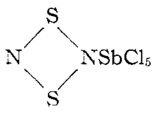
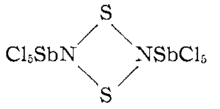
and 723 (mw) cm^{-1} are expected from the lowering of symmetry resulting from the nonequivalence of the nitrogen atoms. Distinction between the possible configurations of the S_2N_2 group [planar ring (C_{2v}), puckered ring (C_s), or chain ($C_{\infty v}$, C_s, or C_1)] is not possible inasmuch as five or six infrared-active modes are predicted for each configuration. That the ring is broken (chain), however, is unlikely because of the ease of interconversion of $S_2N_2SbCl_5$ and $S_2N_2(SbCl_5)_2$, the similarity to the S_2N_2 modes, and the lack of higher frequency bands expected for terminal N–S groups. The 1005-cm^{-1} band can be reasonably assigned to an S–N ring system, because bands have been observed[2] for the S–N ring system in $S_4N_4SbCl_5$ in the same region (at 1060 and 968 cm^{-1}).

The possibility that the compounds $S_2N_2(SbCl_5)_2$ and $S_2N_2SbCl_5$ are tetra- and diadducts of S_4N_4 was considered. However, the observed bands showed no correlation with those of S_4N_4 or $S_4N_4SbCl_5$, and the forms of highest symmetry for $S_4N_4(SbCl_5)_4$ (planar ring, D_{4h}) and $S_4N_4(SbCl_5)_2$ (planar ring, D_{2h}) predict four and eight observed modes, respectively. The lack of correlation in frequency and number of observed modes makes these formulations unlikely.

The infrared and chemical evidences support the formulation of $S_2N_2SbCl_5$ and $S_2N_2(SbCl_5)_2$ as adducts of the difunctional Lewis base S_2N_2 with the structures



(puckered or planar ring)



(planar ring)

A recent X-ray diffraction study of $S_2N_2(SbCl_5)_2$ confirms the second of these predicted structures.[15]

Acknowledgment.—This work was supported by the United States Atomic Energy Commission.

[15] R. L. Patton and K. N. Raymond, unpublished work.

Contribution from the Department of Chemistry of the University of California and the Inorganic Materials
Research Division of the Lawrence Radiation Laboratory, Berkeley, California 94720

Reactions of Disulfur Dinitride with Boron Trifluoride and Boron Trichloride

By R. LYLE PATTON and WILLIAM L. JOLLY

Received October 28, 1968

Disulfur dinitride reacts with boron trichloride in dichloromethane to form the following compounds (each of which can be obtained as the principal product by suitable choice of reaction conditions): $S_4N_4BCl_3$, $S_2N_2(BCl_3)_2$, and an apparently polymeric material $(S_2N_2BCl_3)_x$. At 0°, $S_2N_2(BCl_3)_2$ loses BCl_3 to form a simple adduct $S_2N_2BCl_3$ which can be reconverted to the diadduct by treatment with BCl_3 at −78°. Whereas $SbCl_5$ displaces BCl_3 from $S_2N_2BCl_3$ to form $S_2N_2(SbCl_5)_2$, the polymeric material $(S_2N_2BCl_3)_x$ is inert toward both BCl_3 and $SbCl_5$. The properties of $S_2N_2BCl_3$ and $S_2N_2(BCl_3)_2$ indicate that the S_2N_2 ring structure remains intact. Reaction of S_2N_2 with BF_3 yields only $S_4N_4BF_3$.

In a study of the reactions of S_2N_2 with $SbCl_5$ we have shown that S_2N_2 forms the adducts $S_2N_2SbCl_5$ and $S_2N_2(SbCl_5)_2$, in which the S_2N_2 ring remains intact.[1] To explore further the reactions of S_2N_2 as a Lewis base and the effects of coordination upon its stability, this study has been extended to include boron trifluoride and boron trichloride.

