believed due to molecular transitions rather than to transitions of the Np(IV) ion in a crystalline field.

The improved magnetic susceptibility measurements on $U(COT)_2$, which show a second crystal field level at 9°K, can be rationalized by either of two explanations. The approximate crystal field model originally proposed[6] predicts $J_z = \pm 4$ as the lowest level for the U^{4+} ion in a D_{8h} field, with the next level, $J_z = \pm 3$, several hundred reciprocal centimeters higher. Assuming LS coupling and $\mu_{eff} = g_j | J_z | \beta$, $\mu_{eff} = 3.20$ BM for $J_z = \pm 4$ and 2.40 BM for $J_z = \pm 3$. The experimental values are 3.33 BM for the ground level and 2.31 BM for the first excited level, an excellent agreement with this model. However, the energy matrix[6] predicts levels at $-28B_2{}^\circ$, $-17B_2{}^\circ$, and $8B_2{}^\circ$ for $J_z = \pm 4$, ± 3, and ± 2, respectively. ($B_2{}^\circ$ is the second-order crystal field parameter.) For a quantitative agreement, the crystal field level for $J_z = \pm 2$ would be expected at ~20°K. The absence of this level suggests that the predictions of the approximate model cannot be applied in this detail, and the apparent agreement between calculated and experimental magnetic susceptibility values is probably fortuitous.

The failure in detail of the approximate crystal field model requires consideration of an alternate explanation; the most reasonable of which is the probability that the ground state of U^{4+} is split by low-symmetry components in the crystal.[11] This alternative recognizes that, although the molecular symmetry of $U(COT)_2$ is D_{8h}, the $U(COT)_2$ crystal has a monoclinic cell[4,5] and, therefore, has low-symmetry components from the crystal imposed upon the molecule. Splitting of the ground level from these components is reasonable for U^{4+}. Np^{4+}, whose ground state is a Kramers doublet, cannot be split by an electric field and experimentally is not split; Pu^{4+} ($J_z = 0$) cannot be split by any field. The low symmetry of the crystal can show an effect only on U^{4+} in $U(COT)_2$, and splitting of the lowest crystal field level in U^{4+} conforms to this probability. This explanation for the lowest crystal field level of $U(COT)_2$ appears preferable to an explanation based on the approximate crystal field model.

Experimental evidence from absorption spectra, Mossbauer spectra, and nmr studies indicates that the most reasonable theoretical treatment of the actinide(IV)-COT compounds should be on a molecular orbital model. Although an approximate crystal field model[6] can account qualitatively for magnetic susceptibility results, a molecular orbital treatment by Hayes and Edelstein[11] appears successful quantitatively as well. The extension of a molecular orbital treatment to other properties of the actinide(IV)-COT compounds appears promising when additional experimental data are available.

Registry No. $U(COT)_2$, 11079-26-8; $U(EtCOT)_2$, 37274-10-5; $U(BuCOT)_2$, 37274-12-7; $Np(COT)_2$, 37281-22-4; $Np(EtCOT)_2$, 37281-25-7; $Np(BuCOT)_2$, 37281-27-9, $Np(TMCOT)_2$, 12715-86-5; $Pu(COT)_2$, 37281-23-5; $Pu(EtCOT)_2$, 37281-26-8; $Pu(BuCOT)_2$, 37281-28-0.

Acknowledgments. The author is grateful to J. A. Stone for the Mossbauer spectra of the Np(IV)-COT compounds and to N. Edelstein, Lawrence Berkeley Laboratory, for helpful discussions and communication on work in progress. C. A. Harmon and A. Streitwieser, Jr., of the University of California provided a sample of BuCOT for early experiments. R. D. Fischer, University of Erlangen, Nuremberg, proposed the possibility of a lower magnetic state for $U(COT)_2$.

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[11] R. G. Hayes and N. Edelstein, *J. Amer. Chem. Soc.*, 94, 8688 (1972).

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Syntheses and Raman Spectra of Chlorodiiodinium[1] and Bromochloroiodinium Hexachloroantimonates

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Received September 22, 1972

The salts chlorodiiodinium hexachloroantimonate, $I_2Cl^+SbCl_6{}^-$, and bromochloroiodinium hexachloroantimonate, $BrICl^+SbCl_6{}^-$, have been prepared by the direct combination of the suitable halogens in the presence of antimony pentachloride. The Raman spectra of these salts have been studied and the mass spectra of their gaseous dissociation products have been observed.

