

antimony Dichloride.—A solution of 2.1 g. (0.0050 mole) of triphenylantimony dichloride in 50 ml. of benzene was added to a suspension of 2.7 g. (0.010 mole) of sodium diphenyldithiocarbamate in 50 ml. of acetonitrile. The reaction mixture was stirred at room temperature for 2 hr. and then was filtered to give a solid which was stirred with hot benzene. The hot mixture was filtered to give a solid, which did not melt at 350° and gave a positive silver nitrate test.

Upon cooling, the benzene filtrate yielded needles which were collected on a filter to give 2.0 g. (83%) of tetraphenylthiuram disulfide, m.p. 217° dec. (lit.¹⁸ 217.6° dec.).

Anal. Calcd. for $C_{26}H_{20}N_2S_4$: C, 63.91; H, 4.09; N, 5.74. Found: C, 63.51; H, 3.87; N, 5.59.

The infrared spectrum had C–N, 1493 cm^{-1} . The ultraviolet spectrum (chloroform) had λ_{max} 243 $m\mu$ (ϵ_{max} 1.16×10^4) and 280 $m\mu$ (ϵ_{max} 3.17×10^4).

The solvent from the original benzene–acetonitrile filtrate was removed *in vacuo*, and the solid residue was recrystallized from methanol to give 1.0 g. (60%) of triphenylantimony, m.p. 47–50°, no depression on admixture with authentic triphenylantimony, infrared spectrum superimposable on that of authentic triphenylantimony.

CONTRIBUTION FROM BELL TELEPHONE LABORATORIES, INCORPORATED,
MURRAY HILL, NEW JERSEY

Color and Nonintegral Valence in Niobium and Tantalum Subhalides

By M. B. ROBIN AND N. A. KUEBLER

Received February 1, 1965

The electronic spectra of the Ta and Nb subhalide ions, $M_6X_{12}^{2+}$, have been interpreted using a molecular orbital scheme involving both metal–metal and metal–ligand interactions. The only reasonable analysis follows from assuming that the Nb complexes are built upon an Nb_6 framework having octahedral symmetry, whereas the corresponding Ta complexes are tetragonally elongated. This conclusion follows from the fact that certain degenerate transitions in the Nb series are split in the Ta series as would be expected for a descent in symmetry. Two-electron oxidation of the Ta complexes yields ions having a tetragonally flattened geometry, as judged by the criterion just mentioned.

A spate of recent crystallographic work on the Re^{3+} halides indicates that a great many of the structures are built upon a common unit, the trinuclear species $Re_3X_{12}^{3-}$.¹ As yet unpublished work by Schäfer on Nb and Ta halides demonstrates that in a good many cases one again has a common polynuclear building block, the stoichiometry here being M_6X_{12} .² As is also the situation with the Re compounds, halide ions are shared between the M_6X_{12} units in the crystal, the number shared being determined by the over-all stoichiometry of the substance. This paper is concerned with the relationship between the color and the molecular and electronic structure of the $M_6X_{12}^{2+}$ building block ions.

The $M_6X_{12}^{2+}$ ions, where $M = Nb$ or Ta and $X = Cl$, Br , or I , are of special interest because they provide compact units of known geometry which exhibit not only metal–metal bonding and nonintegral valence, but offer for study a stable “monomeric” unit which may be taken as one of a large class of X_6Y_{12} polynuclear complexes having M_6 octahedral metal frameworks in common. As of the moment, this class includes the $M_6X_{12}^{2+}$ ions mentioned above, Mo_6Cl_{12} ,³ $Rh_6(CO)_{16}$,⁴ Pt_6Cl_{12} ,⁵ and the nontransition metal complex $Bi_6(OH)_{12}^{+6}$.⁶

That the $M_6X_{12}^{2+}$ ions of Nb and Ta exhibit strong metal–metal bonding is evident not only from overlap considerations, but also from the metal–metal distances, which are observed to be approximately those of the pure metal. As for the nonintegral valence phenomenon, consider that the twelve halogens contribute a -12 formal charge to the complex, and that the net charge of $+2$ then leads to the six metal atoms contributing a $+14$ formal charge. Thus the average formal valence of the metal atoms is $+2\frac{1}{3}$. This phenomenon of average nonintegral valence has been studied previously⁷ in Prussian blue, $KFe_2(CN)_6$, where it was shown that the two iron ions of average valence $+2\frac{1}{2}$ in fact have the integral valences $+2$ and $+3$. The integral valence results from the fact that a nonintegral valence situation can be expected only for ions in equivalent or near equivalent environments, and in the Prussian blue crystal the two iron ions are in distinctly different sites. By analogy with Prussian blue, if we are to know the correct valences of the metal ions in the $M_6X_{12}^{2+}$ complex we must first investigate the equivalence of the geometries of the local ligand fields. If the metal atoms are all in equivalent ligand fields within the complex, then the formal valence at each metal must be taken as $+2\frac{1}{3}$, whereas nonequivalent ligand fields at the metals will tend to trap the integral valences. A most likely configuration for the latter would result from a tetragonal distortion of the M_6 octahedron yielding four ions of $+2$ and two of $+3$ formal valence.

(1) F. A. Cotton and S. J. Lippard, *J. Am. Chem. Soc.*, **86**, 4497 (1964).

(2) H. L. Schäfer, quoted in *Proc. Chem. Soc.*, 207 (1964).

(3) J. C. Sheldon, *J. Chem. Soc.*, 1007, 3106 (1960).

(4) E. R. Corey, L. F. Dahl, and W. Beck, *J. Am. Chem. Soc.*, **85**, 1202 (1963).

(5) K. Brodersen, *Angew. Chem. Intern. Ed. Engl.*, **3**, 519 (1964).

(6) H. A. Levy, M. D. Danford, and P. A. Agron, *J. Chem. Phys.*, **31**, 1458 (1959).

(7) M. B. Robin, *Inorg. Chem.*, **1**, 337 (1962).