Experimental Section

General Data.—The methods for the manipulation and characterization of volatile and moisture-sensitive materials and for the preparation of S_2N_2 have been described.[1] Boron trichloride and boron trifluoride (Matheson) and antimony pentachloride (J. T. Baker Co.) were purified by vacuum-line fractional condensation. The observed 0° vapor pressure of the BCl_3 was 477 mm (lit.[2] 477 mm). The observed −111.6° vapor pressure of BF_3 was 310 mm (lit.[3] 312 mm). Boron trifluoride was measured by pressure–volume methods, and BCl_3, $SbCl_5$, and S_2N_2 were measured by weight loss of tared storage bulbs after distillation *in vacuo* into reaction vessels.

Reactions were normally carried out in a vacuum-line reactor consisting of a small erlenmeyer flask attached by a 14/20 ground joint (sealed with Kel-F wax) to a Delmar–Urry 0–4-mm O-ring stopcock. The absence of grease prevented absorption of solvents and allowed use of the reactor as a tared vessel for determining solid product weights. In a typical study, S_2N_2 and CH_2Cl_2 were distilled into the reactor, warmed to 20° to dissolve the S_2N_2, and then rapidly frozen at −196°. The volatile Lewis acid was then distilled in, and the reactor was warmed to the desired reaction temperature. The solvent and volatile products were removed and separated *in vacuo*, and the remaining nonvolatile solids were weighed and then removed in the glove bag. Antimony pentachloride and BF_3 could be cleanly fractionated from CH_2Cl_2 and directly measured, whereas BCl_3 could not and was determined by hydrolysis and titration of the boric acid with standard NaOH in the presence of mannitol.

Reaction of S_2N_2 with BF_3.—Disulfur dinitride (0.71 mmol), BF_3 (3.175 mmol), and CH_2Cl_2 (4 ml) were distilled into a reactor at −196°. Upon warming to −78°, a white suspension formed which became yellow at −45°, brown at 0°, and slowly formed an intense burgundy solution at 20°. The CH_2Cl_2 and excess BF_3 (2.817 mmol) were pumped off, leaving 84 mg

---

[1] R. L. Patton and W. L. Jolly, *Inorg. Chem.*, **8**, 1389 (1969).
[2] A. Stock and O. Pries, *Chem. Ber.*, **47**, 3109 (1914).
[3] O. Ruff, A. Braida, O. Bretschneider, W. Menzel, and H. Plaut, *Z. Anorg. Allgem. Chem.*, **206**, 59 (1932).

of a burgundy solid which was identified as $S_4N_4BF_3$ on the basis of its infrared spectrum,[4] its melting point of 145° (lit.[4] mp 145–147°), and its characteristic of slowly losing BF_3 when pumped on at room temperature. Complete conversion of S_2N_2 to $S_4N_4BF_3$ requires 0.355 mmol of BF_3 (obsd, 0.358 mmol), forming 83 mg of $S_4N_4BF_3$.

S_2N_2–BCl_3 Reaction at 0°.—Disulfur dinitride (1.55 mmol), BCl_3 (4.97 mmol), and CH_2Cl_2 (10 ml) were frozen together in a reactor at −196°. The mixture was held at −78° for 2 hr while the CH_2Cl_2 melted and the solution above the white solid became slightly yellow. The mixture was then warmed slowly to 0° while stirring. Only slight darkening of the suspension occurred until the temperature reached −35°, above which the suspension turned, in rapid succession, yellow, gray, gray-green, black, brown, and yellow. Then with brief effervescence, a dark red solution formed. During 0.5 hr at 0° this solution slowly turned light orange, and a slight film of an orange plastic material appeared. The appearance of the solution was then unaffected by warming to 20° or cooling to −78°. The reaction mixture was held at −78° while BCl_3 was distilled off *in vacuo* and then warmed to 0° while removing the remaining CH_2Cl_2. A slight amount of N_2 (0.017 mmol) was evolved in the reaction. No precipitation occurred during the solvent removal, but as the last of the CH_2Cl_2 distilled off, the solution darkened to orange-brown and finally left 0.314 g of a solid plastic-like layer (calcd for 1.55 mmol of $(S_2N_2BCl_3)_x$: 0.324 g). Repeated cooling to −196° and warming to 0° broke up this solid, but no further gases were evolved.

