decrease in the energy separation between the ground state and the excited states leads to an increase in χ_{TIP} as observed. Certain absorption maxima in the electronic spectra also exhibit a shift to lower energy upon successive unit oxidation of the cluster ions from 2+ to 4+. Accordingly, one might expect the 4+ ion to exhibit the largest value of χ_{TIP}. Comparison of values for analogous niobium and tantalum compounds containing the ions $(M_6Cl_{12})Cl_6{}^{n-}$ with $n = 2$ and 3, however, reveals no trend of this type within the uncertainty of the data. Such a trend may be obscured by compensating changes in χ_D which are not accounted for in the method used here for estimating this quantity. Alternately, the effect of oxidation upon the electronic levels contributing to χ_{TIP} is too small to give a discernible trend in these data.

It does appear that a small increase in χ_{TIP} results when Br is substituted for Cl in the cluster compounds. This can be seen by comparing the values for the compounds in the $(Ta_6X_{12})X_6{}^{2-}$ series and for $Nb_6X_{14}\cdot 8H_2O$ with X = Cl or Br. Again this effect correlates with observed changes in the electronic spectra, where a small shift of the "metal–metal" bands toward lower energy by *ca.* 1000 cm^{-1} results on replacement of Cl with Br in the cluster ions.[16] A further structural feature that might be expected to have some effect on the magnetic properties is the symmetry of the cluster species. No discernible effect on χ_{TIP} is evident, however, when values for the hydrated or terminally substituted derivatives are compared with the values for the corresponding clusters having O_h symmetry, *viz.*, the $R_n[(M_6X_{12})X_6]$ compounds. As demonstrated by the two tungsten cluster compounds[37] included in Table IV there is a large decrease in χ_{TIP} on switching from the $M_6X_{12}{}^{n+}$ series to the $M_6X_8{}^{4+}$ series. The bonding levels in the latter clusters for M = Mo or W are known to be more stable, and the excited states are at higher energies, as evidenced by the absence of bands in the visible region of their electronic spectra.

In conclusion it is noted that the values derived here for χ_D and χ_{TIP} may be useful in correcting the molar susceptibilities of new paramagnetic derivatives of the $M_6X_{12}{}^{n+}$ cluster ions prior to a calculation of the magnetic moment, especially in those cases where the temperature dependence of χ_M is not determined. In the case of diamagnetic derivatives measured values of χ_M may be compared with χ_M calculated from appropriately chosen values of χ_D and χ_{TIP} to test for the presence of paramagnetic impurities. Finally, when a more accurate knowledge of the molecular orbital structure of these interesting species becomes available it should be possible to calculate the magnetic susceptibility components for comparison with experiment.

Acknowledgment.—The authors are grateful to J. L. Meyer, P. B. Fleming, T. A. Dougherty, and R. D. Hogue for making samples available to us for this study and to J. B. Hamilton for the epr measurements.

[37] R. D. Hogue and R. E. McCarley, *Inorg. Chem.*, **9**, 1354 (1970).

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Chemistry of Polynuclear Metal Halides. VII. Characterization of the Tantalum Chloride and Bromide Phases $TaX_{2.8}$ as Mixed-Valence Compounds[1]

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It has been shown that during equilibration of $TaCl_4$ or $TaBr_4$ at temperatures above their decomposition points TaX_3 phases are initially produced, but continued equilibration leads ultimately to phases of composition $TaX_{2.80}$. Data derived from reactions in aqueous solution, reflectance spectra (300–1000 nm), infrared spectra (50–400 cm^{-1}), epr, and magnetic susceptibilities indicate that the mixed-valence formulation $2Ta_6X_{15}\cdot 3TaX_4$ best describes the stoichiometry and structural features of the $TaX_{2.80}$ phases. Examination of the intermediate TaX_3 phases by similar methods revealed marked structural differences between $TaCl_3$ and $TaBr_3$. Apparently the $TaCl_3$ phase does not contain Ta_6Cl_{12} cluster units, in contrast to $TaBr_3$ which may be formulated as $(Ta_6Br_{12}{}^{2+})(TaBr_6{}^-)_2$.

Introduction

Compounds in the tantalum–tantalum chloride, bromide, and iodide systems have been investigated by Schäfer, *et al.*, and the lower phases $TaCl_4$, $TaCl_3$, Ta_6Cl_{15} in the chloride[2] system; $TaBr_4$, $TaBr_3$, and Ta_6Br_{15} in the bromide[3] system; and TaI_4 and Ta_6I_{14} in the iodide[4] system were reported. Each of these lower phases was obtained in crystalline form *via* deposition from vapor species formed in chemical transport reactions between the appropriate gaseous tantalum(V) halide and tantalum metal under the influence of a care-

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[1] Work performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

[2] H. Schäfer, H. Scholz, and R. Gerken, *Z. Anorg. Allgem. Chem.*, **331**, 154 (1964).

[3] H. Schäfer, R. Gerken, and H. Scholz, *ibid.*, **335**, 96 (1965).

[4] D. Bauer, H. G. Schnering, and H. Schäfer, *J. Less-Common Metals*, **8**, 388 (1965).

fully chosen temperature gradient. In this method the reactants were arranged in a three-compartment, sealed tube. The tantalum metal usually was maintained at ≥600° in one of the end compartments, the tantalum(V) halide was held at a temperature chosen to provide a specified vapor pressure in the other end, and the choice of temperature in the middle compartment governed the lower halide phase which was deposited by the chemical transport. Under these conditions only equilibrium phases in the respective systems should be expected to deposit, and in the case of most of the lower tantalum halides this has been confirmed, as noted below.

