The Tantalum–Tantalum Iodide System.—The outstanding feature of this system is its simplicity. Yet some comments are necessary in order to clarify previously reported observations on the tantalum iodides. This work establishes that TaI_4 and $(Ta_6I_{12})I_2$ are the only equilibrium phases in the system. The latter compound provides the green aqueous solutions which were attributed to a subiodide corresponding to TaI_4,[25] and which Körösy[15] had obtained from solids having a composition in the range $TaI_{2.75}$–$TaI_{2.45}$. As noted under Results pure TaI_4 does not produce green aqueous solutions; rather it hydrolyzes to yield the hydrated, brown tantalum(IV) oxide. It is difficult to obtain TaI_4 in a state entirely free of either TaI_5 or $(Ta_6I_{12})I_2$. The method of preparation of TaI_4 used in this work, while satisfactory for purposes reported here, probably left some TaI_5 in the product. At the temperatures necessary to separate TaI_5 by sublimation (*ca.* 350°) some decomposition of TaI_4 may result. The product TaI_3, previously reported by us[11] as resulting from the reduction of TaI_5 with tantalum, can be accounted for in terms of a mixture of TaI_4 and $(Ta_6I_{12})I_2$.

There is a striking contrast between the lower phases present in the niobium iodide and tantalum iodide systems. In the equilibrium niobium iodide system only NbI_4 and Nb_3I_8 were identified[24] with NbI_3 occupying an anomalous position. Thus there is little apparent resemblance between the two systems in the lower phase region. It is possible, however, that Nb_3I_8 may have the polynuclear structure and be formulated as $(Nb_6I_{12})I_4$. Evidence has been obtained that indicates the related anhydrous phases $(Nb_6Cl_{12})Cl_2$ and $(Nb_6Br_{12})Br_2$ do exist[26] and that the ion $Nb_6Cl_{12}{}^{2+}$ can be oxidized to $Nb_6Cl_{12}{}^{4+}$ in aqueous solution.[18]

(25) R. F. Rolsten, *J. Am. Chem. Soc.*, **80**, 2952 (1958).

(26) R. E. McCarley, P. B. Fleming, and L. A. Mueller, to be published.

Notes

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ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY,
IOWA STATE UNIVERSITY, AMES, IOWA, AND
THE DEPARTMENT OF CHEMISTRY,
MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
CAMBRIDGE, MASSACHUSETTS

The Two-Electron Oxidation of Metal Atom Cluster Species of the Type $[M_6X_{12}]^{2+}$

BY R. E. MCCARLEY,[1a] B. G. HUGHES,[1b] F. A. COTTON,[1c] AND R. ZIMMERMAN[1c]

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The oxidation–reduction behavior of metal atom cluster species, such as $[Ta_6X_{12}]^{2+}$, $[Nb_6X_{12}]^{2+}$, and $[Mo_6X_8]^{4+}$, under circumstances in which the cluster remains intact, are of interest for various reasons. Of particular pertinence to the question of chemical bonding in the clusters is the question of the extent and the ease with which the Nb and Ta species mentioned may be oxidized. A recently published molecular orbital treatment[2] of the $[Mg_6X_{12}]$ systems led to the result that the highest filled bonding MO is an A_{2u} level. When it is noted that this level is not very strongly bonding and that in a solvent such as water an increase in over-all charge from +2 to +4 should result in additional energy of solvation, a two-electron oxidation of $[M_6X_{12}]^{2+}$ leading to a diamagnetic product, $[M_6X_{12}]^{4+}$, might be expected to proceed at a relatively low potential. Conversely, the observation of such a process might be taken to substantiate, in some degree, the correctness of the order of molecular orbitals.

Oxidation reactions of the kind described have been observed for both the $[Nb_6Cl_{12}]^{2+}$ and the $[Ta_6X_{12}]^{2+}$ (X = Cl or Br) ions. In the case of the latter solid compounds such as the sulfates have been isolated.

Experimental

Standard Solutions of Dodeca-μ-halo-hexatantalum Sulfate.—Aqueous solutions of the $[Ta_6X_{12}]^{2+}$ halides were passed through a 2 cm. × 30 cm. column of strong anion-exchange resin, Amberlite IRA-401, in the sulfate form. After discarding the first 50 ml., the eluate was collected in a 250-ml. volumetric flask and diluted to the mark. The solutions were standardized by analyzing aliquots for tantalum and halide. Ratios of halide to tantalum for various solutions ranged from 1.97 to 2.00.