Vaughan, Sturdivant, and Pauling⁸ first determined the structures of a series of $M_6X_{12}^{2+}$ ions using X-ray scattering from solutions with the result shown in Figure 1.⁹ They demonstrated that the polynuclear complexes consist of six metal atoms at the vertices of a regular octahedron with halide ions bridging the edges. Locally, each metal ion is in an approximately square-coplanar field of halide ions, with all nearest neighbor metal-halide distances being equal. Though a non-integral valence of $+2\frac{1}{3}$ is implied by this symmetrical structure, the inexact nature of the earlier experiment does not rule out the possibility of small distortions of the octahedral framework in some ions. Indeed, we shall show that the spectra of the ions in solution strongly suggest that some of them do have a symmetry lower than octahedral.

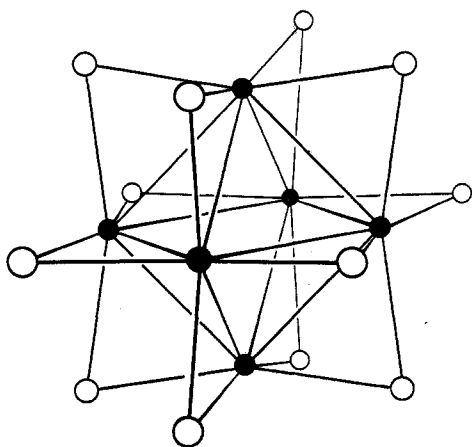


Figure 1.—The molecular structure of the $M_6X_{12}^{2+}$ ions. The solid spheres represent metal atoms, empty spheres represent bridging halide ions.

Spectroscopically, the polynuclear complex ions are unique in that they can show electronic transitions which are necessarily absent in the mononuclear complexes. Though both types of complex will show ligand-to-metal charge-transfer transitions, the polynuclear complex can also have metal-metal transitions; *i.e.*, transitions between molecular orbitals which differ primarily in their nodal patterns between metal atoms. Thus polynuclear complexes will show transitions which are quite unrelated to those of the mononuclear components. In general, such metal-metal transitions can occur with large intensity only if the electron jumps between m.o.'s composed of a.o.'s having the same n , l , and m_z quantum numbers. Obviously, such a shell of fixed n , l , and m_z must be only partially filled if there is to be a transition within it. These requirements are most easily met in the mixed valence compounds, which is why these compounds exhibit unusual colors. Note, however, that the appearance of strong colors is far from diagnostic for mixed valence.

(8) P. A. Vaughan, J. H. Sturdivant, and L. Pauling, *J. Am. Chem. Soc.*, **72**, 5477 (1950).

(9) R. B. Corey, R. H. Stanford, R. E. Marsh, Y. C. Leung, and L. M. Kay, *Acta Cryst.*, **15**, 1157 (1962), have recently used the $Nb_6Cl_{12}^{2+}$ and $Ta_6Cl_{12}^{2+}$ ions as heavy-atom scatterers in an attempt to solve the crystal structure of wet lysozyme chloride.

Experimental

The M_6X_{14} compounds were prepared by reduction of the appropriate pentahalide with Cd metal filings at about 500°. The cooled solid masses were worked up as suggested by Harned, *et al.*,¹⁰ giving hydrated complexes which were then analyzed by X-ray fluorescence techniques and found to have metal:halide ratios of $(6.00 \pm 0.03):14$. Though H_2O was not determined directly, the metal-halide analyses lead to the general formula $M_6X_{14} \cdot 7H_2O$ for these complexes. Oxidation of the Ta complexes¹¹ was carried out by adding a drop or two of 30% H_2O_2 to an ethanolic solution of the complex acidified with a drop of $HClO_4$ and allowing the solution to sit at room temperature for 24 hr. Reduction of the oxidized species was easily effected by the addition of zinc dust. On the other hand, the niobium complexes resist oxidation by this means, and stronger conditions slowly yield a product that is apparently a hydrous oxide.

Spectra of the complexes were determined in aqueous and C_2H_5OH solutions at room temperature and in C_2H_5OH at -100° using a Cary Model 14 spectrophotometer. The low-temperature spectra were obtained using a filled 1-cm. cell supported within a cylindrical quartz dewar, the inside of which was continuously purged with cooled nitrogen. Whereas the cold solution spectra were quite useful in determining the presence and frequencies of weak bands, the integrated transition moment values were more easily derived from the room-temperature spectra, where concentrations are better determined.

The magnetic susceptibilities were kindly measured for us by Dr. E. Koubek using a pendulum magnetometer. He found that the uncorrected susceptibilities at room temperature were approximately zero to within the rather large error incurred in measuring such small currents. A more intensive study of $Nb_6Cl_{14} \cdot 7H_2O$ showed that the molar susceptibility remained at 240×10^{-6} c.g.s. over the temperature range 42–290°K. A diamagnetic correction estimated to be 610×10^{-6} c.g.s.¹² yields a final value of 850×10^{-6} c.g.s. for the temperature-independent paramagnetic susceptibility of this complex. Earlier work by Krylov¹³ showed temperature-dependent susceptibilities for this compound that suggested a few spins per ion; this is contrary to our conclusion that the complexes have a singlet ground state.

Electronic Structure of the Complexes

The large size of both the complex ions and the atoms within them precludes any but the most elementary discussion of their electronic structure. What we offer is in effect an ordering of one-electron energy levels according to the nodal patterns of molecular orbitals involving both metal-metal and metal-ligand interactions. In those places where an ambiguity arises as to the level ordering, we appeal to the experimental evidence for help. Though we readily admit that this is circular reasoning, we believe that the argument is not *ad hoc* and that the consequences of our inferences from experiment lead to some very interesting results. In any event, though we really have not predicted the spectra, the end result of our approach is a consistent, unique explanation of both the spectra and electronic structure of the complexes.

Specifically, we consider the case of $Nb_6Cl_{12}^{2+}$.

(10) H. S. Harned, C. Pauling, and R. B. Corey, *J. Am. Chem. Soc.*, **82**, 4815 (1960).

(11) R. E. McCarley, P. J. Kuhn, and B. G. Hughes, Abstracts, 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April 6–10, 1964, abstract No. 92, p. 36L.

(12) P. W. Selwood, "Magnetochemistry," Interscience Publishers, Inc., New York, N. Y., 1956, p. 78.

(13) E. I. Krylov, *Nauch. Dokl. Vysshei Shkoly, Khim. i Khim. Tekhnol.*, 676 (1958); *Chem. Abstr.*, **53**, 5790d (1959).