The equilibrium tantalum–tantalum bromide and –tantalum iodide phase diagrams were investigated by McCarley and Boatman[5] using thermal analysis and thermal equilibration techniques. The lower phases $TaBr_4$, $TaBr_{2.83}$, Ta_6Br_{15}, Ta_6Br_{14}, TaI_4, and Ta_6I_{14} were identified under conditions which also should lead to formation of equilibrium phases. As can be seen, the two methods gave concordant results for the equilibrium bromides and iodides except for $TaBr_3$, on one hand, and $TaBr_{2.83}$, on the other. (In the experiments[3] of Schäfer, *et al.*, temperatures sufficiently high for formation of Ta_6Br_{14} were not employed.) Thus the principal concern is with the TaX_3 and $TaX_{2.83}$ phases, since the results reported here show that a similar anomaly exists with the corresponding chlorides.

According to Schäfer, *et al.*, the phases $TaCl_3$ and $TaBr_3$ each had a small homogeneity range and were structurally similar to the $NbCl_{3.1-2.67}$ phase,[6] which had the indicated composition limits. At the lower composition limit the $NbCl_3$ phase may be formulated as Nb_3Cl_8 to reflect the trimeric units of metal atoms included between the closest packed chloride layers.[7] On the other hand it was proposed by McCarley and Boatman[5] that $TaBr_{2.83}$ should be formulated as $(Ta_6Br_{12})Br_5$ because chemical evidence indicated that the compound contained the Ta_6Br_{12} moiety in some form. Thus the purpose of this investigation was to understand the relationship of the TaX_3–$TaX_{2.83}$ phases and to characterize better the structural features and properties of the $TaX_{2.83}$ phases. In the subsequent discussion these latter compounds will be referred to as $TaX_{2.80}$ because of results reported here.

Experimental Section

Materials.—The tantalum(V) halides were prepared from direct combination of the elements in evacuated Pyrex tubes by passing the halogen over the metal heated to 400°. Purification was effected by sublimation under 5–10 mm pressure of argon to prevent entrainment of impurities. Subsequent handling of these and all the lower halides was always done on a vacuum line at *ca.* 10^{-5} Torr or in the glove box under an atmosphere of argon.

Tantalum(IV) Halides.—Large amounts of $TaCl_4$ were prepared by aluminum reduction of $TaCl_5$ in an $AlCl_3$ melt. An excess of $TaCl_5$ combined with aluminum turnings and $AlCl_3$ was sealed in an evacuated Pyrex tube and heated in a 230–200° thermal gradient for 6 days. Excess $TaCl_5$ and $AlCl_3$ were removed by sublimation at 150° for 24 hr. Preparation of $TaBr_4$ was similar to that of $TaCl_4$ except that the reaction was carried out at 250°.[5] Excess $TaBr_5$ and $AlBr_3$ were removed by sublimation at 225° for 24 hr.

Tantalum Chloride (2.80) Phase.—This phase was discovered as a result of an investigation of the thermal behavior of $TaCl_4$. Differential thermal analyses of $TaCl_4$, performed as previously described,[5] revealed an endothermic peak at 337 ± 1° which indicated possible decomposition of $TaCl_4(s)$ into new phases. Subsequently mixtures containing $TaCl_4$ (2 g) and $TaCl_5$ (1 g) were sealed in small evacuated Pyrex ampoules and equilibrated at 365 ± 1° for varying times (2–30 days). When the equilibrations were terminated, $TaCl_5$ was removed from the products by sublimation at 150° and the residues subjected to analyses, X-ray powder patterns, and tests of chemical behavior. A sample equilibrated for 30 days provided the single product $TaCl_{2.80}$. *Anal.* Calcd for $TaCl_{2.80}$: Ta, 64.57. Found: Ta, 64.69. An equilibration stopped after 2 days showed primarily lines of $TaCl_4$ in the X-ray powder pattern. Another, terminated after 5 days, dissolved partially in methanol (~30 wt %) leaving a black insoluble residue. The X-ray powder pattern of this residue was in good agreement with that of $TaCl_3$ prepared by chemical transport.

Tantalum Bromide (2.80) Phase.—The phase $TaBr_{2.80}$ was prepared by the disproportionation of tantalum(IV) bromide at 405–410° with sufficient $TaBr_5$ present to maintain its equilibrium pressure over the solid $TaBr_4$. In a typical preparation, $TaBr_4$ (15 g) and $TaBr_5$ (5 g) were sealed in an evacuated Pyrex tube *ca.* 3 in. long and 0.5 in. in diameter. The reaction vessel was placed in a vertical position in the furnace with an aluminum liner to smooth out thermal gradients. A temperature of 405 ± 2° was maintained over the sample with the upper portion slightly warmer than the bottom. After 25 days a brown powder remained. The material was transferred in the drybox to another tube *ca.* 8 in. long. The excess $TaBr_5$ was removed at 225° for 24 hr. Analytical data for two different preparations are given below. *Anal.* Calcd for $TaBr_{2.80}$: Ta, 44.71. Found: (1) Ta, 44.31, 44.56; (2) Ta, 44.44, 44.48; Br:Ta (average), 2.83.

Tantalum Trichloride Phase.—This compound was prepared by the chemical transport method.[2] A sample of composition $TaCl_{3.03}$ was prepared by reaction of Ta and $TaCl_5$ in a thermal gradient of 630–300° for 7 days. The product was black and insoluble in water. *Anal.* Found: Ta, 62.55; Cl, 37.18; Cl:Ta, 3.03. A comparison of X-ray diffraction *d* spacings of this compound with those given by Schäfer[2] for $TaCl_3$ proved the compounds were identical.

Tantalum Tribromide Phase.—Initial evidence for this phase was obtained from X-ray powder patterns of mixtures resulting from the incomplete equilibration of $TaBr_4$. It was found that the material could be prepared by aluminum reduction of $TaBr_5$ in sealed tubes under a 430–320° thermal gradient. The products were green and provided solutions of $Ta_6Br_{12}^{2+}$ when treated with water. Also further treatment of these products in a 550–25° thermal gradient provided $(Ta_6Br_{12})Br_2$, as described previously.[8]

For a sample of composition $TaBr_{3.01}$ the following *d* spacings (Å) (relative intensities in parentheses) were observed in the *X*-ray powder pattern: 9.22 (9), 8.45 (9), 6.18 (8), 3.20 (2), 3.05 (2), 3.02 (5), 2.88 (3), 2.62 (10), 2.40 (2), 2.21 (5), 2.16 (4), 2.09 (4), 1.86 (7), 1.85 (7).

