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Infrared Absorption Spectra of Inorganic Solids.[1] IV. Hexafluorosilicates. Raman Spectra of Aqueous SiF_6^{2-}

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Infrared absorption spectra of 11 solid hexafluorosilicates and the Raman spectra of aqueous solutions of some of these compounds have been investigated. Two intense bands observed in the infrared regions have been assigned as $\nu_4(F_{1u})$ of SiF_6^{2-} at 485 cm^{-1} and $\nu_3(F_{1u})$ of SiF_6^{2-} at 740 cm^{-1}. The three Raman bands have been assigned as $\nu_1(A_{1g})$ at 656 cm^{-1}, $\nu_5(F_{2g})$ at 395–400 cm^{-1}, and $\nu_2(E_g)$ at 465 cm^{-1}. By comparison with other AB_6 molecules and ions and observed combination bands, one estimates $\nu_6 \approx 325$ cm^{-1}.

The infrared absorption spectra of 11 solid hexafluorosilicates have been examined in a continuation of studies of infrared absorption spectra of inorganic solids.

Spectra were recorded with a Beckman IR-9 double-beam recording spectrometer over the range, 400–4000 cm^{-1}, with the samples in a standard KBr matrix, *i.e.*, 0.4–0.5 mg of substance in 200 mg of KBr powder, ground in a vibrating mill and pressed in a 0.5-in. diameter die at a pressure of 1000 psi to form a thin disk.

All of the compounds studied were commercially available (Analytical grade), and the spectra were recorded without any further purification, except for evacuating and heating to 120° to remove adsorbed water.

Attempts to record Raman spectra of these solid hexafluorosilicates in pure form or in KBr matrices[2] in various proportions failed, but the Raman spectra of saturated aqueous solutions (zinc, cadmium, ammonium, and lithium fluorosilicates) were recorded with a Cary Model 81 Raman spectrometer.

All of the compounds showed two strong infrared absorption bands in the regions of 490 and 740 cm^{-1}. Those containing water molecules in the crystal (that is, all except the sodium, potassium, silver, and ammonium salts) also had strong bands around 1620 and 3400 cm^{-1}. The ammonium salt had a strong band at 1400–1410 cm^{-1}, and the silver salt had one at 1380 cm^{-1}. For all excepting the lithium and sodium salts, the 490-cm^{-1} band is a sharp peak. In place of a single peak the lithium salt has two strong peaks of equal intensity at 475 and 508 cm^{-1}. The sodium salt shows a broader strong band extending from 450 to 540 cm^{-1}, with peaks at 477, 485, 498, and 522 cm^{-1}. In the ammonium salt the 1400-cm^{-1} band had a sharp double maximum at 1402 and 1408 cm^{-1}, with subsidiary peaks at 1422, 1425, 1432, 1439, and 1460 cm^{-1}. Some weak bands were also observed as indicated in Table I. The Raman spectra of the four aqueous solutions all had a strong sharp band close to 656 cm^{-1} and a very weak broad band at 395–400 cm^{-1}. The band at 656 cm^{-1} is polarized whereas the band at 395–400 cm^{-1} is not.