Introduction

Interhalogen compounds can react with either Lewis acids or bases to form cationic or anionic species, respectively. These reactions can be formally described as the self-ionization processes

$$2XY_n \rightleftarrows (XY_{n-1})^+ + (XY_{n+1})^- \quad n = \text{odd, not 1} \tag{1a}$$

$$2XYZ_m \rightleftarrows (XYZ_{m-1})^+ + (XYZ_{m+1})^- \quad m = \text{even} \tag{1b}$$

where X is the central halogen in each case. The specific conductance of ICl is consistent with the formulation of a polyatomic cation and anion

$$3XY \rightleftarrows X_2Y^+ + XY_2{}^- \quad n = 1 \tag{2}$$

and there is no evidence for monoatomic Cl^+, Br^+, or I^+.[3]

Both I_2Cl^+ and $BrICl^+$ are additions to the family of non-fluorine-containing interhalogen cations of which $ICl_2{}^+$, reported by Vonk and Wiebenga in 1959,[4] had been the only known member. These all can be considered derivable from

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[1] For a preliminary report, see J. Shamir and M. Lustig, *Inorg. Nucl. Chem. Lett.*, 8, 985 (1972).

[2] On sabbatical leave from the Department of Inorganic and Analytical Chemistry, The Hebrew University, Jerusalem, Israel.

[3] R. J. Gillespie and M. J. Morton, *Quart. Rev., Chem. Soc.*, 25, 553 (1971).

[4] C. G. Vonk and E. H. Wiebenga, *Recl. Trav. Chim. Pays-Bas*, 78, 913 (1959).

equilibria 1 and 2. Consequently, the sequence of cations $(\mathrm{I{-}I{-}Cl})^+$, $(\mathrm{Br{-}I{-}Cl})^+$, $(\mathrm{Cl{-}I{-}Cl})^+$ now exists.

Experimental Section

Reagents. The halogens chlorine, bromine, and iodine (resublimed) were obtained from the Matheson Co., Merck and Co., Inc., and the B & A Laboratory Chemical Department, Allied Chemical Corp., respectively, and were used without further purification. The antimony pentachloride and pentafluoride were procured from B & A and Alpha Inorganics, Division of Ventron, respectively. Iodine monobromide was synthesized by a known method.[5]

Apparatus and Equipment. A standard Pyrex-glass vacuum apparatus, equipped with Quickfit Rotaflow TF2/18 Teflon valves, was used for transfer of volatile materials. Otherwise, a dry-nitrogen glove bag was employed for transferring chemicals. The reactors were Pyrex vessels fitted with either stopcocks or Fischer-Porter Teflon valves depending whether subatmospheric or high pressures were required for the reaction conditions.

The Raman spectra were recorded with an instrument consisting of a Spectra-Physics Model 125 helium-neon laser and a Spex Model 1401 double monochromator. The samples were vacuum sealed in Pyrex tubes and excited by the 6328-Å laser line. The mass spectra were measured with a Varian Associates Model CH-7 mass spectrometer operating at 70 eV; the gas inlet system was at ambient temperature. Visible spectra were recorded with a Cary Model 14 spectrophotometer.

A. Preparation of $I_2Cl^+SbCl_6^-$. Antimony pentachloride (2.98 g, 10.0 mmol) and iodine (2.53 g, 9.97 mmol) were weighed into a 50-ml round-bottom Pyrex bulb containing several side arms and a stopcock attachment. A large excess of chlorine (*ca.* 5 ml) was distilled onto the reactants at −196°. The mixture was allowed to stand for 2 hr at −80°. The unreacted chlorine was distilled away while holding the reactor at the same temperature. A black solid was formed, but after slow sublimation, deep burgundy red crystals were obtained. The reaction was nearly quantitative and only a trace of $ICl_2^+SbCl_6^-$, visually observed by the characteristic color of the crystals, was also produced. Crystals of the two salts grow separately. The $I_2Cl^+SbCl_6^-$ was allowed to sublime into the side arms, kept at a slightly cooler than ambient temperature, which were sealed off *in vacuo*. The samples were then analyzed.

B. Preparation of $BrICl^+SbCl_6^-$. Antimony pentachloride (4.70 g, 15.7 mmol) and iodine monobromide (3.25 g, 15.8 mmol) were weighed into a 100-ml thick-walled Pyrex container with several side arms and equipped with a Fischer-Porter Teflon valve. Then chlorine (1.11 g, 15.7 mmol) was distilled into the reactor at −196°. The reactor was allowed to warm to room temperature over a period of several hours. The reactor was briefly vented and the $BrICl^+SbCl_6^-$ was allowed to sublime as above. Large dark red crystals were formed and the yield was substantially quantitative.