Another sample, prepared in the same manner and having the composition $TaBr_{3.15}$, was used to obtain both magnetic susceptibility and far-infrared spectral data. Each preparation of this material provided samples of slightly different composition, but in the composition range $TaBr_{3.01}$ to $TaBr_{3.43}$ all samples gave X-ray powder pattern data which were in substantial agreement. Thus this phase appears to have a very limited homogeneity range.

Analytical Procedure.—Tantalum and halogen analyses were

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(5) R. E. McCarley and J. C. Boatman, *Inorg. Chem.*, **4**, 1486 (1965).

(6) H. Schäfer and K. D. Dohmann, *Z. Anorg. Allgem. Chem.*, **300**, 1 (1959).

(7) H. G. Schnering, H. Wohrle, and H. Schäfer, *Naturwissenschaften*, **48**, 159 (1961).

(8) P. J. Kuhn and R. E. McCarley, *Inorg. Chem.*, **4**, 1482 (1965).

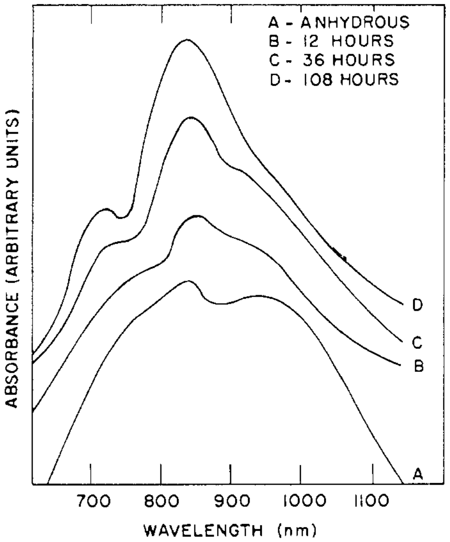

Figure 1.—Reflectance spectrum of $TaBr_{2.80}$ before and after exposure to air.

performed as described previously[5] for air-sensitive samples. For more accurate tantalum analyses the sample was weighed into a tared fused-silica thimble, heated to 100–110° for 24 hr with nitric acid in a sealed tube, and subsequently weighed as Ta_2O_5 after ignition in air at *ca.* 800°.

X-Ray Diffraction Data.—Powder patterns were obtained with a 114.59-mm Debye–Scherrer camera. Finely powdered samples were packed and sealed into 0.2-mm Lindemann glass capillaries in the glove box. Samples were exposed to Ni-filtered Cu $K\alpha$ radiation for 24–30 hr. Relative intensities of lines were estimated visually by comparison with the most intense lines.

Spectra.—Near-infrared spectra were obtained on solutions using a Cary Model 14 recording spectrophotometer and 1-cm fused silica cells. The wavelength range investigated was 600–1200 nm which provided qualitative identification of the cluster ions. Reflectance spectra were obtained with a Beckman Model DU spectrophotometer equipped with the Beckman 2580 reflectance attachment. Potassium bromide was used as dilutant and reference material. The sample was contained in a cell provided with a fused-silica window and sealed from the atmosphere by an "O" ring.

Far-infrared spectra (40–600 cm^{-1}) were obtained using a Beckman IR-11 grating spectrophotometer in a double-beam operation on Nujol mulls. The mulled sample was sandwiched between thin polyethylene windows and sealed with an "O" ring.

Oxidation State Determinations.—A sample of $TaCl_{2.81}$ was mixed with an aliquot of standard iron(III) solution under an argon atmosphere and stirred overnight. The solution was separated from a red-brown solid, shown to be a $Ta_6Cl_{12}^{4+}$ derivative, by filtration and diluted to volume. Two aliquots were placed in volumetric flasks, 1,10-phenanthroline was added to one of the solutions, and they were diluted to volume. The absorbance of the $Fe(o\text{-phen})_3^{2+}$ complex was measured at 512 nm using the solution without indicator as a reference solution. The concentration of iron(II) was determined by comparison with the absorbance of standard solutions.

Magnetic Susceptibility.—Magnetic susceptibilities were obtained using the Faraday method with equipment previously described.[9] Measurements were obtained at five field strengths between 6 and 12 kOe to correct for field dependence of ferromagnetic impurities. Correction for the diamagnetism of the container was applied in all cases. All data were processed on an IBM 360 computer to obtain a least-squares fit to the equation of Honda and Owen.[10]

Electron Paramagnetic Resonance.—The *g* factors used in this work were obtained from epr spectra measured at room temperature. Spectra were obtained on a Strand Model 601 spectrometer equipped with an AFC system which locked the microwave oscillator frequency to the instantaneous cavity frequency of the cylindrical TE_{011} cavity. Magnetic field measurements were made with a proton magnetometer and frequency counter.

Results

The phases $TaCl_{2.80}$ and $TaBr_{2.80}$ provided X-ray powder patterns which strongly suggest their isomorphism. The *d* spacings and relative intensities (in parentheses) for corresponding reflections in each pattern are given in Table I.

TABLE I[a]
X-RAY DIFFRACTION *d* SPACINGS FOR $TaX_{2.80}$ (X = Cl, Br)

$TaCl_{2.80}$	$TaBr_{2.80}$	$TaCl_{2.80}$	$TaBr_{2.80}$
9.15(10)	9.33(10)	2.44(6)	2.54(5)
...	6.68(8)	2.33(8)	2.43(5)
6.37(10)	6.49(6)	2.30(8)	2.40(5)
4.48(6)	4.65(4)	2.22(8)	2.32(5)
4.04(3)	4.21(4)	2.17(8)	2.26(5)
3.95(3)	4.11(4)	2.14(4)	2.24(3)
3.44(8)	3.56(6)	2.01(4)	2.10(4)
2.85(3)	2.96(5)	1.95(4)	2.04(4)
2.49(8)	2.60(8)		

[a] *d* spacings in ångströms; relative intensities in parentheses.