Most of the observed bands are interpretable as vibrational transitions of the species SiF_6^{2-}, NH_4^+, and H_2O. The small frequency differences between the different salts are attributed to differences in the environments of these species in the different crystals. The strong bands at 1405 and 3160 cm^{-1} of the ammonium salt correspond to the F_2 fundamentals (ν_3 and ν_4) of the ammonium ion NH_4^+ quoted by Herzberg[3] as 1397 and 3134 cm^{-1}. Similarly the strong 1620- and 3450-cm^{-1} bands are fundamentals of the water molecules in the hydrates. Herzberg[4] quotes 1595, 3652, and 3736 cm^{-1} for the gaseous molecule. The observed single broad band at around 3450 probably contains the two high-frequency fundamentals, which are merged into one band in the solid. The remaining two strong bands at 485 and 750 cm^{-1} are presumed to be the F_{1u} fundamentals of the hexafluorosilicate ion SiF_6^{2-}, assuming that it has octahedral symmetry. Following the reasoning in previous papers on many XY_6 molecules,[5] the higher frequency infrared band at ~740 cm^{-1} is designated as the stretching vibration ν_3, and the lower frequency band at 485 cm^{-1} is designated as the bending vibration ν_4. The 656-cm^{-1} Raman band is assigned as the A_{1g} fundamental (ν_1) of SiF_6^{2-}, in agreement with the 646-cm^{-1} band in the Raman spectrum of a single crystal of ammonium hexafluorosilicate observed by Mathieu and Mathieu.[6] They also observed the other Raman-active fundamentals $\nu_2(E_g)$ at 466 cm^{-1} and $\nu_5(F_{2g})$ at 403 cm^{-1}. Thus, the weak Raman band at 395 to 400 cm^{-1} is probably ν_5. The spectrum of zinc hexafluorosilicate solution did have a very weak Raman band around 465 cm^{-1} which could be ν_2. That these two fundamental bands were observed only weakly is attributed in part to the experimental difficulties of obtaining Raman spectra for these dilute solutions.

The observed splitting of the ν_4 band in the case of the sodium and lithium salts is thought to be an effect

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[1] For paper III in this series see K. Sathianandan, L. McCory, and J. L. Margrave, *Spectrochim. Acta*, **20**, 957 (1964).

[2] J. R. Ferraro, *ibid.*, **17**, 802 (1961); **20**, 901 (1964).

[3] G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1945, pp 167, 182.

[4] See ref 3, p 281.

[5] For example, see J. Gaunt, *Trans. Faraday Soc.*, **49**, 1122 (1953).

[6] L. Couture-Mathieu and J. P. Mathieu, *J. Chim. Phys.*, **49**, 226 (1952).

TABLE I

OBSERVED FREQUENCIES FOR HEXAFLUOROSILICATES[a]

$(NH_4)_2SiF_6$

400 (20) 17 R; 487 (12) 88; 656 (14) 100 R; 744 (75) 100; 1402 (60) 79; 1408 (60) 70; 1422 (S) 56; 1439 (S) 46; 1460 (S) 29; 3150 (280) 22; 3380 (30) 3

$Li_2SiF_6 \cdot 2H_2O$

400 (· · ·) R; 475 (20) 34; 508 (20) 41; 662 (12) 100 R; 730 (150) 100; 1640 (65) 37; 3440 (280) 27

Na_2SiF_6

415 (S) 6; 478 (S) 69; 485 (S) 70; 497 (35) 85; 522 (S) 27; 725–765 (115) 100; 1108 (80) 10; 1220 (70) 7

K_2SiF_6

425 (S) 6; 491 (15) 100; 610 (10) 3; 621 (10) 3; 745–780 (80) 100; 1100 (30) 3; 1138 (30) 3; 1224 (30) 7; 1640 (60) 7

$Cu(H_2O)_6 \cdot SiF_6$

419 (S) 6; 488 (20) 95; 736–784 (100) 100; 1220 (30) 13; 1617 (70) 51; 1622 (70) 51; 3400 (500) 31

Ag_2SiF_6

486 (15) 100; 718 (S) 75; 740 (115) 100; 790 (S) 83; 831 (S) 20; 842 (10) 22; 1370–1395 (70) 70; 1435 (S) 18; 1766 (15) 3

$Zn(H_2O)_6 \cdot SiF_6$

395 (20) 26 R; 418 (S) 7; 465 (· · ·) R; 487 (12) 60; 656 (12) 100 R; 740–770 (70) 100; 1110 (80) 10; 1220 (25) 5; 1615 (25) 14; 1620 (50) 50; 3550 (200) 20

