for the $BiCl_3$ solvent in these dilute solutions[2-5] are hazardous in view of the probable ionization of chloride from the product to form chlorobismuthate complexes such as are found in the solid, since other investigations have shown rather drastic nonideality of $BiCl_3$ in such cases.[46]

It would appear highly probable that the species Bi_9^{5+} will become important in the more concentrated solutions of metal in $BiCl_3$ at the lower temperatures, although no direct evidence for this or any other entity has been published. However, in the study of the oxidation–reduction process in solution by means of concentration cells,[6] the strange decrease in the Nernst *n* from 8 to about 2 over the range of about 8 to 22% Bi may be a result of increasing partition of the solute into species such as Bi_9^{5+} that are not in equilibrium with Bi^{3+} at the electrodes. The properties of the concentrated solutions, that is, the high viscosity, slow equilibration, and pronounced supercooling at the $BiCl_{1.167}$ peritectic, are also indicative of the presence of large groups. A study of the X-ray scattering by these solutions may elucidate something of the nature of the solute.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF MINNESOTA, MINNEAPOLIS 14, MINNESOTA

Structure of the Polyanions of the Transition Metals in Aqueous Solution: The Hexatantalate[1]

BY WILFRED H. NELSON AND R. STUART TOBIAS

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Alkaline solutions of tantalum(V) have been studied by spectrophotometric, e.m.f., and light scattering techniques. The position of the charge-transfer band at about 2000 Å. did not change as the total tantalum concentration was varied from 1.2 to 60×10^{-4} *M* or as the hydroxide ion concentration was varied from 6 to 350×10^{-4} *M*. The e.m.f. measurements indicated that the compound $K_8Ta_6O_{19}\cdot 16H_2O$ dissolves in dilute KOH solutions without appreciable protonation. The experimental value for the number of protons bound per tantalum was constant in the pH range 10 to 13 and had a value of 0.12. These data indicate that the dissolved solute has essentially the same stoichiometry as the crystalline $K_8Ta_6O_{19}$ and that neither protonation–deprotonation reactions nor the concomitant condensation–depolymerization processes are occurring in the range $13 \geqslant \text{pH} \geqslant 10$. The light scattering investigation indicated that the solute species contains about 6 tantalum atoms, that this value was pH independent in the range studied, and that the species charge is reduced appreciably by the binding of counter-ions from the 1 *M* KCl medium used in the measurements. The scattering of potassium 12-tungstosilicate was also studied as a check on our procedure. On the basis of the results, it appears very likely that the tantalate solutions contain a monodisperse species and that this anionic species has the same structure as the $[Ta_6O_{19}]^{-8}$ anion found in tantalate crystals. An examination of the structure and bonding of this anion indicates that it should be somewhat resistant to protonation. Comparisons are made with structures for other poly-cations and anions which are found at high concentrations in monodisperse systems.

Introduction

Recently there has been some interest in the isopolyanions formed in aqueous solutions of the transition metals, primarily with the group V-A and VI-A elements. Studies on solutions of vanadium(V) by e.m.f. techniques have indicated that a decavanadate $[V_{10}O_{28}]^{-6}$ exists in aqueous solutions together with the protonated species $[HV_{10}O_{28}]^{-5}$ and $[H_2V_{10}O_{28}]^{-4}$ in the range of hydrogen ion concentration 10^{-4} to 10^{-6} *M*.[2,3] Studies by other experimental methods including measurements of the visible absorption spectrum,[4] ultracentrifugation,[5] and cryoscopic studies[6,7] have tended to confirm these results. E.m.f. studies have also indicated that the smaller poly- and mononuclear anions $[V_3O_9]^{-3}$, $[HV_2O_7]^{-2}$, and $[HVO_4]^{-2}$ also exist in solutions in the pH range 8 to 10.[8] Unfortunately, because of the very complicated stereochemistry of

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(1) This report is based on portions of a doctoral dissertation to be submitted by W. H. Nelson to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy. The work has been supported by grant NSF-G14173 from the National Science Foundation and by the Graduate School of the University of Minnesota. Presented before the Division of Inorganic Chemistry of the American Chemical Society, Los Angeles, California, April, 1963.

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vanadium(V),[9] rather little can be said about the structure of these ions.

Few studies have been carried out with the heavier V-A elements, primarily because their extremely basic nature makes such experiments difficult. Jander and Ertel[10] reported that strongly alkaline solutions of niobium(V) contain an anion $[Nb_6O_{19}]^{-8}$ and that this could be protonated to give $[HNb_6O_{19}]^{-5}$ and $[H_2Nb_6O_{19}]^{-4}$; on the other hand, similar studies made on solutions of Ta(V) led to the postulation of a pentatantalate.[11] These conclusions were drawn largely from measurements of diffusion coefficients and cryoscopic studies. Both of these experimental methods have been criticized, for there appears to be no theoretical basis for the assumed relation between diffusion coefficient and ionic weight[12] and cryoscopic methods become rather inaccurate when the polyions contain more than two or three metal atoms.[13] Recently additional preparative work on the niobates and tantalates has been reported by Kennedy,[14] who was, however, unable to obtain any experimental information on the nature of the species in solution.

Since the stereochemistry of tantalum in oxygen compounds is rather simple, it was decided to study alkaline tantalate solutions as a model system for the investigation of polyanion formation. The potassium tantalate $K_8Ta_6O_{19}\cdot 16H_2O$ is extremely soluble in aqueous solution and appeared suitable for e.m.f. and light scattering studies. The preparation of this and related salts has been studied previously by many workers.[11,15,16] Halla, *et al.*,[17] first investigated the structure of the tantalate obtained by fusing KOH and Ta_2O_5 together and crystallizing the product from water; they determined that there were four $4K_2O\cdot 3Ta_2O_5\cdot 16H_2O$ formula units in the monoclinic unit cell. These authors chose to formulate the compound as $K_{16}[Ta_{12}O_{36}](OH)_4\cdot 30H_2O$, apparently because of a belief that the structure would involve chains of tetrahedrally coordinated tantalum atoms analogous to the polyphosphates. Lindqvist and Aronsson later carried out a single crystal X-ray investigation[18] which indicated that discrete anions containing six tantalum atoms arranged at octahedral vertices existed in the crystals. On this basis, the compound is formulated $K_8[Ta_6O_{19}]\cdot 16H_2O$.

