[Contribution from the Istituto di Chimica Generale e Inorganica, Universita' di Firenze, Firenze, Italy]

Far-Infrared Spectra of Some Tetrahalo Metal Complexes

By A. Sabatini and L. Sacconi

The far-infrared spectra (400–70 cm.$^{-1}$) of twenty-seven tetrahedral tetrahalogenmetallates(II), $R_2[MX_4]$ (R = univalent organic cation; M = Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II); X = Cl$^-$, Br$^-$, I$^-$), have been examined. In the chloro and bromo compounds the two infrared active fundamental vibrations of the F_2 species (ν_3 and ν_4) were observed, whereas in the iodo compounds only the ν_3 appeared in the spectra. Owing to the distorted symmetry, a splitting of the absorption bands was observed in the copper(II) compounds. The vibration frequencies of the $[ZnCl_4]^{2-}$ and $[ZnBr_4]^{2-}$ ions have been calculated using a simplified ionic model. The agreement between the calculated and observed frequencies is satisfactory.

Introduction

During the last few years a considerable number of salts of tetrahedral tetrahalogenmetallates, $R_2[MX_4]$ (R = univalent organic cation; M = bivalent first row transition metal; X = Cl$^-$, Br$^-$, and I$^-$), have been prepared and characterized.[1,2] Extensive studies of their magnetic and spectral properties, as well as some X-rays investigations, have also been recently reported.[1-3] We have now measured the far-infrared spectra of a series of these complex salts (with R = tetramethylammonium, $(Me_4N)^+$, tetraethylammonium, $(Et_4N)^+$, and tetra-n-propylammonium, $(n$-$Pr_4N)^+$; M(II) = Mn, Fe, Co, Ni, Cu, Zn; X = Cl$^-$, Br$^-$, I$^-$), with the aim to observe their vibrational frequencies and to determine, if possible, which of the complex anions have a regular and which a distorted tetrahedral configuration.

When the present research was nearly completed, two papers appeared which reported the infrared spectra of inorganic complex halides down to 190 cm.$^{-1}$,[4] and assigned the metal–chlorine and metal–bromine stretching vibrations. In our investigation, extended down to 70 cm.$^{-1}$, we were able to observe also the metal–iodine stretching vibrations, as well as the X–M–X bending vibrations. In addition, we calculated the vibrational frequencies of the $[ZnCl_4]^{2-}$ and $[ZnBr_4]^{2-}$ ions on the basis of an ionic model involving non-polarizable charged spheres interacting with repulsive forces of the Lennard-Jones type.

Experimental

The tetramethyl- and tetraethylammonium salts were prepared according to the literature[1,2] by mixing anhydrous ethanol solutions of the metal halides and tetraalkylammonium halides. The tetra-n-propylammonium salts, which in general cannot be easily crystallized from their ethanol solutions, were prepared using isoamyl alcohol or sec-octyl alcohol as solvents, except for $(n$-$Pr_4N)_2[ZnBr_4]$ which separated from ethanol, and for $(n$-$Pr_4N)_2[FeBr_4]$ and $(n$-$Pr_4N)_2[FeI_4]$ which were obtained from their ethanol solutions by dilution with ethyl acetate in a nitrogen atmosphere. The compounds $(Me_4N)_2[NiCl_4]$ and $(n$-$Pr_4N)_2$-$[CuBr_4]$ could not be obtained in a sufficiently pure state. The analytical data for the investigated compounds are listed in Table I.

The infrared spectra were taken with a Perkin-Elmer 301 double beam spectrophotometer, employing Nujol mulls supported on polyethylene windows. The 400–70 cm.$^{-1}$ region was investigated.

Results and Discussion

The frequencies of the absorption bands of the complex salts $R_2[MX_4]$ are listed in Table II. The spectra of the corresponding tetraalkylammonium halides, RX, were also measured for comparison and are listed in Table III. The absorptions observed in the spectra of

(1) N. S. Gill and R. S. Nyholm, J. Chem. Soc., 3997 (1959).

(2) N. S. Gill, ibid., 3512 (1961); C. Furlani and G. Morpurgo, Z. physik. Chem. (Frankfurt), 28, 93 (1961); D. M. L. Goodgame, M. Goodgame, and F. A. Cotton, J. Am. Chem. Soc., 83, 4161 (1961); F. A. Cotton, D. M. L. Goodgame, and M. Goodgame, ibid., 83, 4690 (1961).