$Cd(H_2O)_6 \cdot SiF_6$

395 (20) 21 R; 421 (10) 2; 487 (15) 92; 588 (20) 3; 608 (25) 4; 656 (12) 100 R; 730–785 (90) 100; 985 (20) 2; 1138 (20) 4; 1218 (24) 15; 1388 (30) 3; 1396 (30) 3; 1622 (50) 9; 3480 (240) 7

$Mn(H_2O)_6 \cdot SiF_6$

434 (15) 2; 488 (15) 62; 748 (75) 100; 788 (S) 70; 1222 (20) 4; 1626 (70) 56; 3400 (450) 40

$Co(H_2O)_6 \cdot SiF_6$

485 (11) 80; 600 (35) 4; 745–780 (80) 100; 1110 (60) 6; 1220 (20) 4; 1604 (S) 50; 1628 (60) 60; 1655 (5) 32; 3400 (420) 69

$Ni(H_2O)_6 \cdot SiF_6$

430 (S) 4; 486 (11) 66; 635 (90) 26; 745–780 (70) 100; 1222 (20) 4; 1618 (S) 66; 1628 (45) 92; 1668 (S) 24; 3400 (440) 80

[a] The first number is the absorption (or Raman scattering) frequency in cm^{-1}. The number in parentheses is the width of the band in cm^{-1} at half the peak height, a shoulder or subsidiary peak being indicated by "S." The third number is the peak intensity as a percentage of the intensity of the highest peak in the spectrum, which, in all cases, is the ν_3 infrared band of SiF_6^{2-}, and the ν_1 Raman band of SiF_6^{2-}. R indicates a Raman line.

of the crystal structure of these two salts associated with the relative smallness of the Na^+ and Li^+ cations compared with the K^+, NH_4^+, and $M(H_2O)_6^{2+}$ ions, and the resultant lattice symmetry. The ν_4 band of the ion GeF_6^{2-} is a single peak in the cesium and ammonium salts but is split into two peaks in the barium salt[7] similar to the observed spectrum for Li_2SiF_6. The observed splitting in $BaGeF_6$ is interpreted by Griffiths and Irish in terms of a site symmetry for the GeF_6^{2-} ion of D_{3d} rather than O_h. This removes the threefold degeneracy of the F_{1u} modes. A similar effect is consistent with the crystal structure of Na_2SiF_6[8] in which the site symmetry of SiF_6^{2-} is D_{3d} rather than O_h. In addition, the Na_2SiF_6 structure[8] contains SiF_6^{2-} ions in two different environments, which could be the reason why the ν_4 band shows four peaks in this case. The Li_2SiF_6 ν_4 band indicates D_{3d} symmetry for the SiF_6^{2-} site, but only one kind of site for the anions, unlike Na_2SiF_6. In the crystal structure of $Fe(H_2O)_6 \cdot SiF_6$, and presumably in the other transition metal hexafluorosilicates $M(H_2O)_6 \cdot SiF_6$, the SiF_6^{2-} ions do have the O_h site symmetry.[9]

A surprising feature of these spectra is the absence of most of the allowed binary combination bands[10] since some of these (notably $\nu_2 + \nu_6$, $\nu_5 + \nu_6$, $\nu_2 + \nu_3$, $\nu_1 + \nu_3$, and $\nu_2 + \nu_4$) occur with high intensity in the spectrum of SF_6.[11] The ν_3 band does have subsidiary peaks in some cases as indicated in Table I. This suggests that it is not simply the ν_3 fundamental but is a superposition of ν_3 with some other bands. To assign $\nu_2 + \nu_6$ and $\nu_5 + \nu_6$, one looks for two combination bands which are separated by a frequency of $\nu_2 - \nu_5 \approx 70$ cm^{-1} and which are not simpy $\nu_2 + \nu_3$ and $\nu_5 + \nu_3$ or $\nu_2 + \nu_4$ and $\nu_5 + \nu_4$. Such a pair of peaks occurs in several of the spectra but is most distinct as side bands of ν_3 in the spectrum of Ag_2SiF_6 (718 and 790 cm^{-1}). This assigns the value 323–325 cm^{-1} to ν_6.

