bands at 2073, 2040, 2006, 1998, and 1957 cm.$^{-1}$, might be a partially desulfurized complex analogous to the $C_4H_4Fe_2(CO)_6$ formed from thiophene itself.[1]

Anal. Calcd. for $C_{14}H_6O_6SFe_2$: C, 40.61; H, 1.46; S, 7.74; mol. wt., 414. Found: C, 39.80; H, 1.58; S, 6.21; mol. wt., 458.

Reaction between *o*-Aminobenzenethiol and Triiron Dodecacarbonyl.—A mixture of 2.50 g. (20 mmoles) of *o*-aminobenzenethiol and 6.0 g. (12 mmoles) of triiron dodecarbonyl in 60 ml. of cyclohexane was stirred for 45 min. in a bath at 80°. The cooled mixture was chromatographed on alumina. (Filtration of other runs yielded quantities of intractable, insoluble, pyrophoric, red solids.) The eluates obtained with pentane were discarded; a 1:1 pentane-dichloromethane mixture eluted a deep red solution, which was evaporated to a sticky orange solid. Impurities were sublimed away (70° (0.1 mm.)) and the residue was crystallized (pentane) to 200 mg. of brick-red solid, m.p. 106–108° (2.5% yield).

Anal. Calcd. for $C_{12}H_5O_6NSF_2$: C, 35.76; H, 1.25; N, 3.47; S, 7.95; mol. wt., 403. Found: C, 35.58; H, 1.60; N, 3.55; S, 7.86; mol. wt., 420.

In addition to the carbonyl stretching bands the infrared spectrum (CS_2 solution, NaCl optics) showed bands at 3330 (N–H stretching), 3067, 2959 (C–H stretching), and 746, 725 (C–H deformation) cm.$^{-1}$. Thermal decomposition of an acetone solution of the complex gave primarily aniline, identified by mass spectrometric techniques.[12]

CONTRIBUTION FROM THE CHEMISTRY DIVISION,
OAK RIDGE NATIONAL LABORATORY,
OAK RIDGE, TENNESSEE

Hydrolysis of Tantalum(V): Equilibrium Ultracentrifugation and Raman Spectra of Potassium Tantalate[1]

BY J. AVESTON[2] AND JAMES S. JOHNSON

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The comparative dearth of information on the solution chemistry of tantalum is in marked contrast to the abundance of data in the literature on the hydrolytic behavior of the elements in adjacent groups. This stems from the fact that the oxide is soluble only in complexing media such as hydrofluoric acid, or in strongly basic solution, where the degree of hydrolysis of the tantalate species appears to be essentially constant. The more popular methods which have been used to establish both the stoichiometry and degree of aggregation of such species in solution, such as potentiometric and conductometric titrations, are therefore inapplicable, and the use of some direct method for the determination of ionic weight is especially indicated.

Jander and Ertel,[3] on the basis of measurements by the much criticized diffusion method, reported that in alkaline solutions of Ta(V), the $Ta_5O_{16}{}^{7-}$ ion predominates. More recently, Nelson and Tobias[4] (who review the literature more extensively than we do here), using light-scattering techniques, obtained evidence for the hexatantalate ion ($Ta_6O_{19}{}^{8-}$) in the pH range 10–13. This species is consistent with the formulation $K_8(Ta_6O_{19})\cdot 16H_2O$ for crystalline potassium tantalate advanced by Lindqvist and Aronsson[5] from a single-crystal X-ray diffraction study. Very recently, Nelson and Tobias[6] have also centrifuged tantalate in KCl supporting electrolyte.

We present here further evidence, obtained by equilibrium ultracentrifugation, for a hexatantalate ion, together with the Raman spectra of crystalline $K_8(Ta_6O_{19})\cdot 16H_2O$ and the corresponding solution; the latter indicate a similar structure for the species in the crystal and in the solution. Although the ultracentrifugation study duplicates to some extent that of Nelson and Tobias,[6] we shall report it briefly. Our results, which encompass some conditions not investigated by them (KOH supporting electrolyte), confirm theirs.