C. Direct Synthesis of $ICl_2^+SbCl_6^-$. A more simplified synthetic approach to $ICl_2^+SbCl_6^-$ than previously reported[4] which involved the separate preparation of ICl_3 is the following. Antimony pentachloride (7.00 g, 23.4 mmol) and iodine (2.90 g, 11.4 mmol) and an excess of chlorine (*ca.* 10 ml) were added to a reactor similar to that described in B. The mixture was allowed to react over a 20-hr period at 23°. The unreacted chlorine was pumped away at −80°. The synthesis was practically quantitative, although a trace of $I_2Cl^+SbCl_6^-$ was visually observed. The dichloroiodate salt can be purified by sublimation from the slight excess $SbCl_5$. A mixture of $I_2Cl^+SbCl_6^-$ and $ICl_2^+SbCl_6^-$ could be obtained by allowing antimony pentachloride and iodine in a 2:1 molar ratio to combine in excess liquid chlorine at −80°. In a typical experiment antimony pentachloride (1.70 g, 5.70 mmol) and iodine (0.72 g, 2.83 mmol) in an excess of liquid chlorine were permitted to interact at −80° for 3 hr in a reactor as in A. Roughly similar quantities of both salts were formed and some $SbCl_5$ remained. Crystals of the two salts grew separately from each other and the $SbCl_5$ mother liquor on standing and could be separated with tweezers.

D. Attempted Synthesis of the ICl_4^+ Cation. With $SbCl_5$. A reactor like that described in B was loaded with antimony pentachloride, iodine, and excess chlorine in a manner similar to method C ($SbCl_5$:I_2 = 2:1). The mixture was heated to 100° for several days, but the only product was $ICl_2^+SbCl_6^-$.

With SbF_5. A reactor like that in method B was loaded with antimony pentafluoride (3.85 g, 17.8 mmol) and iodine (2.26 g, 8.90 mmol) and excess chlorine (*ca.* 3 ml). The reactor was heated at 100° for 24 hr. The unreacted chlorine was pumped out at −80°. The increase in weight corresponded to a take-up of 2.05 g (28.9 mmol) of chlorine. A red-orange gelatinous mass was formed whose stoichiometry approximates $ICl_2^+SbF_5Cl^-$, *i.e.*, $I_2 + 2SbF_5 + 3Cl_2 \rightarrow 2ICl_2^+SbF_5Cl^-$.

Table I. Mass Spectra

Mass no.	Species	Rel abund I_2Cl^+	Rel abund $BrICl^+$	Rel abund ICl_2^+
35	$^{35}Cl^+$	55	63	72
36[a]	$H^{35}Cl^+$	70	50	80
37	$^{37}Cl^+$	20	30	40
38[a]	$H^{37}Cl^+$	31	23	55
63.5	I^{2+}	5	15	15
70	$^{35}Cl_2^+$	36	35	53
72	$^{35}Cl^{37}Cl^+$	26	23	37
74	$^{37}Cl_2^+$	3	3	4
79	$^{79}Br^+$		20	
81	$^{81}Br^+$		21	
114	$^{79}Br^{35}Cl^+$		28	
116	$^{79}Br^{37}Cl^+$, $^{81}Br^{35}Cl^+$		33	
118	$^{81}Br^{37}Cl^+$		6	
127[b]	I^+	100	100	100
158	$^{79}Br_2^+$		5	
160	$^{79}Br^{81}Br^+$		9	
162	$^{81}Br_2^+$ and/or $I^{35}Cl^+$	40	83	42
164	$I^{37}Cl^+$	13	33	14
206	$I^{79}Br^+$		11	
208	$I^{81}Br^+$		11	
254	I_2^+	35	20	25

[a] Due to hydrogen abstraction on the walls of the mass spectrometer. [b] The 127 mass ion is assigned a relative intensity of 100 in each case.

Elemental Analyses. Glass tubes in which samples were sealed were introduced into 1 *N* NaOH solutions containing excess potassium tartrate and sodium sulfite. After breaking the sealed tubes the solutions were allowed to stand for *ca.* 1 hr, then neutralized with dilute sulfuric acid, and finally boiled for several hours to ensure the complete removal of the SO_2. The solutions were diluted to known volumes. Aliquots were then measured and the halogens determined by potentiometric titration with silver nitrate using calomel and silver electrodes. *Anal.* Calcd for Cl_7I_2Sb: I, 40.7; Cl, 39.8. Found: I, 40.8; Cl, 39.8. Calcd for $BrCl_7ISb$: Br, 13.9; Cl, 43.0; I, 22.0. Found: Br, 14.8; Cl, 42.7; I, 21.7. The equivalence point for the bromide was somewhat obscured.