(3) B. Morosin and E. C. Lingafelter, Acta Cryst., 12, 611 (1959); B. Morosin and E. C. Lingafelter, J. Phys. Chem., 65, 50 (1961).

(4) R. J. H. Clark and T. M. Dunn, J. Chem. Soc., 1198 (1963); D. M. Adams, J. Chatt, J. M. Davidson, and J. Gerrat, ibid., 2189 (1963).

Table I

Analytical Data

Compound	Metal, % Calcd.	Metal, % Found	Halogen, % Calcd.	Halogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
$(Me_4N)_2[MnCl_4]$	15.92	15.80	41.10	41.01		
$(Me_4N)_2[FeCl_4]$	16.15	16.31	41.00	40.81		
$(Me_4N)_2[CoCl_4]$	16.89	16.79	40.63	40.49		
$(Me_4N)_2[CuCl_4]$	17.97	17.89	40.10	40.03		
$(Me_4N)_2[ZnCl_4]$	18.39	18.49	39.89	39.75		
$(Et_4N)_2[MnCl_4]$	12.01	11.92	31.02	31.10	6.13	6.30
$(Et_4N)_2[FeCl_4]$	12.19	12.17	30.96	30.89		
$(Et_4N)_2[CoCl_4]$	12.78	12.76	30.75	30.66	6.07	6.08
$(Et_4N)_2[NiCl_4]$	12.73	12.72	30.76	30.64		
$(Et_4N)_2[CuCl_4]$	13.63	13.46	30.44	30.19	6.01	5.89
$(Et_4N)_2[ZnCl_4]$	13.97	13.80	30.32	30.27	5.99	5.96
$(Et_4N)_2[MnBr_4]$	8.65	8.55	50.33	50.30	4.41	4.20
$(Et_4N)_2[FeBr_4]$	8.78	8.37	50.25	50.34		
$(Et_4N)_2[CoBr_4]$	9.22	9.03	50.02	49.90	4.38	4.21
$(Et_4N)_2[NiBr_4]$	9.18	9.13	50.04	49.81	4.39	4.23
$(Et_4N)_2[CuBr_4]$	9.87	9.88	49.66	49.52		
$(Et_4N)_2[ZnBr_4]$	10.13	10.04	49.52	49.30	4.34	4.40
$(n$-$Pr_4N)_2[MnBr_4]$	7.35	7.15	42.78	42.30		
$(n$-$Pr_4N)_2[FeBr_4]$	7.46	7.30	42.72	42.35		
$(n$-$Pr_4N)_2[CoBr_4]$	7.84	7.74	42.55	42.47		
$(n$-$Pr_4N)_2[NiBr_4]$	7.83	7.68	42.56	42.05		
$(n$-$Pr_4N)_2[ZnBr_4]$	8.63	8.51	42.19	42.09		
$(n$-$Pr_4N)_2[MnI_4]$	5.87	5.85	54.28	54.38		
$(n$-$Pr_4N)_2[FeI_4]$	5.96	5.81	54.22	54.54		
$(n$-$Pr_4N)_2[CoI_4]$	6.27	6.13	54.05	53.90		
$(n$-$Pr_4N)_2[NiI_4]$	6.25	6.48	54.06	53.61		
$(n$-$Pr_4N)_2[ZnI_4]$	6.92	6.84	53.68	53.58		

the tetraalkylammonium halides, RX, cannot correspond to internal vibrations of the organic cations, for they are considerably shifted toward lower wave numbers as the atomic weight of the halide ion increases. We attribute these absorptions to lattice modes. The frequencies listed in Table II are assigned to vibrations of the tetrahalogenmetallate ions, as confirmed by the fact that salts of the same anion with different cations have approximately the same absorptions.