Herman and Skillman¹⁴ have tabulated a 4d Hartree-Fock-Slater a.o. for the neutral Nb atom and we have fitted this by eye with the normalized analytic function

$$\psi(\text{Nb}) = 2.35r^3e^{-1.75r} - 1.65r^2e^{-1.75r}$$

The Cl atomic orbital used here is the simple 3p Slater function recommended by Clementi and Raimondi.¹⁵ Using these functions as basis, a molecular orbital calculation was then carried through in which the off-diagonal Hückel elements were simply taken as proportional to the appropriate overlap with reversed sign. Clearly the only aspect of such an investigation that may have any significance is the determination of the ordering of the levels, but this is our goal.

We proceed in steps. The five a.o.'s on each metal are expressed as linear combinations of the momentum eigenfunctions, yielding the a.o.'s.¹⁶ Following this, the first step is the mixing of each particular type of a.o. with its own type on all six centers and with the appropriate ligand a.o.'s.

The calculation of the necessary overlaps was aided considerably by the compilation by Cotton and Haas of geometric factors involved in nonaligned metal-metal interactions.¹⁷ A compilation of overlaps calculated over the metal and ligand momentum functions is given in Table I. This, together with the relations quoted in ref. 16 and the cautious use of the Cotton and Haas compilation allows one to calculate the a.o. overlaps.

TABLE I

OVERLAPS APPROPRIATE TO THE NbCl_2^{2+} COMPLEX ION

$S(d_0d_0)$ <i>trans</i> = 0.148	$S(d_0d_0)$ <i>cis</i> = 0.171
$S(d_{+1}d_{+1})$ <i>trans</i> = 0.083	$S(d_{+1}d_{+1})$ <i>cis</i> = 0.324
$S(d_{+2}d_{+2})$ <i>trans</i> = 0.012	$S(d_{+2}d_{+2})$ <i>cis</i> = 0.096
$S(d_0p_0)$ = 0.278	$S(d_{+1}p_{+1})$ = 0.211

Assuming a regular geometry and taking the orbital sets one at a time, we find first that d_{z^2} does not mix with the ligands due to symmetry but that the $d_{x^2-y^2}$ orbitals are split apart by metal-metal overlap, as shown in Figure 2. The orbital order a_{1g} , t_{1u} , e_g ¹⁸ found here is contrary to that of Cotton and Haas, who claim a_{1g} , e_g , t_{1u} for this system.

In the case of the d_{xy} orbitals, we have both metal-metal and d_{xy} metal-p π ligand interactions. The metal-metal interaction, taken by itself, yields the metal m.o. ordering a_{2u} , t_{2g} , e_u , whereas if we consider metal-ligand interaction solely, the inverted order e_u , t_{2g} , a_{2u} is obtained. Thus there are opposing effects in this system having magnitudes which we are not prepared to evaluate, especially since the metal and ligand a.o.

matrix elements differ by an unknown amount on the diagonal and it is this quantity together with the relative strengths of metal-metal and metal-ligand interaction which determine the order. Fortunately, as we shall see below, the electronic spectrum can be used to settle this point. The "experimental" ordering is e_u , t_{2g} , a_{2u} ; supposedly the metal-ligand overlaps are sufficiently large to determine the metal m.o. ordering even though the ligands are out of resonance with the metal a.o.'s.

Within the $d_{x^2-y^2}$ set there is an unusually large metal-ligand overlap of the σ type which lifts the $d_{x^2-y^2}$ manifold bodily upward without splitting it. An unusually small metal-metal overlap then splits the elevated manifold yielding the orbital order depicted in Figure 2.

The situation within the $d_{xz}d_{yz}$ set is qualitatively like that for $d_{x^2-y^2}$. The ligands contribute an upward shift to the metal a.o. manifold by virtue of the π bonding of the ligand σ a.o.'s. $d_{xz}d_{yz}$ splitting then results from direct interactions among the metal a.o.'s and is not inappreciable.

For the second stage of this calculation, the theory demands that the m.o.'s of the same symmetry be mixed. Thus $d_{z^2}(t_{1u})$ is to be mixed with $d_{xz}d_{yz}(t_{1u})$, $d_{z^2}(e_g)$ is to be mixed with $d_{x^2-y^2}(e_g)$, $d_{xy}(t_{2g})$ is to be mixed with $d_{xz}d_{yz}(t_{2g})$, and $d_{x^2-y^2}(t_{2u})$ is to be mixed with $d_{xz}d_{yz}(t_{2u})$. The result of this mixing is the following: though the over-all m.o. symmetry allows mixing between the above m.o. symmetry pairs, the local a.o. symmetry can forbid it, with the consequence that the only nonzero interorbital mixing is between the last mentioned t_{2u} m.o.'s. Because all other mixing elements are of the kind $\beta(d_{xy}d_{z^2})$, they are zero by symmetry, regardless of the assumptions used in evaluating the one-electron matrix element. Except for this mixing at one point, which will prove to be of no consequence in our naive explanation, what we have here is a set of independent subsystems separated by symmetry in a way reminiscent of π - σ separation in aromatic hydrocarbons. This remarkable separability has many other consequences which will be pointed out below.¹⁹

We now place the 16 valence electrons into low-lying orbitals so as to give a spin singlet configuration as shown in Figure 2. The Cotton and Haas ground-state configuration $d_{z^2}(a_{1g})^2d_{xy}(a_{2u})^2d_{xz}d_{yz}(t_{1u})^6(t_{2g})^6$ seems outwardly like a reasonable one, but our experience in trying to match the spectra to an orbital scheme reveals that the ground-state configuration $d_{xy}(e_u)^4d_{xz}d_{yz}(t_{1u})^6(t_{2g})^6$, Figure 2, leads to a more natural explanation of the spectra. Evidently, the stabilization attained by giving the $d_{xy}(e_u)$ orbital its full complement of four electrons and thereby closing a shell is sufficient to overcome the promotion energy incurred in raising two electrons from $d_{z^2}(a_{1g})$ to $d_{xy}(e_u)$. That the low-lying $d_{z^2}(a_{1g})$ orbital is not occupied in our

(14) F. Herman and S. Skillman, "Atomic Structure," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1963.

