Metal Cluster Halide Complexes. I. Efficient Synthesis of Hydrated Hexanuclear Niobium and Tantalum Cluster Halides $M_6X_{14} \cdot 8H_2O$[1]

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Niobium and tantalum cluster halides $M_6X_{14} \cdot 8H_2O$ may be synthesized in high yields *via* ternary halides $A_4M_6X_{18}$ (A = alkali; M = Nb, Ta; X = Cl, Br) by a one-step conproportionation reaction from the metal M, its pentahalide MX_5, and a suitable alkali halide AX. The apparent stability of the higher valent ternary halides formed in the initial stages of the reaction makes it possible to run the reaction in Vycor tubes without the interference from silicon dioxide usually experienced in reactions involving niobium or tantalum and its halides. Important factors which favor the formation of $A_4M_6X_{18}$ over the competing compounds A_2MX_6, $A_3M_2X_9$, and AM_4X_{11} are use of an excess of the metal and of a stoichiometric amount of the alkali halide, the particular alkali halide used, and the temperature. It appears that conproportionation reactions of this general type may be of importance for the syntheses of other polynuclear metal cluster halides and of ternary halides in low oxidation states.

Introduction

Hydrated hexanuclear metal cluster halides $[(M_6X_{12})X_2 (H_2O)_4] \cdot nH_2O$ (M = Nb, Ta; X = Cl, Br), usually formulated as $M_6X_{14} \cdot 8H_2O$, are representatives of a particular class of coordination compounds that are based on $(M_6X_{12})^{n+}$ cluster units as central cations. M_6X_{12} cations contain metal–metal bonded M_6 octahedra with halogens bridging over the 12 octahedral edges.[2] Each metal atom has one site open for attachment of a terminal ligand. Negative, neutral, and positive complexes may be prepared with the M_6X_{12} central cation in various oxidation states. Crystal structures,[3-8] spectra,[9-16] and magnetic properties[17,18] of a number of such complexes have been the subject of recent investigations. The syntheses of complexes containing M_6X_{12} central cations are based on the hydrates $M_6X_{14} \cdot 8H_2O$ as starting materials. The need for a fast and efficient method for the preparation of these hydrates brought about this investigation.

Syntheses of the hydrates $M_6X_{14} \cdot 8H_2O$ generally involve high-temperature reactions yielding products that contain $(M_6X_{12})^{2+}$ cations. These products are extracted, and from the purified aqueous solutions the hydrates are precipitated with concentrated aqueous HX. Harned's method,[19] which is generally used, involves the reduction of niobium or tantalum pentahalide with cadmium metal, possibly with the formation of $Cd_2[(M_6X_{12})X_6]$

$$6MX_5 + 8Cd \rightarrow Cd_2[(M_6X_{12})X_6] + 6CdX_2 \qquad (1)$$
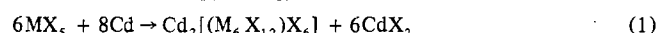
This method supplies only small amounts of cluster material. A variation of Harned's method was developed by Fleming.[20] Lithium halide–potassium halide melts were used as reaction media for the reduction of niobium pentahalides with cadmium or aluminum metal. This molten salt variation provides higher yields and requires lower temperatures. However, upon extraction of the reduction products, vast quantities of salts accompany the cluster material into aqueous solution.

A second method, due to McCarley and coworkers,[21] involves the high-temperature disproportionation of Nb_3X_8 in the presence of an alkali halide

$$14AX + 5Nb_3X_8 \rightarrow 3A_2NbX_6 + 2A_4[(Nb_6X_{12})X_6] \qquad (2)$$
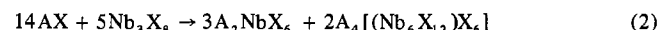
In niobium tubes or in the presence of niobium metal, the disproportionation is replaced by an outright reduction of Nb_3X_8 by niobium metal

$$16AX + 7Nb_3X_8 + 3Nb \rightarrow 4A_4[(Nb_6X_{12})X_6] \qquad (3)$$
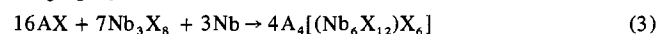
Broll, Juza, and Schafer[22] have extended this procedure to the preparation of $(Ta_6X_{12})^{2+}$-containing materials. A disadvantage of this method is the need for the lower halide M_3X_8 as a starting material, since it has to be prepared from the corresponding pentahalide.

