tions influence the stereochemical behavior of the molybdenum(IV) and vanadium(IV) dithiocarboxylates. The general problem is that the detailed structural features of a given eight-coordinate complex are the result of many energy terms, none of which is separately observable since they operate in concert and in opposing ways to produce simply a single observed result. Particularly for the dithiocarboxylato complexes it appears that any understanding of the structural facts must parallel understanding of the unique electronic structure. In this respect, the electronic spectra of these complexes clearly indicate that any treatment which only includes the metal and ligand ground states cannot provide definite conclusions regarding stereochemistry, bond lengths, and particularly total π-bonding effects.

Registry No. $(TBA)_3MoCl_6$, 19964-31-9; $(TEA)_3MoCl_6$, 52175-52-7; $Mo(dtb)_4$, 52175-53-8; $Mo(mdtb)_4$, 52175-54-9; $Mo(dtpa)_4$, 52175-55-0.

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Oxofluoro Complex Anion Equilibria in Aqueous Hydrofluoric Acid. I. Tellurate(IV)

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The hydroxotetrafluorotellurate(IV) anion, $Te(OH)F_4^-$, is characterized by Raman and infrared spectroscopy in solid $KTe(OH)F_4$ and in aqueous solution. The spectra show that the OH group is in the apical position although there is considerable departure from the spectrum expected for a C_{4v} ion. Raman spectra indicate that aqueous hydrofluoric acid solutions of TeO_2 contain only TeF_5^- and $Te(OH)F_4^-$ ions and the equilibrium constant for the hydrolysis of TeF_5^- to $Te(OH)F_4^-$ has been estimated. Aqueous solutions of $KTe(OH)F_4$ and $KTeF_5$ show only the spectrum of the $Te(OH)F_4^-$ ion.

Introduction

Between the traditional interest in oxo anion behavior in aqueous solutions and, more recently, interest in fluoro anion equilibria in 100% HF,[1] equilibria in aqueous hydrofluoric acid have been comparatively little studied. Moreover, as a general rule, inorganic fluorine chemists exclude water, as far as possible, from systems under study and products showing hydrolysis are avoided. The subject of this series of papers is the fluoro anions formed by the heavier nonmetals of groups V–VII in aqueous hydrofluoric acid and the compounds containing such anions.

Aqueous hydrofluoric acid solutions of Te(VI) have been studied by Kolditz and Fitz,[2] who found species formed with up to four fluorines coordinated to tellurium. It is interesting that these authors were able to separate the species chromatographically indicating that the compounds formed have considerable kinetic stability. Pentafluorotelluric acid, $HOTeF_5$,[3] was not formed, however, in these aqueous solutions.

Prideaux and Millott[4] and Metzner[5] in their early studies on solutions of TeO_2 in 40% aqueous hydrofluoric acid isolated some hydrated oxofluoro compounds. Substances with F:Te ratios up to 2:1 were obtained. Pentafluorotellurates, M^ITeF_5, may be prepared from M^IF and TeO_2 in 40% hydrofluoric acid.[6] Compounds containing the two recently reported fluorotellurate(IV) anions $TeOF_4^{2-}$ and $TeO_2F_2^{2-}$ are prepared under anhydrous conditions and cannot be made from aqueous solutions.[7] This paper concerns itself with the behavior of Te(IV) in aqueous hydrofluoric acid solutions and the fluorotellurates which may be isolated from such solutions.

Experimental Section

Materials and Apparatus. Tellurium dioxide, 99.9% (Fisher), potassium fluoride, 98% (BDH), and potassium hydrogen carbonate (Analar, BDH) were used directly. Hydrofluoric acid, 50% (J. T. Baker), and perchloric acid (Analar, BDH) were standardized with phenolphthalein as indicator and used directly.

Ir spectra were taken as mulls in Nujol, using CsBr plates, on a Beckman IR-20A spectrometer. Raman spectra were recorded on a Jarrell-Ash series 300 spectrometer. A Spectra-Physics argon ion laser was used and detection was by a cooled photomultiplier tube. A spike filter was used to remove plasma lines from the spectra of the solids. Solid samples were contained in 0.5-mm o.d. Pyrex tubes, and, for solutions, a cylindrical sapphire cell 10 cm long and with 5-mm i.d. (Tyco, Sapphikon Division), closed with a plastic cap, was used. Slit widths were 5 cm^{-1} for solid samples and 10 cm^{-1} for solutions. A Raman spectrum of 50% HF showed no bands that interfered with the spectra of the anions studied. Integrated peak intensities of the Raman bands were measured with a planimeter and were accurate to within ±3%. All integrated peak intensities were relative to 0.34 M ClO_4^- = 100.