Both compounds produced deep green to blue-green solutions of the $Ta_6X_{12}^{2+}$ ions when combined with water, thus indicating the presence of the $Ta_6X_{12}^{n+}$ cluster units in their structure. After prolonged stirring with water an insoluble fraction constituting *ca.* 20–25% of the total tantalum was shown to contain a mixture of tantalum(IV) oxide and tantalum(V) oxide. Decomposition of the $Ta_6X_{12}^{2+}$ ions is sufficiently slow under these conditions that the insoluble oxides must have resulted from hydrolysis of noncluster species contained in the compounds.

A search for more suitable solvents showed that $TaBr_{2.80}$ was either insoluble or reacted in a manner similar to that above in most solvents. Previous experience, however, with the behavior of tantalum halides in acetonitrile suggested that this solvent might be used to purify the $TaBr_{2.80}$ compound. As this material is prepared by equilibration in the presence of $TaBr_5$, a small amount of $TaBr_4$ always must be left in the preparation. The phase diagram[5] in the region of the temperature used in the equilibration indicates the liquid in contact with this phase should have a composition of *ca.* $TaBr_{4.8}$. Hence when $TaBr_5$ is removed by sublimation, a small amount of $TaBr_4$, *i.e.*, the quantity needed to lower the liquidus composition to $TaBr_{4.80}$, should remain to contaminate the desired compound. This impurity would thus give somewhat false indication of the true Br:Ta ratio in the phase which was reported originally as $TaBr_{2.83}$.[5] Prolonged leaching of a sample having the composition $TaBr_{2.83}$ with acetonitrile, in which $TaBr_4$ is soluble, removed this impurity and provided new material with the analytical composition $TaBr_{2.79}$. As noted in the Experimental Section prolonged equilibration of $TaCl_4$ provided $TaCl_{2.80}$ of better purity.

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(9) J. G. Converse and R. E. McCarley, *Inorg. Chem.*, **9**, 1361 (1970).

(10) As given by L. F. Bates, "Modern Magnetism," 3rd ed, Cambridge University Press, Cambridge, England, 1951, pp 133–136.

Further information was obtained from the reflectance spectra of the $TaX_{2.80}$ compounds. As shown in Figure 1 the anhydrous $TaBr_{2.80}$ did not provide a very useful spectrum, but after exposure to the atmosphere for increasing periods the material gave a well-defined spectrum with maxima at 730 and 850 nm and a shoulder near 935 nm. On the other hand even the anhydrous $TaCl_{2.80}$ furnished a good spectrum with maxima at 740, 900, and 960 nm (sh). These data clearly indicate that the cluster species in the crystalline phases are $Ta_6Cl_{12}^{3+}$ and $Ta_6Br_{12}^{3+}$; the strong maximum at *ca.* 640 nm[8] for the ions $Ta_6X_{12}^{2+}$ is notably absent and the observed maxima are in accord with those for the Ta_6X_{15} phase reported by Spreckelmeyer.[11]

Because of the reaction in water whereby the cluster species is reduced to the 2+ state, the noncluster species was indicated to be a good reducing agent. On the assumption that the latter is a species of Ta(IV), the compounds may be formulated as $(Ta_6X_{15})_2(TaX_4)_3$ or $2Ta_6X_{15} \cdot 3TaX_4$. In the oxidation state determinations the reaction of $TaCl_{2.81}$ with Fe(III) provided 1 mol of Fe(II)/3 mol of $TaCl_{2.81}$. This result is in agreement with the suggested formulation since excess Fe(III) oxidizes the cluster to the 4+ state,[12] and Ta(IV) to Ta(V). Thus 5 mol of Fe(II)/mol of $2Ta_6Cl_{15} \cdot 3TaCl_4$ should be formed and was observed in the experiments

In order to gain further insight into the possible structural features of the $TaX_{2.80}$ phases, their magnetic susceptibilities and infrared spectra were investigated. Both the chloride and bromide were paramagnetic, but their susceptibilities exhibited a slight deviation from Curie law behavior at lower temperatures as shown in Figure 2. Molar susceptibilities were calculated for the $2Ta_6X_{15} \cdot 3TaX_4$ model and are listed in Table II, along with χ_g and μ_{eff}. From plots of χ_M^{-1} *vs.* T values of Θ were found to be -16 and $-23°$, respectively, for $TaCl_{2.80}$ and $TaBr_{2.80}$. The values of χ_D listed in the footnotes of Table II were calculated as described in the previous paper[9] dealing with this term and χ_{TIP} in the metal cluster compounds. If it is assumed that the deviation from Curie behavior is caused by intermolecular exchange interactions and a value of *ca.* 500×10^{-6} cgsu/mol of Ta_6X_{12} in the compounds is taken for χ_{TIP},[9] then magnetic moments may be calculated from the relation $\mu = 2.828[(\chi_M - \chi_{TIP} - \chi_D)(T - \theta)]^{1/2}$. The relatively constant moments calculated in this way were 2.20 ± 0.03 BM for the chloride and 2.48 ± 0.02 BM for the bromide. Epr measurements on powdered samples provided spectra which showed a nearly isotropic signal with $\bar{g} = 1.91$ for both $TaCl_{2.80}$ and $TaBr_{2.80}$.