A third synthetic route is the conproportionation of niobium or tantalum metal with its pentahalide in the presence of an alkali halide. McCarley and coworkers[21,23] allowed niobium metal, niobium pentachloride, and excess potassium chloride or lithium chloride to react for 4–6 days in electron beam sealed niobium tubes and showed the obtained reac-

(1) Presented at the XIVth International Conference on Coordination Chemistry, Toronto, Canada, June 1972. A preliminary account of certain aspects of this work has been published: J. A. Parsons, A. Vongvusharintra, and F. W. Koknat, *Inorg. Nucl. Chem. Lett.*, 8, 281 (1972).

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(23) B. G. Hughes, J. L. Meyer, P. B. Fleming, and R. E. McCarley, *Inorg. Chem.*, 9, 1343 (1970).

tion products to contain $K_4[(Nb_6Cl_{12})Cl_6]$ or the corresponding lithium compound $Li_4[(Nb_6Cl_{12})Cl_6]$ (see eq 4).

$$20KCl + 14NbCl_5 + 16Nb \rightarrow 5K_4[(Nb_6Cl_{12})Cl_6] \quad\quad (4)$$
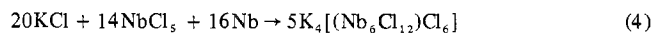
Obvious disadvantages of this synthesis were the long reaction time of 4-6 days, the low yield due to incomplete reduction, and the apparent need to work in electron beam sealed niobium tubes. In spite of these drawbacks, a conproportionation reaction appeared to be a promising synthetic route for several reasons. First, it employs readily available starting materials. Second, even at low yields it supplies rather large amounts of cluster material, since both oxidizing and reducing agents are transformed into the desired product. Third, since the reducing agent is the metal itself, an excess of the reducing agent cannot overreduce the pentahalide to the metal.

Consideration of the conditions that favor the formation of $(Nb_6Cl_{12})^{2+}$ cluster cations and their implementation have now made it possible to run a conproportionation reaction in glass vessels with almost quantitative yields within 24 hr. The method has been extended as a general synthesis for hydrated cluster halides of the formula $M_6X_{14} \cdot 8H_2O$. It has been particularly valuable for the preparation of $Nb_6Br_{14} \cdot 8H_2O$, which was available previously only in minute quantities.[19,21,22,24] These syntheses will now be outlined.

Experimental Section

Materials and Apparatus. Niobium and tantalum pentahalides were purchased from Research Organic/Inorganic Corp. and used without further purification. They were stored in a drybox under nitrogen. Niobium metal (E. I. du Pont de Nemours and Co.) was used in the form of pellets of approximately 1-mm diameter; tantalum metal (Research Organic/Inorganic Corp.), as a 325-mesh powder. Vycor reaction tubes were carefully outgassed on a vacuum line before being filled in the drybox.

X-Ray powder photographs were taken in 0.2-mm diameter Lindemann capillaries with tungsten as an internal standard, using an Enraf-Nonius general-purpose camera of 114.6-mm diameter. The radiation used was Cu $K\alpha$.

$Nb_6Cl_{14} \cdot 8H_2O$ *via* $Na_4Nb_6Cl_{18}$. Stoichiometric amounts of niobium pentachloride (37.8 g, 0.14 mol) and sodium chloride (11.7 g, 0.20 mol) were intimately mixed by grinding in a mortar. The mixture was placed in a Vycor reaction tube, and excess niobium metal (60 g, 0.65 mol) was added. The reaction vessel was sealed under vacuum and shaken for several minutes in order to mix its contents thoroughly. Within 6-8 hr, it was heated to 850° and left at this temperature overnight. The complex $Na_4Nb_6Cl_{18}$, identified by its X-ray powder pattern,[22] was extracted with five 2000-ml portions of water to which 1 ml of concentrated hydrochloric acid had been added. The intensely green solutions were filtered, treated with equal volumes of concentrated hydrochloric acid, and heated with stirring until precipitation of $Nb_6Cl_{14} \cdot 8H_2O$ was completed. During this process, 5 g of solid stannous chloride was added periodically in small portions to prevent air oxidation to $(Nb_6Cl_{12})^{3+}$ containing material. The black product was filtered over a fritted glass filter, washed with concentrated hydrochloric acid and ether, and dried *in vacuo* over phosphorus pentoxide; yield 55.3 g, 92%. *Anal.* Calcd for $Nb_6Cl_{14} \cdot 8H_2O$: Cl, 41.43; Nb, 46.53. Found: Cl, 41.22; Nb, 45.97; Cl:Nb, 14.10:6.00.