The X-ray powder photographs were taken in Lindemann tubes using Cu Kα irradiation. A Debye–Scherrer camera of 11.5-cm diameter was used.

Preparation of the Compounds. M^ITeF_5. The method of Greenwood, *et al.*,[6] was used for these preparations.

$KTe(OH)F_4$. A 6.4-g amount of TeO_2 (0.040 mol) and 4 g of $KHCO_3$ (0.040 mol) were weighed into a Teflon dish, and 6.2 ml of 26.0 M hydrofluoric acid was added (0.160 mol). Twenty milliliters of water was added and the mixture was heated to give solution. After filtering to remove traces of suspended material, the solution was allowed to cool. The large crystals which separated were collected by suction filtration and recrystallized from water. The product was dried in a vacuum desiccator over $CaCl_2$. *Anal.* Calcd for $KTe(OH)F_4$: F, 29.26; Te, 49.13. Found: F, 29.34; Te, 49.14. A second recrystallization proved impossible since dissolution in water was accompanied by some additional hydrolysis. However, dissolution of $KTe(OH)F_4$ in a dilute hydrochloric acid solution (Te:Cl = 1:1) yielded back $KTe(OH)F_4$ on crystallization indicating the stability of the $Te(OH)F_4^-$ anion in dilute acid solution.

The compound was also prepared by forced hydrolysis of $KTeF_5$ in acetonitrile: $KTeF_5 + H_2O + KF = KTe(OH)F_4 + KHF_2$. Equimolar amounts of the reactants $KTeF_5$, H_2O, and KF were refluxed

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(1) M. Kilpatrick and J. G. Jones in "The Chemistry of Non-aqueous Solvents," J. J. Lagowski, Ed., Academic Press, New York, N. Y., 1967.

(2) L. Kolditz and I. Fitz, *Z. Allg. Anorg. Chem.*, **349**, 175 (1967).

(3) A. Engelbrecht and F. Sladky, *Angew. Chem., Int. Ed. Engl.*, **3**, 383 (1964).

(4) E. B. R. Prideaux and J. O. Millott, *J. Chem. Soc.*, 2703 (1929).

(5) R. Metzner, *Ann. Chim. Phys.*, **15**, 203 (1898).

(6) N. N. Greenwood, A. C. Sharma, and B. P. Straughan, *J. Chem. Soc. A*, 1446 (1966).

(7) J. B. Milne and D. Moffett, *Inorg. Chem.*, **12**, 2240 (1973).

for 2 hr in a glass apparatus. An ir spectrum of the dried filtered product showed the Te–OH stretching vibration at 698 cm^{-1} and the characteristic bands of KHF_2 at 1200 and 1475 cm^{-1}.

$CsTe(OH)F_4$ and $NaTe(OH)F_4$. Attempts to prepare the cesium salt by the analogous method yielded a mixture of the pentafluorotellurate(IV) and the hydrolyzed product $CsTe(OH)F_4$ which could not be separated by recrystallization. It was also not possible to prepare the sodium compound by the above method, since even highly concentrated solutions could not be made to crystallize.

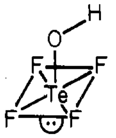
Analysis. Fluoride analysis was done as previously described[7] and tellurium was determined volumetrically, using $KMnO_4$ and back-titrating with ferrous ion.[8]

Solutions. Solutions were made up from TeO_2 and 26.0 *M* hydrofluoric acid in F:Te stoichiometric ratios of interest and diluted with distilled water. The solutions were filtered after complete dissolution of the TeO_2 and the spectra were run. $KTeF_5$ and $KTe(OH)F_4$ were dissolved in water and spectra were run immediately since upon standing the $KTe(OH)F_4$ solution slowly deposited TeO_2.

Results and Discussion

$KTe(OH)F_4$. X-Ray powder data for $KTe(OH)F_4$ have been deposited with the American Society for Testing and Materials. It is not apparent from a comparison of the powder photographs for $KTeF_5$ and $KTe(OH)F_4$ that the two compounds are isomorphous, and the $KTe(OH)F_4$ data cannot be satisfactorily indexed in the orthorhombic system.