To predict the number of infrared active fundamental vibrations of molecules or ions in crystals, it is sufficient in general to know the space group of the crystals and the number of molecules per unit cell.[5] Of all the compounds investigated by us, only $(Me_4N)_2$-$[CoCl_4]$, $(Me_4N)_2[CuCl_4]$, and $(Me_4N)_2[ZnCl_4]$ have known crystal structures.[3] They belong to the space group D_{2h}^{16}-Pnma, with four molecules per unit cell. The site symmetry at the metal ion is C_s. The $[Co$-$Cl_4]^{2-}$ and $[ZnCl_4]^{2-}$ ions have an almost perfect tetrahedral structure, the four M–Cl distances being identical within experimental accuracy, and the bond angles being very close to the tetrahedral value of 109° 28′. The $[CuCl_4]^{2-}$ ion, on the other hand, is a flattened tetrahedron, the four Cu–Cl distances being almost

(5) D. F. Hornig, J. Chem. Phys., 16, 1063 (1948); H. Winston and R. S. Halford, ibid., 17, 607 (1949).

Table II
Far-Infrared Absorption Frequencies (cm.⁻¹) of R₂[MX₄] Compounds

Compound	Assignment	Mn	Fe	Co	Ni	Cu	Zn
(Me₄N)₂[MCl₄]	ν_3 (M–Cl stretching)	284 s	284 s	296 s		281 s 237 m	276 s
	ν_4 (Cl–M–Cl bending)	123 m	126 m	131 m		145 w 128 vw	133 m
	ν_2 (Cl–M–Cl bending) or lattice vibration	79 w	81 w	85 w		83 w	84 w
(Et₄N)₂[MCl₄]	ν_3 (M–Cl stretching)	284 s	286 s	297 s	289 s	267 s 248 sh	277 s
	ν_4 (Cl–M–Cl bending)	118 m	119 m	130 m	112 m	136 sh 118 m	130 m
	ν_2 (Cl–M–Cl bending) or lattice vibration	78 w	77 w	82 w	79 m	77 w	80 w
(Et₄N)₂[MBr₄]	ν_3 (M–Br stretching)	221 s	219 s	231 s	231 sh 224 s	216 s 174 m	207 s
	ν_4 (Br–M–Br bending)	85 m	84 m	91 m	83 m	85 w	92 m
(n-Pr₄N)₂[MBr₄]	ν_3 (M–Br stretching)	216 s	215 s	230 sh 222 s	228 sh 219 s		206 sh 199 s
	ν_4 (Br–M–Br bending)	81 m	91 m	87 m	71(?)m		88 m
(n-Pr₄N)₂[MI₄]	ν_3 (M–I stretching)	185 s	186 s	197 sh 192 s	189 s		165 s

Table III
Far-Infrared Absorption Frequencies (cm.⁻¹) of Tetraalkylammonium Halides

(Me₄N)Cl	(Me₄N)Br	(Et₄N)Cl	(Et₄N)Br	(n-Pr₄N)Br	(n-Pr₄N)I
115 m	98 m	103 w	<70	104 w	<70
83 m	<70			71 m	

identical, two opposite angles of about 128° and the others of about 100°.

Figure 1 shows the relationships among the vibrational classes of the free [MX₄]²⁻ ions, those of the ions subjected to a crystal field of site symmetry Cs, and those of the four ions in the unit cell (factor group D₂h).

of D₂d symmetry, each of these vibrations is expected to split, as shown in Fig. 1, into one vibration of B₂ species and one of E species, and in fact the spectrum shows four bands at 281, 237, 145, and 128 cm.⁻¹.

It is true, however, that the bands observed in the spectra of the tetrahalogenmetallates are in general rather diffuse and it is possible that, under different experimental conditions, for example by measurements on single crystals in polarized light, a larger number of bands may appear in agreement with the theory of vibrational spectra in crystals.[5]

The assignment of the bands observed in the spectra of the other complex anions follows directly from the

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Symmetry of the ions          Symmetry of the ion
[CoCl₄]²⁻ and [ZnCl₄]²⁻            [CuCl₄]²⁻              Site symmetry      Factor group symmetry
       Td                            D₂d                      Cs                     D₂h

                                                                                Ag (6 vibr., Raman)
(1 vibr., Raman) A₁              A₁                                             B1g (6 vibr., Raman)
                                 (2 vibr.)               A'
                                 (Raman)                 (6 vibr.)              B2u (6 vibr., I.R.)
                                                         (I.R., Raman)
(1 vibr., Raman) E               B₁                                             B3u (6 vibr., I.R.)
                                 (1 vibr.)
                                 (Raman)                                        Au (3 vibr.)