Several similar reactions were run with variations in the time held at −80°, the rate of warming, and the time held at 0°. The visual observations of the reactions and products were the same. All of the results are summarized in Table I. Only N_2, CH_2Cl_2, BCl_3, and slight traces of S_2Cl_2 were distilled from the reactions, leaving a product of composition $(S_2N_2BCl_3)_x$.

TABLE I

REACTIONS OF S_2N_2 WITH BCl_3 AT 0°

$[S_2N_2]$, mmol	$[BCl_3]/[S_2N_2]$	N_2 evolved, mmol	Product wt, mg	Calcd wt for $(S_2N_2BCl_3)_x$, mg
0.54	5.1	Trace	108	113
0.77	4.8	0.003	161	161
1.16	2.6	0.011	240	242
1.42	3.2	0.015	300	297
1.55	3.2	0.017	314	324
2.90	3.2	Trace	607	607

Nujol mulls of these products all absorbed strongly throughout the region 670–1350 cm^{-1} with prominences on this general broad absorption occurring at 1300, 1240, 1080, 970, and 730 cm^{-1}. Broad absorptions also occurred at 640 and 510 cm^{-1}. These absorption maxima differed slightly in different samples in position and relative intensity.

After removal from the reactor, the product did not redissolve in either CH_2Cl_2 or CCl_4 at 20°, although some darkening of the solvent and S_2Cl_2 evolution occurred. Distillation of CH_2Cl_2 back into the reactor once resulted in slight coloring of the solvent and release of S_2Cl_2 and, in another case, in vigorous N_2 evolution at −10°.

In a sealed capillary the $(S_2N_2BCl_3)_x$ remained solid on heating to 360°, becoming brown above 120° and shrinking with evolution of a yellow liquid above 160°. When $(S_2N_2BCl_3)_x$ was held at 20° for 4 weeks or at 55° for 4 days, considerable decomposition occurred, with formation of BCl_3, S_2Cl_2, N_2, and traces of SCl_2. Pyrolysis at 90° or higher yielded S_2Cl_2, SCl_2, N_2, and only traces of BCl_3. (Passing the volatile products through a −80, −112, −196° fractionation train stopped S_2Cl_2, SCl_2, and BCl_3, respectively, which were then identified by their infrared spectra.[3]) The relative amounts of the volatile products and the empirical composition of the residue did not correspond to any unique stoichiometry.

Liquid boron trichloride (10.70 mmol) was distilled onto 161 mg of $(S_2N_2BCl_3)_x$, and the mixture was held at 0° for 2 hr, then cooled to −78°, and held for 1 hr before pumping off the BCl_3 at that temperature. Exactly 10.70 mmol of BCl_3 was recovered, indicating that no BCl_3 uptake by $(S_2N_2BCl_3)_x$ occurred at −78°. Antimony pentachloride (3.11 mmol) was then distilled onto the $(S_2N_2BCl_3)_x$, and the mixture was twice held at 20° for 30 min followed by cooling to −78° and pumping. No gases were removed. The reactor was then warmed to 20° while pumping to remove all of the free $SbCl_5$. No BCl_3 or other gases were removed and the product weight remained 161 mg. Antimony pentachloride obviously did not displace BCl_3 from or add to the $(S_2N_2BCl_3)_x$.