The frequencies of the infrared and Raman bands for $KTe(OH)F_4$ and their assignment are given in Table I. The vibrational frequencies for $KTeF_5$ and Cs_2TeOF_4 are given for comparison. The Raman spectrum of $KTe(OH)F_4$ below 850 cm^{-1} is given in Figure 1, trace a, and, the ir, in Figure 2, trace B. The absence of a sharp strong Raman line at 611 cm^{-1}, corresponding to a Te–F (axial) stretching mode, and the close similarity of the Te–F (basal) stretching and bending modes of the $Te(OH)F_4^-$ ion to those of TeF_5^- in both position and order of intensities indicate that the OH group in $Te(OH)F_4^-$ is in the apical position and the anion has the shape



The $TeOF_4$ skeleton of $Te(OH)F_4^-$ approximates to C_{4v} symmetry but the presence of the nonlinear TeOH group will cause deviations from the C_{4v} selection rules for vibrational spectra. The skeletal modes are expected to be close to those of TeF_5^- except that ν_1 and ν_8, the Te–F (axial) stretch and wag, should lie at higher frequencies corresponding to the lower mass of oxygen (or OH) to fluorine. Moreover some of the E modes in C_{4v} symmetry might be split, especially ν_8, since this Te–(OH) wagging mode would be affected by inter- or intraionic hydrogen bonding. Bearing these differences in mind, the assignment of the skeletal modes was made by analogy with the assignment for $KTeF_5$. As expected ν_1 and ν_8 are displaced by the substitution of the axial fluorine by an OH group. The shift in ν_1 is greater than that expected for a mass effect alone and suggests that the Te–(OH) bond is stronger than the Te–F (axial) bond. Furthermore, ν_8 is split into two bands. The ir spectrum of $KTe(OH)F_4$ shows two bands at 425 and 465 cm^{-1}, while only one band appears in the ir spectrum of $KTeF_5$. Two possible assignments of the additional band are possible. The ν_4 mode, which in C_{4v} symmetry should be active only in the Raman spectrum, may become active in the ir, or ν_7, which is a doubly degenerate mode, may be split under re-

Table I. Raman and Ir Spectra of $Te(OH)F_4^-$ and Related Species (cm^{-1})

$KTe(OH)F_4$[a]		$KTeF_5$[b]		Cs_2TeOF_4[c]		$Te(OH)F_4^-$ (soln)[d]	TeF_5^-(soln)[e]	Assignment	
Raman	Ir	Raman	Ir	Raman	Ir	Raman	Raman	(C_{4v})	Approx description of mode (XZY_4)
697 vs	689 m	611 vs	618 ms	837 vs	840 s	700 vs, p	636 vs, p	$\nu_1(A_1)$	$\nu(XZ)$
502 vs	505 sh, w	504 s	(466 vs, br)	461 m	480 m	505 s, p	528 s, p	$\nu_2(A_1)$	$\nu_{sym}(XY_4)$ in phase
266 w	250 sh	282 mw	283 m		265 m	265 w, sh, p	273 m, p	$\nu_3(A_1)$	$\delta_{sym}(XY_4)$ umbrella
465 m	(465 vs, sh)	(472 s)		390 m		460 m, sh	(508 s, sh, br)	$\nu_4(B_1)$	$\nu_{sym}(XY_4)$ out of phase
205 sh, vw							238 sh	$\nu_5(B_1)$	$\delta_{asym}(XY)$ in plane out of phase
223 w		231 mw		190 w		225 w, sh	225 m	$\nu_6(B_2)$	$\delta_{sym}(XY_4)$ in phase
427 w	(465 vs, sh) 425 vs, br	(472 s)	(466 vs, br)	335 m	330–360 vs, br	425 w, sh	(508 s, sh, br)	$\nu_7(E)$	$\}\nu_{asym}(XY_4)$
378 w 342 w	375 s, br 335 m	338 mw	336 m			340 w, br	333 m	$\nu_8(E)$	$\}\delta(ZY_4)$ wag
125 w, sh			164 mw	129 w			168 sh	$\nu_9(E)$	$\delta_{asym}(XY_4)$ in phase

[a] Additional bands (cm^{-1}) in the spectra of $KTe(OH)F_4$: Raman, 647 vw, br (δ_{OH}(wag)); ir, 630 w, br (δ_{OH}(wag)), 1130 mw, br (δ_{OH}(bend)), 2240 w, vbr (2 δ_{OH}(bend)), 3285 m, vbr (ν_{OH}). [b] K. O. Christe, E. C. Curtis, C. J. Schack, and D. Pilipovich, *Inorg. Chem.*, **11**, 1679 (1972). [c] Reference 7. [d] $KTe(OH)F_4$ in water. [e] TeO_2 (2 *M*) in 26.0 *M* HF.