Experimental

Synthesis.—Reagent grade Ta_2O_5 containing less than 1% niobium and produced by H. C. Starch, A.G., was fused with KOH in a silver crucible to form the crude tantalate. The cold melt was dissolved in a minimum amount of hot water, and the product was freed from the insoluble Ag_2O which resulted from attack on the crucible. Polyethylene vessels were used throughout to avoid contamination by silicates. The partially purified product was precipitated by the addition of ethanol. This material was recrystallized three more times from dilute KOH; the crystals were dissolved in water and passed three times through a Millipore filter with a pore diameter of 4500 Å. Finally, pure crystals were obtained by precipitation with ethanol, and the product was dried in a vacuum desiccator. The product was stored and transferred under a nitrogen atmosphere. Tantalum was determined by precipitation of the hydrous oxide from an aqueous solution of the salt with HCl. The precipitate was washed with 2% NH_4NO_3, ignited, and weighed as Ta_2O_5. Potassium was determined by precipitating the tantalum with sulfuric acid, separating the hydrated Ta_2O_5 by filtration, evaporating the solution, and weighing the residue as K_2SO_4. Differential thermal and gravimetric analyses were run to determine the water of crystallization. The weight loss upon ignition was constant from 400 to 700°. Typical analytical results were: Calcd. for $K_8Ta_6O_{19}\cdot 16H_2O$: Ta, 54.5; K, 15.9; H_2O, 14.5. Found: Ta, 56.3; K, 15.7; H_2O, 14.5. The product was shown to be free of carbonate by the absence of any band in the infrared spectrum in the range 1425–1475 cm.$^{-1}$. The X-ray powder pattern was determined for the product using a General Electric XRD-3 diffractometer. The observed reflections corresponded to those calculated using the monoclinic cell dimensions given by Lindqvist and Aronsson.[18]

Tungstosilicic acid was prepared by dissolving reagent grade $SiO_2\cdot 12WO_3\cdot 26H_2O$ in ether, the ether adduct was decomposed with water, and the acid crystallized from the aqueous solution in a desiccator over sulfuric acid. The water content of the crystals was determined initially by titration with Karl Fischer reagent and subsequently by ignition to a constant weight, as the latter procedure was found to yield satisfactory results.

Infrared and Ultraviolet Spectra.—The infrared spectrum for the potassium tantalate was determined with both mineral oil mulls and KBr disks using a Perkin-Elmer Model 421 spectrometer. The ultraviolet absorption spectra of solutions of the potassium tantalate were determined with a Cary Model 11 recording spectrophotometer and with a Beckman DU spectrophotometer.

E.m.f. Measurements.—The general cell design and the potentiometer–vibrating reed electrometer circuit used to measure the cell potentials have been described earlier.[19] In some cases a Radiometer PHM-4 was also used to measure the potentials. The cell was thermostated at 25 ± 0.1°, and the measurements were made in a thermostat room maintained at 25 ± 2°. Standard Beckman lithium glass Type "E" electrodes (No. 40495) as well as a special "E" electrode with a large envelope (No. 78074) were used for the measurements. KCl was added to all of the solutions to provide a constant ionic medium with $[Cl^-] = 0.5\ M$. The cell was calibrated by KOH–HCl titrations, and these data were fitted with the equation $E = E^{0\prime} + 59.15 \log [OH^-]$, $[OH^-]$ in mM. Calibration curves were drawn giving $E^{0\prime}$ as a function of E. The medium with $[Cl^-] = 0.5\ M$ was chosen, since deviations of the glass electrodes from the behavior of a hydrogen electrode became more pronounced at higher KCl concentrations. The precision of the measurements in these highly alkaline solutions was an order of magnitude lower than that of the usual measurements in acid–neutral solutions.[19] Care was taken to protect the solutions at all times from CO_2 using a nitrogen atmosphere.

Light Scattering Measurements.—Measurements of the turbidity of the solutions were made with unpolarized 4358 Å. light using a Brice-Phoenix photometer. Calibration of the instrument was carried out using the opal glass diffuser supplied by the manufacturer. All measurements were made with 1 M KCl as the supporting electrolyte, and the turbidity of the supporting electrolyte in the tantalate solutions was approximated by that of 1 M KCl. This was subtracted from the total turbidity of the tantalate

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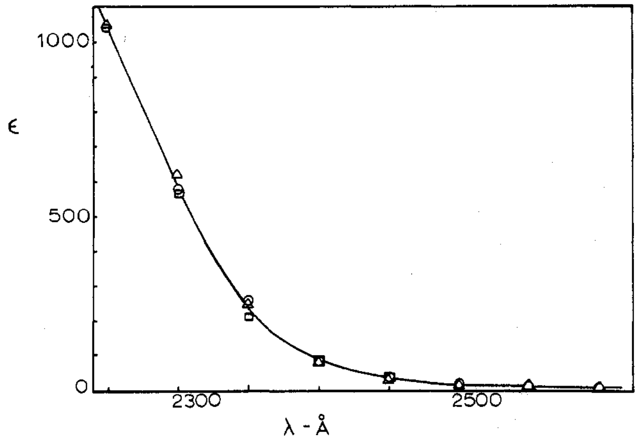

Fig. 1.—The electronic absorption spectrum of solutions of $K_8Ta_6O_{19} \cdot 16H_2O$: ○, 6.2×10^{-3} mono*M* Ta(V), 1.62×10^{-2} *M* OH^-; △, 2.48×10^{-3} mono*M* Ta(V), 1.62×10^{-2} *M* OH^-; □, 6.02×10^{-4} mono*M* Ta(V), 1.62×10^{-2} *M* OH^-.

solutions to give the turbidity τ^* due to the tantalate species. Semioctagonal cells and a cylindrical cell were used to determine the dissymmetry of scattering.