Experimental

(1) **Ultracentrifugation.**—Details of the centrifugation technique and of the computational procedure used in the interpretation of results have been presented elsewhere.[7] For the tantalate centrifugations, the temperature was 25°, the speed was 17,250 r.p.m., and interference optics was used. The cells were 30 mm. for 0.008 *M* Ta(V) and 12 mm. for the other concentrations; centerpieces were of epoxy resin (not metal filled). The stoichiometric potassium concentration was *ca.* 1 *M* in all solutions; the free K^+ concentration will be slightly less if there is any counterion binding. Approximate constancy of this concentration is important in the estimation of charge by comparison of results obtained with different solutions.

(2) **Density and Refractive Index Measurements.**—Apparent molal volumes of the tantalate solute were computed from density data obtained with a *ca.* 24-ml. pycnometer. Refractive index increments of the tantalate in the appropriate supporting electrolyte and also of KOH were measured with a Brice-Phoenix differential refractometer. The apparent molal volume of the tantalate was found to be, within experimental uncertainty, independent of concentration; a mean volume of 216 ml./mole of $K_8Ta_6O_{19}$ was used to compute the partial specific volume, $\bar{v}$, necessary for interpretation of the centrifugation results. Similarly, the refractive index increment of the tantalate species showed no significant concentration dependence and a mean value of $\Delta n/c$ of 0.0295 l./mole at 546 mμ was used in both supporting electrolytes. Both volumes and refractive index increments are corrected for the small amount of excess base in the solid (see section 4). The corresponding constants for KCl were obtained from literature density and refractive index data.[8] The values used were as follows: KCl, $dn/dc = 0.009322$ l./mole, $\bar{v} = 0.403$; for KOH, $dn/dc = 0.00999$ l./mole, and $\bar{v} = 0.164$, for 1 *M* KOH.

(3) **Raman and Infrared Spectra.**—Raman spectra were obtained with a Cary Model 81 spectrophotometer, with 436 mμ exciting radiation. The cell used for the crystalline spectrum was developed by Keller.[9] A standard Cary 7-mm. cell was used for the solution. The scan speed was 0.25 cm.$^{-1}$/sec. for the solid

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(1) This document is based on work performed for the U. S. Atomic Energy Commission at the Oak Ridge National Laboratory, operated by Union Carbide Corporation.

(2) Guest Scientist, Oak Ridge National Laboratory, during 1963.

(3) G. Jander and D. Ertel, *J. Inorg. Nucl. Chem.*, **14**, 71 (1960).

(4) W. H. Nelson and R. S. Tobias, *Inorg. Chem.*, **2**, 985 (1963).

(5) I. Lindqvist and B. Aronsson, *Arkiv Kemi*, **7**, 49 (1955).

(6) W. H. Nelson and R. S. Tobias, *Inorg. Chem.*, **3**, 653 (1964).

(7) J. S. Johnson, G. Scatchard, and K. A. Kraus, *J. Phys. Chem.*, **63**, 787 (1959). For more recent details of the computational program, see O. E. Esval, Thesis, University of North Carolina, 1962.

(8) Volumes: H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Co., New York, N. Y., 1958, p. 361. Refractive index: A. Kruis, *Z. Physik. Chem.*, **B34**, 13 (1936).

(9) O. L. Keller, Jr. and R. H. Busey, *J. Chem. Phys.*, in press.