Further experiments showed that prolonged heating of the reaction mixture causes considerable reaction of niobium metal or its chlorides with the glass wall of the reaction tube, thereby decreasing the yields. Reaction mixtures heated for 3 and 5 days gave yields of 82 and 72%, respectively.

$Nb_6Br_{14} \cdot 8H_2O$ *via* $K_4Nb_6Br_{18}$. A vacuum-sealed Vycor reaction tube containing an intimate mixture of 13.8 g (28 mmol) of niobium pentabromide, 4.75 g (40 mmol) of potassium bromide, and 15 g (160 mmol) of niobium pellets was gradually brought to 720° within 6-8 hr and left at this temperature for 15 hr. The product, $K_4Nb_6Br_{18}$, was extracted twice with 300-ml portions of warm water.

(24) R. J. Allen and J. C. Sheldon, *Aust. J. Chem.*, **18**, 277 (1965).

The filtered, dark green solutions were treated with equal volumes of concentrated hydrobromic acid with stirring and heating, and 5 g of solid stannous bromide was added in small portions to prevent air oxidation of the cluster material. The black $Nb_6Br_{14} \cdot 8H_2O$ was filtered over a frit, washed with concentrated hydrobromic acid and ether, and dried *in vacuo* over phosphorus pentoxide; yield 14.8 g, 81%. *Anal.* Calcd for $Nb_6Br_{14} \cdot 8H_2O$: Br, 61.46; Nb, 30.62. Found: Br, 61.29; Nb, 30.35; Br:Nb, 14.09:6.00.

Selection of the proper temperature is critical for the success of the reaction leading to $K_4Nb_6Br_{18}$. The maximum yield of 81% was obtained at 720°. Yields of 51 and 38% were obtained for reaction temperatures of 830 and 620°, respectively. Prolonged reaction times and temperatures above 800° caused considerable reaction with the glass wall of the container.

$Ta_6Cl_{14} \cdot 8H_2O$ *via* $Na_4Ta_6Cl_{18}$. An intimate mixture of tantalum pentachloride (25.08 g, 70 mmol), sodium chloride (5.84 g, 100 mmol), and excess tantalum powder (58 g, 320 mmol) in a vacuum-sealed Vycor reaction tube was gradually heated to 700° within a 10-hr period and kept at this temperature overnight. The solid reaction product, $Na_4Ta_6Cl_{18}$, was ground in a mortar and extracted four times with 1500-ml portions of water. The filtered solutions were treated with equal volumes of concentrated hydrochloric acid, and a total of 5 g of stannous chloride was added in small portions with stirring and heating. The dark green precipitate was filtered over a frit, washed twice with 150 ml of concentrated hydrochloric acid and twice with 150 ml of ether, and dried *in vacuo* over phosphorus pentoxide; yield 37.9 g, 88%. *Anal.* Calcd for $Ta_6Cl_{14} \cdot 8H_2O$: Cl, 28.75; Ta, 62.90. Found: Cl, 28.94; Ta, 63.06; Cl:Ta, 14.05:6.00.

Again the reaction temperature is critical for the success of the preparation. Thus a reaction run at 850° gave only a 4% yield.

$Ta_6Br_{14} \cdot 8H_2O$ *via* $K_4Ta_6Br_{18}$. An intimate mixture of 16.25 g (28 mmol) of tantalum pentabromide, 4.76 g (40 mmol) of potassium bromide, and 18.1 g (100 mmol) of tantalum metal in a vacuum-sealed Vycor reaction tube was allowed to react at 700° for 15 hr after a gradual initial heating over 10 hr. The reaction product, $K_4Ta_6Br_{18}$, was found to be isostructural with $K_4Nb_6Br_{18}$ by visual comparison of X-ray powder patterns. The $K_4Ta_6Br_{18}$ obtained was extracted with four 250-ml portions of water, and from the filtered solutions $Ta_6Br_{14} \cdot 8H_2O$ was precipitated in the same way as described above for $Nb_6Br_{14} \cdot 8H_2O$; yield 22.4 g, 95%. *Anal.* Calcd for $Ta_6Br_{14} \cdot 8H_2O$: Br, 47.64; Ta, 46.23. Found: Br, 47.81; Ta, 46.82; Br:Ta, 13.87:6.00.

