chlorine bridges in a manner similar to that found for β-$ClC_2H_4TeCl_3$.

Solid-state spectra of I–III were therefore examined in order to discern shifts indicative of fluorine bridging. In going from solution to the solid state, substantial broadening of peaks occurs for I, II, and III; aryl ring absorptions are broadened to the same extent as Se–F absorptions, however. For I–II the largest frequency shift (solid vs. solution) for an Se–F mode is 14 cm^{-1}, although most Se–F modes show much smaller shifts. For example, the modes associated with Se–F equatorial stretching for I and II shift by 3–5 cm^{-1} to higher frequency in going from solution to the solid state. A very broad absorption not observed in solution is found for I and II at 430 and 417 cm^{-1}, respectively.

The close similarity between the solid-state and solution spectra of I–II militates against pentacoordination via strong fluorine bridge bonding as found for TeF_4.[24] Our results are in contrast to the behavior of SF_4, SeF_4 and other main group fluorides[17,26,27] in which fluorine bridge bonding brings about large shifts in M-F stretching modes. However the broad weak-medium absorption for I–II at ca. 420 cm^{-1} may be an Se–F mode resulting from limited fluorine bridging. Our data do not permit an unambiguous statement in this regard.

No absorption corresponding to the Se–F equatorial stretching mode observed at 572 cm^{-1} in solution is found for III in the solid state. This corresponds to a shift to lower frequency of at least 37 cm^{-1}, assuming this absorption occurs in the vicinity of the strong, broad absorption at 535 cm^{-1}. Intermolecular fluorine bridging trans to the equatorial fluorine may be responsible for lowering this A′ mode to a position obscured by the very intense and broad absorption at 535 cm^{-1}.

Very little change occurs in the position, number, and contour of the Se–F bands of V in going from solution to solid state. In solution and solid state, the Se–F apical stretching frequency occurs at 522 cm^{-1}. The constancy of infrared frequencies observed in solution and in the solid state for V is explained by the persistence in the solid state of structure **4**. Here, the potential Se acceptor site for fluorine bridge formation is occupied through intramolecular coordination by one of the oxygens on the NO_2 group. Direct evidence for *o*-nitro coordination has been obtained through X-ray crystal structures of (*o*-nitrobenzene)selenenyl thiocyanate,[30] methyl *o*-nitrobenzenesulfenate[31] and bis(*o*-nitrophenyl) disulfide.[32] Supporting *o*-NO_2 coordination in V are the observed shifts to lower frequency of the asymmetric and symmetric NO_2 stretching modes in going from *o*-bromonitrobenzene to V. For *o*-$NO_2C_6H_4Br$ the asymmetric and symmetric frequencies are observed in the IR at 1532 and 1355 cm^{-1}, respectively. These bands are shifted to 1513 and 1323 cm^{-1}, respectively, in V.

Conclusions

The synthetic method reported here for the preparation of arylselenium trifluorides should prove generally applicable for the conversion of aryl diselenides which are soluble in Freon 113 or chloroform and which do not contain reactive functional groups.

The steric restriction of fluorine exchange observed for (*o*-ethylphenyl)selenium trifluoride and the coordinative restriction of fluorine exchange observed for (*o*-nitrophenyl)-selenium trifluoride may be expected to be observed in other systems such as arylphosphoranes and -sulfuranes. Systematic study of substituted organyl main-group fluorides may thus provide an additional approach for obtaining information concerning the mechanism of F exchange and for controlling the exchange process.

Registry No. I, 76773-18-7; II, 76773-19-8; III, 76773-20-1; IV, 76773-21-2; V, 76773-22-3; VI, 76773-23-4; $(PhSe)_2$, 1666-13-3; $(p\text{-}CH_3C_6H_4Se)_2$, 21856-94-0; $(p\text{-}FC_6H_4Se)_2$, 52673-29-7; $(o\text{-}C_2H_5C_6H_4Se)_2$, 76773-24-5; $(o\text{-}NO_2C_6H_4Se)_2$, 35350-43-7; $C_6H_5SeO_2H$, 6996-92-5; AgF_2, 7783-95-1.