Mass Spectra. The results are recorded in Table I.

Visible Spectra. Spectra have been recorded by shining light through crystals in sealed tubes. The spectrum of $ICl_2^+SbCl_6^-$ has a maximum at 470 nm and a shoulder at 590 nm. That of $I_2Cl^+SbCl_6^-$ shows a maximum at 450 nm. Dissolved in oleum, the latter shows absorptions 642 and 460 nm.

Results and Discussion

The first mention of a substance having a composition I_2SbCl_7 from the combination of ICl and $SbCl_5$ was by Ruff.[6a] In a later study of the $AlCl_3$-ICl phase system, it was reported that a eutectic point existed corresponding to the composition $AlCl_3 \cdot 2ICl$.[6b] A recent nqr study of this composition suggests the ionic formulation $I_2Cl^+AlCl_4^-$.[7] The cation also has been reported in solution.[8] Still, no viable synthesis of salts containing this cation has been reported. It has now been found that when antimony pentachloride and iodine in a 1:1 molar ratio react at −80° in liquid chlorine, $I_2Cl^+SbCl_6^-$ results in high yield. When the ratio is changed to 2:1, then mixtures of $I_2Cl^+SbCl_6^-$ and $ICl_2^+SbCl_6^-$ are produced under similar conditions. However, at room temperature and consequently higher chlorine pressure, $ICl_2^+SbCl_6^-$ is nearly quantitatively synthesized. It is interesting to note, therefore, that once I_2Cl^+ is formed, there is

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(5) G. Brauer, "Handbook of Preparative Inorganic Chemistry," Vol. 1, 2nd ed, Academic Press, New York, N. Y., 1963, p 291.

(6) (a) O. Ruff, J. Zedner, and L. Hecht, *Ber.*, 48, 2073 (1915); (b) Ya. A. Falkov and O. I. Shor, *Zh. Obshch. Khim.*, 19, 1787 (1949).

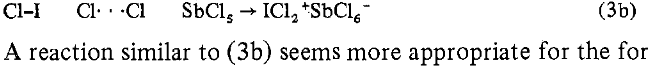
(7) D. J. Merryman, P. A. Edwards, J. D. Corbett, and R. E. McCarley, *J. Chem. Soc., Chem. Commun.*, 779 (1972).

(8) R. A. Garrett, R. J. Gillespie, and J. B. Senior, *Inorg. Chem.*, 4, 563 (1965).

resistance to further oxidation to ICl_2^+, even though the conditions are otherwise right for further chlorination to take place. Both ICl and ICl_3 are formed by allowing the reactants to combine at $-80°$, the formation of either being dependent on the relative reactant concentrations; *i.e.*, in the presence of excess chlorine ICl_3 is formed. Therefore, one would expect the formation of ICl_2^+ in the presence of $SbCl_5$ and excess chlorine. Nevertheless, if the proper ratio of I:Sb = 1:1 is used, the reaction yields $I_2Cl^+SbCl_6^-$ which can be considered a derivative of ICl even though enough chlorine is present to form ICl_3. This would indicate that once I_2Cl^+ is formed, it is stabilized as the ionic salt and further chlorination at $-80°$ is resisted.

Two routes to $ICl_2^+SbCl_6^-$ are apparent, one involving ICl_3 and the other ICl in the presence of chlorine in a three-body reaction, *i.e.*

$$ICl_3 + SbCl_5 \rightarrow ICl_2^+SbCl_6^- \quad (3a)$$



$$Cl\text{-}I \quad Cl\cdots Cl \quad SbCl_5 \rightarrow ICl_2^+SbCl_6^- \quad (3b)$$

A reaction similar to (3b) seems more appropriate for the formation of I_2Cl^+, *i.e.*, reaction between antimony pentachloride and either two molecules of ICl or a molecule each of chlorine and iodine. Two plausible routes to the formation of $BrICl^+$ are suggested. One involves the intermediate $BrICl_2$, in a reaction similar to (3a) and based on equilibrium 1b, which has never been isolated, although a report alludes to it.[9] In a separate experiment, an orange-yellow solid is formed at $-80°$ according to the equation

$$2IBr + Cl_2\ (\text{excess}) \overset{?}{\rightarrow} BrICl_2$$

but decomposes on warming. Reaction 3b involving IBr could also yield the desired product. Combining antimony pentachloride or pentafluoride, iodine, and chlorine at elevated temperatures and pressures did not facilitate the stabilization of iodine(V) chloride as a cation. Only iodine(III) was produced.