S_2N_2–BCl_3 Reaction at −78°.—When suspensions of S_2N_2, CH_2Cl_2, and excess BCl_3 were held for extended periods at −78° and then subjected to pumping at that temperature to remove the CH_2Cl_2 and excess BCl_3, measurement of the unreacted BCl_3 showed that products approaching the composition $S_2N_2(BCl_3)_2$ were obtained. The reaction times and calculated $[BCl_3]/[S_2N_2]$ ratios for the products for several runs were: 6 hr, 1.67; 15 hr, 1.83; 2.5 days, 1.865; 5 days, 1.96; 6.5 days, 1.83. When the product of the 6.5-day run (containing 0.86 mmol of S_2N_2 and 1.57 mmol of BCl_3) was warmed slowly while pumping, the creamy white solid evolved 0.70 mmol of BCl_3 between −35 and 0°. Further pumping at 0° for 2 hr evolved 1 mg of S_2Cl_2 and no BCl_3. These data correspond to an empirical product composition $S_2N_2 \cdot 1.01BCl_3$; the product weight (178 mg) was also in good agreement with that calculated for the formation of $S_2N_2BCl_3$ (179 mg). (In each of the above runs, similar evolution of BCl_3 on warming to 0° left a product composition of $S_2N_2BCl_3$.) The remaining solid was treated with a measured excess of BCl_3 in CH_2Cl_2 at −78° for 2 hr, and then the reaction mixture was evacuated at that temperature. The product retained 0.625 mmol of the BCl_3, but all of this BCl_3 was evolved when the product was again warmed to 0° *in vacuo*. In a repetition of this procedure without CH_2Cl_2, 0.615 mmol of BCl_3 was retained at −78° and then evolved at 0°. In a second repetition of the procedure, 0.56 mmol of BCl_3 was retained at −78° and then evolved at 0°. Then the remaining product was treated with 3.90 mmol of antimony pentachloride at 20° for 1 hr. After cooling to −78° for 0.5 hr, the reactor was evacuated at −78°, and BCl_3 was removed. The reactor (still containing the $SbCl_5$) was twice warmed to 20°, returned to −78° for further BCl_3 removal, and then warmed to 20° to pump off the $SbCl_5$. The total BCl_3 removed (0.55 mmol) corresponded to the BCl_3 reversibly absorbed in the previous treatment (0.56 mmol). The weight gain, corrected for the BCl_3 lost, corresponded to the absorption of 1.08 mmol of $SbCl_5$.

A similar sequence of experiments, in which BCl_3 was absorbed at −78° and removed at 0°, was performed on the product of the 15-hr run mentioned above containing originally 1.30 mmol of S_2N_2. The final BCl_3 treatment, in which 1.03 mmol of BCl_3 was evolved at 0°, was again followed by treatment with excess $SbCl_5$. A 0.99-mmol amount of BCl_3 was evolved while 2.05 mmol of $SbCl_5$ was retained. The infrared spectrum of the products after treatment with $SbCl_5$ showed the presence of $S_2N_2(SbCl_5)_2$.[1] Extraction of the product with dichloromethane yielded a solution from which pure $S_2N_2(SbCl_5)_2$ was obtained (identified by its infrared spectrum[1]) and left some residue with the appearance and infrared spectrum of $(S_2N_2BCl_3)_x$.

The creamy white products of composition $S_2N_2BCl_3$ yellowed slightly when warmed at 0° during the course of subsequent BCl_3 treatments and slowly darkened to orange with evolution of S_2Cl_2 when warmed above 0°. However, at −15° in sealed tubes the material remained stable indefinitely without darkening or change in its infrared absorptions. In a sealed capillary it turned red-orange at 50° before melting at 55° with decomposition.

When dichloromethane was distilled onto $S_2N_2BCl_3$ at −196° and warmed to −78°, the conversion of $S_2N_2BCl_3$ to $(S_2N_2BCl_3)_x$

---

(4) K. J. Wynne and W. L. Jolly, *Inorg. Chem.*, **6**, 107 (1967).

occurred relatively rapidly, with rapid darkening of the solution. Whenever excess BCl_3 was present, darkening of the solution did not occur until around −35°.

In Nujol mulls, the infrared spectra of fresh samples of $S_2N_2BCl_3$ showed the following peaks (in cm^{-1}): 1115 (ms), 950 (w), 840 (m), 788 (wm), 728 (s, b), 682 (mw), 610 (ms), and 467 (m). An $S_2N_2BCl_3$ sample was allowed to stand 24 hr at 20° and a Nujol mull was taken; the $S_2N_2BCl_3$ absorptions were gone and absorptions characteristic of $(S_2N_2BCl_3)_x$ had appeared.

Addition of BCl_3 to S_2N_2 at 20°.—Slow addition of a BCl_3 (2.20 mmol) solution to S_2N_2 (1.58 mmol) in CH_2Cl_2 at 20° in the glove bag resulted in a black, opaque suspension which cleared after several minutes to a dark red solution which finally turned orange-red. Concentration and cooling of this solution yielded pure crystals of $S_4N_4BCl_3$ as shown by its infrared spectrum[4] and melting point of 136° (lit.[4] mp 137–138°). Infrared spectrometry indicated that the residue from evaporation of the remaining solvent consisted of $S_4N_4BCl_3$, with no S_4N_4 or $S_2N_2BCl_3$ impurity.