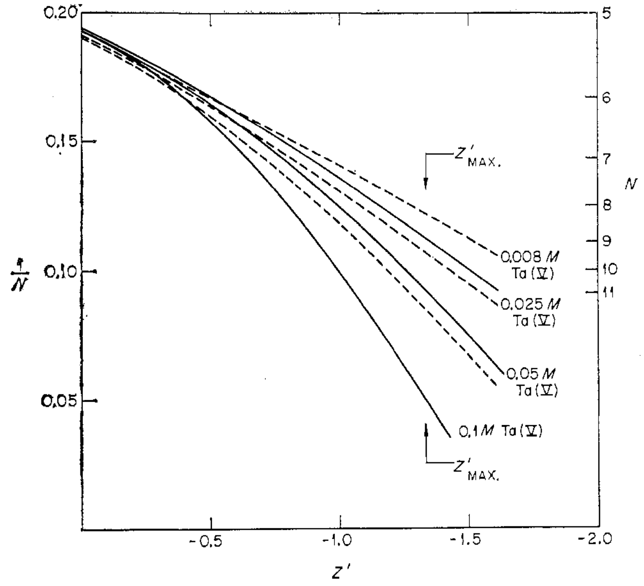

Fig. 1.—Reciprocal of degree of polymerization, N, of Ta(V) computed as a function of assumed charge per monomer unit, z'. Solid lines refer to 1 M KCl and broken lines to 1 M KOH supporting electrolytes.

and 0.05 cm.$^{-1}$/sec. for the solution. Infrared spectra were obtained with a Grubb Parsons GS3 and DM2 instrument, in KBr down to 400 cm.$^{-1}$ and in Nujol from 400 to 200 cm.$^{-1}$.

(4) **Materials.**—Reagent grade Ta_2O_5 (A. D. Mackay, Inc.) was fused with KOH in a nickel crucible, the melt extracted with hot water, and the solution crystallized by removing water through suction. The product was recrystallized from water in an atmosphere of N_2. Tantalum was determined by precipitating the hydrous oxide with hydrochloric acid, igniting the precipitate at 950°, and weighing as Ta_2O_5. Potassium was determined by evaporating the filtrate and weighing as KCl. The water was estimated by difference. The analysis corresponded to the composition $4.1K_2O \cdot 3Ta_2O_5 \cdot 16H_2O$, *i.e.*, *ca.* 3 mole % excess base over $K_8Ta_6O_{19} \cdot 16H_2O$. A second sample used to obtain infrared spectra had the composition $3.9K_2O \cdot 3Ta_2O_5 \cdot 16H_2O$. Spectrographic analysis indicated the product contained 0.5–1 mole % Nb. Reagent grade KCl and KOH were used without further purification.

Results and Discussion

(1) **Ultracentrifugation Results.**—In principle, it is possible to determine both the molecular weight and the charge (which may be different from the maximum charge implied by complete dissociation of counterions) from the radial distribution of an ionized solute at centrifugation equilibrium in the presence of an excess of supporting electrolyte.[7] The procedure for a monodisperse solute is to carry out centrifugations at varying solute to supporting electrolyte ratios, compute apparent degrees of polymerization, N, as a function of assumed charge, z, and find the value of the charge for which the degree of polymerization is independent of concentration.

In the present case, graphs of $\ln n^*$ *vs.* x^2, where n^* is the difference in refractive index between solution and background and x is radius, were linear or concave downward for individual centrifugations in both KCl and KOH supporting electrolyte. Such behavior usually indicates that the solutes are monodisperse, and degrees of polymerization were therefore computed according to the above procedure. The values of N obtained for the separate experiments (Fig. 1) are most nearly the same for $N \sim 6$ or a little less. The value of the charge per tantalum appears to be no more than 0.5, or much less than the maximum value of 1.33 for complete ionization of $K_8Ta_6O_{19}$. There thus appears to be a substantial binding of potassium ions by the tantalate species.

The monomer unit was assumed to be $K_{8/6}TaO_{19/6}$ in the computation of the curves of Fig. 1. Nelson and Tobias, on the basis of acidity measurements, have suggested that the polytantalate may bind *ca.* $^1/_6$ proton per tantalum in KCl supporting electrolyte. A few measurements of ours appear to confirm these results. Acidity measurements in this range (pH 10–12) should of course be regarded with caution; however, if one assumes that the component in 1 M KCl is $K_7HTa_6O_{19}$, and adjusts the measured values of volumes and refractive index increments accordingly, the value of N in KCl solution would be raised by *ca.* 8%. Agreement between the results in KOH and KCl would not be greatly worse than shown in Fig. 1, since the values of N in 1 M KOH appear to be a little higher than in 1 M KCl. Differences in activity coefficient gradients with radius (which are assumed to be zero) for individual solutions could easily be large enough to account for any residual discrepancy.