TABLE II

MAGNETIC SUSCEPTIBILITIES FOR $TaX_{2.80}$ PHASES[a]

$TaCl_{2.80}$[b]				$TaBr_{2.80}$[c]			
T, °K	$10^6\chi_g$, cgsu	$10^6\chi_M$, cgsu	μ_{eff}[d]	T, °K	$10^6\chi_g$, cgsu	$10^6\chi_M$, cgsu	μ_{eff}[d]
296	0.291	1220	2.62	295	0.2246	1364	2.81
274	0.328	1380	2.59	241	0.3030	1839	2.75
242	0.388	1630	2.54	203	0.3767	2287	2.67
222	0.443	1860	2.51	183	0.4279	2597	2.62
195	0.518	2180	2.45	142	0.5820	3533	2.53
166	0.637	2680	2.41	126	0.6704	4069	2.50
133	0.845	3550	2.37	116	0.7309	4437	2.46
113	1.00	4220	2.33	113	0.7430	4510	2.44
77	1.47	6170	2.20	77	1.080	6558	2.31

[a] χ_M and χ_D calculated on the basis of the formula $2Ta_6X_{15} \cdot 3TaX_4$. [b] χ_D(calcd) = -1660×10^{-6} cgsu. [c] χ_D(calcd) = -2090×10^{-6} cgsu. [d] Calculated from the formula $\mu_{eff} = 2.828[(\chi_M - \chi_D)T]^{1/2}$.

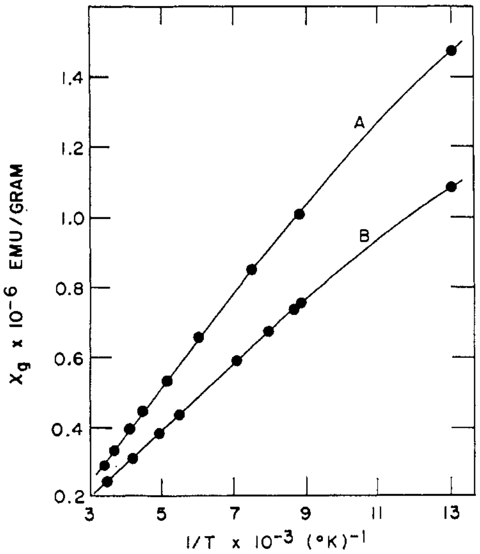

Figure 2.—Magnetic gram-susceptibilities of $TaCl_{2.80}$ (A) and $TaBr_{2.80}$ (B).

The compound of composition $TaBr_{3.15}$ was diamagnetic with $10^6\chi_g$ values of -0.109, -0.123, and -0.141 cgsu at 77, 114, and 298°K, respectively. These data agree with the value -0.1×10^{-6} cgsu/g (90–295°K) reported by Schäfer, *et al.*,[3] for $TaBr_{3.16}$. In contrast these authors reported for $TaBr_{2.90}$ (at the lower limit of the "$TaBr_3$" phase) $10^6\chi_g$ values of $+0.56$, $+0.12$, and -0.03 cgsu at 90, 195, and 297°K, respectively. It is noteworthy that the temperature dependence of the latter data is similar to that of $TaBr_{2.80}$ (Table II), but the magnitude of the susceptibilities is somewhat smaller for the reported $TaBr_{2.90}$.

The results of the infrared measurements over the region 40–600 cm^{-1} on the $TaX_{2.80}$ phases and related compounds are given in Tables III and IV.

Discussion

Originally the $TaBr_{2.83}$ phase was proposed to be $Ta_6Br_{12}Br_3$[5] for the following reasons, other than its composition. When this phase was combined with water, the $Ta_6Br_{12}^{2+}$ ion was identified in solution by its electronic spectrum and the red-brown insoluble residue was identified as tantalum(IV) oxide. Observation that the $Ta_6X_{12}^{4+}$ ions decomposed in neutral aqueous solution suggested that the $Ta_6X_{12}^{5+}$ ions also would be unstable in solution. A slow step rupture of the 5+ cluster ion could produce reducing fragments which could in turn yield $Ta_6Br_{12}^{2+}$ ions by rapid reduction of other 5+ ions.

The results of this investigation, however, clearly

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[11] B. Spreckelmeyer, *Z. Anorg. Allgem. Chem.*, **365**, 225 (1969).

[12] J. H. Espenson and R. E. McCarley, *J. Am. Chem. Soc.*, **88**, 1063 (1966).

Table III

Infrared Spectra (cm^{-1}) of the Lower Tantalum Chloride Phases[a]

$TaCl_4$	$TaCl_{3.03}$	$TaCl_{2.80}$	Ta_6Cl_{15}
386 s	387 w	400 m	
	372 w		
363 s	356 vs	359 s	
		338 vs	331 vs
	311 m	303 w	300 m
	271 w		280 vw
	249 s	250 s	254 m
247 vs		242 s	
	234 s		235 s
	227 s		
212 vw	191 w		191 vw
172 m		177 w	173 w
	164 m		166 vw
	140 w	142 w	143 m
127 m			137 w
	108 vw	117 vw	
100 s	93 vw	95 vw	93 w

[a] Relative intensities: vs, very strong; s, strong; m, medium; w, weak; vw, very weak.

Table IV

Infrared Spectra (cm^{-1}) of the Lower Tantalum Bromide Phases[a]

$TaBr_4$	$TaBr_{3.15}$	$TaBr_{2.80}$	Ta_6Br_{15}	Ta_6Br_{14}
268 s		272 s	271 m	
253 s		242 s		237 s
	231 vs	233 vs	230 vs	228 vs
220 w	212 w			212 s
		197 s	197 s	192 w
174 vs	184 s			182 s
159 m		165 w	164 m	159 m
	154 vs	150 vs	152 s	147 m
	128 m		144 s	133 s
		122 w		120 w
116 w		115 w		
	106 vw	106 w	108 w	107 m
	101 w	98 w	100 vw	100 w
91 m	92 m	92 vw	94 w	93 w
73 w	68 w		79 w	84 w
	66 w	62 m	63 m	63 vw
57 vw	56 m			
	48 vw	51 vw	48 vw	48 w

[a] Relative intensities: vs, very strong; s, strong; m, medium; w, weak; vw, very weak.

show that the 3+ ion rather than the 5+ ion of the Ta_6X_{12} moiety is present in the $TaX_{2.80}$ phases. The chemical behavior of these materials leads one to conclude that the $TaX_{2.80}$ phases are best described as mixed-valence compounds. It is possible to deduce some structural features from the magnetic and infrared spectral data.