The solutions were clarified by filtration through either 0.45 μ Millipore ultrafilters in an all-glass system or through 0.10 μ Gelman filters in a stainless steel system, in both cases under an atmosphere of nitrogen. Each sample was passed through the filter from 5 to 10 times and was discarded if any trend was observed in the turbidities from filtration to filtration.

The absence of fluorescence was demonstrated by the method of Brice, Nutting, and Halwer.[20] Depolarization was found to be negligibly small by the method of Maron and Lou.[21]

Refractive index increments were determined at 4358 Å. with a Brice-Phoenix differential refractometer which was calibrated with sucrose solutions.

Results

Spectra.—The only absorption observed for aqueous solutions of the potassium tantalate in the region 2000 to 8000 Å. was a charge-transfer band below 3000 Å.[11] Spectra were obtained for solutions with different total tantalum concentrations and different hydroxide ion concentrations. No appreciable change was noted in the spectrum as the total tantalate concentration was varied from 1.2 to 60×10^{-4} monomolar (concentration computed in terms of tantalum). The hydroxide ion concentration was varied from 6 to 380×10^{-4} *M*, also without effect. The band maximum was below 2000 Å., and at 2100 Å. the molar extinction coefficient was 2.6×10^4 l. per monomole cm. The data are shown in Fig. 1. From these data, it appears very likely that no change occurs in the tantalate species with these changes in concentration, for protonation and the subsequent condensation reactions of the anionic molybdate species have been observed to shift the charge-transfer band to longer wave lengths.[22]

The infrared spectrum showed sharp bands at 965, 910, 822, and 710 cm.$^{-1}$ as well as others at lower frequencies. Barraclough, Lewis, and Nyholm[23] have

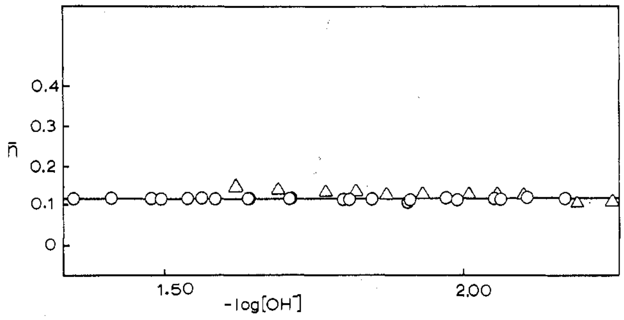

Fig. 2.—The number of protons bound per tantalum atom, $\bar{n}$, as a function of log $[OH]^-$: ○, 60 mono*M* Ta(V); △, 24 mono*M* Ta(V).

discussed the infrared absorption spectra of analogous compounds containing metal–oxygen bonds. It was found that strong metal–oxygen double bonding led to a sharp absorption band in the range 950–1050 cm.$^{-1}$. This is especially apparent in complexes of the vanadium(IV) ion where there is one strong bond to oxygen and four or five weak ones, and the following absorptions are observed: $(NH_4)_2VO(ox)_2 \cdot 2H_2O$, 976 cm.$^{-1}$; $(NH_4)_2VO(mal)_2 \cdot 4H_2O$, 977 and 967 cm.$^{-1}$; $VO(acac)_2$, 995 cm.$^{-1}$ (mal, ox, and acac are the malonato, oxalato, and acetylacetonato groups). For K_2MoOCl_5, a band is observed at 967 cm.$^{-1}$.

E.m.f. Measurements.—Although very concentrated solutions of tantalate can be prepared by dissolving the $K_8Ta_6O_{19} \cdot 16H_2O$, the addition of an acid will precipitate hydrous Ta_2O_5. For this reason, the procedure used in the measurements was to add a strongly alkaline tantalate solution to a weakly alkaline solution with the same total tantalate concentration. In this way, the total tantalate concentration was maintained constant while the pH was varied. The data were used to calculate the number of protons bound per tantalum, $\bar{n} = ([OH^-]_{exptl} - [OH^-]_{anal})/[Ta]_{total}$, in the range $13 \geq pH \geq 10$ with total tantalum concentrations of from 0.024 to 0.060 monomolar. It proved to be impossible to obtain pH values appreciably less than 10 without the formation of a precipitate. The measurements were not continued above pH 13 because of the rather large errors in the equilibrium hydroxide ion concentrations obtained from the cell e.m.f.'s. The "analytical" hydroxide ion concentration, $[OH^-]_{anal}$, was calculated with the assumption that the average charge per tantalum was -1.33, *i.e.*, that it was the same as in $[Ta_6O_{19}]^{-8}$ Data for two total tantalum concentrations are given in Fig. 2. The small value of *n*, *ca.* 0.12, observed indicates that the degree of proton binding by the tantalate species must be small if any occurs at all. This small value could also be caused by traces of KOH in the crystals of the tantalate, for it is notoriously difficult to remove such impurities completely. The constancy of $\bar{n}$ as the pH was varied indicates that no change occurs in the tantalate species in the range studied.