Titration of the $[Ta_6X_{12}]^{2+}$ Standard Solutions.—Oxidation–reduction titrations of the $[Ta_6X_{12}]^{2+}$ solutions were carried out indirectly using iron(III) ammonium sulfate solution as the oxidant and back titrating the iron(II) formed with standard ammonium tetrasulfatocerate(IV) solution. Aliquots of the standard, ion-exchanged solutions were added directly to excess iron(III) solution or passed through a Jones reductor into excess iron(III) solution. It was necessary to filter and wash the insoluble sulfate which formed on oxidation of the $[Ta_6X_{12}]^{2+}$ solutions in order to keep it from interfering with the subsequent titration.

Sulfate Derivatives of $[Ta_6X_{12}]^{4+}$.—An aqueous solution of $[Ta_6Cl_{12}]^{2+}$ acidified with sulfuric acid was oxidized with chlorine gas or iron(III) sulfate solution. The insoluble red-brown product was filtered, washed with ethanol and ether, and air dried.

Anal. Found: Ta, 59.23; Cl, 22.62; SO_4, 9.07; Cl/Ta, 1.95; SO_4/Ta, 0.288.

In a similar way, an aqueous solution of $[Ta_6Br_{12}]^{2+}$ acidified with sulfuric acid was oxidized with bromine water or iron(III) sulfate solution. The chocolate-brown precipitate was washed with ethanol and ether and air dried.

Anal. Found: Ta, 45.67; Br, 39.24; SO_4, 7.08; Br/Ta, 1.95; SO_4/Ta, 0.292.

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(1) (a) Department of Chemistry, Iowa State University, Ames, Iowa; (b) Department of Chemistry, Western Illinois University, Macomb, Ill.; (c) Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Mass.

(2) F. A. Cotton and T. E. Haas, *Inorg. Chem.*, **3**, 10 (1964); there is a typographical error in Figure 3 of this paper. The lower $T_{2g}(xz,yz)$ level is actually $T_{1g}(xz,yz)$.

Titration of $[Nb_6Cl_{12}]^{2+}$ Solutions with I_2 and Fe^{3+}.—An aqueous solution (approximately 10^{-3} *M*) of $[Nb_6Cl_{12}]^{2+}$ was prepared by dissolving $Nb_6Cl_{14}\cdot 7H_2O$ in water. Aliquots of this solution were titrated using an aqueous solution of iron(III) ammonium sulfate and a methanol solution of iodine.

Polarographic Study of $[Nb_6Cl_{12}]^{2+}$ Oxidation.—Approximately 10^{-3} *M* solutions of $Nb_6Cl_{14}\cdot 7H_2O$ with 1 *M* $KClO_4$ as supporting electrolyte were used, with a standard calomel electrode (s.c.e.) as the reference electrode. An oxidation wave was found with $E_{1/2} = +0.426$ v. on the hydrogen scale; the maximum accessible potential is about 0.60 v.

Results and Discussion

Solutions of $[Ta_6X_{12}]^{2+}$ in which the ionized halide had been exchanged for nitrate or perchlorate proved to be unsuitable for quantitative studies of the oxidation. The nitrate solutions were unstable with respect to oxidation of $[Ta_6X_{12}]^{2+}$ by nitrate ion, and a perchlorate solution, evaporated to near dryness on a hot plate, detonated. Therefore, sulfate-exchanged solutions were chosen for study. Nitrate solutions of $[Nb_6Cl_{12}]^{2+}$ were also found to be unstable, decomposing to liberate Cl^-.

Direct titrations of the $[Ta_6X_{12}]^{2+}$ solutions were unsatisfactory because the disulfate which precipitated during the titration formed an impervious coating on the platinum electrode, producing erratic results. Indirect titrations allowed removal of this product by filtration and so were free of interference. However, direct titrations of the $[Nb_6Cl_{12}]^{2+}$ ion in the presence of Cl^- ion were carried out with both aqueous Fe(III) and methanolic I_2.

The titration of aged solutions (*ca.* 1 week) of $[Ta_6Cl_{12}]^{2+}$ and $[Ta_6Br_{12}]^{2+}$ with iron(III) gave Fe/Ta_6X_{12} ratios in the range of 1.90 to 1.81. However, on passing these solutions through a Jones reductor or titrating freshly prepared solutions Fe/Ta_6X_{12} ratios in the range 1.97 to 2.03 were obtained. Direct titrations of $[Nb_6Cl_{12}]^{2+}$ with methanolic iodine or aqueous iron(III) sulfate gave Fe/Nb_6Cl_{12} or ${}^1/_2I_2/Nb_6Cl_{12}$ ratios of 1.97 to 2.06.