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(8) A. I. Vogel, "Quantitative Inorganic Analysis," Longmans, Green and Co., London, 1966, p 302.

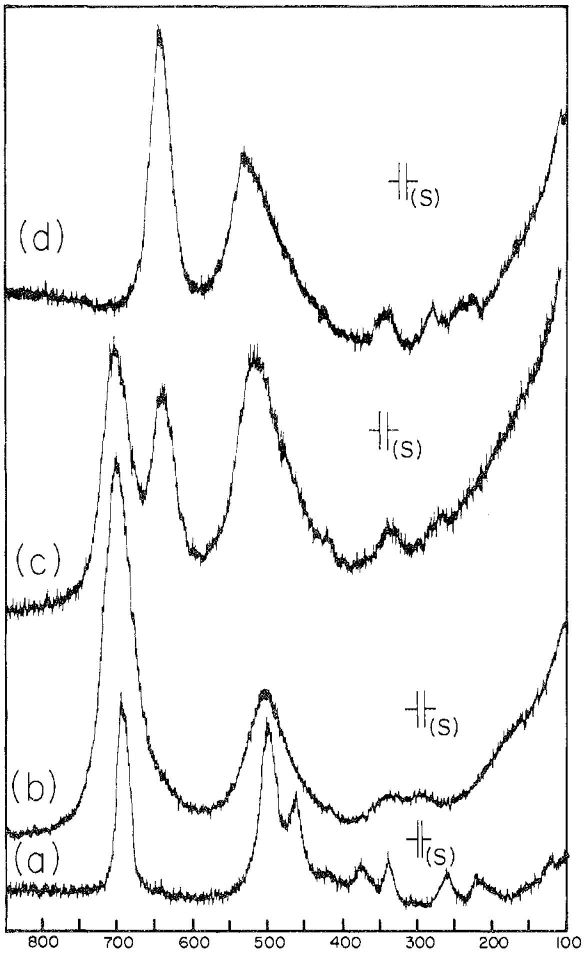

Figure 1. Raman spectra of solid $KTe(OH)F_4$ and TeO_2 solutions in aqueous HF: (a) solid $KTe(OH)F_4$; (b) 2 *M* TeO_2 in 8 *M* HF; (c) 2 *M* TeO_2 in 10 *M* HF; (d) 2 *M* TeO_2 in 26 *M* HF. (S) indicates slit width.

duced symmetry. The Raman spectrum of $Te(OH)F_4^-$ shows a band at 205 cm^{-1}, which does not correspond to any peak in the Raman spectra of the known square-pyramidal pentafluoro or oxotetrafluoro species.[7] This peak is probably ν_5 which has grown in intensity as a result of reduced symmetry. The corresponding in-plane asymmetric deformation in XeF_4 comes at 235 cm^{-1} [9] and the calculated position for ν_5 in IF_5 is at 257 cm^{-1}.[10]

The presence of a hydrogen bonded to the oxygen of the $TeOF_4$ skeleton will introduce three additional modes: ν_{OH}, δ_{OH}(bend), and δ_{OH}(wag). The OH stretching mode appears at 3285 cm^{-1} and the bending mode is at 1130 cm^{-1} in good agreement with similar modes in telluric acid and tellurates.[11] Moreover, the first overtone of the bending mode, which is observed for the tellurates and telluric acid,[11] is also found as a broad weak absorption at 2240 cm^{-1} in the ir spectrum of the $Te(OH)F_4^-$ ion. The one remaining unassigned band at 630 cm^{-1} in the ir spectrum is assigned as the OH wag. This mode appears at 675 cm^{-1} in the spectrum of HSO_4^- [12] and at 744, 812 cm^{-1} in $Sn(OH)_6^{2-}$.[13] In all cases this mode is broad and appears more strongly in the ir than in the Raman spectrum. There is a possibility that this band is due to the presence of a small amount of TeF_5^- which would not be detected by analysis because its presence would cause only a small change in per cent F and virtually no change in per cent tellurium. However, the three most intense lines for $KTeF_5$ were not observed in the X-ray powder pattern of $KTe(OH)F_4$. Furthermore, the position of the peak (ir, 630 cm^{-1}; Raman, 647 cm^{-1}) is high for ν_1 of TeF_5^- and it appears relatively more strongly in the ir spectrum than in the Raman spectrum, unlike ν_1 of TeF_5^- which is strong in the Raman effect and weak in the ir.