$(SN)_x$–BCl_3 Reaction.—Samples of $(SN)_x$ underwent reaction with BCl_3 during several days at 20° to give what appeared to be $(S_2N_2BCl_3)_x$, on the basis of infrared studies.

Results and Discussion

Reaction with Boron Trifluoride.—When disulfur dinitride is added to excess boron trifluoride in dichloromethane, only $S_4N_4BF_3$ is formed, whereas the analogous reaction with $SbCl_5$ yields an adduct of S_2N_2. We believe the difference may be explained by the relative weakness of BF_3 as a Lewis acid compared with $SbCl_5$ and by the assumption that the S_4N_4 acid adduct is formed by a second-order reaction

$$S_2N_2 + S_2N_2\cdot(\text{acid}) \longrightarrow S_4N_4\cdot(\text{acid}) \qquad (1)$$

In the case of $S_2N_2SbCl_5$, the equilibrium concentration of S_2N_2 is too low for this reaction to proceed at an appreciable rate unles an excess of S_2N_2 is added to the system. In the case of $S_2N_2BF_3$, the equilibrium concentration of S_2N_2 is high enough for the reaction to proceed and to prevent the isolation of $S_2N_2BF_3$.

Reactions with Boron Trichloride at 0°.—The results of the reactions in which S_2N_2 and BCl_3 were warmed to 0° in dichloromethane show that a product of composition $(S_2N_2BCl_3)_x$ was formed. However, the broad, diffuse, varying infrared spectra of these products showed no correspondence to known S_2N_2, S_4N_4, or BCl_3 adducts. Also, it was not possible to displace BCl_3 from $(S_2N_2BCl_3)_x$ with $SbCl_5$ as might have been expected for a simple adduct inasmuch as $SbCl_5$ is a stronger Lewis acid than BCl_3 and does effect this displacement on $S_4N_4BCl_3$.[2] Thus it appears that $(S_2N_2BCl_3)_x$ is not an adduct involving intact S_2N_2 and BCl_3 units but rather that polymerization has occurred, possibly with partial chlorination of the sulfur atoms. The inability of the product to dissolve after removal of the dichloromethane suggests that the degree of polymerization increased in the solid or highly concentrated state.

The reaction of polymeric sulfur nitride, $(SN)_x$, with boron trichloride gives a material having the same properties and approximately the same composition as the $(S_2N_2BCl_3)_x$ prepared from S_2N_2 and BCl_3 at 0°. However the $(SN)_x$–BCl_3 reaction must be carried out at temperatures around 20°, and at these temperatures side reactions take place, precluding the isolation of a pure product.

Reactions with Boron Trichloride at −78°.—The data for reactions performed at −78°, in which the solvent and excess BCl_3 were removed at that temperature, indicate the formation of a simple labile diadduct $S_2N_2(BCl_3)_2$ and a small amount of $(S_2N_2BCl_3)_x$. The $S_2N_2(BCl_3)_2$ dissociates reversibly on warming to 0° to BCl_3 and a monoadduct $S_2N_2BCl_3$. The ability of $S_2N_2BCl_3$ to add BCl_3 at low temperatures distinguishes it from $(S_2N_2BCl_3)_x$, which is inert to addition of a second mole of BCl_3. The slight decrease in the BCl_3 reversibly absorbed after each successive BCl_3 replacement was probably caused by a slight amount of the irreversible rearrangement (polymerization) $S_2N_2BCl_3 \rightarrow (S_2N_2BCl_3)_x$ occurring at temperatures near 0°. This latter reaction occurs readily in dichloromethane solution whenever excess boron trichloride is absent, even at low temperatures. Apparently the polymerization is blocked when both nitrogens of S_2N_2 are coordinated to BCl_3. The amount of BCl_3 reversibly absorbed is a measure of the monoadduct $S_2N_2BCl_3$ present in a mixture of $S_2N_2BCl_3$ and $(S_2N_2BCl_3)_x$, as evidenced by the displacement, on treatment with $SbCl_5$, of BCl_3 in only the amount equal to that reversibly absorbed in the previous BCl_3 treatment. This displacement of BCl_3 to form the known[1] disulfur dinitride adduct $S_2N_2(SbCl_5)_2$ is in agreement with the relative Lewis acid strengths of $SbCl_5$ and BCl_3 and supports the formulation of $S_2N_2BCl_3$ and $S_2N_2(BCl_3)_2$ as adducts of S_2N_2. The residue of $(S_2N_2BCl_3)_x$ left after washing out the $S_2N_2(SbCl_5)_2$ further confirms its presence as the inert material. The data presented correspond quantitatively to the reactions