Light Scattering Measurements.—Since the previous measurements indicated that the nature of the tantalate species did not change with the total tantalate concentration or with the pH in the range 10 to 13, a light

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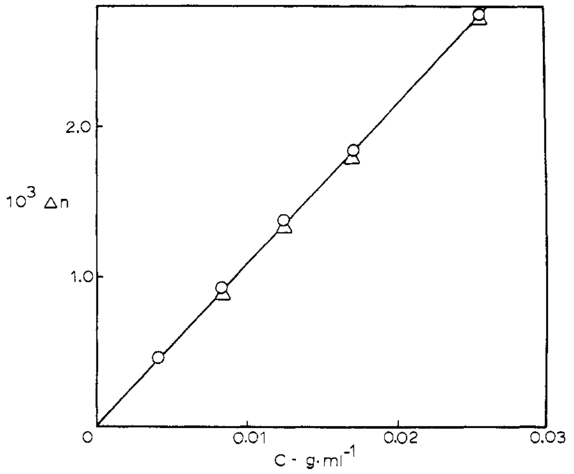

Fig. 3.—Refractive index of the tantalate solutions as a function of concentration: ○, 0.5 M KCl; △, 1.0 M KCl; tantalate concentrations in g. of $K_8Ta_6O_{19}$ per ml. of solution.

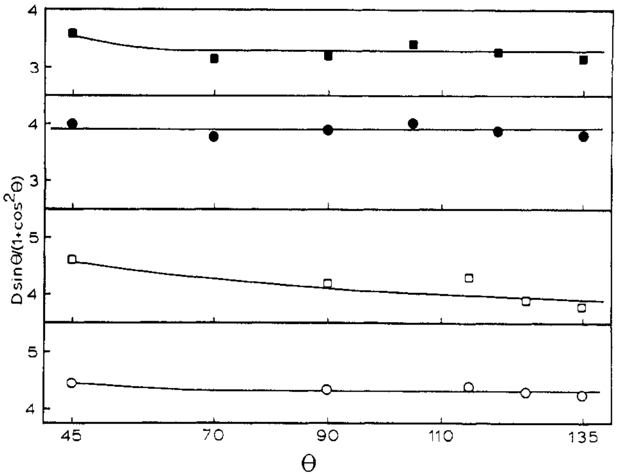

Fig. 4.—Angular dependence of scattering: ■, 0.032 mono$M$ Ta; ●, 0.064 mono$M$ Ta; □, 0.0062 M tungstosilicate; ○ 0.0281 M tungstosilicate.

scattering study was carried out to ascertain the size of the tantalate species. The general method used was that described by Tobias and Tyree[24] and applied to a study of the polycation that exists in hydrolyzed bismuth(III) solutions.[25]

As a check on our entire procedure, we determined the scattering of the 12-tungstosilicic acid $H_4SiW_{12}O_{40}$. The light scattering of this large polyanion has been investigated by different workers,[26,27] and it appears to give essentially the correct value for the formula weight of the solute when the measurements are carried out on solutions with supporting electrolyte. X-Ray diffraction studies on 0.3095 M $H_4SiW_{12}O_{40}$ solutions have confirmed that the single polyanion existing in these solutions is the same as that found in tungstosilicate crystals, *i.e.*, $[SiW_{12}O_{40}]^{-4}$.[28] The supporting electrolyte used in our work was 0.5 M KCl. The value of dn/dc in ml. g.$^{-1}$ at 4358 Å. was determined to be 0.106 ± 0.001 by measurements on solutions containing 0.5 M KCl which were neutralized to a stoichiometry of $K_{3.9}[H_{0.1}SiW_{12}O_{40}]$. Johnson, Kraus, and Scatchard[27] reported 0.1065 ± 0.0014 and Kronman and Timasheff[26] gave 0.107, both for the free acid in water. We also determined the value for solutions containing no supporting electrolyte and obtained the value of 0.1065 given by Johnson, Kraus, and Scatchard. The main experimental error in these determinations arises from the difficulty in determining the water content of the 12-tungstosilicic acid, since this is quite variable and must be determined for each sample.

A plot of Hc/τ^* *vs.* c, where the concentrations are in g. ml.$^{-1}$, gave a straight line corresponding closely to that obtained by Kronman and Timasheff[26] for solutions 0.3 M in NaCl. The reciprocal of the intercept obtained by extrapolation to infinite dilution was 3.01 × 10³ compared to 2.86 × 10³ reported for the NaCl solutions. Since the appreciable positive slope of the lines obtained in these plots indicates that the polymeric solute species carries an appreciable charge, the values obtained by this treatment correspond only approximately to the solute formula weight.[24] The comparable values for NaCl solutions of the free acid obtained by ultracentrifugation are 2.8 × 10³ (sedimentation-Archibald procedure[26]) and 2.91 × 10³ (sedimentation velocity[29]).

The refractive index increments for the tantalum species were obtained from measurements on solutions with known concentrations of KOH and KCl. The contributions of these latter species to the gross Δn values could be calculated using known refractive indices of KOH and KCl solutions, and these were subtracted from the gross Δn to give the Δn due to tantalate. A plot of the Δn due to tantalate *vs.* the tantalate concentration in g./ml. is shown in Fig. 3 The experimentally determined value of dn/dm' was 0.0304 l. monomole^{-1} for solutions 0.5 M in KCl and 0.0300 l. monomole^{-1} for solutions 1.0 M in KCl. The constancy of dn/dm' with varying tantalate and hydroxide ion concentrations also indicated that the nature of the tantalate species did not vary in the solutions.

