m(F)</td>
<td>122m</td>
<td>124m</td>
<td>118m</td>
<td>123m</td>
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<tr>
<td></td>
<td>53 m</td>
<td>55m</td>
<td>---</td>
<td>70m</td>
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</tbody>
</table>

\(^a\)S = strong, m = medium, w = weak, v = very, b = broad, sh = shoulder.

\(^b\)McCarley, R. E., Ames, Iowa. On the far infrared spectrum of Cs\(_2\)Ta\(_6\)Cl\(_{18}\). Private communication. 1968.

\(^c\)(F) designates band as fundamental according to reference (41).

\(^d\)Data from reference (41).
In the case of the 4-2 complex, the symmetry could be $C_{2v}$ or $D_{4h}$ corresponding to a cis or trans arrangement, respectively, of the molybdenum atoms in the cluster. For $C_{2v}$ symmetry, the total reducible representation is given by Equation 6 in terms of the irreducible representations it contains. The $A_2$ modes are not infrared active and one $A_1$ mode, two $B_1$ modes, and two $B_2$ modes are accounted for by translation and rotation of the ion. Therefore, fifty four infrared bands should appear in the spectrum. The total reducible representation for the 4-2 complex ion in $D_{4h}$ symmetry is given by Equation 7. Only the $A_{2u}$ and $E_u$ modes are infrared active however, and one $A_{2u}$ mode and one $E_u$ mode are accounted for by translations of the ion. This leaves six $A_{2u}$ and ten $E_u$ modes for a total of sixteen bands to be expected in the spectrum. In the actual spectrum eight bands are clearly visible. The band at 348 cm$^{-1}$ is very broad however and probably represents more than one absorption.

Upon close examination of the data in Table 4, it becomes apparent that the far infrared spectra of the mixed-metal clusters closely resembles the spectra of the tantalum cluster species given in the table. Structural studies already dis-
cussed have shown that the tantalum clusters can be considered to have $O_h$ symmetry. The close resemblance of the spectra of the tantalum clusters and the mixed-metal clusters indicates that the effective symmetry of the mixed-metal clusters must also be $O_h$. As a precedent for this contention, Mattes (63) has noted from his own work and references (57, 59, and 60) that the far infrared spectra of $M_6X_8Y_6^{2-}$ species ($O_h$ symmetry) and $M_6X_8Y_4$ species ($D_{4h}$ symmetry) differ only slightly. Hogue and McCarley (64) made a similar comment about the spectra of $W_6Cl_8Cl_4(CH_3CH)_2$ and $W_6Cl_8Cl_6^-$. Also, there is extensive mixing of the normal modes of vibration in $M_6X_12^{3+}$ derivatives (41) and this mixing could serve to moderate the effect of the change of one or two of the metal atoms. If the effective symmetry of the clusters is $O_h$, six fundamental bands should be seen in the spectra (38, 95).

Further examination of the data in Table 4 reveals that five of the bands designated as fundamentals in the spectrum of Cs$_2$Ta$_6$Cl$_{18}$ (41) are clearly present in all the other spectra listed. These bands are listed as B, C, E, I, and J in the table. The lower energy of bands B, C, and E in the spectra of derivatives of $3^+$ clusters is consistent with the data of McCarley et al. (41) and Schneider and Mackay (38). The identity of the sixth fundamental at 165 cm$^{-1}$ in the spectrum of Cs$_2$Ta$_6$Cl$_{18}$ is certainly less clear in the other spectra.

Bands A, D, G, and H in Table 4 are seen to be unique to
the spectra of the mixed-metal species. Band D appears only in the spectra of the 5-1-2 complexes while band H is medium to strong in the spectra of the 5-1-2 complex, weak in the 4-2 spectrum and absent in the 5-1-3 spectrum. This could indicate that band H is also unique to the 5-1-2 spectra and appears in the 4-2 spectrum as the result of contamination of the 4-2 sample by some 5-1-2 complex. In light of the epr data however, this is probably not the case.