                                 B₂                                             B1u (3 vibr., I.R.)
(2 vibr., I.R., Raman) F₂        (2 vibr.)               A''
                                 (I.R., Raman)           (3 vibr.)              B2g (3 vibr., Raman)
                                                         (I.R., Raman)
                                 E                                             B3g (3 vibr., Raman)
                                 (2 vibr.)
                                 (I.R., Raman)
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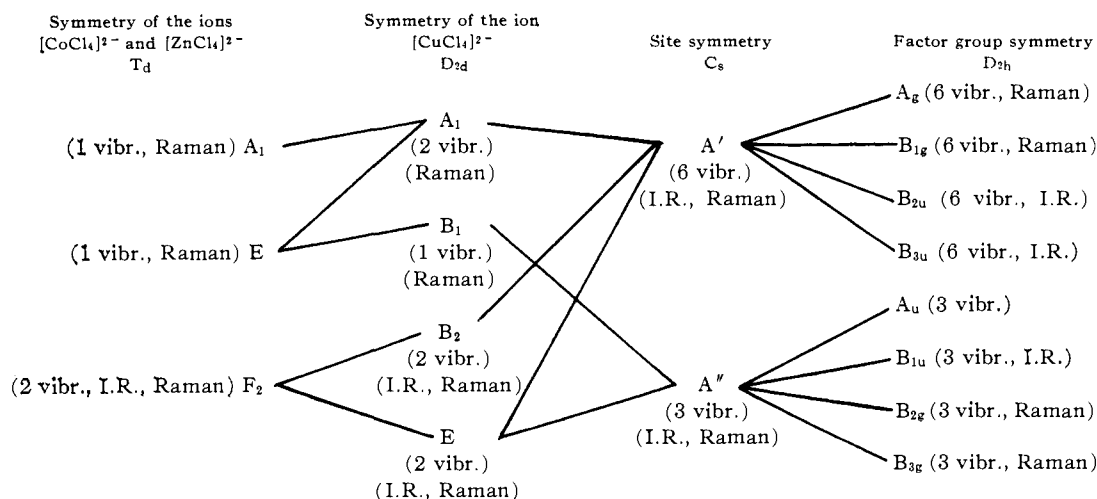
Fig. 1.—Relationships among the vibrational classes of the free ions, those of the ions subjected to the perturbations of the crystal field, and those of the four ions in the symmetry of the unit cell.

The number of observed absorptions is much smaller than that theoretically expected for molecules and ions in crystals and corresponds essentially to the number expected on the basis of the symmetry of the free ions. For the ions [CoCl₄]²⁻ and [ZnCl₄]²⁻, of Td symmetry, the two vibrations of the F₂ species, which are infrared active, can be confidently assigned to the observed bands at 296 and 131 cm.⁻¹ for [CoCl₄]²⁻ and at 276 and 133 cm.⁻¹ for [ZnCl₄]²⁻. For the [CuCl₄]²⁻ ion,

above considerations, except for the absorption present at about 80 cm.⁻¹ in the tetrachlorometallates which requires some additional discussion. This band may be assigned to the ν_2 frequency, activated by site symmetry, or alternatively to a lattice mode. If the 80 cm.⁻¹ band were the ν_2 frequency, we should expect to observe also the ν_1 band, as well as a splitting of the two vibrations of F₂ species; this is not observed. If the 80 cm.⁻¹ band were a lattice mode we should ex-

pect it to vary appreciably for the two series of tetramethyl- and tetraethylammonium salts, which again is not observed. However, the Raman spectrum of $[ZnCl_4]^{2-}$ in aqueous solution[6] appears to support the former assignment. In fact the ν_2 (E species) band appears at 82 cm.$^{-1}$ in the Raman spectrum, and at 84 and 80 cm.$^{-1}$ in the infrared spectra of $(Me_4N)_2[ZnCl_4]$ and $(Et_4N)_2[ZnCl_4]$, respectively.

The metal–halogen stretching vibration appears as a single band, which in a few complexes is accompanied by a shoulder on the high frequency side separated by only a few cm.$^{-1}$ from the center of the main peak. Only in the copper(II) complexes, for which a distorted tetrahedral structure has been found, is the splitting fairly large, and for a few compounds two well separated bands appear. We therefore conclude that all complexes, except those of copper(II), very likely have a regular tetrahedral configuration, and that the shoulders observed in some spectra arise from solid state interactions.