Cotton and Lippard[13] reported the mixed-valence compound $(C_9H_7NH^+)_2(Re_3Br_9)(ReBr_6^{2-})$ containing both a trimeric rhenium cluster unit and the $ReBr_6^{2-}$ ion. In a similar manner one may formulate a model for $TaX_{2.80}$ as $(Ta_6X_{12}^{3+})_2(TaX_6^{2-})_3$. The model $(TaX_2^{2+})_3(Ta_6X_{12}X_6^{3-})_2$ could be a reasonable choice, also, in view of the $(Ta_6Cl_{12})Cl_6]^{n-}$ derivatives prepared by Hughes, *et al.*[14] In these cases the halide acceptor strength of $Ta_6X_{12}X_3$ *vs.* TaX_4 should be significant in determining which model would be favored. The alternative to a distinct molecular species of course would be a mixed-crystal formulation of the type found by Schäfer and Schnering[15] for $NbCl_3$ over its homogeneity range, where both trimeric and dimeric metal atom clusters were located between closest packed halide layers.

The magnetic susceptibilities and epr results support the mixed-valence formulation. The observed *g* factors closely correspond to the value of 1.922 for $((C_2H_5)_4N)_2[(Ta_6Cl_{12})Cl_6]$.[9] The fact that little evidence was found for anisotropy in the epr spectra indicated the absence of any large distortion within the $Ta_6X_{12}^{3+}$ units. An epr spectrum from Ta(IV) at room temperature was considered only a remote possibility. Even if such a resonance peak was observed, it should be at much lower *g* values because of the strong spin–orbit interaction acting on this ion.

Treatment of the magnetic susceptibility data depends upon the molecular configuration of the compound. The magnetic moment can be calculated from the molar susceptibility which depends on the molecular weight of the compound. Thus the molar susceptibility calculated for $(Ta_6X_{12})X_5$ is different from that obtained for $2Ta_6X_{15}\cdot 3TaX_4$. (The models $(Ta_6X_{12}^{3+})_2(TaX_6^{2-})_3$, $(TaX_2^{2+})_3(Ta_6X_{18}^{3-})_2$, and the mixed-crystal model all yield the same molar susceptibility.) Rationalization of the magnetic properties of the components for these models can then be used to select the most accurate representation.

The magnetic moment can be calculated from the *g* factor if one assumes the total spin quantum number *S* is $^1/_2$ for both the 5+ and 3+ cluster units. The Cotton–Haas[16] molecular orbital scheme and diamagnetism of the 4+ cluster unit[9] indicate this would be a correct assumption. The product $g[S(S + 1)]^{1/2}$ yields a moment of 1.65 BM for the $(Ta_6X_{12})X_5$ model as compared to a moment of 1.42 BM determined from susceptibility data. The large difference between these moments lends further support to the contention that $(Ta_6X_{12})X_5$ is not an accurate representation of the $TaX_{2.80}$ phase.

In order to compare esr and bulk susceptibility data for the formulation $2Ta_6X_{15}\cdot 3TaX_4$ moments of both the cluster component and the Ta(IV) component must be estimated. The total magnetic moment then is given by the expression $\mu_T = (2\mu_C^2 + 3\mu_{Ta(IV)}^2)^{1/2}$. Because of strong spin–orbit coupling the moment of the Ta(IV) component is expected to be quite low. For example, it was found by Torp[17] that $\mu = 0.20$ BM in the compound K_2TaCl_6. No resonance signal in the esr spectrum would be observed for such a Ta(IV) species at the frequency and field strengths investigated here. Thus the observed esr spectrum is attributed only to the $Ta_6X_{12}^{3+}$ component with $g = 1.91$. Proceeding with calculations based on these considera-

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[13] F. A. Cotton and S. J. Lippard, *Inorg. Chem.*, **4**, 59 (1965).

[14] B. G. Hughes, J. L. Meyer, P. B. Fleming and R. E. McCarley, *ibid.*, **9**, 1343 (1970).

[15] H. Schäfer and H. G. Schnering, *Angew. Chem.*, **76**, 833 (1964).

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

[17] B. A. Torp and R. E. McCarley, unpublished research.

tions we obtain $\mu_C = 1.65$, $\mu_{Ta(IV)} \approx 0.2$, and $\mu_T = 2.36$ BM. The latter value compares favorably with the moments of 2.20 and 2.48 BM, for the chloride and bromide, respectively, which were calculated from the molar susceptibilities based on the formula $2Ta_6X_{15} \cdot 3TaX_4$.

Among the possible models which may be used to represent the coordination of the cluster and Ta(IV) components, the one formulated as $(TaX_4^{2+})_3[(Ta_6X_{12})X_6^{3-}]_2$ seems the least likely. In particular the occurrence of a two-coordinate Ta(IV) ion is clearly unreasonable. On the other hand, the representation as $(Ta_6X_{12}^{3+})_2(TaX_6^{2-})_3$ may be more plausible. Here the lack of a completed coordination sphere about the $Ta_6X_{12}^{3+}$ unit is not so objectionable since the charge density per tantalum atom is low. Moreover the occurrence of Ta(IV) as TaX_6^{2-} is well known,[18] and the $^2T_{2g}$ ground state of the octahedral anion leads to a magnetic moment near zero when strong spin–orbit coupling prevails.[19] Even Ta(IV) complexes of lower symmetry, such as $TaX_4(C_5H_5N)_2$,[20] have magnetic moments less than *ca.* 0.7 BM. The magnetic data do indicate that there is very little contribution to the total moment from the Ta(IV) species in these phases.