There are two bands, A and G, which are unique to the mixed-metal cluster spectra and appear in the spectra of all four mixed-metal compounds. Band A is seen as a shoulder at about 350 cm\(^{-1}\) in the spectra of the 5-1 complexes and probably as a component of the broad absorption at 348 cm\(^{-1}\) in the spectrum of the 4-2 complex. Bands A and B have probably coalesced in the spectrum of the 4-2 complex. Band G occurs at about 200 cm\(^{-1}\) in the spectra of all four mixed-metal complexes. No definite assignments can be made on the basis of the data available, but either band A or G probably derived from a molybdenum-terminal chlorine stretching vibration; the other band is likely attributable to an \(\text{M}_6\text{Cl}_{12}\) mode.
SUGGESTIONS FOR FUTURE WORK

A continuation of this work could take any of several directions. The most obvious is to extend the cluster series Ta₆, Ta₅Mo, Ta₄Mo₂ to include Ta₃Mo₃, Ta₂Mo₄ and TaMo₅ clusters. Continued investigation of the clusters already prepared might be of more immediate value however.

The difficulty encountered in this work in preparing pure compounds points out the need for further preparative studies. If pure compounds cannot be prepared directly, further attempts to purify the compounds might be fruitful. Purification of the compounds might be facilitated by some definite knowledge of the identity of the contaminants.

Even though the presence of the impurities had no apparent gross effect on the spectra of the mixed-metal derivatives, such an effect may appear in low temperature spectra of the derivatives. Electronic spectra at liquid helium temperature are needed to clarify which of the observed bands are actually allowed and which are vibronically allowed. This information would be of significant help in assigning the spectral bands to specific electronic transitions. Low temperature far infrared spectra might have sufficiently better resolution to show additional bands or at least provide better data on the 350 cm⁻¹ shoulders in the Ta₅Mo spectra and the broad 348 cm⁻¹ band in the spectrum of Ta₄Mo₂.

Further assistance in assigning the bands in the far
infrared spectra would be provided by the preparation of mixed-halogen derivatives where the terminal chloride ions have been replaced by other halide ions or possibly by some other anions. Preparation of bromide analogs of the type $\text{M}_6^{-x}\text{M}_x\text{Br}_{12}^{n+}$ is also a possibility in this regard.

Further work is needed to determine whether the $\text{Ta}_4\text{Mo}_2\text{Cl}_{12}^{4+}$ cluster contains *cis* or *trans* molybdenum atoms in the metal core, or if the samples so far prepared are mixtures of the two isomers. If the samples are mixtures, separation of the isomers would be desirable.

A preliminary investigation of the crystal structure of the compounds would be in order. It is quite possible that disorder of the molybdenum atoms will prevent detailed analyses of the molecular structures.

In this thesis, nothing was said about the other products of the coreduction of the pentachlorides of tantalum and molybdenum. Since yields of the mixed-metal clusters are low (ten to twenty percent of theoretical) and since it is unlikely that pentavalent tantalum or molybdenum would survive the reaction, there must be some other products of the reaction which contain these metals in a low oxidation state. Identification and isolation of these other products might provide some interesting results.

Finally, it now seems likely that preparation of mixed metal cluster compounds containing other pairs of transition metals is possible.
BIBLIOGRAPHY


42. Hellriegel, W., German Patent 703,895, 1941.


APPENDIX
<table>
<thead>
<tr>
<th>$T(°K)$</th>
<th>$\chi_M(\text{emu}\times 10^{-4})$</th>
<th>$1/T(°K\times 10^{-4})$</th>
<th>$\chi_g(\text{emu}\times 10^{-7})$</th>
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Derivation of Equation 4

\( x = \text{weight fraction of the paramagnetic component of a mixture containing one paramagnetic and one diamagnetic component} \)

\( M = \text{molecular weight} \)