Analytical Procedures. Niobium and tantalum were determined gravimetrically as the oxides, M_2O_5. Samples were weighed directly into tared crucibles, decomposed, dried, and ignited. The bromides were decomposed with dilute hydrogen peroxide; the chlorides, by treatment with ammoniacal hydrogen peroxide and thereafter with concentrated nitric acid. Halides were determined by potentiometric titration with standard silver nitrate solution after decomposition of the cluster compounds with dilute sodium hydroxide.

Discussion

The above experiments show that complex metal cluster halides $A_4M_6X_{18}$ can be readily synthesized in glass vessels and in almost quantitative yields by high-temperature conproportionation of niobium or tantalum metal with its pentachloride or pentabromide, in the presence of the proper alkali halide. The conditions which effect a fast and quantitative formation of the cluster species will now be briefly discussed.

The formation of $(M_6X_{12})^{2+}$ cluster material in a high-temperature synthesis is facilitated if the cluster is stabilized, by complexation, into an $(M_6X_{18})^{4-}$ anion. This is accomplished by addition of an alkali halide

$$20AX + 14MX_5 + 16M \rightarrow 5A_4M_6X_{18} \quad\quad (5)$$
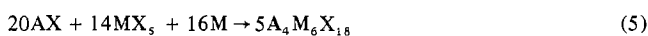
The formation of $A_4M_6X_{18}$ requires an alkali halide:metal pentahalide ratio of 10:7. It can be assumed to be in competition with the reactions
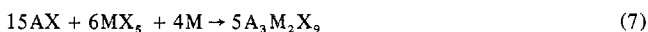
$$10AX + 4MX_5 + M \rightarrow 5A_2MX_6 \quad\quad (6)$$

$$15AX + 6MX_5 + 4M \rightarrow 5A_3M_2X_9 \quad\quad (7)$$

$$AX + 2MX_5 + 2M \rightarrow AM_4X_{11} \quad\quad (8)$$

Table I. Ternary Alkali Niobium Chlorides

$Na_4Nb_6Cl_{18}{}^a$			$Na_2NbCl_5{}^f$	$Na_2NbCl_6{}^i$	$NaNbCl_6{}^{l,m}$
$K_4Nb_6Cl_{18}{}^{b,c}$			$K_2NbCl_5{}^{f,g}$	$K_2NbCl_6{}^{g,i}$	$KNbCl_6{}^{l,m}$
	$RbNb_4Cl_{11}{}^d$		$Rb_2NbCl_5{}^{g,h}$	$Rb_2NbCl_6{}^{j,k}$	$RbNbCl_6{}^{n,o}$
$Cs_4Nb_6Cl_{18}{}^a$	$CsNb_4Cl_{11}{}^d$	$Cs_3Nb_2Cl_9{}^e$	$Cs_2NbCl_5{}^{g,h}$	$Cs_2NbCl_6{}^{j,k}$	$CsNbCl_6{}^{n,o}$

a Reference 22. *b* Reference 21. *c* Reference 4. *d* A. Broll, A. Simon, H. G. Schnering, and H. Schafer, *Z. Anorg. Allg. Chem.*, 367, 1 (1969). *e* A. Broll, H. G. Schnering, and H. Schafer, *J. Less-Common Metals*, 22, 243 (1970). *f* V. V. Safonov, B. G. Korshunov, T. N. Zimina, and Z. N. Shevtsova, *Zh. Neorg. Khim.*, 11, 2139 (1966). *g* T. J. Beresneva, G. P. Gosteva, and A. N. Ketov, *ibid.*, 16, 397 (1971). *h* V. V. Safonov, B. G. Korshunov, and T. N. Zimina, *ibid.*, 11, 906 (1966). *i* B. G. Korshunov and V. V. Safonov, *ibid.*, 6, 753 (1961). *j* V. V. Safonov, B. G. Korshunov, and Z. N. Shevtsova, *ibid.*, 7, 1979 (1962). *k* E. K. Smirnova and I. V. Vasilkova, *Vestn. Leningrad. Univ., Fiz., Khim.*, 161 (1965). *l* A. P. Palkin and N. D. Chikanov, *Zh. Neorg. Khim.*, 7, 1370 (1962). *m* O. R. Gavrilov and L. A. Niselson, *ibid.*, 11, 209 (1966). *n* K. Huber, E. Jost, E. Neuenschwander, M. Studer, and B. Roth, *Helv. Chim. Acta*, 41, 2411 (1958). *o* T. I. Beresneva, G. P. Gosteva, and A. N. Ketov, *Zh. Neorg. Khim.*, 15, 3274 (1970).