(15) E. Clementi and D. L. Raimondi, *J. Chem. Phys.*, **38**, 2686 (1963).

(16) H. Byrning, J. Walter, and G. E. Kimball, "Quantum Chemistry," John Wiley and Sons, New York, N. Y., 1954, p. 89.

(17) F. A. Cotton and T. E. Haas, *Inorg. Chem.*, **3**, 10 (1964).

(18) The symmetry representations of the metal m.o.'s are those of the O_h point group. The ligand m.o.'s are assigned O_h representations in accordance with their ability to mix with the metal m.o.'s. For example, any symmetry-adapted linear combination of ligand a.o.'s which mixes with a metal m.o. of symmetry t_{2g} is given the symmetry label t_{2g} .

(19) Actually, some mixing is possible through the agency of ligand orbitals shared in common by metal m.o.'s of different subsystems. The resulting departure from separability will have only a small effect on our arguments and we choose to ignore it.

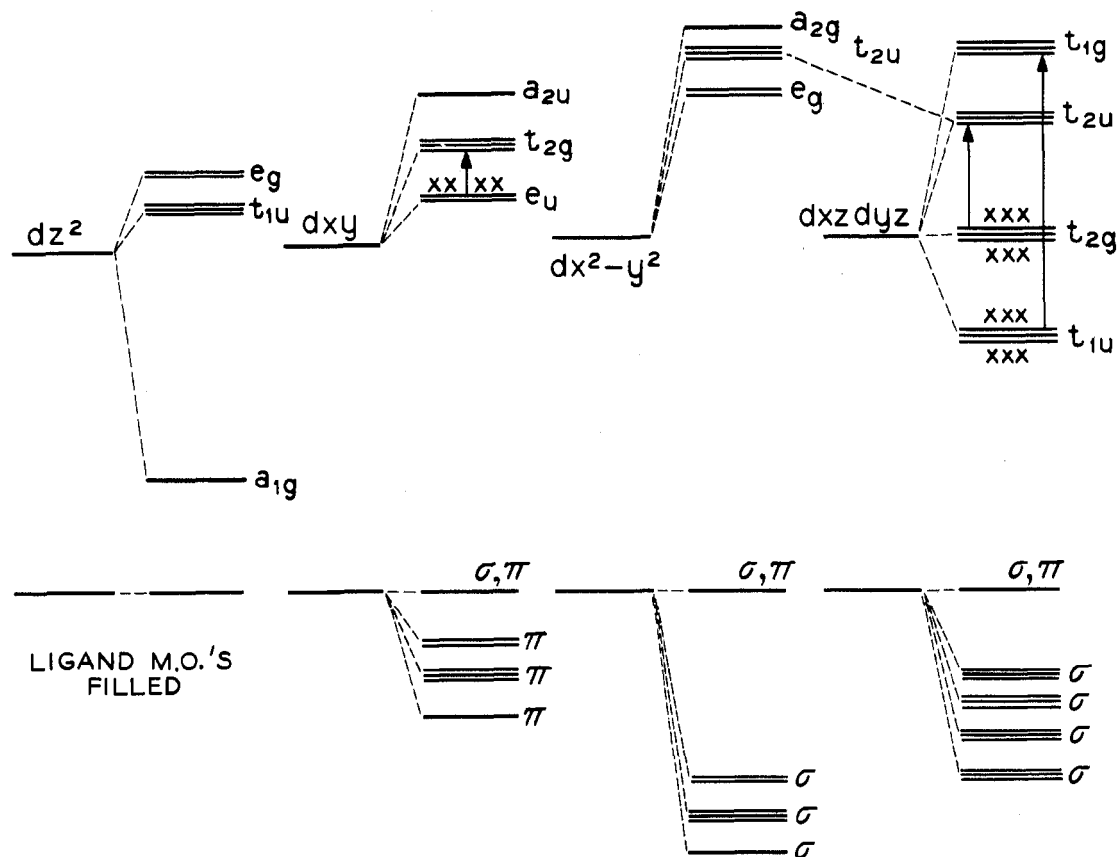


Figure 2.—The molecular orbital scheme deduced for the $M_6X_{12}^{2+}$ ion. The predominantly ligand m.o.'s denoted by π and σ are each doubly filled in the ground state.

scheme follows from the consequent spin triplet property expected for such a configuration, in contrast to the observed singlet character of the ions. Considering the crudity of our approach, it would not be unreasonable to suppose that $d_{z^2}(a_{1g})$ is not as low as shown in Figure 2.

Each of the occupied subsystems will have an allowed metal-metal transition as shown by the arrows. These transitions will have a transition moment which is dependent only upon molecular geometry, which is the same for all subsystems, of course. Moreover, the possibility that this equality of transition moments will be upset by configuration interaction mixing of the metal-metal excited states is quite small, again because the separability leads to mixing matrix elements of the form

$$\langle d_{xz}d_{xy} (1) \left| \frac{e^2}{r_{12}} \right| d_{xz}d_{xy} (2) \rangle$$

which, in the Mulliken approximation, are zero. Another consequence of the subsystem separability is the fact that transitions between subsystems are forbidden regardless of m.o. symmetry. This follows again from the orthogonality of the a.o.'s in different subsystems.

We can make only a few comments on ligand-to-metal charge-transfer bands in this system. Over-all symmetry permitting ($A_{1g} \rightarrow T_{1u}$), the charge-transfer moment will depend directly upon the overlap of metal and ligand orbitals so that transitions from ligand σ to

$d_{x^2-y^2}$ m.o.'s may be very strong, those from ligand π to $d_{xz}d_{yz}$ and d_{xy} less strong, and those to d_{z^2} very weak, regardless of symmetry. Energetically, it would appear from Figure 2 that transitions to d_{z^2} would be lowest, those to $d_{x^2-y^2}$ highest, and the others intermediate. Thus the charge-transfer spectrum may very well consist of a set of bands which increase rapidly in intensity with increasing frequency.