The mass spectra of the vapor phases in equilibrium with the solids show that the three salts considered herein dissociate to a small extent to molecular species. This is consistent with the reported dissociation of $ClF_2^+BF_4^-$ [10] as well as the ease of their sublimation. As can be seen from Table I, halogen and interhalogen species are generated from these cations. Although the spectra of the ICl_2^+ and I_2Cl^+ salts show similarities, it is observed that the relative intensities of the ions generated from chlorine are greater in the spectrum of the former. This suggests but does not prove that ICl_3 is formed from $ICl_2^+SbCl_6^-$ and is the precursor to ICl and Cl_2. A sample of ICl_3 in the mass spectrometer produced a similar spectrum. Also, the ICl^+ ion is more intense than the IBr^+ ion in the spectrum of $BrICl^+SbCl_6^-$. This is to be expected based on the interhalogen bond dissociation energies.

The implication of the visible spectra is not clear, although the maxima for $I_2Cl^+SbCl_6^-$ at 642 and 460 nm are close to the principal absorptions of I_2^+ (646 nm) and ICl (460 nm).

Raman Spectra. Most Raman data collected so far have been relevant to the various interhalide anions, although only recently the spectrum of $ICl_2^+SbCl_6^-$ was studied.[11] The materials examined in the present work are very deeply colored, from deep red in the case of $BrICl^+$ to a deeper, darker burgundy red in the case of I_2Cl^+. The latter crystals are almost black when viewed through thick areas, although the He-Ne laser (6328 Å) could be used to study these materials. One more difficulty was encountered because these crystals sublime at room temperature and the heat from the laser creates volatilization.

The Raman spectra of both $I_2Cl^+SbCl_6^-$ and $BrICl^+SbCl_6^-$ are presented in Figure 1, and the numerical data from the observed spectra and the spectra of related compounds are summarized in Table II. The spectra will be discussed separately.

A. $I_2Cl^+SbCl_6^-$. The spectrum of this salt exhibits the three expected Raman-active fundamentals (one of which is split) of the O_h symmetrical anion. These frequencies are measured at 334 (ν_1), 296, 260 (ν_2, doublet), and 177 cm^{-1} (ν_5). The lowest frequency absorption appears as a broad band on the low-frequency side of the narrower and more intense peak at 190 cm^{-1}. All the above frequencies are in good agreement with those of other salts containing the hexachloroantimonate ion.[12] The remaining lines are assigned to the cation. This ion, whether linear or bent, could be formulated as having a symmetric $(I\text{-}Cl\text{-}I)^+$ structure or an asymmetric $(I\text{-}I\text{-}Cl)^+$ structure. Since three Raman lines are observed, a symmetric cation must be bent with C_{2v} symmetry. In this case, both stretching frequencies, asymmetric and symmetric, should be close together providing the bond angle approaches 90°, but this is not the case in the observed spectrum. Only one band at 356 cm^{-1}, with a shoulder at 350 cm^{-1}, assigned to the I-Cl stretching frequency, is present. The splitting into a doublet results from the isotopic effect of ^{35}Cl and ^{37}Cl and would be expected to be manifest in the I-Cl stretching absorption. Based on a two-mass model, the calculated ratio is $\nu(I\text{-}^{35}Cl)/\nu(I\text{-}^{37}Cl) = 1.02$, which is actually the observed ratio. Other bands at 190 and 126 cm^{-1} are assigned to the I-I stretching and the ionic bending modes, respectively. Both stretching modes are at slightly lower frequency than those of the ICl and I_2 molecules. This feature will be discussed in greater detail below. Consequently, the I_2Cl^+ cation has an asymmetric I-I-Cl structure, but it cannot be deduced whether the ion is linear or bent. In either case, all three vibrations are Raman active. However, based on the structure of other interhalogen cations such as ICl_2^+,[13] Cl_2F^+,[14,15] and ClF_2^+,[16] the best assumption is an angular configuration. The splitting of the ν_2 (E_g) of the $SbCl_6^-$ is attributed to the removal of the degeneracy in the solid state and indicates that this anion is distorted from O_h symmetry or could possibly result from site symmetry lowering. Similar splittings of this nature are observed in the spectra of other hexafluoro anions like AsF_6^- and SbF_6^-.[15,16] In the latter cases the splitting has been attributed to fluorine bridging between the cation and anion, reducing the octahedral symmetry of the ion. Similarly, it can be suggested that chlorine bridging exists in $I_2Cl^+SbCl_6^-$ which has been indicated by X-ray examination.[13] The absorption at 91 cm^{-1} is probably due to a lattice vibration.