In order to verify that contributions to the 90° scattering due to colloidal impurities were not significant, the angular dependence of the scattering was investigated from θ = 45 to 135° using a cylindrical cell. The normalized scattering envelope was calculated by multiplying the observed galvanometer deflections, D, by $\sin \theta/(1 + \cos^2 \theta)$. Examples of typical data for both high and low concentrations of the scattering solute are given in Fig. 4. These data indicate that there was no appreciable contribution to τ^* from colloidal impurities, and the experimental values of τ^* are the same as those obtained by extrapolation from the large angle scattering for all solutions except the

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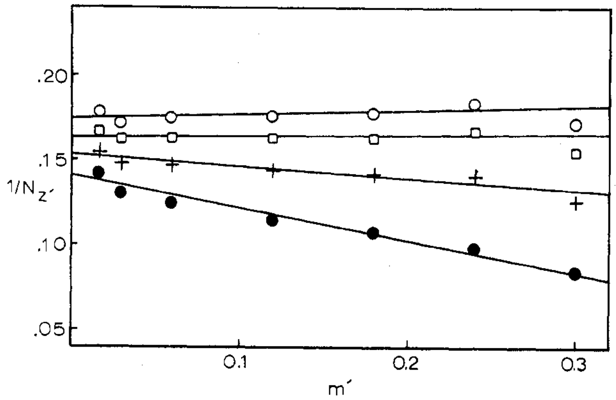

Fig. 5.—$1/N_{Z'}$ *vs.* the monomolar concentration of Ta(V) with Z' as a parameter: ○, $Z' = 0$; □, $Z' = -0.2$; +, $Z' = -0.4$; ●, $Z' = -0.6$.

most dilute tungstosilicate solutions. The turbidity of the tantalate solutions was also independent of the hydroxide ion concentration, within the experimental error, over a 5-fold variation in the hydroxide ion concentration up to a maximum value of 30 m*M*.

In order to calculate the number of tantalum atoms in the polyanion, it is convenient to define a "monomer unit" containing a single tantalum atom and having the proper charge per tantalum required by the stoichiometry of the species in solution. Since the e.m.f. measurements indicated that the stoichiometry of the tantalate solute is essentially the same as in crystalline $K_8Ta_6O_{19}$, the monomer unit is defined as $[K_{\bar{\nu}}\,TaO_{3.17} + (1.34 - \bar{\nu})K^+]$. In this electrically neutral unit, the anion monomer is written with $\bar{\nu}K^+$ ions to allow for a reduction in the anionic charge to $(1.34 - \bar{\nu}) = Z'$.

The experimental data were used to compute the values of the deviation function

$$1/N_{Z'} = \frac{\phi H''\Psi'^2 m'}{\tau^*} - \frac{Z'^2 m'}{2(m_3 + m_5)} \qquad (1)$$

for different trial values of the charge per monomer unit.[24,25] In this equation, $N_{Z'}$ is the number of the monomer units contained in the polyanion, m' is the tantalum concentration in monomoles per liter, Ψ' is the value of dn/dm' for the monomeric scattering component, H'' is the usual constant, ϕ is the volume fraction of solvent computed for 1 *M* KCl for the tantalate and 0.5 *M* KCl for the tungstosilicate, and m_3 and m_5 are the concentrations of added electrolytes KCl and KOH, respectively. The concentration of KOH was small in comparison to that of KCl in all solutions, so the system is essentially a three-component one. When the correct value of the charge per monomer unit, Z', has been chosen, $N_{Z'}$ will be independent of concentration. The data are illustrated in Fig. 5, which shows $1/N_{Z'}$ as a function of concentration with Z' as the parameter for the tantalate solutions and in Fig. 6 and 7 which show $1/N_{Z'}$ as a function of Z' with concentration as a parameter for the tantalate and 12-tungstosilicate, respectively. From an examination of the tantalate data, it is apparent that the effective charge per monomer unit, Z', is much smaller than the maximum possible charge of -1.34 and is approximately -0.3. This value was not determined accurately, for charge effects were small in the 1 *M* KCl solutions. This extensive reduction in charge, presumably as a result of the binding of counter-ions from the medium, has also been observed in the studies on the light scattering of molybdate solutions in a medium with 3 *M* $NaClO_4$.[30] The best value for the charge of the tantalate species per monomer unit appears to be between -0.2 and -0.4, giving a degree of polymerization, *N*, in the range 6.0 to 6.5.

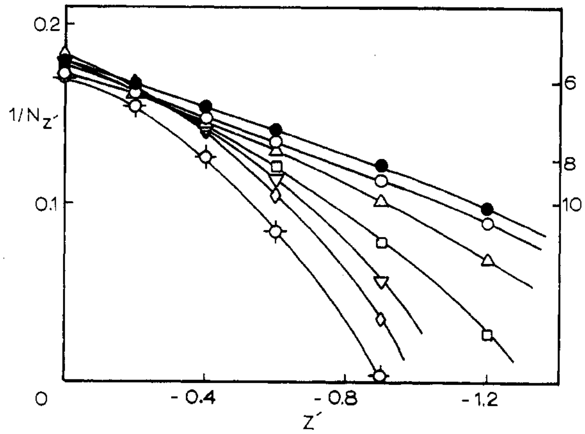

Fig. 6.—$1/N_{Z'}$ *vs.* Z' with concentration as a parameter for the tantalate: ●, 18 m*M*; ○, 30 m*M*; △, 60 m*M*; □, 120 m*M*; ▽, 180 m*M*; ◇, 240 m*M*; ⌖, 302 m*M* Ta(V).

The data for the 12-tungstosilicate solutions indicate that the degree of polymerization is about 1.05. The fact that this value differs slightly from unity is not surprising considering the uncertainties in the light scattering method. The activity cross terms are neglected in the derivation of eq. 1, and the lower the concentration of supporting electrolyte, the poorer this approximation is likely to be. Because of the low solubility of the potassium salt, measurements could not be made with greater supporting electrolyte concentrations than 0.5 *M*, and the low formula weight of the tungstosilicate required that rather high concentrations of solute be employed. There are also certain small uncertainties in the absolute values of the turbidities as determined with the Brice-Phoenix photometer. Recently several workers[31–34] have indicated that the value of the residual refraction correction supplied by the manufacturer is slightly too large, resulting in turbidities which are *ca.* 3% too large. The smaller correction factor recommended by these authors was used in our work.