In anticipation of the experimental results, we consider here the spectral consequences of a tetragonal distortion. The allowed metal-metal bands are characterized by the state symbols $A_{1g} \rightarrow T_{1u}$ in the octahedral symmetry. On tetragonal distortion, the T state splits into A and E components having an intensity ratio, from the ground state, of 1:2 for the elongated tetragonal and 2:1 for the flattened tetragonal geometry. For a given distortion, all allowed metal-metal bands must split with the same intensity pattern and, for small splits, transition moment will be conserved. As for the effects of tetragonality on the charge-transfer spectrum, the allowed ligand-to-metal bands are necessarily $A_{1g} \rightarrow T_{1u}$, but, unlike the metal-metal bands, are *not* necessarily split on distortion. This interesting result follows from the assumption that the ligands do not overlap among themselves so that relative displacements of the nuclei do not split degenerate ligand m.o.'s. Thus an allowed ligand-to-metal transition from, say, ligand t_{2g} to metal a_{2u} will not be split energetically in any geometry. If, however, the charge-

transfer transition is to a metal m.o. of symmetry e or t , then splitting is expected for distorted geometries.

With this background we turn now to the spectra where the first problem to be met is the sorting out of the metal-metal bands from the ligand-to-metal bands, both of which can be strong in a polynuclear complex. The distinction is accomplished by comparing the spectra of $M_6Cl_{12}^{2+}$ and $M_6Br_{12}^{2+}$ ions, the idea being that a change of ligands will have a large effect on ligand-to-metal bands but only a small effect on metal-metal bands. In Figure 3, we show the spectra of $Nb_6Cl_{12}^{2+}$ and $Nb_6Br_{12}^{2+}$ ions in ethanol at -100° ; it is clear that there is a close correspondence of the bands within the spectra and that the frequency shifts appear in two groups, the one having a few hundred cm^{-1} shift, the other shifted by about 1000 cm^{-1} . Thus, by this criterion, the small shift bands centered at $10,870$ and $35,650\text{ cm}^{-1}$ in $Nb_6Cl_{12}^{2+}$ are the first two metal-metal bands and the bands centered at $16,670$, $20,410$, $24,690$, $31,250$, and $46,390\text{ cm}^{-1}$ are ligand-to-metal charge-transfer transitions, their shift being in the expected direction. We confirm the hypothesis that the $10,870$ and $35,650\text{ cm}^{-1}$ bands are metal-metal transitions by deriving the transition moment lengths of these bands from the spectra and finding that they are indeed equal (0.62 and 0.63 \AA ., respectively) as predicted by the m.o. model. Looking on the darker side of this aspect of the spectrum, the transition moment²⁰ of the metal-metal bands can be calculated using the Pauling bond distances and the Mulliken approximation and gives a predicted length of 2.9 \AA . The m.o. theory is well known to exaggerate the magnitude of this quantity, but the disagreement appears beyond reasonable bounds and will be discussed further below.

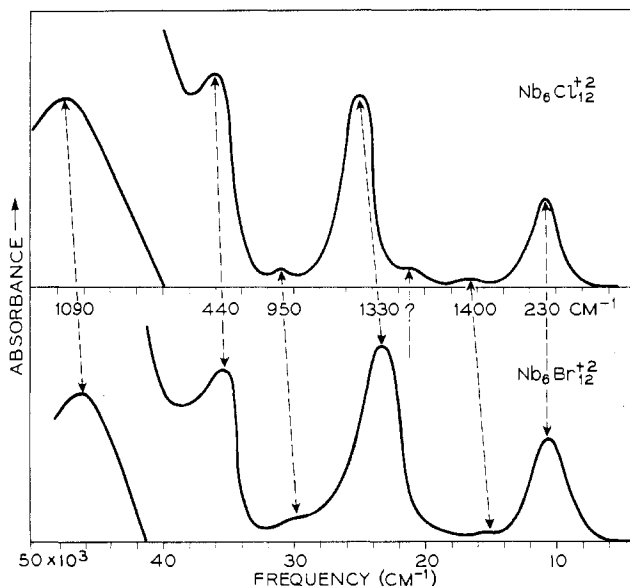


Figure 3.—The absorption spectra of $Nb_6Cl_{12}^{2+}$ and $Nb_6Br_{12}^{2+}$ in ethanol at -100° .

There is nothing in the $Nb_6X_{12}^{2+}$ spectra which suggests that the geometry of the ions is anything other

than regular, and it is reasonable to expect the analogous $Ta_6X_{12}^{2+}$ ions to show spectra quite similar to those of the Nb complexes. It is most significant to note then (see Figure 4) that the bands in the spectra of the Nb and Ta complexes cannot be brought into 1:1 correspondence unless it is assumed that certain of the bands in the Nb complexes are split into two components in the Ta series. Thus the two metal-metal bands at $10,870$ and $35,650\text{ cm}^{-1}$ in the $Nb_6X_{12}^{2+}$ complexes are split into two components with maxima appearing at $13,000$ and $15,290\text{ cm}^{-1}$ for the first metal-metal band and at $37,170$ and $40,480\text{ cm}^{-1}$ for the second in the Ta complexes, Figure 4. As would be expected for such a splitting, a comparison of the $Ta_6Cl_{12}^{2+}$ and $Ta_6Br_{12}^{2+}$ spectra shows that both components of a split band have the smaller shift characteristic of metal-metal transitions.

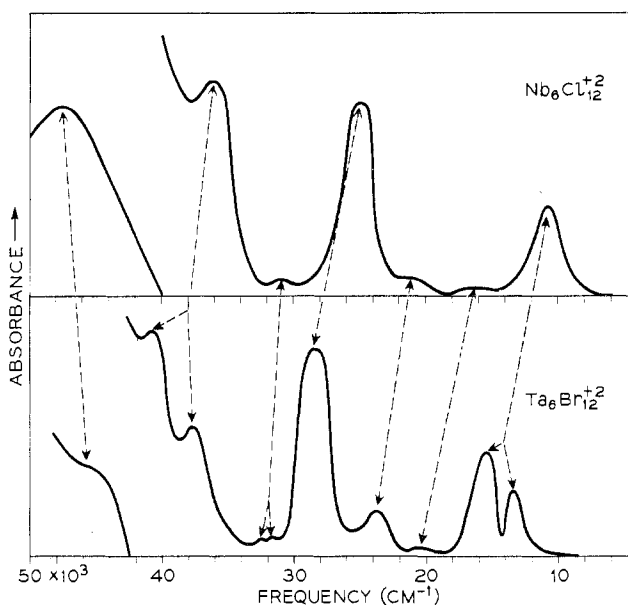


Figure 4.—The absorption spectra of $Nb_6Cl_{12}^{2+}$ and $Ta_6Br_{12}^{2+}$ in ethanol at -100° .