B. $BrICl^+$. In the spectrum of $BrICl^+SbCl_6^-$, again three of the observed lines 323 (ν_1), 268 (ν_2), and 177, 170 cm^{-1} (ν_5) are from the anion. The remaining are assigned to the cation. Their frequencies would vary with regard to the cen-

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[9] M. Pasternak and T. Sonnino, *J. Chem. Phys.*, 48, 1967 (1968).

[10] H. Selig and J. Shamir, *Inorg. Chem.*, 3, 294 (1964).

[11] J. Shamir and R. Rafaeloff, to be submitted for publication.

[12] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," 2nd ed, Wiley-Interscience, New York, N. Y., 1970, p 123.

[13] C. G. Vonk and E. H. Wiebenga, *Acta Crystallogr.*, 12, 859 (1959).

[14] A. J. Edwards and R. J. C. Sills, *J. Chem. Soc. A*, 2697 (1970).

[15] R. J. Gillespie and M. J. Morton, *Inorg. Chem.*, 9, 616 (1970).

[16] R. J. Gillespie and M. J. Morton, *Inorg. Chem.*, 9, 811 (1970).

Table II. Raman Frequencies of Related Species, $\Delta\nu$ (cm^{-1})

ICl[a]	IBr[a]	I_2[b]	$ICl_2^+SbCl_6^-$ [11]	$BrICl^+SbCl_6^-$	$I_2Cl^+SbCl_6^-$	Assignment for anion	Assignment for cation
382			372 (asym)	370[d] (100)[c]	356[d] (100)		I–Cl str
			366 (sym)	362[d] sh	350[d] sh		
			324	323 (47)	334 (28)	ν_1 (A_{1g})	
			271	268 (22)	296 (11)	ν_2 (E_g)	
					260 (12)		
	262			255 (37)			I–Br str
		205			190 (21)		I–I str
			176	177 (16)	177 (9)	ν_5 (F_{2g})	
				170 (19)			
			149	149 (16)	126 (20)		Bend
				125	91		Lattice vib
				70			

[a] H. Siebert, "Anwendung der Schwingungsspektroskopie in der Anorganischen Chemie," Springer-Verlag, Berlin, 1966, p 40. [b] J. Shamir and H. H. Claassen, to be submitted for publication. [c] The numbers in parentheses are relative intensities. [d] Isotope splitting from ^{35}Cl and ^{37}Cl.

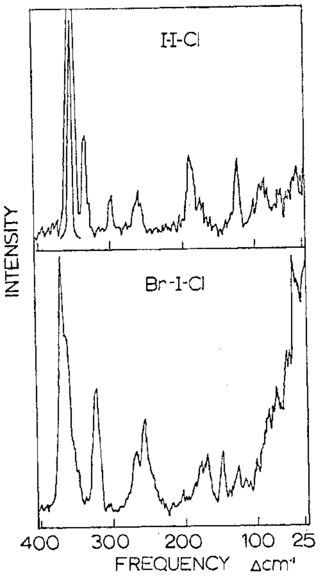

Figure 1. Raman spectra of $I_2Cl^+SbCl_6^-$ and $BrICl^+SbCl_6^-$ using the 6328-Å exciting line.

tral atom, being one of the three halogens: I $(Br–I–Cl)^+$, II $(I–Br–Cl)^+$, or III $(Br–Cl–I)^+$. In this spectrum an I-Cl stretching frequency at 370 cm^{-1} is present, ruling out structure II. It has been observed already that the halogen–halogen frequencies for the cations are slightly lower than those for the neutral molecules. Therefore, it would be expected that the Br-Cl frequency of structure III should be in the 425-435-cm^{-1} range, close to the stretching frequency of the Br-Cl molecule. Since no band is present in this region, structure III is unlikely as well. Finally, the spectrum does show a band at 255 cm^{-1}, just slightly lower than the frequency of the I-Br molecule as would be expected. Therefore, the spectral data are most consistent with structure I, which fits into the general pattern of the central atom being the most electropositive. The I-Cl stretching frequency, which is observed at 370 cm^{-1} having a shoulder at 362 cm^{-1}, shows the expected splitting resulting from the isotope effect that has been reported above. From the spectrum itself, again, it cannot be deduced whether the cation is linear or bent, for, in both cases, all three vibrations are Raman active. However, based on arguments similar to those presented in section A, the $BrICl^+$ cation is probably bent. One band at 125 cm^{-1} does not consistently appear in all spectra of this salt. If it is real, then it is likely to be a lattice vibration as is also that at 70 cm^{-1}.