$$(2 + y)BCl_3 + (1 + y)S_2N_2 \xrightarrow[-78°]{CH_2Cl_2} S_2N_2(BCl_3)_2 + (y/x)(S_2N_2BCl_3)_x \qquad (2)$$

$$S_2N_2(BCl_3)_2 \underset{-78°}{\overset{0°}{\rightleftharpoons}} S_2N_2BCl_3 + BCl_3 \qquad (3)$$

$$S_2N_2BCl_3 \xrightarrow[0°]{\text{slow}} (S_2N_2BCl_3)_x \qquad (4)$$

$$S_2N_2BCl_3 + 2SbCl_5 \longrightarrow S_2N_2(SbCl_5)_2 + BCl_3 \qquad (5)$$

Formation of $S_4N_4BCl_3$.—The formation of $S_4N_4BCl_3$ by the addition of BCl_3 to an S_2N_2 solution is analogous to the formation of $S_4N_4SbCl_5$[1] and $S_4N_4BF_3$ from S_2N_2. In each of these reactions, the mechanism is probably the initial formation of an adduct of the type $S_2N_2\cdot$(acid), followed by reaction 1.

In adducts in which the boron atom of BCl_3 is bonded directly to the central atom of a Lewis base molecule, a broad infrared absorption envelope characteristic of the BCl_3 portion of the adduct is found with maxima in the 700–800-cm^{-1} region.[5,6] Also, sulfur–nitrogen compounds usually have strong absorptions in and near this region. For example, S_2N_2,[7] S_2N_2-

---

(5) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley & Sons, Inc., New York, N. Y., 1963.

(6) K. J. Wynne and J. W. George, *J. Am. Chem. Soc.*, **87**, 4750 (1965).

(7) J. R. W. Warn and D. Chapman, *Spectrochim. Acta*, **22**, 1371 (1966).

$SbCl_5$,[1] and $S_2N_2(SbCl_5)_2$[1] have absorptions at 795 and 663, 800 and 723, and 818 cm^{-1}, respectively. It seems likely that all of the infrared absorptions of $S_2N_2BCl_3$ near this region (at 840 (m), 788 (wm), 728 (s, b), and 682 (mw) cm^{-1}) may result from combinations of S–N and BCl_3 modes. The remaining $S_2N_2BCl_3$ absorptions (at 1115, 950, 610, and 467 cm^{-1}) correspond closely in position and shape to absorptions in $S_2N_2SbCl_5$. Thus the infrared and chemical evidences support formulation of $S_2N_2BCl_3$ and $S_2N_2(BCl_3)_2$ as adducts of the same type as those of S_2N_2 with $SbCl_5$.[1]

Acknowledgment.—This research was supported by the U. S. Atomic Energy Commission.

Contribution from the William Ramsay and Ralph Forster Laboratories,
University College, London, W.C.1, United Kingdom

Infrared Spectra, Laser Raman Spectra, and Force Constants of the Metal–Hexahalo Species $R_2M^{IV}X_6$, $RM^{V}X_6$ [$R = (C_2H_5)_4N$ or Cs; M^{IV} = Ti, Zr, or Hf; M^{V} = Nb or Ta; X = Cl or Br], and WCl_6