Solutions. Solutions of TeO_2 up to 2.32 *M* in 26.0 *M* hydrofluoric acid give the Raman spectrum of the TeF_5^- ion shown in Table I and Figure 1, trace d. That TeF_5^- is the only species present is confirmed by the linearity of a plot of the integrated peak intensity of ν_1 of TeF_5^- against TeO_2 concentration in 26.0 *M* hydrofluoric acid given in Figure 3 and Table II (solutions 1, 2, and 3). Moreover, there is excellent agreement with the Raman spectrum of TeF_5^- in acetonitrile[14] with the single exception of the peak at 590 cm^{-1}, which was not observed in this work. A weak band at 579 cm^{-1} has also been reported in a single-crystal Raman spectrum of the TeF_5^- ion.[15a] It was not possible to resolve ν_4 and ν_7, which constitute the strong, broad peak at 508 cm^{-1}. Assignment of this peak to ν_4 and ν_7 accords well with the change of position of these two modes as one moves along the sequence SbF_5^{3-}, TeF_5^-, IF_5 as discussed earlier.[7,15b] The observed polarization of the two highest frequency bands and the band at 273 cm^{-1} confirms the assignment of these bands to ν_1, ν_2, and ν_3 in $KTeF_5$.

As the mole ratio of HF to TeO_2 decreases, the Raman spectrum of a new species appears and increases in intensity as the spectrum of TeF_5^- decreases. This is shown in Figure 1. This new spectrum is the same as that observed for a solution of $KTe(OH)F_4$ in water and, on the basis of the close analogy with the Raman spectrum of solid $KTe(OH)F_4$, is attributed to the $Te(OH)F_4^-$ ion. The agreement between the spectrum in solution and that in the solid is excellent. The two highest frequency bands in the solution spectrum are both polarized as expected for A_1 modes. The weakness and breadth of the band at 265 cm^{-1} ($\nu_3(A_1)$) precludes a definite decision on the degree of polarization. The Raman spectrum of a solution of $KTeF_5$ in distilled water taken immediately after preparation shows only bands for the $Te(OH)F_4^-$ ion indicating rapid displacement of the apical F of TeF_5^- by OH. No evidence was found for the presence of lower fluorotellurates such as may be derived from the $TeO_2F_2^{2-}$ ion.[7] A mixture which was made up with 3:1 HF:TeO_2 yielded a clear solution on warming, but upon cooling, a white precipitate, which gave an ir spectrum of TeO_2, was deposited. The clear supernate showed only the spectrum of the $Te(OH)F_4^-$ ion. The absence in all the solution spectra of a peak at 840 cm^{-1} indicates that the $Te(OH)F_4^-$ ion is not significantly dissociated to $TeOF_4^{2-}$. The close similarity of the solution Raman spectrum of $Te(OH)F_4^-$ to that in solid $KTe(OH)F_4$ and the absence of bands which cannot be attributed to the $Te(OH)F_4^-$ ion indicate that no significant amount of H_2OTeF_4 is formed and that H_2OTeF_4 is, at least, a moderately strong acid.

The changing intensities of the spectra of TeF_5^- and Te-

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(9) H. H. Claassen, C. L. Chernick, and J. G. Malm, *J. Amer. Chem. Soc.*, **85**, 1927 (1963).

(10) G. M. Begun, W. H. Fletcher, and D. F. Smith, *J. Chem. Phys.*, **42**, 2236 (1965).

(11) H. Siebert, *Z. Anorg. Allg. Chem.*, **301**, 161 (1959).

(12) H. Siebert, "Anwendungen der Schwingungsspektroskopie in der anorganischen Chemie," Springer-Verlag, Berlin, 1966, p 100.

(13) V. Lorenzelli, T. Dupuis, and J. LeComte, *C. R. Acad. Sci.*, **259**, 1057 (1964).

(14) C. J. Adams and A. J. Downs, *J. Chem. Soc. A*, 1534 (1971).