Subscript \( a \) indicates apparent value for mixture

Subscript \( d \) indicates value for diamagnetic component

Subscript \( p \) indicates value for paramagnetic component

\[
\chi_{g,a} = x\chi_{g,p} + (1-x)\chi_{g,d}
\]

\[
\chi_{M,a} = \chi_{g,a} \frac{M_a}{M}
\]

\[
= xM_a \chi_{g,p} + (1-x)M_a \chi_{g,d}
\]

\[
= xM_a \frac{\chi_{M,p}}{M_p} + (1-x)M_a \frac{\chi_{M,d}}{M_d}
\]

Substituting

\[
\chi = \frac{nB^2\mu^2}{3kT} + \chi_{\text{TIP}}
\]

\[
\chi_{\text{TIP},a} + \frac{nB^2\mu^2}{3kT} = \frac{xM_a}{M_p} \frac{nB^2\mu^2}{3kT} + \chi_{\text{TIP},p} + \frac{(1-x)M_a}{M_d}
\]

\[
\chi_{\text{TIP},a} = x\chi_{\text{TIP},p} + (1-x)\chi_{\text{TIP},d}
\]

\( \mu_d \approx 0 \)
\[ \frac{n_{b}^{2} \mu_{a}^{2}}{3kT} = \frac{n_{p}^{2} \mu_{p}^{2}}{3kT M_{p}} \]

\[ \mu_{p}^{2} = \frac{x_{M_{a}}}{M_{p}} \mu_{p}^{2} \]

\[ x = \frac{\mu_{a}^{2}}{2} \frac{M_{p}}{\mu_{p}^{2}} \frac{M_{a}}{2} \]
Computer program for Gaussian analysis of electronic spectra