It was this splitting that we were anticipating in our earlier discussion of the effects of tetragonal distortions. The simple orbital theory predicts that for small distortions, the transition moment of the unsplit band should equal that of the split components integrated as though they were one band, and that the moment ratio of the low to high energy components of the split is either $\sqrt{2}$ or $\sqrt{0.5}$ depending upon whether the tetragonality is elongated or flattened. Such comparisons are most easily carried out on the low-frequency metal-metal band since it is not overlapped from either side. Comparing the unsplit band of $Nb_6Br_{12}^{2+}$ with the split metal-metal band of $Ta_6Br_{12}^{2+}$ we find the moment lengths for the two ions to be 0.72 and 0.77 \AA . The agreement is quite adequate considering that the $Ta_6Br_{12}^{2+}$ ion is slightly larger and should thereby have a larger moment. The two components of the first metal-metal band in $Ta_6Br_{12}^{2+}$ can be decomposed easily and integrated to yield a moment ratio of $\sqrt{1.96}$, in accord with a tetragonal elongation in the Ta com-

(20) G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., New York, N. Y., 1950, p. 199.

plexes. Though we can give no quantitative data, we do see that for the second metal-metal band splitting, the lower energy component is weaker than the higher, as it must be in the m.o. theory.

Using the conclusion that the Nb complexes are symmetric but the Ta complexes show a tetragonal elongation, one can proceed to an assignment of the electronic transitions in these systems. As we said above, the small shift on ligand substitution and intensity arguments support the 10,000 cm^{-1} band system as being metal-metal. According to Figure 2, the lowest energy metal-metal band is confined to the d_{xy} subsystem, but this conclusion may be pushing the "calculation" further than is reasonable. If we translate the calculated transition moment of 2.9 Å. for this $\text{Nb}_6\text{Cl}_{12}^{2+}$ band into molar extinction, we find an anticipated extinction of approximately 100,000, to be compared with the observed 3500! Such a large discrepancy outwardly indicates either that the metal electrons are not as delocalized as we have pictured them above or that the geometry of the triply degenerate excited state is grossly different from that of the ground state. If we assume that any distortions from regular geometry are only small ones, then the former explanation does not seem reasonable in view of the phenomenon of quantum mechanical resonance. The nonvertical transition argument in turn appears as a plausible one but quite difficult to prove or disprove. The excited state distortion would be accompanied by vibrations of such low frequency that we would not expect to resolve them. That the splitting of this band in the Ta series has an internal origin is shown by the fact that the split separation is completely independent of the basicity of the solvent, which was varied from glacial acetic acid to water to dimethyl sulfoxide to pyridine.

The next two transitions, at 15,000 and 21,000 cm^{-1} , are low-energy, symmetry-forbidden charge-transfer bands wherein the accepting metal orbital is nondegenerate. This last statement follows from the fact that these bands are not split in the distorted Ta complexes. It is most logical from Figure 2 to assign these bands to transitions originating somewhere within the nonbonding ligand m.o. manifold and terminating in $d_{z^2}(a_{1g})$. In the simplest energy level picture, the effect of substituting Br_{12} for Cl_{12} would be a uniform elevation of the ligand orbitals with respect to the metal m.o.'s and a consequent shift of all charge-transfer bands by the same amount toward lower frequencies. Such would seem to be the case here; however, the shift of *ca.* 1000 cm^{-1} is rather smaller than one might expect judging from the spectra of other transition metal chlorides and bromides.

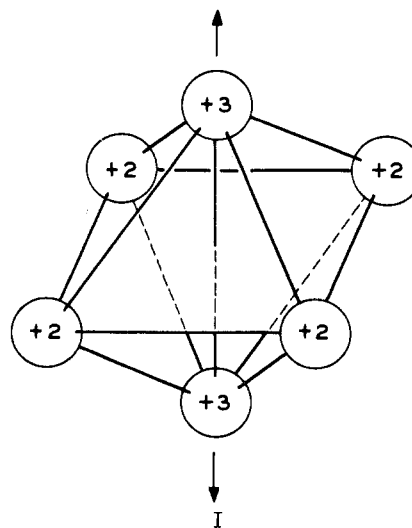
The first symmetry-allowed ligand-to-metal charge transfer falls at about 25,000 cm^{-1} . As is obvious from its high intensity, the a.o.'s of the originating and terminating m.o.'s must have an appreciable overlap. Since the metal m.o. involved must also be nondegenerate, it seems most likely that this band is assignable as ligand $\pi(t_{2g}) \rightarrow d_{xy}(a_{2u})$. Arguing in the same manner, the very strong, high-energy charge transfer at

47,000 cm^{-1} would appear to be ligand $\sigma(t_{2u}) \rightarrow d_{x^2-y^2}(a_{2g})$. It was at this point in our work that we found simultaneously that the Cotton and Haas ground-state occupation would necessarily lead to a splitting of each of these bands and that the ordering within d_{xy} was in question. We therefore altered the Cotton and Haas orbital ordering and occupation in a reasonable way, thereby accommodating the observed lack of splitting and resolving a theoretical ambiguity by experiment.

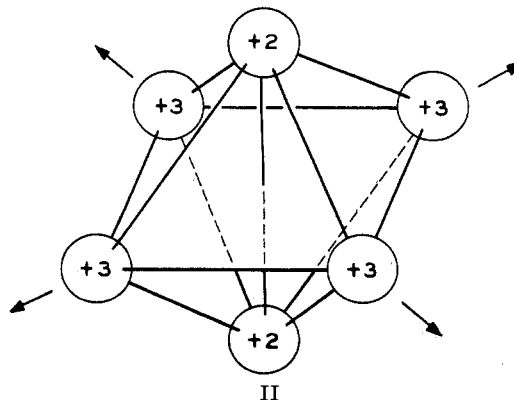
A second metal-metal band, $t_{2g} \rightarrow t_{2u}$ in $d_{xz}d_{yz}$ at 37,000 cm^{-1} , is characterized in a way identical with that used for the 10,000 cm^{-1} band. A third metal-metal band, $t_{1u} \rightarrow t_{1g}$ in $d_{xz}d_{yz}$, is not observed in our spectrum and presumably has a frequency greater than 50,000 cm^{-1} .