Conclusions

The e.m.f. measurements indicate that the solute

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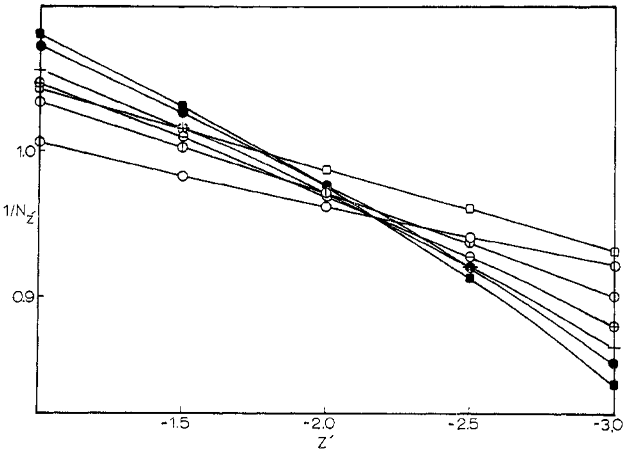

Fig. 7.—$1/N_{Z'}$ *vs.* Z' with concentration as a parameter for the 12-tungstosilicate: ○, 3.16 m*M*; □, 6.32 m*M*; ⦶, 9.48 m*M*; ⊖, 12.6 m*M*; +, 15.8 m*M*; ●, 19.0 m*M*; ■, 22.1 m*M* $[SiW_{12}O_{40}]^{-4}$.

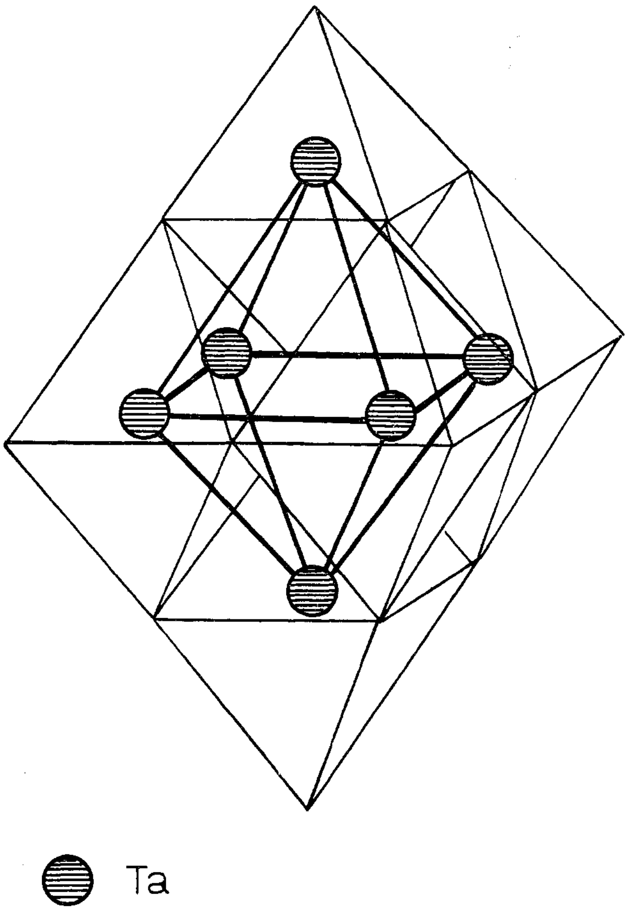

Fig. 8.—Structure of the hexatantalate anion, $[Ta_6O_{19}]^{-8}$.

$K_8Ta_6O_{19} \cdot 16H_2O$ dissolves in alkaline solutions without appreciable protonation, so that the stoichiometry of the tantalate species in solution must be essentially the same as in the crystals. This stoichiometry is constant throughout the range $13 \geq pH \geq 10$ in which measurements could be made. Since the polymerization and depolymerization reactions which would lead to different polyanions invariably involve a change in the degree of protonation, this indicates that the discrete anions $[Ta_6O_{19}]^{-8}$ which exist in the crystals prepared from aqueous solutions probably exist in the solutions.

The light scattering measurements show that there are about six tantalum atoms in the polyanion, and this too indicates that the tantalate dissolves to give $[Ta_6O_{19}]^{-8}$ anions. The effective charge of these anions is reduced to a value no greater than about -3 by the binding of counter-ions, K^+.

It is not surprising that the hexatantalate anion in the crystals of $K_8Ta_6O_{19} \cdot 16H_2O$ also exists in aqueous solution if the structure of this anion is examined. Figure 8 gives this structure[18] in terms of the packing of TaO_6 octahedra in the $[Ta_6O_{19}]^{-8}$ anion. It should be noted that the X-ray studies[18] show only that there are six tantalum atoms arranged with cubic symmetry in discrete anions of which there are four per unit cell. The oxygen reflections are too weak to be of value in fixing the location of the oxygen atoms, and their positions are inferred from the usual Ta–O distances and the requirement of six-coordination for tantalum with respect to oxygen. In this anion there are 19 oxygen atoms, and 1 is shared by all 6 octahedra, 12 are shared by 2 octahedra, and only 6 of the oxygen atoms are unshared. The site symmetry of the tantalum(V) is C_{4v}. Since p_π–d_π donation is quite pronounced at the beginning of each transition series and this is especially so with the penta- and hexavalent metals, one would expect that the electron density at the peripheral, unshared oxygens would be rather low. The "p" donation leaves much "s" character in the lone pair oxygen electrons, and this is unfavorable for binding protons. The individual octahedra would also be expected to show a tetragonal distortion giving one long bond to the central oxygen, four intermediate bonds to the oxygens shared between two octahedra, and one short bond to the unshared peripheral oxygen. This should reduce the repulsions between the octahedra which otherwise would tend to prevent the sharing of a single oxygen among all six octahedra. An analogous situation involving a tetragonally distorted octahedron, that of the vanadyl cation, has been discussed in some detail recently.[35]

On the basis of this structure, the charge-transfer band observed at about 2000 Å. would result primarily from a transfer of electrons from the peripheral oxygens which are unshared to the Ta(V). This spectrum should be sensitive to changes in the degree of π-bonding, so that either protonation of these peripheral oxygens or further aggregation to larger anions should markedly affect the energy levels and the spectrum. The fact that the charge-transfer band does not change with either the hydroxide ion concentration or the total tantalate concentration is therefore a good indication that no such reactions are occurring in the pH range studied.