Comparative force constant calculations have been carried out for SiF_6^{2-} and other species whose ν_6 fundamental is known.[5,12,13] The details will be published later. For given values of the active fundamentals ν_1 to ν_5, variation of ν_6 affects the two bend–bend interaction constants. $F_{\theta\theta}$ and $F_{\theta'\theta}$ are approximately equal at 0 to 0.2 mdyne/A. The allowed ranges for PtF_6,[13] PtF_6^{2-}, and SiF_6^{2-}, with ν_6 300, 325, and 350 cm^{-1}, are shown in Table II.

TABLE II

	ν_6, cm^{-1}	$F_{\theta\theta}$, mdyne/A Min	$F_{\theta\theta}$, mdyne/A Max	$F_{\theta'\theta}$, mdyne/A Min	$F_{\theta'\theta}$, mdyne/A Max
PtF_6	211	0.0295	0.2524	0.0082	0.2310
PtF_6^{2-}	143	0.0251	0.1554	0.0274	0.1577
SiF_6^{2-}	300	−0.0106	0.0936	0.0148	0.1189
SiF_6^{2-}	325	0.0004	0.1045	0.0038	0.1080
SiF_6^{2-}	350	0.0122	0.1163	−0.0796	0.0962

Platinum hexafluoride was selected for comparison because it is the only case where the fundamentals of the ion and the neutral molecule are both known. The range of the PtF_6^{2-} ion is less than that for the PtF_6 molecule so that the relatively small range of 0–0.1 mdyne/A for SiF_6^{2-} is expected. From the range variation with ν_6 it follows that ν_6 for SiF_6^{2-} may be in the range 300–350 cm^{-1} and is probably close to 325 cm^{-1} if the relationship between $F_{\theta\theta}$ and $F_{\theta'\theta}$ is similar to that in other hexafluorides. The assignment of ν_6 as 325 cm^{-1} is further supported by the interpretation of the 610-cm^{-1} band as $2\nu_2 - \nu_6 = 606$ cm^{-1} and of the 415–430-cm^{-1} band as $\nu_3 - \nu_6$.

Other combination bands which may be assigned are

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(7) J. E. Griffiths and D. E. Irish, *Inorg. Chem.*, **3**, 1134 (1964).

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(11) R. T. Lagemann and E. A. Jones, *ibid.*, **19**, 534 (1951).

(12) L. A. Woodward and M. J. Ware, *Spectrochim. Acta*, **19**, 775 (1963).

(13) B. Weinstock, H. H. Classen, and J. G. Malm, *J. Chem. Phys.*, **32**, 181 (1960).

$\nu_1 + \nu_4$ or $\nu_5 + \nu_3$ at 1108–1138 cm^{-1}, $\nu_2 + \nu_3$ at 1220–1224 cm^{-1}, and $\nu_1 + \nu_3$ at 1370–1396 cm^{-1}.

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Notes

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Preparation of an Iron(0) Complex with 2,2′-Bipyridine[1]

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The preparation of tris(2,2′-bipyridine)iron(0) has been reported[2] but no quantitative data concerning elemental analyses or physical properties have been published. In this note we report data on Fe, Na, Cl$^-$, C, and N quantitative analyses. Furthermore, it is of interest to inquire as to whether this compound should be regarded as an ionic complex of Fe^{3+} and three bipyridine anions, bipy$^-$, or as a covalent complex with essentially uncharged ligands.

The compound was prepared in anhydrous 1,2-dimethoxyethane[3] (DME) by adding a solution of Na$^+$(bipy$^-$) in slight excess to solid anhydrous $FeCl_3$ under moisture-free, oxygen-free conditions in an evacuated vessel. The black product precipitate was filtered and washed with pure anhydrous DME in the same vessel.