Table III. Force Constants (10^5 dyn cm^{-1})

	I_2Cl^+	$BrICl^+$	ICl	I_2	IBr
f(I-Cl)	2.07	2.23	2.35		
f(I-I)	1.35			1.60	
f(I-Br)		1.88			1.98

C. Stretching Frequencies Related to Mass, Oxidation Numbers, and Coordination Numbers. By comparing the I-Cl stretching frequencies in the series $X–I–Cl^+$ (X = Cl, Br, I), it is found that as X becomes heavier, ν(I-Cl) generally decreases, *i.e.*, $\nu(ICl_2^+) \approx \nu(BrICl^+) > \nu(I_2Cl^+)$, using $(372 + 366)/2 = 369$ for ICl_2^+, 370 for $BrICl^+$, and 356 cm^{-1} for I_2Cl^+, respectively. Furthermore, it has been shown that stretching frequencies usually increase with an increase of oxidation number of the central atom and decrease with an increase of coordination number of the central atom.[16] To compare the stretching frequencies I-Cl, I-Br, I-I of the cations to those of the molecules ICl, IBr, I_2, two opposing effects must be considered. An increase in the oxidation number of the central iodine tends to increase the frequency, whereas an increase in its coordination number causes a decrease in the frequency. In the observed spectra of the cations, the stretching frequencies are slightly lower than those of the related molecules. Hence, the change in coordination number is a greater influence than the change in oxidation number.

It is also interesting to note that the relative changes of the two stretching frequencies in the same cation compared to those of the corresponding neutral molecules are similar. To illustrate for the I_2Cl^+ cation

$$\frac{\nu(\text{I-Cl})}{\nu(\text{ICl})} = 0.93, \quad \frac{\nu(\text{I-I})}{\nu(\text{I}_2)} = 0.93$$

and for the $BrICl^+$ cation

$$\frac{\nu(\text{I-Cl})}{\nu(\text{ICl})} = 0.97, \quad \frac{\nu(\text{I-Br})}{\nu(\text{IBr})} = 0.97$$

The I-^{35}Cl stretching frequency is used in each case. These changes indicate that treating the I-Cl and I-X stretching frequencies separately as a two-mass model is valid to the first approximation. Actually, some coupling of the vibrations in the cation will cause slight variations in the frequencies.

D. Force Constants. According to Siebert,[17] it is possible to calculate approximate force constants by using the principal vibrational frequency and neglecting coupling with other frequencies. On this basis, force constants were calculated for the various cationic stretching vibrations. These are close

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(17) H. Siebert, "Anwendung der Schwingungsspektroskopie in der Anorganischen Chemie," Springer-Verlag, Berlin, 1966, p 33.

to those of the binary molecules as illustrated in Table III.

Registry No. I_2, 7553-56-2; Cl_2, 7782-50-5; IBr, 7789-33-5; $SbCl_5$, 7647-18-9; $(I_2Cl)SbCl_6$, 38656-79-0; $(BrICl)SbCl_6$, 38656-80-3; $(ICl_2)SbCl_6$, 38656-81-4.

Acknowledgments. J. S. thanks the National Science Foundation for having granted him a Senior Foreign Scientist Fellowship. We thank Argonne National Laboratory, Chemistry Division, for making available its laser Raman equipment. We also thank Dr. L. Katzin of the same division for helpful discussions and Mrs. A. Silberstein of the Nuclear Research Center, Soreq, Israel, for technical assistance.