These reactions lead to products containing the metal in oxidation states higher than +2.33 and require alkali halide:metal pentahalide ratios of 10:4, 10:4, and 10:20, respectively. To favor the formation of $A_4M_6X_{18}$, it is essential to use strictly the exact alkali halide:metal pentahalide ratio of 10:7, given by eq 5.

It is also essential to employ an excess of the metal. This not only favors the low oxidation state of +2.33 in $A_4M_6X_{18}$ but also compensates for any loss of metal due to reaction with the glass walls.[25,26]

$$14Ta + 5SiO_2 \rightarrow 5Ta_2Si + 2Ta_2O_5 \tag{9}$$

$$11Nb + 3SiO_2 \rightarrow Nb_5Si_3 + 6NbO \tag{10}$$
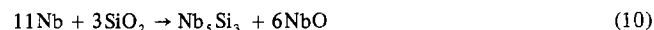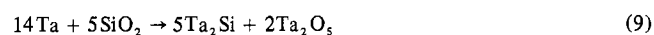
A third essential factor is the selection of the alkali halide AX, since the relative stabilities of the compounds A_2MX_6, $A_3M_2X_9$, and AM_4X_{11} that are competing with $A_4M_6X_{18}$ are functions of the particular alkali ions A^+. The considerations that were made for ternary alkali niobium chlorides (A = Na, K, Rb, Cs; see Table I) are given as an example. All compounds $A_4Nb_6Cl_{18}$ (except for $Rb_4Nb_6Cl_{18}$) are known. Of the species ANb_4Cl_{11}, only the cesium and rubidium compounds have been prepared, and Broll, *et al.*,[27] reported that, in spite of repeated attempts, KNb_4Cl_{11} could not be synthesized. For compounds $A_3Nb_2Cl_9$, only $Cs_3Nb_2Cl_9$ has been reported and characterized by an X-ray structure determination.[28] However, compounds A_2NbCl_5 have been described as the only double salts occurring in the systems alkali chloride-niobium trichloride.[29-31] Since $A_3Nb_2Cl_9$ (60 mol % ACl) is quite close in composition to A_2NbCl_5 (66.7 mol % ACl) and since the maxima in the described phase diagrams are rather broad, there is a possibility that the reported compounds A_2NbCl_5 are actually of the type $A_3Nb_2Cl_9$. Table II shows melting points of compounds in the systems alkali chloride-niobium trichloride and alkali chloride-niobium tetrachloride. Whereas sodium chloride itself is the highest melting alkali chloride, its double salts Na_2NbCl_5 and Na_2NbCl_6 have melting points that are at least 200° lower than the melting points of their heavier analogs. This can be interpreted as indicating a lower stability for the ternary sodium chlorides Na_2NbCl_5 and Na_2NbCl_6. Since the sodium compounds which compete

(25) H. Schafer and K.-D. Dohmann, *Z. Anorg. Allg. Chem.*, 299, 197 (1959).

(26) H. Schafer, E. Schibilla, R. Gerken, and H. Scholz, *J. Less-Common Metals*, 6, 239 (1964).

(27) A. Broll, A. Simon, H. G. Schnering, and H. Schafer, *Z. Anorg. Allg. Chem.*, 367, 1 (1969).

(28) A. Broll, H. G. Schnering, and H. Schafer, *J. Less-Common Metals*, 22, 243 (1970).

(29) V. V. Safonov, B. G. Korshunov, T. N. Zimina, and Z. N. Shevtsova, *Zh. Neorg. Khim.*, 11, 2139 (1966).

(30) T. J. Beresneva, G. P. Gosteva, and A. N. Ketov, *Zh. Neorg. Khim.*, 16, 397 (1971).