(15) (a) L. E. Alexander and I. R. Beattie, *J. Chem. Soc. A*, 3091 (1971); (b) K. O. Christe, E. C. Curtis, C. J. Schack, and D. Pilipovich, *Inorg. Chem.*, **11**, 1679 (1972).

Table II. Calculation of the Hydrolysis Constant K_h, of TeF_5^- Ion

Soln. no.	C_{HF}, ml^{-1}	Total Te(IV), ml^{-1}	Int[a] TeF_5^-	$[TeF_5^-]$, ml^{-1}	$[TeF_4(OH)^-]$, ml^{-1}	M_{HF}, ml^{-1}	[HF], ml^{-1}	a_{H_2O}	K_h,[b] ml^{-1}
1	26.0	0.94	194	0.94		21.3			
2	26.0	1.44	299 292	1.44		18.8			
3	26.0	2.32	482	2.32		14.4			
4	21.17	3.75	475	2.29	1.46	3.88	3.25	0.947	2.19
5	18.82	3.75	330	1.60	2.15	2.22	1.94	0.965	2.70
6	15.29	2.25	231	1.12	1.13	2.82	2.41	0.957	2.54
7	12.94	2.31	226	1.09	1.22	2.61	2.24	0.959	2.61
8	12.94	1.98	235	1.14	0.84	3.88	3.25	0.947	2.52
9	8.83	1.91	88	0.43	1.48	0.76	0.75	0.975	2.65

[a] Integrated peak intensity relative to ν_1 0.34 *M* $HClO_4$ (928 cm^{-1}) = 100. [b] Mean $K_h = 2.5 \pm 0.1$ ml^{-1}.

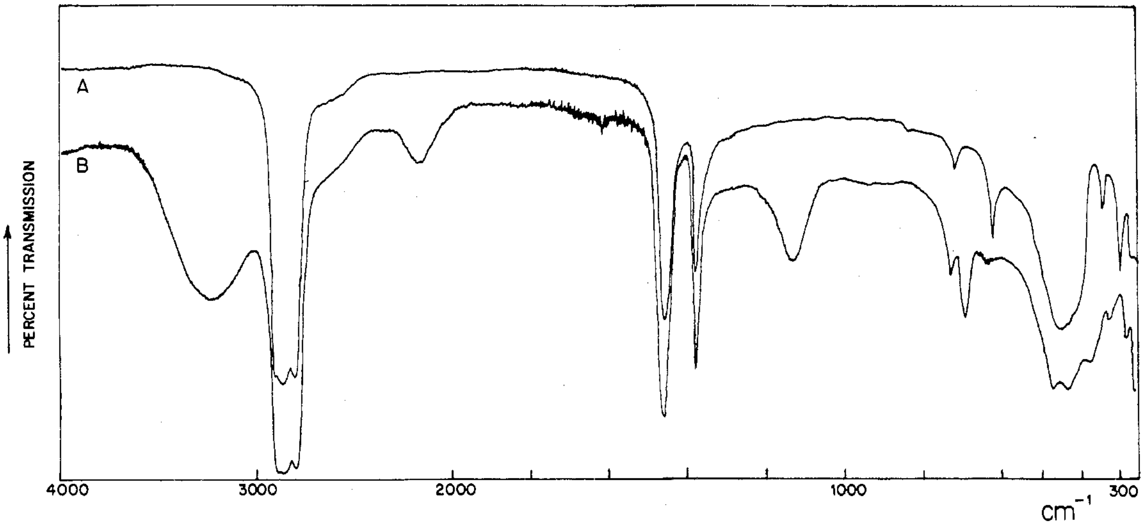

Figure 2. Ir spectra of solid $KTe(OH)F_4$ and $KTeF_5$: A, $KTeF_5$; B, $KTe(OH)F_4$.