The weak, split band at 30,000 cm^{-1} can be assigned in a multitude of ways and we claim here only that it is a forbidden charge transfer involving either an e or t metal m.o. in the upper state.

Thus, through a comparison of Nb and Ta complex ion spectra, we conclude that whereas the Nb complexes have a regular octahedral geometry, the Ta complexes show an elongated tetragonal distortion of this geometry. Such a distortion implies formal charges having the pattern shown below (I), in which the arrows give the sense of the distortion. If we now perform a two-



electron oxidation on such a system, we are left with four +3 and two +2 ions, which might well tend to distort as shown in II. We feel this follows logically



from the above, for in both cases the distortion has been assumed to prefer those displacements which further separate those ions of highest like charge while tending to trap integral valences.

The distortion of the oxidized species (flattened) is the opposite of that of the reduced (elongated) and as such would be expected simply to invert the intensity ratio of the tetragonally split components of the metal-metal bands. The spectra of the reduced and oxidized material are compared in Figure 5, and we find that, indeed, on oxidation, the intensity ratios of the components of both metal-metal bands are inverted. Surprisingly, the only features of the spectra that do change on oxidation are the above-mentioned ratios. The positive and negative ions of an aromatic hydrocarbon show such spectral similarity, but this arises from an electron-hole equivalence which is not at all possible in the complex ions. The unexpected spectral similarity of oxidized and reduced species can perhaps be explained once again as a consequence of the orbital separability. Under the flattened tetragonal distortion, the filled $d_{xz}d_{yz}(t_{2g})$ orbital of the reduced ion splits into a lower e_x and an upper b_{2x} level. Oxidation then removes the two electrons in $d_{xz}d_{yz}(b_{2x})$ while the remaining four electrons can still undergo transitions up to $d_{xz}d_{yz}(t_{2u})$, which splits into e_u (lower) and b_{2u} (upper). Thus a pair of valence electrons can be lost without the loss of a split metal-metal band or gross alteration of the spectrum.

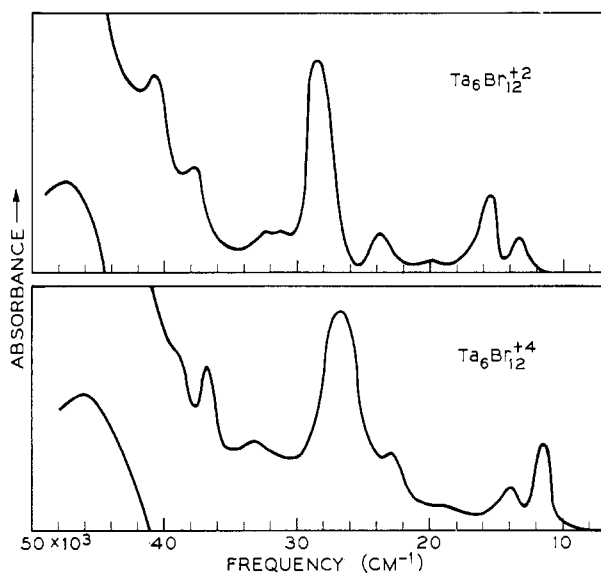


Figure 5.—The absorption spectra of the $Ta_6Br_{12}^{2+}$ and $Ta_6Br_{12}^{4+}$ ions in ethanol at -100° .

We conclude then from a simple orbital analysis of the electronic spectra that the $Nb_6X_{12}^{2+}$ ions most likely have a regular octahedral Nb_6 geometry while the corresponding $Ta_6X_{12}^{2+}$ ions have their Ta_6 structure elongated tetragonally, and the $Ta_6X_{12}^{4+}$ ions are flattened tetragonally. A more direct kind of evidence for such distortions rests in demonstrating that any or all of the split metal-metal component bands show *any* polarized

absorption, an effect we have been unable to measure, as yet.

As our final topic, we offer a highly speculative and abbreviated discussion of the geometries of these complex ions. In view of the totally symmetric nature of the ground-state wave function, it is not at all clear why the Ta complexes appear not to have regular geometries or why the same effect is not observed in the Nb series. That the lowering of the symmetry is not due to external solvent influence was demonstrated by the fact that the splitting is identical in a large number of solvents of widely varying basicity.

There is, however, an internal mechanism imaginable wherein Coulomb forces tend to distort the ion. The d electrons within a $M_6X_{12}^{2+}$ complex are involved in metal-metal bonding and their energy is lowered through this one-electron interaction. There are also nuclear-nuclear and two-electron Coulomb terms in the energy which can be interpreted as expressing among other things the repulsions of the positively charged Ta ions taken at the vertices of an octahedron. Giving all the ions a charge of $+n$ yields a Coulomb energy

$$E_1 = 3n^2f(R) + 12n^2f(r)$$

where $f(R)$ is the potential of two spherical charge distributions, each of unit positive charge, with center-to-center separation equal to the *trans* octahedral distance, R , and $f(r)$ is similarly defined with the separation being equal to the *cis* distance, r . Consider the situation now where four of the ions in a plane each lose a charge $+\delta$ and the two remaining ions increase their charge by 2δ . In this case the Coulomb energy is

$$E_2 = (3n^2 + 6\delta^2)f(R) + (12n^2 - 12\delta^2)f(r)$$

and

$$E_2 - E_1 = 6\delta^2f(R) - 12\delta^2f(r)$$

Since a *cis* repulsion would necessarily have to be larger than a *trans*, $f(r)$ is larger than $f(R)$ and therefore any shift of charge out of the plane and toward the poles will result in a decrease in the Coulombic repulsion. We must add that according to this way of looking at the problem, the minimum energy is achieved by transferring all of the charge to the poles. Clearly we need also to consider the internal energies of the ions as charge is transferred to or from them. Perhaps it would be safe enough to transfer just enough charge to keep the species recognizably familiar, *i.e.*, $+2$ and $+3$. From this point, it is perhaps not too unbelievable that the complex achieves this transfer of charge by a relative outward displacement of the two highest like charges. Thus we have come full circle to the tetragonally elongated species. A similar argument can be made in the case of the oxidized material. Indeed, if it has any validity at all, the argument would seem to be of some significance to the geometry of all compounds with nonintegral valence. Our attempt to put the above on a somewhat firm quantum mechanical basis will be reported in the future.