//C261BJM2 JOB 'A0241,TIME=7,SIZE=128K',JLMeyer
//STEPONE EXEC FORTG,REGION,GO=128K,TIME,GO=5
//FORT,SYSSIN DD *
COMMON N,A(64),D(64),PX(64),CY(99),X(99),Y(99),NP,NG
DIMENSION WLMM(99),ABSU(99),YS(99,6),XL(5),YL(5),GL(5),DL(5),TITLE
1(19)
READ(1,51)TITLE
1 READ(lt2) NP,NG,C
2 FORMAT(2I10,F10.0)
IF(NP)4,4,6
4 STOP
6 N=NG*3
READ(1,7)(A(I),I=1,N)
7 FORMAT(3F10.0)
READ(1,8)(WLMM(I),ABSU(I),I=1,NP)
8 FORMAT(8(F5.3,F5.3))
DO 10 I=1,NP
X(I)=1./WLMM(I)*1.E+7
10 Y(I)=ABSU(I)/C
CALL FUNFIT(.001,2)
WRITE(3,51)TITLE
51 FORMAT!'1',19A4)
WRITE(3,48)
48 FORMAT('0*10X*EXTC(MAX)*10X*WLRC(MAX)*12X*DEL(I)*')
42 WRITE(3,44)(A(I),I=1,N)
44 FORMAT(3F20.5)
READ(1,45)XL,YL,GL,DL
45 FORMAT(20A4)
CALL GRAPH(NP,X,Y,3,1,10.,10.,0,0,0,XL,YL,GL,DL)
CALL GRAPH(NP,X,CY,4,1,0,0,0,0,0,0,0,0,0,0)
DO 50 I=1,NG
DO 46 J=1,NP
V=(X(J)-A(3*I-1))/A(3*I)
46 YS(J,I)=A(3*I-2)/EXP(V*V)
50 CALL GRAPH(NP,X,YS(1,I),0,2,0,0,0,0,0,0,0,0,0,0)
WRITE(3,52)
52 FORMAT(1H0,1X10HLAMBDA(MUI,2X6HCM(-1),4X5HABSU,3X10HEXTC(DBS) ,10H
1EXTC(CALC),5X7HEXTC(I))
DO 54 I=1,NP
54 WRITE(3,56)WLMM(I),X(1),ABSU(I),Y(I),CY(I),(YS(I,J),J=1,NG)
56 FORMAT(IHO,F6.0,F13.3,F9.3,7F10.2)
GO TO 1
END
SUBROUTINE FUNFIT(DLIM,IP)
COMMON NP,A(1)
DIMENSION DA(99)
CALL FCN(ER)
POEL=.L
SQ2=SQRT(2.)/2.
2 DO 4 I=1,NP
4 DA(I)=A(I)*PDEL
6 IS=1
ER1=1.E70
ER2=ER1
DO 28 I=1,NP
A(I)=A(I)+DA(I)
CALL FCN(ER3)
A(I)=A(I)-DA(I)
IF(ER3-ER)14,14,10
14 A(I)=A(I)-DA(I)
CALL FCN(ER4)
A(I)=A(I)+DA(I)
IF(ER4-ER3)12,14,14
12  ER3=ER4
    DA(I)=DA(I)
14  IF(ER3-ER2)16,28,28
16  IF(ER3-ER1)18,20,20
18  I2=I1
    ER2=ER1
    I1=I
    ER1=ER3
    GO TO 28
20  ER2=ER3
    I2=I
28  CONTINUE
30  COSX=DA(I1)*SQ2
    SINX=DA(I2)*SQ2
    A(I1)=A(I1)+COSX
    A(I2)=A(I2)+SINX
    Y0=ER1
    CALL FCN(Y1)
    Y2=ER2
    A(I1)=A(I1)-COSX
    A(I2)=A(I2)-SINX
    IF((Y1-(Y0+Y2)*.5)31,305,305
305  Z=2.
    GO TO 32
31  C2=(4.0*Y1-Y2-3.0*Y0)*.5
    C3=Y1-Y0-C2
    Z=-C2/(C3*4.)
    IF(Z)32,38,38
32  GO TO (34,36),IS
34  IS=2
    DA(I2)=-DA(I2)
    A(I2)=A(I2)+DA(I2)
    CALL FCN(ER3)
    A(I2)=A(I2)-DA(I2)
    GO TO 30
36  SINX=0.
COSX=DA(I1)
A(I1)=A(I1)+COSX
ER3=YO
GO TO 40
SINX=(1.570627*Z-.6432292*Z*Z+.0727102*Z*Z*Z*Z)*DA(I2)
A(I2)=A(I2)+SINX
Z=Z-1.
COSX=(-1.570627*Z+.6432292*Z*Z-.0727102*Z*Z*Z*Z)*DA(I1)
A(I1)=A(I1)+COSX
CALL FCN(ER3)
IF(ER3-ER)42,44,44
ER=ER3
A(I2)=A(I2)+SINX
A(I1)=A(I1)+COSX
CALL FCN(ER3)
IF(ER3-ER)42,43,43
A(I2)=A(I2)-SINX
A(I1)=A(I1)-COSX
WRITE(3,7)(A(I),I=1,9I,ER,Z,I1,I2
7 FORMAT(11F10.2,2I5)
GO TO 6
A(I2)=A(I2)-SINX
A(I1)=A(I1)-COSX
IF(PDEL-DLIM)70,62,62
PDEL=.3*PDEL
GO TO 2
70 CONTINUE
CALL PDUMP(I,COSX,4,I,COSX,5)
RETURN
END
SUBROUTINE FCN(ER)
COMMON N,A(64),D(64),PX(64),CY(99),X(99),Y(99),NP,NG
ER=0
DO 50 I=1,NP
CY(I)=0.
DO 40 J=1,NG
V=(A(3*J-1)-X(I))/A(3*J)
IF(ABS(V)-13.2>39,39,40
39 CY(I)=CY(I)+A(3*J-2)/EXP(V*V)
40 CONTINUE
CYY=CY(I)-Y(I)
ER=ER+CYY*CYY
50 CONTINUE
RETURN
END

//GO.FTL4F001 DD SPACE=(800, (120, 15)), DISP=(, PASS), DSNAME=&SM, UNIT=DISK
//GO.SYSIN DD *

NP = number of data points (wavelength-absorbance couples).
NG = number of Gaussian components.
WLMM = wavelength in nanometers.
ABSU = absorbance units.
C = concentration in moles per liter.
EXTC = extinction coefficient.
WLRC = wave length as reciprocal centimeters.
DEL = delta, peak half width at half height.