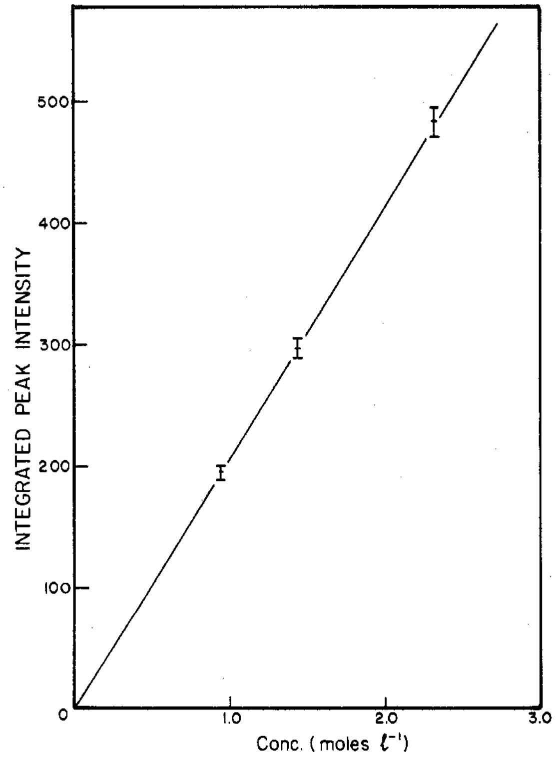

Figure 3. Dependence of integrated peak intensity of ν_1 (636 cm^{-1}) on concentration of TeO_2 in 26.0 *M* HF.

$(OH)F_4^-$ with the changing $HF:TeO_2$ mole ratio shown in Figure 1 indicate that the two anions are in equilibrium: $TeF_5^- + H_2O = Te(OH)F_4^- + HF$. The equilibrium constant is given by

$$K_h = \frac{a_{Te(OH)F_4^-}a_{HF}}{a_{TeF_5^-}a_{H_2O}} = \frac{f_{Te(OH)F_4^-}}{f_{TeF_5^-}}\frac{[Te(OH)F_4^-]f_{HF}[HF]}{[TeF_5^-]a_{H_2O}}$$

Since the two complex ions are similar in charge and structure, the factor of their activity coefficients may be set equal to unity as a good approximation. Similarily it is assumed that $f_{HF} = 1$. The equilibrium constant may be evaluated by quantitative determination of Te(IV) anion concentrations from integrated Raman peak intensities for solutions of known stoichiometry.[16] Integrated peak intensities are referenced to ν_1 of the ClO_4^- ion at 0.34 *M*. Figure 3 shows that the integrated peak intensity of ν_1 of TeF_5^- (636 cm^{-1}) is directly related to TeF_5^- concentration. A variation of only 3% in integrated peak intensity was found upon changing the position of the sample in the laser beam, the gain, and the time constant for the spectrum. Solutions with fluoride to tellurium ratios of approximately 5:1 and 4:1 were prepared for the determination of K_h. Exact concentrations and integrated peak intensities of ν_1 for the TeF_5^- ion are given in Table II. The $Te(OH)F_4^-$ ion and HF concentrations were determined from stoichiometry

$$[Te(OH)F_4^-] = C_{TeO_2} - [TeF_5^-]$$

$$M_{HF} = C_{HF} - 5[TeF_5^-] - 4[Te(OH)F_4^-]$$

where C_{TeO_2} and C_{HF} represent total initial molarities of both species. Equilibrium molalities of HF in aqueous so-

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(16) D. E. Irish, *Raman Spectrosc.*, 1 (1967).

lutions have been measured up to 4 m[17] and [HF] has been evaluated from these data by interpolation and using density data in ref 18. While water activities in aqueous HF solutions have not been measured, values for a_{H_2O} may be obtained from the vapor pressure measurements of Fredenhagen.[19] The validity of this approach has been demonstrated for aqueous HCl solutions where a_{H_2O} values from vapor pressure measurements agree within experimental error with those obtained by emf methods.[20] The effect on a_{H_2O} and [HF] of a relatively small concentration of $HClO_4$ in these solutions has not been taken into consideration but its effect must be small in view of the satisfactory agreement between K_h values for the solutions given in Table II. The hydrolysis constant K_h, was found to be 2.5 ± 0.1 ml^{-1}.

It is interesting that the apical F is replaced in the hydrolysis of TeF_5^-. This behavior parallels that observed for substitution reactions with IF_5 where the apical F is readily replaced by OMe[21] and OH.[22] The apical fluorine is more strongly bonded to the central atom than the basal fluorines are, judging from their respective bond distances.[23,24] It would appear that the facile displacement of the apical fluorine may arise from the ease of attack at the trans position. Secondary bonding in several fluorine-containing solids such as $XeF_2 \cdot IF_5$ has been observed to take place at this position.[25]

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Registry No. $KTe(OH)F_4$, 52279-46-6; $KTeF_5$, 52279-47-7; $Te(OH)F_4^-$, 52279-48-8; TeF_5^-, 37419-76-4; HF, 7664-39-3.