The infrared spectra indicated the presence of tantalum–oxygen bonds with double bond character, which is also in agreement with the bonding picture. Since

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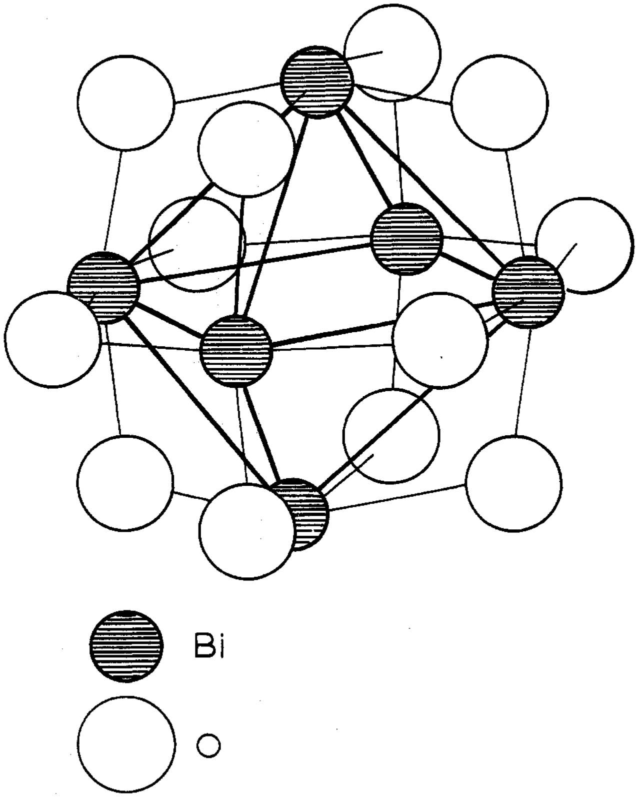

Fig. 9.—Structure of the cation $[Bi_6(OH)_{12}]^{+6}$.

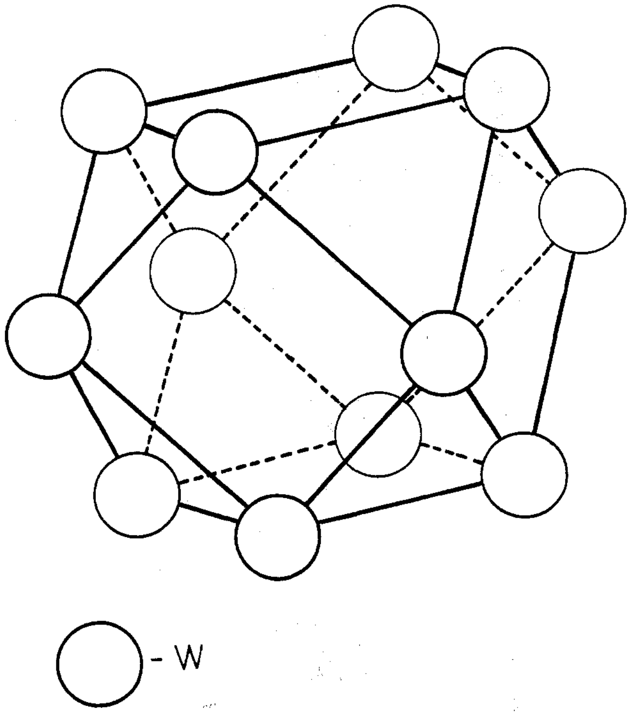

Fig. 10.—Structure of the anion $[SiW_{12}O_{40}]^{-4}$.

there is bound to be coupling of the tantalum oxygen vibrations, there is some doubt whether the compounds cited by Barraclough, Lewis, and Nyholm[23] are really good standards for comparison. From the complexity of the spectrum, it is apparent that the crystal lacks the full symmetry of the anion.

The absence in the light scattering measurements of any measurable depolarization of the 90° scattering is also in accord with the cubic symmetry of the anion $[Ta_6O_{19}]^{-8}$.

From the studies which have been made on solutions containing polynuclear complexes thus far, it is clear that two general types of behavior occur. In most systems, the conjugate acids or bases condense to give several polynuclear complexes of low degrees of polymerization. In many cases, only the dimer is formed in sufficient concentration in solution to be studied by equilibrium methods. With these systems, the formation of appreciable concentrations of large polyions is generally prevented by the low solubility of such species. Many examples of these systems have been given by Sillén in a review.[36]

The second type of behavior which has been observed is that of the high solubility of a large polyion which has a structure of rather high symmetry. Thus solutions with the composition $[Bi(OH)_2]^+$ can be prepared with quite high total bismuth concentrations, and these solutions have been shown to contain a hexameric cation, $[Bi_6(OH)_{12}]^{+6}$ or $[Bi_6O_6\ xH_2O]^{+6}$, by various experimental methods.[25,37-39] X-Ray studies on 5.81 monomolar $[Bi(OH)_2]^+$ solutions have shown that the arrangement of the bismuth atoms in the hexameric cation has cubic symmetry,[40] and the ionic structure is probably based on the cuboctahedron as shown in Fig. 9. This structure seems especially logical in view of the fact that the ions with an "inert pair" generally occur in structures with only three or four bonds, probably because of s–p mixing.[41] In this bismuth polycation, there should be only weak bonds between the Bi(III) ions and adjacent water molecules which would stabilize the hexamer by retarding further growth to larger species.