A mixed-crystal model whereby both the $Ta_6X_{12}^{3+}$ cluster and the Ta(IV) ions complete their coordination sphere by sharing halogen atoms would seem to be the most realistic possibility. Neither component need be strongly distorted from its ideal octahedral symmetry in such crystals. Also the halogen bridging may provide a path for magnetic exchange coupling similar to that found in the compounds $(Ta_6X_{12})X_{6/2}$.[9] Evidence of magnetic exchange is provided by the Θ values (Curie–Weiss) of -16 and -23°K for $TaCl_{2.80}$ and $TaBr_{2.80}$, respectively.

The infrared spectra in the region 50–600 cm^{-1} arise primarily from metal–halogen vibrations and should provide useful information about the possible structural features of the $TaX_{2.80}$ phases. Band assignments for the Ta_6X_{12} cluster species have been considered elsewhere.[21] Thus the bands listed in Table III for $TaCl_{2.80}$ at 338, 250, 177, and 142 cm^{-1} may be considered to arise from $Ta_6Cl_{12}^{3+}$ cluster vibrations. In this spectrum the bands at 303 and 117 cm^{-1} may arise from vibrations of chlorine atoms coordinated in the terminal positions of the cluster. With the exception of the band at 117 cm^{-1} each of these bands appears at a similar wave number in the spectrum of Ta_6Cl_{15}, which corroborates their assignment. The bands at higher wave number, *viz.*, at 400 and 359 cm^{-1}, have no counterpart in the spectrum of Ta_6Cl_{15}. However these bands are matched by bands in similar positions in the spectrum of $TaCl_4$, and, accordingly, they are assigned as the Ta–Cl stretching modes of the Ta(IV) species in $TaCl_{2.80}$. The assignment of the band at 242 cm^{-1} is uncertain because bands of similar wave number appear in the spectra of both $TaCl_4$ and Ta_6Cl_{15}. In regard to the spectrum of "$TaCl_3$" (as represented by $TaCl_{3.03}$ in Table III) we note only that the absence of a strong band at *ca.* 330 cm^{-1} appears to rule out the presence of Ta_6Cl_{12} clusters in the trichloride phase.

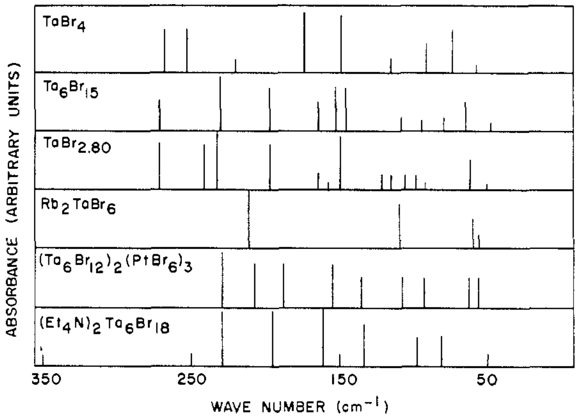

Figure 3.—Infrared spectra of $TaBr_{2.80}$ and some related tantalum bromide compounds.

A more extensive study was made of the infrared spectra of the different tantalum bromide phases. In addition to the data given in Table IV, the spectra of Rb_2TaBr_6[17] and $(Ta_6Br_{12})_2(PtBr_6)_3$ were obtained for testing the $(Ta_6Br_{12})_2(TaBr_6)_3$ model of $TaBr_{2.80}$. The $PtBr_6^{2-}$ derivative was obtained by mixing aqueous solutions of $(Ta_6Br_{12})Br_3$ and H_2PtBr_6, followed by slow evaporation and crystallization. *Anal.* Calcd for $Ta_{12}Pt_3Br_{42}$: Ta, 35.5. Found: Ta, 34.5. Because no bands arising from the vibrations of H_2O were observed in the infrared spectrum (50–4000 cm^{-1}), the compound $(Ta_6Br_{12})_2(PtBr_6)_3$ was considered to be anhydrous. A comparison of the spectra of $TaBr_4$, Ta_6Br_{15}, $TaBr_{2.80}$, Rb_2TaBr_6, $(Ta_6Br_{12})_2(PtBr_6)_3$, and $((C_2H_5)_4N)_2[(Ta_6Br_{12})Br_6]$[21a] is provided in Figure 3.

In the spectrum of Rb_2TaBr_6 strong bands were observed at 212 and 110 cm^{-1}, which corresponded, respectively, to the T_{1u} stretching and bending modes of $TaBr_6^{2-}$. The absence of a band near 212 cm^{-1} in the spectrum of $TaBr_{2.80}$ indicates that the ion $TaBr_6^{2-}$ is not present *per se* in this compound. By contrast the spectrum of $(Ta_6Br_{12})_2(PtBr_6)_3$ exhibited strong bands at 208 and 108 cm^{-1} attributed to $PtBr_6^{2-}$ and bands at 230, 188, 155, 135, and 93 cm^{-1} which were attributed to $Ta_6Br_{12}^{3+}$. Thus, because the latter spectrum indicated the individual ions could retain their identity in a compound of similar stoichiometry and the spectrum of $TaBr_{2.80}$ indicated the absence of $TaBr_6^{2-}$, the formulation as $(Ta_6Br_{12}^{3+})_2(TaBr_6^{2-})_3$ was regarded as a poor model.

The bands at 233, 197, 165, 150, 98, and 62 cm^{-1} in the spectrum of $TaBr_{2.80}$ correspond closely with bands observed in the spectra of Ta_6Br_{15} and Ta_6Br_{14} and hence are associated with vibrations of the $Ta_6Br_{12}^{3+}$

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[18] V. V. Safonov, B. G. Korshunov, Z. N. Shevtsova, and L. G. Shadrova, *Zh. Neorgan. Khim.*, **9**, 1406 (1964); **10**, 669 (1965); E. K. Smirnova and I. V. Vasil'kova, *ibid.*, **12**, 566 (1967).