When chemical analyses of the product were desired, the reaction compartment was opened to the air. The black precipitate formed from the reaction of Na$^+$(bipy$^-$) and $FeCl_3$ immediately turned red, presumably the result of oxidation to a compound of Fe(bipy)$_3^{2+}$ by oxygen and/or water of the air. The red precipitate in the reaction compartment was dissolved in water and transferred to a volumetric flask, and the red solution was brought to volume. The spectrum of the red solution agreed with that of Fe(bipy)$_3^{2+}$ formed by standard methods. Chemical analyses for sodium, iron, and chloride ion were performed on aliquots of this solution as described below. In other instances samples of the red precipitate were also submitted to the microanalysis laboratory for carbon and nitrogen analyses so that the C:N ratio could be obtained.

Sodium ion in aqueous solution was determined by the sodium zinc uranyl acetate method. Iron and chloride ion analyses were performed on the same aliquot of aqueous solution. The iron(II) was oxidized to iron(III) with hydrogen peroxide (the red color of Fe(bipy)$_3^{2+}$ was lost), and hydrous ferric oxide was precipitated with ammonia. The filtrate from the filtration and washing of this precipitate was heated to decompose the excess hydrogen peroxide and analyzed for chloride ion by the gravimetric silver chloride method. If the excess hydrogen peroxide was not completely decomposed, oxidation of Ag$^+$ to Ag(II) occurred in the presence of 2,2′-bipyridine, and the silver chloride precipitate was discolored. The hydrous ferric oxide was dissolved in a small amount of 1 *M* HCl and analyzed for iron by the oxine method or by titration with standard potassium dichromate after reduction with stannous chloride. Sodium, iron, chloride, carbon, and nitrogen analyses gave Na:Cl ratios of 0.98, 0.99, and 0.98 (theoretical 1.00), Na:Fe ratios of 2.94, 2.96, and 2.93 (theoretical 3.00), C:Fe ratios of 29.8, 28.7, and 27.0 (theoretical 30.0), and N:Fe ratios of 6.0, 6.4, and 6.6 (theoretical 6.00). The microanalyses for C and N lacked the high precision of the Na, Cl$^-$, and Fe analyses since the carbon analyses indicated slightly less than three bipyridine groups per Fe atom whereas the nitrogen analyses indicated slightly more than three bipyridine groups per Fe atom.

No soluble chlorides were formed in the reaction between Na$^+$(bipy$^-$) and $FeCl_3$ since no trace of Cl$^-$ passed through the filter out of the reaction compartment. Because the ratio of Na:Cl was 1:1 and the ratio of Na:Fe was 3:1, the reaction

$$3Na^+(bipy^-) + FeCl_3 = Fe(bipy)_3(s) + 3NaCl(s)$$

apparently went to completion. Under certain conditions the Na:Cl ratio was 1:1, but the Na:Fe ratio was greater than 3:1, indicating that reduction could be carried beyond iron(0) to form soluble products, perhaps by a reaction such as

$$Na^+(bipy^-) + Fe(bipy)_3(s) \longrightarrow Na^+[Fe(bipy)_3{}^-] + bipy$$

In order to establish that Na$^+$(bipy$^-$) was the only reductant present in the bipyridine solution, the changes in the spectrum of 2,2′-bipyridine in DME were studied as the reduction by sodium progressed. An isosbestic point at 299 mμ was observed in the reduction of the neutral molecule to Na$^+$(bipy$^-$). In the

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[1] Abstracted in part from the M.S. thesis of Frank S. Hall, University of Minnesota, 1965.

[2] S. Herzog and H. Präkel, 8th International Conference on Coordination Chemistry, Vienna, Sept 7–11, 1964, p 214.

[3] M. T. Jones and S. I. Weissman, *J. Am. Chem. Soc.*, **84**, 4269 (1962).