(31) V. V. Safonov, B. G. Korshunov, and T. N. Zimina, *Zh. Neorg. Khim.*, 11, 906 (1966).

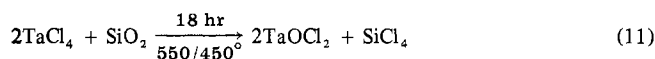**Table II.** Melting Points (°C) in the Systems $ACl-NbCl_3$ and $ACl-NbCl_4$

NaCl	800	Na_2NbCl_5	450^a	Na_2NbCl_6	582^b
KCl	772	K_2NbCl_5	718^a	Na_2NbCl_6	782^b
RbCl	717	Rb_2NbCl_5	753^c	Rb_2NbCl_6	$802^{d,e}$
CsCl	642	Cs_2NbCl_5	762^c	Cs_2NbCl_6	822^d

a Footnote *f* of Table I. *b* Footnote *i* of Table I. *c* Footnote *h* of Table I. *d* Footnote *j* of Table I. *e* Footnote *k* of Table I.

with $Na_4Nb_6Cl_{18}$ either are not even formed or have lower stabilities than their heavier analogs, $Nb_6Cl_{14}\cdot8H_2O$ may be best synthesized *via* $Na_4Nb_6Cl_{18}$. Similar considerations can be made for the corresponding tantalum systems. For the bromide systems, corresponding data are rare. It appears reasonable that Na^+ may be replaced by the heavier K^+.

The presence of an alkali halide in a reaction mixture containing a niobium or tantalum pentahalide has several beneficial side effects. In the initial stages of the reaction volatile pentahalides or tetrahalides are complexed to nonvolatile alkali hexahalometalates, AMX_6 or A_2MX_6. The lack of excessive pressure in the initial stages makes it possible to reach the final reaction temperature within several hours.

In addition it appears that the ternary halides that are formed react substantially slower with the glass walls of reaction vessels than binary niobium or tantalum halides. Schafer and coworkers[26,32,33] observed a number of reactions involving tantalum chlorides and the silicon dioxide of reaction tubes, *i.e.*

$$2TaCl_4 + SiO_2 \xrightarrow[550/450°]{18\ hr} 2TaOCl_2 + SiCl_4 \tag{11}$$

$$11Ta + Ta_6Cl_{15} + 5SiO_2 \xrightarrow[800°]{15\ hr} 5Ta_2Si + 2Ta_2O_5 + 3TaCl_5 \tag{12}$$

$$14Ta_6Cl_{15} + 15SiO_2 \xrightarrow[800°]{3\ days} 15Ta_2Si + 6Ta_2O_5 + 42TaCl_5 \tag{13}$$

$$2TaCl_5 + SiO_2 \underset{1000°}{\rightleftharpoons} 2TaOCl_3 + SiCl_4 \tag{14}$$
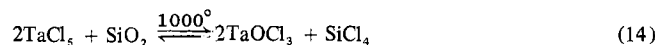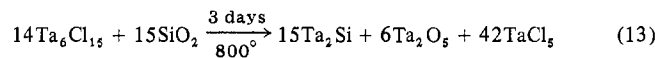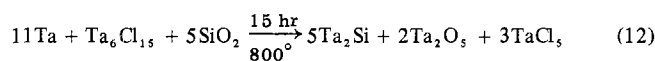
They even used the reaction of powdered silicon dioxide with tantalum metal and tantalum pentachloride for the synthesis of tantalum oxydichloride

$$2Ta + 5SiO_2 + 8TaCl_5 \xrightarrow[4\ days]{550/450°} 10TaOCl_2 + 5SiCl_4 \tag{15}$$
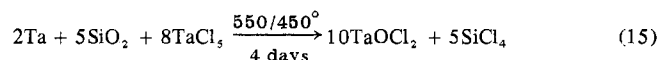
They concluded[33] that at temperatures above 650° side reactions of tantalum chlorides with silicon dioxide become severe. The conproportionation reactions described in this paper however were hardly disturbed by side reactions with

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the glass walls as indicated by the high yields obtained and by the condition of the Vycor tubes after the reactions. Reactions with silicon dioxide of the container seemed to be substantial only if the reaction temperature was above 800° and if the total reaction time exceeded 24 hr.