We carried out a centrifugation of 0.008 M $K_{8/6}TaO_{19/6}$ in 1 M KCl, not shown in Fig. 1. The value of N for $z' = 0$ appeared to be about 5% lower than for the other centrifugations. There was some decomposition of the solution from which the sample centrifuged was taken during the time of the centrifugation, and there appeared to be a slight drift in the interference pattern from day to day after ample time had elapsed for attainment of centrifugation equilibrium. We tentatively conclude that the polytantalate is unstable at the pH of this dilution.

If the rather extreme assumption of zero charge is discounted, the indicated degree of polymerization is six, in agreement with the X-ray data of Lindqvist and the light-scattering studies of Nelson and Tobias. Similar indications of potassium binding were given by the turbidity measurements[4] and the centrifugation measurements of Nelson and Tobias.[6]

(2) **Raman Spectra.**—According to Lindqvist, crystalline potassium tantalate contains discrete $Ta_6O_{19}^{8-}$ ions with the six tantalum atoms arranged octahedrally to form an exceptionally compact and symmetrical structure. From this the point group symmetry is O_h and eleven Raman and seven infrared fundamentals are predicted, if there is no removal of degeneracy in the crystal. The Raman spectra of crystalline potassium tantalate and its saturated solution are shown in Fig. 2. For the solid, lines were observed at 860, 825, 742, 516, 466, 415, *ca.* 260 (shoulder), 210, 173, and 145 cm.$^{-1}$; in solution lines at 857, *ca.* 825 (shoulder), 738, 516, *ca.* 466 (shoulder), 415, *ca.* 210 (shoulder), 170, and 145 cm.$^{-1}$ were found. It is

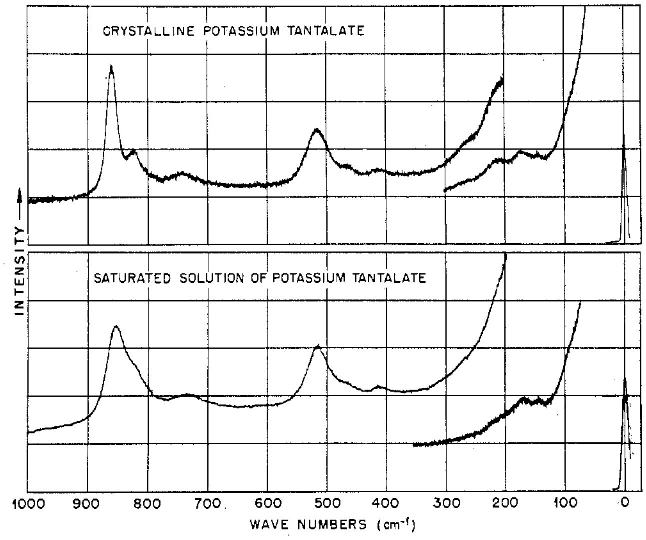

Fig. 2.—Comparison of Raman spectra of potassium tantalate in solution with crystalline $K_8Ta_6O_{19}\cdot 16H_2O$. Left traces, double slit width; right traces, single slit width; all 10 cm.$^{-1}$. Top spectra (crystalline): sensitivity settings, 1 × 100RD4; period controls, left trace, 0.5; right trace, 0.3. Bottom spectra (solution): left trace sensitivity, 1.6 × 100RD4; period, 5.0; right trace sensitivity, 1 × 100RD4; period, 0.