By W. van Bronswyk, R. J. H. Clark, and L. Maresca

Received December 17, 1968

The infrared and laser Raman spectra of a series of metal–hexahalo species of groups IV–VI have been recorded in the range 700–70 cm^{-1}. The compounds are R_2MX_6 [$R = (C_2H_5)_4N$ or Cs; M = Ti, Zr, or Hf; X = Cl or Br], RMX_6 [$R = (C_2H_5)_4N$ or Cs; M = Nb or Ta; X = Cl or Br], and WCl_6. Assignments for the three Raman-active and two infrared-active fundamentals are made; in addition the value for the inactive fundamental ν_6 (t_{2u}) has in some cases been deduced from infrared-active combination bands. Force constants for the hexahalo species have been calculated on the assumption both of a modified Urey–Bradley force field (MUBFF) and of a generalized valence force field (GVFF). The value for ν_6 could thus be calculated and compared with the value deduced from combination bands. For both force fields the average value of the bond stretching force constants for the quadrivalent ions lies below that for quinquevalent ions, which in turn lies below that for WCl_6. For example, on the basis of the MUBFF, K_{av} for the MCl_6^{2-} ions is ~1.0 mdyn/Å, for the MCl_6^{-} ions it is ~1.3 mdyn/Å, and for WCl_6 it is ~1.6 mdyn/Å. This increase in K with increase in the oxidation state of the metal is consistent with previous findings on other complex ions. In addition, $K_{MCl} > K_{MBr}$ in all cases for a given central metal atom. The expected isotopic structure of the a_{1g} mode of an MCl_6 molecule is calculated, but could not, in practice, be resolved for either the $TiCl_6^{2-}$ or the $TaCl_6^{-}$ ions.

Introduction

Although many studies of the vibrational spectra of MX_6 species (X = Cl or Br) of the later transition metals and of the nonmetals have been made, very few have been reported for the corresponding early transition metal species. Recent infrared and Raman spectral measurements[1] on the $TiCl_6^{2-}$ ion have shown that the original data[2] were incorrect and, consequently, that force constant calculations based thereon[3] are unfounded. Accordingly we have recalculated the force constants for this ion, both as the cesium and as the tetraethylammonium salts, in terms (a) of a modified Urey–Bradley force field (MUBFF) and (b) of a generalized valence force field (GVFF). The infrared and Raman data on $ZrCl_6^{2-}$, $HfCl_6^{2-}$, $NbCl_6^{-}$, and $TaCl_6^{-}$ ions, on WCl_6, and also on the corresponding hexabromo species, are nonexistent, fragmentary, or incorrect. We report herein the complete data for all of these ions, usually both as the cesium and as the tetraethylammonium salts, the band assignments, and the force constants according to both the MUBFF and the GVFF bases. The variations of the bond stretching force constants with change of halogen and with change of the oxidation state of the metal atom are delineated. In general, the data have been gathered for the solid state only, owing to the difficulty (if not impossibility) of finding a solvent or solvents in which the species would be both sufficiently soluble and sufficiently stable for adequate spectral measurements to be made. It is recognized that solid-state spectra may be complicated by site symmetry and correlation splitting and also by slight frequency shifts of the normal modes from their values for the isolated ions. However, in those cases for which reliable data in the dissolved as well as the solid states could be obtained ($TiCl_6^{2-}$ ion[1] and $TaCl_6^{-}$ ion, see below) these effects appear to be slight.

Experimental Section

Preparation of Compounds.—The $TiCl_6^{2-}$ and $TiBr_6^{2-}$ ions were prepared as described previously.[1,4]

The tetraethylammonium salts $[(C_2H_5)_4N]_2ZrCl_6$ and $[(C_2H_5)_4N]_2HfCl_6$ were prepared by a modification of the method involving thionyl chloride as solvent.[5] The metal tetrachloride in thionyl chloride was added to a slight stoichiometric excess

---

(1) R. J. H. Clark, L. Maresca, and R. J. Puddephatt, *Inorg. Chem.*, **7**, 1603 (1968).

(2) M.-E. P. Rumpf, *Compt. Rend.*, **202**, 950 (1936).

(3) C. W. F. T. Pistorius, *J. Chem. Phys.*, **29**, 1328 (1958).

(4) R. J. H. Clark, "The Chemistry of Titanium and Vanadium," Elsevier Publishing Co., Amsterdam, 1968.

(5) D. M. Adams, J. Chatt, J. M. Davidson, and J. Gerratt, *J. Chem. Soc.*, 2189 (1963).