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Proton Nuclear Magnetic Resonance Determination of the Cis and Trans Methanol Exchange Rates of $Co(CH_3OH)_5OH_2{}^{2+}$

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Received August 30, 1972

The methanol-exchange rate constants per coordinated solvent molecule for the methanols cis and trans to H_2O in $Co(CH_3OH)_5OH_2{}^{2+}$ were determined by direct observation of the methyl proton resonances of the coordinated methanol. The composition of the sample as a function of temperature was obtained by measuring the relative integrated intensities of the cis aquo complex resonance and that corresponding to $Co(CH_3OH)_6{}^{2+}$. With this information it was possible to interpret the exchange-induced relaxation and shifts of the bulk methanol methyl resonance in terms of an overall solvent-exchange rate constant. Comparison of the exchange data from the coordinated and bulk resonances indicated there was no exchange-induced rearrangement taking place in the aquo complex. The cis and trans sites were found to have equal exchange rate constants *per coordinated methanol* (609 sec^{-1} at $-30°$). The enthalpy and entropy of activation were 12.8 kcal mol^{-1} and 6.9_6 eu, respectively.

It is well established that the measurement and understanding of solvent-exchange rates is, in general, an important key to understanding the kinetics of substitution reactions for labile octahedral complexes.[1] Studies of the methanol-exchange rates of a number of $Co(CH_3OH)_5X^n$ complexes are being undertaken in this laboratory in an attempt to correlate the observed exchange kinetics with the properties of the monodentate ligands X (where n is the charge on the complex).[2] The reasons for studying the $Co(CH_3OH)_5OH_2{}^{2+}$ complex are twofold. First, significant differences between the kinetic parameters observed in this laboratory and those of a previous study were found.[3] Second, water is a common "impurity" in the cobalt(II)-methanol system and for that reason it is desirable to have a firm understanding of its effect on the methanol-exchange rates.

Variable-temperature studies of the transverse relaxation times and shifts of both the coordinated and bulk methanol methyl resonances are reported in this paper. A much more complete study of the bulk solvent resonance than in the previous study[2] was made and yielded more definitive results concerning the kinetic trans effect and internal rearrangements in the aquo complex.

Experimental Section

Sample Preparation. An anhydrous methanol solution of cobaltous perchlorate was prepared by adding cobaltous perchlorate to methanol and treating repeatedly with Linde 3A molecular sieves. The solution was considered sufficiently anhydrous when no coordinated methanol methyl resonance for the cis coordination site in $Co(CH_3OH)_5OH_2{}^{2+}$ could be detected. The concentration of Co^{2+} was determined by an EDTA back-titration with Zn^{2+} using Eriochrome Black T as an indicator.[4] The water was introduced into the sample with a microliter syringe fitted with a device for reproducible ejection of aliquots, and the size of the aliquot was calibrated with mercury. All the shift and relaxation data for the coordinated and bulk solvent resonances were made on samples having a total Co^{2+} concentration of 0.216 M and a total water concentration of 0.470 M. All samples were prepared in a glove bag under dry nitrogen.

Instrumentation and Measurements. All nmr measurements were made on a Jeolco 4H-100 100-MHz instrument. The spectrum was acquired as a 1000 data point digital representation in a minicomputer and was subsequently transferred to a PDP-10 where a total line shape analysis of the spectrum was carried out. A more complete description of the instrument, its modifications, the data acquisition system, and the data processing system is given elsewhere.[2]

The kinetic information is obtained from the nuclear magnetic relaxation times, T_2, and shifts of the methanol methyl resonances of both the coordinated and bulk solvent. T_2 is obtained from line shape analysis of the nmr resonances, where the half-width at half-height, expressed in radians per second, is the reciprocal of T_2. The equations relating the experimental data to the kinetic parameters are most conveniently expressed in terms of line widths, $1/T_2$; therefore, the subsequent presentation of data and their discussion will be expressed in terms of line widths rather than relaxation times. Digital techniques for data acquisition and processing are necessary to obtain accurate values of T_2 and relative integrated intensities of overlapping resonances. Numerical data processing techniques are a necessary adjunct in obtaining accurate shifts of bulk solvent resonances because the maximum of the observed line is a sensitive function of the phasing of the signal (*i.e.*, the amount of dispersion in the signal). The computer programs for processing the data take into account the necessary phasing corrections.

All measurements were carried out under conditions of slow passage and nonsaturation. The temperature was maintained to within ±0.2°.

Data and Results

For the reagent concentrations used in this study, the only nmr resonances observed were for the $Co(CH_3OH)_6{}^{2+}$ and $Co(CH_3OH)_5OH_2{}^{2+}$ complexes. The two most intense resonances observed were, of course, those of the bulk methanol hydroxyl and methyl protons. Three much less intense resonances located downfield relative to the bulk methyl resonance were identified as the methyl resonances of the meth-

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