In all the tetrahalogenmetallates here investigated the values of the metal–halogen stretching frequencies follow the order $Mn \simeq Fe < Co > Ni > Zn$, which, except for Mn, is the same as the order of the tetrahedral ligand-field stabilization energies. Copper(II) is not included in the sequence as its complexes depart from the true tetrahedral configuration. The value of ν_3 is greater for the Mn complexes than for the Zn ones, contrary to what we would expect on the basis of the stability of these complexes.[1] This fact can be attributed to the greater atomic mass of Zn compared with Mn. In fact the value of this frequency depends also on the mass of the central atom, decreasing as the latter increases.

We may point out here a few discrepancies between the frequencies reported by Clark, et al.,[4] and Adams, et al.,[4] and those observed by us. Table IV lists the values obtained independently by us and by

TABLE IV

M–X STRETCHING FREQUENCIES OBSERVED FOR THE $(Et_4N)_2$-[MX$_4$] COMPOUNDS

Complex ion	Clark, et al.	Adams, et al.[a]	This work
	Observed frequencies, cm.$^{-1}$		
$[MnCl_4]^{2-}$	282 s	281	284 s
$[FeCl_4]^{2-}$	282 s	276	286 s
$[CoCl_4]^{2-}$	300 s, 281 sh	295	297 s
$[NiCl_4]^{2-}$	285 s, br	283	289 s
$[CuCl_4]^{2-}$	289 sh, 268 s, 247 m	267	267 s, 248 sh
$[ZnCl_4]^{2-}$	281 m, 273 s	271	277 s
$[MnBr_4]^{2-}$	216 s	221, 210	221 s
$[FeBr_4]^{2-}$	216 s	219, 212	219 s
$[CoBr_4]^{2-}$	227 s	233, 228	231 s
$[NiBr_4]^{2-}$	224 s, br		231 sh, 224 s
$[CuBr_4]^{2-}$	248 sh, 222 s		216 s, 174 m
$[ZnBr_4]^{2-}$	207 m, 203 s		207 s

[a] For bands with an unresolved shoulder the prominent absorption maximum has been recorded.

those authors for the $(Et_4N)_2[MX_4]$ compounds. The small differences in the frequencies can be attributed to the difficulty in estimating accurately the maxima of these rather diffuse bands. The deviations in frequency values for $(Et_4N)_2[FeCl_4]$ are, however, rather large. A few differences in the number of the bands are also observed. For example Clark, et al., report two metal–halogen stretching vibrations for the Zn(II) compounds, and Adams, et al., report two metal–bromine stretching frequencies for the bromo complexes of Mn(II), Fe(II), and Co(II), whereas we observed only one band. Since in this region of the spectrum,

(6) M. L. Delwaulle, Compt. rend., **238**, 2522 (1954).

and under the experimental conditions adopted by us, our instrument is capable of resolving absorptions separated by 1 cm.$^{-1}$, we feel confident that the bands observed by us are truly single bands.

Ionic Model and Vibration Frequencies.—A few attempts have been made to calculate the force constants for the halides of the second group metals on the basis of an ionic model.[7] However the discrepancy between the calculated and the observed values indicates that such a model is not a satisfactory representation of these molecules and that the metal–halogen bonds must be regarded as being largely covalent.

In this work we have calculated the vibrational frequencies of the $[ZnCl_4]^{2-}$ and $[ZnBr_4]^{2-}$ ions on the basis of an ionic model consisting of a nonpolarizable bipositive ion tetrahedrally surrounded by four nonpolarizable mononegative ions. The repulsion forces have been taken to be of the type Br^n, where B is the repulsion force constant, r the distance between two ions, and n an integral number.[8]

The force constants can be easily calculated considering that this model gives a central force field. The force, F_1, acting between the Zn^{2+} and the X^- ions is given by

$$F_1 = \frac{2e^2}{r^2} - \frac{B}{r^n}$$

where e is the electron charge, r the Zn–X distance, and B the repulsion constant between Zn^{2+} and X^-. The derivative of F_1 with respect to r, at equilibrium, is the force constant k_2

$$k_2 = \left(\frac{dF_1}{dr}\right)_{r=r_0} = -\frac{4e^2}{r_0^3} + \frac{nB}{r_0^{n+1}}$$