The heteropolyanions, although rather large, *e.g.*, $[SiW_{12}O_{40}]^{-4}$, are often quite soluble in water. The structure of the 12-tungstosilicate anion in solutions as well as in crystals also is based on the cuboctahedron,[28] and the tungsten positions are illustrated in Fig. 10. Since the tungsten atoms are in WO_6 octahedra, the electron density at the peripheral oxygen atoms should be rather low here too as with the tantalate because of p_π–d_π donation. Again this should lessen the tendency of these oxygens to bind protons, and it is observed that the 12-tungstosilicic acid is a strong acid.[26] On the other hand, these ions do not undergo further condensation, since they are built around the tetrahedrally coordinated hetero-atom; while the hexameric bismuth and tantalum ions can undergo further condensation to insoluble precipitates.

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The fact that no depolymerization of the hexatantalate was observed even in the most alkaline solutions studied is not surprising, for the charge per tantalum would be too high for species like TaO_6^{-7} to be stable, and condensed species are formed. Since tantalum seems to occur only with a coordination number of six for oxygen, monomeric anions like TaO_4^{-3} appear quite unlikely.

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CONTRIBUTION FROM THE PIGMENTS AND ENGINEERING DEPARTMENT, EXPERIMENTAL STATION,
E. I. DU PONT DE NEMOURS AND CO., WILMINGTON, DELAWARE

X-Ray Study and Thermoelectric Properties of the $W_{x/2}Mo_{x/2}Ta_{1-x}Se_2$ System

BY L. H. BRIXNER AND G. TEUFER

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The pseudo-binary system between the compounds $TaSe_2$ and $W_{0.5}Mo_{0.5}Se_2$ has been investigated structurally and with regard to such thermoelectric parameters as Seebeck coefficient, electrical resistivity, and thermal conductivity. Eighteen compositions with x varying from 0.2 to 0.99 have been prepared. With the exception of a narrow two-phase region near $x = 0.7$, all compositions crystallize as single phases, either of the $CdCl_2$ or the MoS_2 type. Compounds of interest for thermoelectric power generation in the intermediate temperature range (500–700°) were found for $x = 0.9$–0.99. As corollaries, the system $W_xMo_{1-x}Se_2$ and some compositions of the five-component system $W_{x/2}Mo_{x/2}Ta_{1-x}Se_yTe_{2-y}$ were also invesitgated.

Introduction

In an earlier paper,[1] we have described the system $W_xTa_{1-x}Se_2$, and we have demonstrated how useful thermoelectric properties can be achieved by finding the optimum for x. Compositions such as $W_{0.97}Ta_{0.03}Se_2$ exhibited respectable Seebeck coefficients and relatively low electrical resistivities, but the thermal conductivity of some 70 mwatts/cm.-deg. was somewhat high and could stand some improvement. This was our major goal during the present investigation, which led us to the more complex $W_{x/2}Mo_{x/2}Ta_{1-x}Se_2$ system. The principle followed was essentially that laid down by Airapetiants.[2] He showed that semiconducting compounds of the type we are dealing with can be regarded as consisting of a cation and anion sublattice, and that electron scattering will be more strongly affected by changes in the anion sublattice, while the converse will be true for holes. The uncharged phonons, on the other hand, show essentially no preference. Since all of the useful compositions in the $W_xTa_{1-x}Se_2$ system were p-type, these considerations suggest that one should introduce substituents in the cation sites in order to reduce the thermal conductivity without affecting the electrical conductivity to an equal degree. Therefore, we were led to the system $W_{0.5}Mo_{0.5}Se_2$–$TaSe_2$, where half the tungsten atoms are replaced by molybdenum. (The practical purpose of the minor amount of tantalum substituted in the cation sites, of course, is to adjust the carrier concentration to the optimum level.) Since tungsten and molybdenum have an atomic mass ratio of almost 2:1, we are introducing a considerable mass fluctuation, which should cause further phonon scattering and therefore lower the thermal conductivity. Although the lattice parameters of both $MoSe_2$ and WSe_2 were well established and complete solid solubility could be expected, we studied the $Mo_xW_{1-x}Se_2$ system in some more detail and these data are also reported. Finally, we also prepared some compositions of the even more complex five-component system $W_{x/2}Mo_{x/2}Ta_{1-x}Se_yTe_{2-y}$ and these data are also included.

Experimental

Preparation.—The routine procedure for the preparation of all solid solutions was to vacuum-seal the constituent elements W, Mo, Ta, and Se, weighed to the nearest 0.1 mg., into a quartz ampoule, 15 mm. in diameter and 20 cm. long. All tubes were carefully heat-treated under vacuum in order to eliminate moisture as much as possible. The constituent elements were of best commercially available purity, usually 99.9+%, and were not given any special purification treatment prior to the reaction. Charges of approximately 20–30 g. were fired at 600–700° for 10–15 hr., after which time usually a black, free-flowing reaction product of apparently high surface area was obtained that could be effectively remixed inside the quartz tube by shaking. A second firing step at 1000–1200° for another 10–15 hr. assured completion of the reaction, and a homogeneous polycrystalline product of gray metallic luster was obtained which could be removed quite easily from the quartz after breaking the ampoule.

Crystallographic Characterization.—All X-ray data are based on powder diffraction patterns obtained with a Phillips 114.6-mm. diameter camera at 25°. The samples, which were taken from the center of the final reaction product, were ground to −325 mesh and were sealed into 2-mm. diameter Lindemann

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