[19] C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 143–146.

[20] (a) R. E. McCarley and J. C. Boatman, *Inorg. Chem.*, **2**, 547 (1963); (b) G. W. A. Fowles, D. J. Tidmarsh, and R. A. Walton, *ibid.*, **8**, 631 (1969).

[21] (a) P. B. Fleming, J. L. Meyer, W. K. Grindstaff, and R. E. McCarley, *ibid.*, in press; (b) P. M. Boorman and B. P. Straughan, *J. Chem. Soc.*, 1514 (1966); (c) R. A. Mackay and R. F. Schneider, *Inorg. Chem.*, **7**, 455 (1968).

cluster or Br atoms coordinated in the terminal positions of the cluster. The strong bands at 272 and 242 cm^{-1} most likely are associated with Ta–Br stretching motions of the Ta(IV) species since they correspond to the bands at 268 and 253 cm^{-1} in the spectrum of $TaBr_4$. Thus the spectra of $TaCl_{2.80}$ and $TaBr_{2.80}$ appear to be related in the same way to spectra of the respective TaX_4 and Ta_6X_{15} phases.

While only a single-crystal structure determination can reveal the structural details of the $TaX_{2.80}$ phases, the combined evidence presented here shows that the constituency of these phases is best represented by the mixed-valence formulation $2Ta_6X_{15}\cdot 3TaX_4$. The chemical behavior and electronic spectra disclose the presence of $Ta_6X_{12}^{3+}$ and Ta(IV) species in the material. Paramagnetism confirms the presence of $Ta_6X_{12}^{3+}$ ions, and evidence of magnetic exchange coupling indicates the presence of atoms bridging between the cluster units. Very likely this bridging arrangement results in the filling of the six octahedral coordination sites on both the $Ta_6X_{12}^{3+}$ and Ta^{4+} ions by sharing of halogen atoms.

The results of the equilibration experiments with $TaCl_4$ at $\geq 365°$, or with $TaBr_4$ at $\geq 400°$, show that phases of composition near TaX_3 are generated as intermediates during the reactions. In both cases the $TaX_{2.80}$ phases are the final products after prolonged equilibration. Thus the TaX_3 phases cannot be considered as equilibrium phases at these temperatures, even though these are also obtained as products of chemical transport reactions.[2,3] The X-ray diffraction data and chemical properties indicate that identical $TaCl_3$ is produced by either method. Evidently $TaCl_3$ does not contain Ta_6Cl_{12} cluster units, and in this regard it is different from $TaBr_3$.

On the basis of results presented here it is proposed that the $TaBr_3$ resulting from the aluminum reduction of $TaBr_5$ in a thermal gradient, or from incomplete equilibration of $TaBr_4$ above 400°, can be represented by the formulation $Ta_6Br_{14}\cdot 2TaBr_5$. This mixed valence species has a Br:Ta molar ratio of 3.00 and as noted above does not appear to have a significant homogeneity range. Failure to remove all $TaBr_5$ or $TaBr_4$ from the sample $TaBr_{3.43}$ may account for the higher composition observed. A reaction between Ta_6Br_{14} and $TaBr_5$ at 350° for 3 days followed by removal of excess $TaBr_5$ at 225° yielded an observable quantity of tribromide determined from an X-ray powder pattern. This reaction suggests that $TaBr_5$ may be taken up by Ta_6Br_{14} *via* acid–base interaction, *e.g.*, with formation of $Ta_6Br_{12}(TaBr_6)_2$, although this phase cannot be the final equilibrium phase formed under these conditions.

In contrast to the inert character of $TaCl_3$, the tribromide is readily soluble in water with production of $Ta_6Br_{12}^{2+}$ ions. The infrared spectrum of $TaBr_{3.15}$ given in Table IV has the following noteworthy features. First, there are no bands above 231 cm^{-1}, which implies the absence of species such as those in $TaBr_4$ or $TaBr_{2.80}$ giving rise to the high-energy bands. Second, the presence of the band at 212 cm^{-1} suggests that the $TaBr_6^-$ ion may be a constituent of the compound. The remaining strong bands in this spectrum may be attributed to vibrations of the Ta_6Br_{12} cluster unit. Since the $TaBr_{3.15}$ was diamagnetic and its reflectance spectrum in the region 300–1000 nm corresponded quite closely to that of Ta_6Br_{14}, the cluster was concluded to be present as $Ta_6Br_{12}^{2+}$. Thus the formula $(Ta_6Br_{12}^{2+})(TaBr_6^-)_2$ is indicated as a reasonable representation of these structural features of the $TaBr_3$ phase.

In conclusion it is interesting to comment on the complicated path followed during equilibrium decomposition of $TaBr_4$. Apparently the first reaction is described by

$$16TaBr_4 = (Ta_6Br_{12})(TaBr_6)_2 + 8TaBr_5 \qquad (1)$$

which converts Ta(IV) into $Ta_6Br_{12}^{2+}$ and Ta(V). In the subsequent reaction electron transfer results in formation of $Ta_6Br_{12}^{3+}$ and conversion of Ta(V) to Ta(IV). The net reaction given by eq 2 indicates that this process must be complicated because more Ta(IV) is required than can be provided by a simple one-electron transfer between $Ta_6Br_{12}^{2+}$ and Ta(V). The additional required Ta(IV) may be furnished by $TaBr_4$ in the equilibrating mixture or by oxidation and disruption of a fraction of the $Ta_6Br_{12}^{3+}$ cluster species. If the latter possibility pertains, the very slow conversion to $TaBr_{2.80}$ may be associated with a high activation energy for disruption of the cluster unit.

$$33TaBr_4 = 2Ta_6Br_{15}\cdot 3TaBr_4 + 18TaBr_5 \qquad (2)$$

Acknowledgment.—We are grateful to Miss Evelyn Conrad for her services in the measurement of the infrared spectra reported here.