CONTRIBUTION FROM THE LOS ALAMOS SCIENTIFIC LABORATORY,
UNIVERSITY OF CALIFORNIA, LOS ALAMOS, NEW MEXICO

Crystal Structures of the Trifluorides, Trichlorides, Tribromides, and Triiodides of Americium and Curium¹

BY L. B. ASPREY, T. K. KEENAN, AND F. H. KRUSE

Received February 22, 1965

The previously unreported lattice constants and crystal symmetries of the trifluoride, trichloride, tribromide, and triiodide of curium are given. Similar data for the isostructural trihalides of americium (except for the trifluoride) have been re-determined to a higher degree of precision. Correlations have been made between these actinide trihalides and the corresponding lanthanide trihalides. Curium trifluoride is hexagonal, LaF_3 -type, space group $P6_3/mmc-D_{6h}^4$. Americium and curium trichlorides are hexagonal, UCl_3 -type, space group $P6_3/m-C_{6h}^2$. The tribromides are orthorhombic, PuBr_3 -type, space group $\text{Cmcm}-D_{2h}^{17}$. The triiodides are hexagonal, BiI_3 -type, space group $R\bar{3}-C_{3i}^2$. When treated with hydrogen at elevated temperatures, no reduction of these trivalent americium or curium trihalides was observed.

Introduction

Since their discovery, there has been a continuing interest in the solid-state chemistry of the actinide elements. With the advent of macro (*i.e.*, multimilligram) amounts of the longer-lived isotopes, Am^{243} and Cm^{244} , it has been possible to carry out quite definitive experiments with these elements. More elegant purification schemes can be employed and the over-all handling difficulties are diminished due to the lower rate of γ emission. In general, such work confirmed the early tracer or microgram scale investigations. Occasionally, some of the early results could not be confirmed. In addition, the availability of modern computer programs for processing X-ray data has aided in the determination of more precise values for various crystal parameters.

Some values for the lattice constants of the trichloride, tribromide, and triiodide of americium were reported some time ago.² However, these results were based on work with Am^{241} , difficult to purify and to use for X-ray data because of its strong γ emission. The crystal properties of AmF_3 have been investigated more recently.³ The purposes of the present work then were threefold: (1) to re-examine the trichloride, tribromide, and triiodide of americium using long-lived Am^{243} , (2) to prepare all the analogous trihalides of curium using Cm^{244} , and (3) to study the possible reduction of these trihalides by hydrogen at elevated temperatures.

Experimental

Unless otherwise stated, all chemicals were of A.R. grade. Americium as Am^{243} and curium as Cm^{244} were purified by conventional means.⁴ Tank hydrogen was purified by passing it through a heated palladium alloy valve using a commercial apparatus.⁵

The insolubility of CmF_3 allowed its preparation directly from aqueous solution. Hydrofluoric acid was added to a solution of $\text{Cm}(\text{III})$; the resulting CmF_3 precipitate was washed with dilute HF, water, methyl alcohol, and acetone. The air-dried pellet

of CmF_3 was treated with HF gas for 5 hr. at 400°. Hydrogen gas was mixed with HF gas for some experiments to study the effect of this reductant. X-Ray capillaries were loaded with the curium fluoride following such equilibrations.

The general technique used for preparing the other actinide halides has been described more fully elsewhere.⁶ The trichloride starting material was formed by evaporation in air of an HCl solution of a 10:1 mole mixture of NH_4Cl and MCl_3 . The ammonium chloride was sublimed from this material in a quartz capillary. The appropriate ammonium halide was then used to convert AmCl_3 or CmCl_3 to the desired halide at 400–450° in a stream of hydrogen. The conversion reaction yielding the desired halide salt was carried out in the same quartz capillary, from which a portion could be sealed for X-ray examination of the final product.

An attempt was made in all cases to reduce MX_3 to MX_2 by hydrogen at elevated temperatures. However, treatment of all of these trihalides with hydrogen (at *ca.* 3 p.s.i.g.) at temperatures up to 900° gave no evidence of reduction. Using samarium as a stand-in resulted in formation of samarium dihalides in good yield.

A Norelco X-ray unit was used with 114.6-mm. Debye-Scherrer cameras and Ilford "G" film. The X-ray films of the trihalide compounds were read three times and the results averaged.

A "proposed" powder pattern (using the information from ref. 2) was initially generated using the POWD⁷ or ANIFAC⁸ programs; this was used for preliminary indexing of lines. Lattice constants from the initial indexing were estimated by least-squares calculations using the MET-124⁹ program. The constants were refined by two or three additional cycles between the programs until the over-all standard deviations and the individual variances of each line reached a satisfactory level.

Results and Discussion

In Table I are listed the values for the lattice constants of these halides. With the exception of the iodides, the actinide contraction is exhibited by all dimensions of the crystal lattices. The larger error for the iodides reflects the greater instability of the iodide compounds, possibly due to the disruptive effect of the α particles. Even using the relatively long-

(1) This work was performed under the auspices of the U. S. Atomic Energy Commission.

(2) W. H. Zachariasen, *Acta Cryst.*, **1**, 265 (1948).

(3) D. H. Templeton and C. H. Dauben, *J. Am. Chem. Soc.*, **75**, 4560 (1953).

(4) T. K. Keenan, *J. Inorg. Nucl. Chem.*, **20**, 185 (1961).

(5) Manufactured by The Milton Roy Co., Monterey Park, Calif.

(6) L. B. Asprey, T. K. Keenan, and F. H. Kruse, *Inorg. Chem.*, **3**, 1137 (1964).

(7) D. K. Smith, "A Fortran Program for Calculating X-ray Powder Diffractions," University of California Report UCRL-7196 (1963).

(8) A. C. Larson, Los Alamos Scientific Laboratory, unpublished work.

(9) M. H. Mueller and L. Heaton, "Determination of Lattice Parameters with the Aid of a Computer," Argonne National Laboratory Report ANL-6176 (1961).