The force acting between two X^- ions is

$$F_2 = -\frac{e^2}{s^2} - \frac{B'}{s^m}$$

where s is the X–X distance and B' the repulsion constant between two X^- ions. The force constant k_1 is then given by

$$k_1 = \left(\frac{dF_2}{ds}\right)_{s=s_0} = \frac{2e^2}{s_0^3} + \frac{mB'}{s_0^{m+1}}$$

whereas k' is

$$k' = \left(\frac{F_2}{s}\right)_{s=s_0} = -\frac{e^2}{s_0^3} - \frac{B'}{s_0^{m+1}}$$

The value of the exponent n in the repulsion term of F_1 is not known, as Lennard-Jones derived the values of n in the case of atoms or ions having an inert gas electronic configuration. In the present work we have carried out two sets of calculations, one assuming $n = 9$ and the other $n = 10$, using the values of m and B' reported in the literature.[8] The value of B is obtained by considering that at the equilibrium the forces acting on each of the X^- ions must cancel one another. Thus we have

$$\frac{2e^2}{r_0^2} - \frac{B}{r_0^n} - \frac{3e^2}{s_0^2}\cos\beta - \frac{sB'}{s_0^m}\cos\beta = 0$$

where β is the angle ZnXX'. The force constants and the parameters used in this calculation are reported in Table V. The calculated vibrational frequencies are listed in Table VI, together with the observed infrared and Raman values.

In spite of the simplicity of the ionic model adopted by us, in which ion polarizations have been completely neglected, the agreement between the calculated

(7) R. S. Berry, J. Chem. Phys., **30**, 286 (1959); R. S. Berry, ibid., **30**, 1104 (1959); R. G. Pearson, ibid., **30**, 1537 (1959); A. Büchler, W. K. Klemperer, and A. G. Emslie, ibid., **36**, 2499 (1962).

(8) J. E. Lennard-Jones and P. A. Taylor, Proc. Roy. Soc. (London). **A109**, 584 (1925); J. E. Lennard-Jones, ibid., **A109**, 584 (1925).

Table V

Force Constants and Parameters Used in Their Calculation

Ion	r_0, Å.	m^c	B'^{c} dynes · Å.^{9}	B'^{c} dynes · Å.^{10}	n^d	B^e dynes·Å.^{9}	B^e dynes·Å.^{10}	k_1, md./Å.	k_2, md./Å.	k', md./Å.
					9	0.573		0.1883	0.8005	−0.0576
[ZnCl$_4$]$^{2-}$	2.24^a	9	4.48							
					10		1.284	.1883	.9808	− .0576
					9	0.877		.1740	.6177	− .0484
[ZnBr$_4$]$^{2-}$	2.39^b	10		30.86						
					10		2.095	.1740	.7658	− .0484

^{a} In solid (Me$_4$N)$_2$[ZnCl$_4$] (ref. 2). ^{b} Mean value of Zn–Br distances in solid Cs$_2$ZnBr$_4$ (B. Morosin and E. C. Lingafelter, *Acta Cryst.*, 12, 744 (1959). ^{c} From ref. 8. ^{d} Assumed. ^{e} Calculated (see text).

Table VI

Observed and Calculated Vibrational Frequencies for [ZnCl$_4$]$^{2-}$ and [ZnBr$_4$]$^{2-}$ Ions

Assignment	[ZnCl$_4$]$^{2-}$ Obsd. frequencies Raman^a	Infrared^b	Calcd. frequencies $n = 9$	$n = 10$	[ZnBr$_4$]$^{2-}$ Obsd. frequencies Raman^a	Infrared^c	Calcd. frequencies $n = 9$	$n = 10$
ν_1 (A$_1$)	282		275	290	172		167	176
ν_2 (E)	82	84?	109	109	61		69	69
ν_3 (F$_2$)		276	282	307	210	207	215	233
ν_4 (F$_2$)	116	133	167	167	82	92	109	110

^{a} Aqueous solution (ref. 6). ^{b} Solid (Me$_4$N)$_2$[ZnCl$_4$]. ^{c} Solid (Et$_4$N)$_2$[ZnBr$_4$].

and the observed values is surprisingly good, especially for $n = 9$. We feel that a more elaborate calculation of the vibrational frequencies of these complex ions is not warranted as a direct comparison of the calculated and observed values is not possible. In fact, the calculated values refer to the [ZnX$_4$]$^{2-}$ ion in the gaseous state whereas the observed values are influenced by solid state interactions in the case of infrared spectra and by solvent interactions for the Raman spectra.