likely that the lines at 170 and 145 cm.$^{-1}$ may not correspond to genuine vibrations for the tantalate ion. With our spectrometer spurious lines in this region are sometimes observed in the spectra of crystals, although in solution these lines, if observed at all, are usually much weaker. The close correspondence of the two spectra, with each of the seven lines (excluding 145 and 170 cm.$^{-1}$) observed in the solution having its counterpart in the solid within about 4 cm.$^{-1}$, strongly supports the conclusion that the same hexatantalate anions present in the crystal are also present in solution. The simplicity of the spectra, compared with those of less symmetrical ions (for example,[10] $Mo_7O_{24}{}^{6-}$) provides further qualitative evidence for the octahedral arrangement of tantalum atoms proposed by Lindqvist. However, for the ion $Ta_6O_{19}{}^{8-}$ with O_h point group symmetry, there is a center of symmetry, which means there should be no coincidence between the Raman lines and infrared bands. The infrared spectrum of $K_8Ta_6O_{19}\cdot 16H_2O$ has been observed[4] and one of the four bands (822 cm.$^{-1}$) has a frequency close to the 825 cm.$^{-1}$ Raman line. Our infrared measurements covering this region and below indicated lines at 843 (sharp), 694 (broad), 535 (medium), 402 (broad), and 355 (weak) cm.$^{-1}$. We checked the region of primary interest here with a Nujol mull, on a different instrument (Perkin-Elmer 221), with the preparation of potassium tantalate used in the Raman and ultracentrifugation work, and again found no indication of an 822 cm.$^{-1}$ line. We therefore believe the attribution of O_h point symmetry is correct, but in any case, our main conclusion, that the $Ta_6O_{19}{}^{8-}$ ion is present both in the solid and solution, is unaffected.

Acknowledgment.—We are indebted to Neva Harrison for technical assistance, and R. H. Busey for helpful discussions.

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[10] J. Aveston, E. W. Anacker, and J. S. Johnson, *Inorg. Chem.*, **3**, 735 (1964).

CONTRIBUTION NO. 324 FROM THE DEPARTMENT OF CHEMISTRY,
TUFTS UNIVERSITY, MEDFORD, MASSACHUSETTS

Isomerism in Some Boron and Boron–Carbon Frameworks

BY T. E. HAAS

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The recent reports of an extensive derivative chemistry of some of the boron hydride anions[1] and the carboranes[2] have shown the desirability of a study of substitution isomers to be derived from the basic boron and boron–carbon frameworks of these compounds. The study of isomerism by group-theoretical methods is the most powerful and elegant method of attacking such a problem. Kennedy, McQuarrie, and Brubaker[3] have recently given a new, point-group formulation and extensive discussion of the technique. Their paper should be consulted for details.

Calculations.—The determination of the number of geometrical isomers and enantiomorphic pairs was carried out by the method of Brubaker, *et al.*, for substitution by one kind of substituent. The structures considered are $B_{10}H_{10}{}^{2-}$, $B_{12}H_{12}{}^{2-}$, and the three possible icosahedral dicarbaclovododecaborane(12) isomers. For the carboranes, calculations were carried out for substitution on all atoms and substitution on borons only. Cycle indices for each of these cases are given in Table I for both the point group of the molecule and its rotation subgroup. The total number of isomers and the number of geometric isomers for each of the structures are given in Table II. Note that as both 1,2- and 1,7-carborane[4] have the same symmetry (C_{2v}) and are of the same degree (12, or 10 for borons only), the cycle indices and number of isomers are the same for both structures, although the isomers are completely different.

Discussion

The first communication on the susceptibility of the boron frameworks in $B_{10}H_{10}{}^{2-}$ and $B_{12}H_{12}{}^{2-}$ to electrophilic substitution[1] suggested that all isomers would not be formed in these reactions. For example, apical substitution in $B_{10}H_{10}{}^{2-}$ seemed to occur first, and this

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[1] W. H. Knoth, H. C. Miller, D. C. England, G. W. Parshall, and E. L. Muetterties, *J. Am. Chem. Soc.*, **84**, 1056 (1962).

[2] See *e.g.*, H. Schroeder, T. L. Heying, and J. R. Reiner, *Inorg. Chem.*, **2**, 1092 (1963).

[3] B. A. Kennedy, D. A. McQuarrie, and C. H. Brubaker, Jr., *ibid.*, **3**, 265 (1964).

[4] These names will be used for brevity's sake to denote 1,2- and 1,7-dicarbaclovododecaborane(12), and the 1,12 isomer will be named similarly.