It seems obvious that the reaction temperature exerts an influence not only on side reactions with the glass walls but also on the main reaction, since the reaction temperature might very well decide which ternary halide is formed as the main product of a conproportionation. This aspect has not been investigated any further, since the preparative efforts were mainly directed at achieving the optimum conditions for the formation of compounds $A_4M_6X_{18}$.

Apart from their significance for the preparation of niobium and tantalum cluster material, conproportionation reactions as those described above should be of general im-

portance for the synthesis of other polynuclear metal cluster halides and, more generally, of ternary halides in very low oxidation states which otherwise might not be easily accessible. Applications of conproportionation reactions to the preparation of $(Mo_6X_8)^{4+}$ and other cluster cations will be described in a later paper.

Spectroscopic Studies of Metal–Metal Bonding. VI. Vibrational Spectra and Analyses of X₃MFe(CO)₄⁻ (X = Cl, Br; M = Ge, Sn)

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The infrared and laser Raman spectra of the ions $Cl_3GeFe(CO)_4^-$, $Cl_3SnFe(CO)_4^-$, and $Br_3SnFe(CO)_4^-$ are reported, and 16-19 of the 20 expected fundamentals for each ion have been observed and assigned on the basis of C_{3v} symmetry. Vibrational analyses of these spectra and those of the isostructural $X_3MCo(CO)_4$ (M = Ge, Sn; X = Cl, Br, I) have been carried out with a uniform set of approximations. There is close "calculated–observed" agreement while holding the force fields for the $M'(CO)_4$ moiety constant through the respective series and varying only the constants associated with the MX_3 moieties. In each of the three isoelectronic pairs between the two series, k_{Fe-M} is in a range higher than that for the analogous k_{Co-M}. For $X_3MFe(CO)_4^-$ the metal–metal force constants determined are k_{Fe-Ge}(X = Cl) = 1.29 ± 0.03, k_{Fe-Sn}-(X = Cl) = 1.36 ± 0.03, and k_{Fe-Sn}(X = Br) = 1.10 ± 0.03 mdyn/Å. The range of approximation over which this result remains valid and the nature of bonding implications which can be drawn from vibrational analysis of such organometallic compounds are evaluated.

Introduction

In earlier work in this series[1,2] we reported the vibrational spectra and normal-coordinate analysis of several metal–metal bonded cobalt carbonyl compounds of the form X_3MM'-$(CO)_4^n$, with $n = 0$; M′ = Co; M = Sn, Ge; and X = Cl, Br, I. The primary objective of those studies was to determine the way the metal–metal force constant, k_{M-Co}, depends on the nature of M and X by varying them independently through the series of compounds. In those and other studies[1-5] attention has been drawn to the fact that both σ and π contributions to the M–M′ bonding can be important.

Since the nature of the M–M′ bonding in these species depends on the relationship of the energies of the available M′ (or M′(CO)₄) orbitals to those of the MX₃ moiety, it is desirable to be able to vary the M′ orbital levels through sets of related compounds. A straightforward method for doing this, and a useful approach to investigating the effect on

$k_{M-M'}$ of varying the participation of the M′ orbitals in X_3-$MM'(CO)_4^n$ species, while leaving the remainder of the molecule essentially unchanged, is to study the vibrational spectra of isoelectronic molecules.

The iron carbonyl derivatives $X_3MFe(CO)_4^-$ (M = Sn, Ge; X = Cl, Br) are isoelectronic with the $X_3MCo(CO)_4$ molecules studied earlier and, on the basis of 5-μ infrared data, are postulated[6] to be isostructural to them. Formally the difference between these sets of compounds is the isoelectronic replacement of Co(0) by Fe(−I), which causes the M′ orbitals to become less stable (higher in energy) relative to MX₃ orbitals than those due to Co(0). The formal result of this is to alter the orbital composition of the $X_3MM'(CO)_4^n$ molecular orbitals and, potentially, to change the relative importance of π bonding in essentially the same manner as that of π^*-(CO) orbitals changes through the Ni(CO)₄, Co(CO)₄⁻, Fe-(CO)₄²⁻ series.[7,8] In the latter case, variations in C–O stretching force constants clearly reflect the changes in π^*(CO) participation in the C–O as well as the overall M(CO)₄ bonding.

In this paper we report the infrared and laser Raman spec-

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