(17) W. J. Hamer and Y. Wu, *J. Res. Nat. Bur. Stand., Sect. A*, **74**, 761 (1970).

(18) "International Critical Tables," Vol. III, McGraw-Hill, New York, N. Y., 1928, p 54.

(19) K. Fredenhagen and N. Wellmann, *Z. Phys. Chem., Abt. A*, **162**, 454 (1932).

(20) M. Randall and L. E. Young, *J. Amer. Chem. Soc.*, **50**, 989 (1928).

(21) G. Oates and J. M. Winfield, *Inorg. Nucl. Chem. Lett.*, **8**, 1093 (1972).

(22) J. B. Milne and D. Moffett, unpublished work.

(23) S. H. Mastin, R. R. Ryan, and L. B. Asprey, *Inorg. Chem.*, **9**, 2100 (1970).

(24) A. G. Robiette, R. H. Bradley, and P. N. Brier, *Chem. Commun.*, 1567 (1971).

(25) N. W. Alcock, *Advan. Inorg. Chem. Radiochem.*, **15**, 1 (1972).

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Stereochemistry of Seven-Coordinate Complexes Containing Three Bidentate Ligands

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Minimization of the repulsive energy around a seven-coordinate metal atom bonded to three rigid chelating bidentate ligands shows that three separate minima occur on the potential energy surfaces. These correspond respectively to the capped octahedron with the unidentate ligand lying on the threefold axis, a very irregular stereochemistry containing no elements of symmetry, and a stereochemistry intermediate between a pentagonal bipyramid and a capped trigonal prism, with the unidentate ligand lying on a mirror plane. These predictions are in agreement with known crystal structures. Factors which may favor particular stereochemistries are briefly discussed.

The stereochemistry of complexes resulting from the introduction of bidentate ligands into the coordination sphere is often significantly different from the stereochemistry of complexes containing only unidentate ligands and cannot be calculated from considerations of metal-ligand bonding. The stereochemistry can, however, be determined with remarkable accuracy and simplicity by minimization of the total "ligand-ligand repulsion energy" or, alternatively, the equivalent bond-bond repulsion energy. Investigations into five-,[1] six-,[2,3] seven-,[4] and eight-coordinate[5] complexes is now continued with the seven-coordinate M(bidentate)$_3$(unidentate) complexes. Some comments on the stereochemistry of lanthanoid shift reagents of this stoichiometry have been made elsewhere.[6]

Method

The position of the unidentate ligand A and of each end of the bidentate ligands BC, DE, and FG on the surface of a sphere of radius r about the metal atom is defined by the spherical coordinates ϕ_i and θ_i. The axes are defined by placing the unidentate ligand A at the "north pole," with $\phi_A = 0°$, and the donor atom B at "zero longitude," $\theta_B = 0°$. The coordinates of the i atom are given by the "latitude" ϕ_i, which is defined as the angle between the metal-ligand M-i bond and the axis incorporating the metal-ligand bond M-A. The "longitude" θ_i is defined as the angle between the vertical plane incorporating MAB and the vertical plane incorporating MAi.

The distance between any two such ligand sites i and j is given by

$$d_{ij} = [2 - 2\cos\phi_i\cos\phi_j - 2\sin\phi_i\sin\phi_j\cos(\theta_i - \theta_j)]^{1/2}r$$

For any general bidentate PQ, the coordinate ϕ_Q was calculated from ϕ_P, θ_P, θ_Q, and the "normalized bite" b of the chelate, which is defined as the distance between the two donor atoms of the chelate divided by the metal-ligand bond length, *i.e.*

$$b = d_{PQ}/r$$

It is again assumed that the repulsive energy u_{ij} between

(1) D. L. Kepert, *Inorg. Chem.*, **12**, 1942 (1973).

(2) D. L. Kepert, *Inorg. Chem.*, **11**, 1561 (1972).

(3) D. L. Kepert, *Inorg. Chem.*, **12**, 1944 (1973).

(4) J. C. Dewan, K. Henrick, D. L. Kepert, K. R. Trigwell, A. H. White, and S. B. Wild, *J. Chem. Soc., Dalton Trans.*, in press.

(5) D. G. Blight and D. L. Kepert, *Inorg. Chem.*, **11**, 1556 (1972).

(6) D. L. Kepert, *J. Chem. Soc., Dalton Trans.*, 617 (1974).