The Preparation of Dioxygenyl Salts from Dioxygen Difluoride

By A. R. Young, II, T. Hirata, and S. I. Morrow

Dioxygen difluoride reacts at temperatures near its melting point (−163.5°) with the pentafluorides of phosphorus, arsenic, and antimony to give solid products which behave as strong oxidizers. Chemical evidence as well as infrared and X-ray diffraction data support a characterization of these solids as dioxygenyl salts, O$_2$MF$_6$ (M = P, As, or Sb). O$_2$PF$_6$ is unstable at room temperature, but O$_2$AsF$_6$ and O$_2$SbF$_6$ are stable to above 100° in an inert atmosphere.

Introduction

The synthesis of the thermally unstable compound, dioxygen difluoride, was first reported by Ruff and Menzel[1] in 1933. Nothing was published about its chemical properties until the recent appearance of reports of its reactions with tetrafluoroethylene,[2] with chlorine monofluoride,[3] and with a variety of inorganic reagents.[4] During the course of a continuing investigation of its chemical properties in our laboratories, dioxygen difluoride has been observed to undergo reactions with the pentafluorides of phosphorus, arsenic and antimony, yielding solid products having moderate thermal stability and considerable oxidizing power. Qualitative studies of the properties of these solids indicated that they might be structurally related to the recently reported[5] dioxygenyl salt, O$_2$PtF$_6$. The results of quantitative studies of reactions with water and with nitrogen dioxide, as well as infrared and X-ray data, appear to support a characterization of the dioxygen difluoride–group V pentafluoride reaction products as dioxygenyl salts of composition O$_2$MF$_6$ (M = P, As, Sb).[5a]

Discussion

The reactions of O$_2$F$_2$ with the group V pentafluorides occur at temperatures slightly above the melting point of dioxygen difluoride (−163.5°). After completion of the reactions, as indicated by a rapid increase in pressure and the disappearance of the orange color of dioxygen difluoride, the gaseous fraction which is not condensable at −196° contains an excess of fluorine over oxygen. The solid products obtained in these reactions are white at room temperature, but at −80° or lower they develop violet-colored areas on their surfaces. They fume in moist air and react violently with water and organic solvents.

Thermal Decomposition.—The products derived from arsenic and antimony pentafluorides are stable at room temperature and ordinary pressures. Rapid decomposition occurs only at temperatures above 100°. When samples of the O$_2$F$_2$–AsF$_5$ or O$_2$F$_2$–SbF$_5$ reaction products are evacuated to 10^{-6} mm. pressure, small mass peaks due to the O$_2$$^+$ are observed in the mass spectra of the vapors above the solids. The O$_2$$^+$ mass peaks increase in intensity as the samples are heated, and eventually peaks are observed which can be attributed to

(1) O. Ruff and W. Menzel, *Z. anorg. allgem. Chem.*, **211**, 204 (1933).

(2) R. T. Holzmann and M. S. Cohen, *Inorg. Chem.*, **1**, 972 (1962).

(3) A. G. Streng and A. V. Grosse, Advances in Chemistry Series, No. 36, American Chemical Society, Washington, D. C., 1962, pp. 159–164.

(4) A. G. Streng, *J. Am. Chem. Soc.*, **85**, 1380 (1963).

(5) N. Bartlett and D. Lohmann, *J. Chem. Soc.*, 5253 (1962).

(5a) Note Added in Proof.—The dioxygenyl salts, O$_2$BF$_4$ and O$_2$PF$_6$, were recently reported by I. J. Solomon, *et al.*, of the Illinois Institute of Technology Research Institute. "Reactions of O$_2$F$_2$ with Lewis Acids," Symposium on Inorganic Fluorine Chemistry, Argonne National Laboratory, Sept. 4–6, 1963.