These results for the freshly prepared or reduced solutions confirm the two-electron oxidation of $[Ta_6X_{12}]^{2+}$ and $[Nb_6X_{12}]^{2+}$. Since the titer of $[Ta_6X_{12}]^{2+}$ solutions which had been stored in air returned to the value expected of the two-electron oxidation after prior reduction with zinc, it is probable that a slow oxidation by oxygen is effective *via* reaction 1. Indeed, solutions of $[Ta_6X_{12}]^{2+}$ in methanol acidified with

$$[Ta_6X_{12}]^{2+} + {}^1/_2O_2 + H_2O = [Ta_6X_{12}]^{4+} + 2OH^- \qquad (1)$$

HCl were observed to oxidize rapidly in air with change of color from green to red. Addition of $SnCl_2$ to these oxidized solutions returned the familiar green color.

Evidence that all of the halogen is retained in the oxidized species is provided by the observation that no silver halide is precipitated when Ag^+ is added to the solution above the freshly oxidized sulfate derivatives. The analytical data of the oxidized sulfate derivatives confirm the X/Ta ratio of 2. However, the low sulfate analyses ($SO_4/Ta_6X_{12} \cong 1.75$) are not understood in view of the titration data which indicate complete oxidation to $[Ta_6X_{12}](SO_4)_2$. Further work on the oxidized derivatives of both $[Ta_6X_{12}]^{2+}$ and $[Nb_6X_{12}]^{2+}$ has been undertaken and will be reported at a later date.

The Oxidation Potential of the $[Nb_6Cl_{12}]^{2+}$ Ion.—Since iodine was observed to oxidize the ion $[Nb_6Cl_{12}]^{2+}$, and the standard potential for the half-cell $I^- = {}^1/_2I_2 + e^-$ is -0.535 v., the potential for $[Nb_6Cl_{12}]^{2+} = [Nb_6Cl_{12}]^{4+} + 2e^-$ must be appreciably more positive than -0.535 v. Moreover, since 0.535 v. lies between the potential of the polarographic oxidation wave and the highest potential applied polarographically, it is virtually certain that the oxidation wave corresponds to the two-electron oxidation of $[Nb_6Cl_{12}]^{2+}$ with $E_{1/2} = 0.426$ v. *vs.* H_2.

When 0.5 *M* potassium oxalate plus sufficient HCl to dissolve it is used as the supporting electrolyte, the oxidation wave appears at $E_{1/2} = 0.341$ v. *vs.* H_2. This indicates that the oxidation product is complexed by oxalate to a greater degree than is $[Nb_6Cl_{12}]^{2+}$.

CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY,
THE UNIVERSITY OF MICHIGAN, ANN ARBOR, MICHIGAN

Isomers of the Dichlorobis(*l*-cyclohexanediamine)cobalt(III) Ion

BY ROBERT G. ASPERGER AND CHUI FAN LIU

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trans-1,2-Cyclohexanediamine (to be abbreviated chxn) was synthesized and resolved by Jaeger and co-workers.[1] The complexes of this ligand were investigated by Jaeger and co-workers,[2] and the results constituted an important part of a series of publications which were the foundation of stereospecificity of coordination compounds. The present study is concerned with the preparation of the two possible geometric isomers of the dichlorobis(*l*-cyclohexanediamine)-cobalt(III) ion. The preparation of this ion was reported by Jaeger and Bijkerk.[2a] They oxidized a 2:1 molar mixture of *l*-cyclohexanediamine and cobalt(II) chloride with hydrogen peroxide. The compound was described as a green viscous mass which was dried in a desiccator and used directly in further reactions. No analyses or optical rotation figures were available. Because of the green color of this compound it was assumed to have the *trans* configuration. Attempts were made during the present investigation to obtain the compound through Jaeger and Bijkerk's method.

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[1] (a) F. M. Jaeger and J. A. van Dijk, *Proc. Acad. Sci. Amsterdam*, **39**, 384 (1936); (b) F. M. Jaeger and L. Bijkerk, *ibid.*, **40**, 12 (1937).

[2] (a) F. M. Jaeger and L. Bijkerk, *ibid.*, **40**, 246 (1937); (b) F. M. Jaeger, *ibid.*, **40**, 2 (1937); (c) F. M. Jaeger and J. ter Berg, *ibid.*, **40**, 490 (1937); (d) F. M. Jaeger and L. Bijkerk, *ibid.*, **40**, 116 (1937); (e) F. M. Jaeger and L. Bijkerk, *ibid.*, **40**, 316 (1937).