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Chloro Complexes in Molten Salts. 8. Potentiometric and Raman Spectroscopic Study of the Systems $NaCl–AlCl_3$, $NaCl–AlCl_3–Na_2O$, $NaCl–AlCl_3–SeCl_4$, and $NaCl–AlCl_3–SeCl_4–Na_2O$ at 175 °C

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By potentiometric measurements with chlorine/chloride electrodes the mole fraction of NaCl in a $NaCl–AlCl_3$ melt saturated with NaCl at 175 °C was found to be 0.50209 (5). Furthermore, in the pCl range of 3.885–5.034, the measured potential of the chlorine/chloride electrode at 175 °C could be rationalized by a combination of three reactions: (i) $2AlCl_4^- \rightleftarrows Al_2Cl_7^- + Cl^-$; (ii) $3Al_2Cl_7^- \rightleftarrows 2Al_3Cl_{10}^- + Cl^-$; (iii) $2Al_3Cl_{10}^- \rightleftarrows 3Al_2Cl_6 + 2Cl^-$. The p*K* values (based on the molar units) of these reactions were found to be 7.052 (7), 6.9, and 14, respectively. By potentiometric measurements combined with Raman spectroscopy it was shown that the only complex of Se(IV) formed in the $NaCl–AlCl_3–SeCl_4$ system at 175 °C in the pCl range 1.183–4.662 was $SeCl_3^+$. In the $NaCl–AlCl_3–SeCl_4–Na_2O$ system it was found that in the basic part of the system (i.e., pCl <2.58) $SeCl_3^+$ reacted with the oxide ions forming an oxochloro compound, whereas in the acidic part (i.e., pCl >2.58) the oxide ions reacted with the chloroaluminate ions (instead of the $SeCl_3^+$ ions) forming oxochloroaluminum compounds.

Introduction

The present investigation was started to find out whether analogous chloro complexes were formed in the $NaCl–AlCl_3–SeCl_4$ system as in the $KCl–AlCl_3–TeCl_4$ system, where the chloro complexes $TeCl_6^{2-}$, $TeCl_5^-$, $TeCl_4$, and $TeCl_3^+$ are formed.[2,3]

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It is known that crystals containing $SeCl_6^{2-}$ such as K_2SeCl_6 and $(NH_4)_2SeCl_6$ can be prepared from solutions of Se(IV) in concentrated hydrochloric acid.[4] The complex ion $SeCl_3^+$ is formed[5] in the binary system $SeCl_4$–$AlCl_3$ and has been characterized by Raman spectroscopy.[6] On the basis of measurements with rotating-disk electrodes, Robinson and Osteryoung[7] have recently suggested that $SeCl_6^{2-}$ and $SeCl_5^-$ can be formed in a NaCl–$AlCl_3$ melt at 175 °C.

The NaCl–$AlCl_3$ system was chosen as the solvent because it generally has a lower melting point than the KCl–$AlCl_3$ system in the composition range 50–60 mol % $AlCl_3$. In connection with using NaCl–$AlCl_3$ as the solvent it was necessary to reexamine the self-dissociation reactions and equilibrium constants for this system at 175 °C.[8-11]

Experimental Section

$AlCl_3$ was made from the pure metal (99.999%) and pure HCl.[12] The NaCl used was analytical reagent grade from Riedel-de Haën purified by treatment in the molten state with HCl followed by filtration.[12] $SeCl_4$ was made by reaction between selenium (99.999%) and chlorine (Fluka >99.9%) and further purified by sublimation in chlorine gas. An analysis of the final product gave as an average of nine measurement a chlorine content of 64.28 (30)% (i.e., 64.28 ± 0.30%); the theoretical value is 64.23%. The Na_2O used was from Merck and not analytical reagent grade. Due to the inherent problems in making Na_2O free of Na_2O_2, we did not try to prepare it ourselves. But although the Na_2O used was not analytical reagent grade, there should be little influence on the results since Na_2O is only used in small quantities. A flame photometric analysis of the Na_2O used gave an Na content of 72.6 (2)%; the theoretical value is 74.18%. The content of Na_2O determined acidometrically was found to be 98.94 (8)%. The impurities in the material used are probably Na_2O_2, NaOH, and Na_2CO_3. Since Na_2O_2, NaOH, and Na_2CO_3 will all behave as oxide donors by reaction with the melt these impurities were not considered to be serious. In order to make sure that $SeCl_4$ and Na_2O were not decomposed during the course of the experiments we kept these materials in small glass ampules until used.

The materials that made up a melt were weighed in a nitrogen-filled glovebox with a measured water content of about 5 ppm. The experimental techniques and equipment used in this investigation were almost the same as those used previously.[2,3]

The electrochemical cells were made of Pyrex with glassy carbon rods (Carbone-Lorraine) fused into the bottom.[2,13] The cells were filled with chlorine (Fluka >99.9%) at 0.5 atm and then sealed vacuum tight. The cells used for the Raman spectra were made either of fused quarts with 5 × 10 mm inside cross section or of Pyrex square tubing (from Vitro Dynamics, Inc.) with 5 × 5 mm inside cross section. The Raman spectra were recorded by using either a Coderg PH1 spectrometer[3] or a JEOL JRS-400D spectrometer with cooled photomultiplier. Two different argon ion lasers were used for exitations of the melts: either Spectra Physics 165 argon ion laser or a Coherent Radiation CR500K laser equipped with a 4-W argon tube both with 514.5 nm exitation and an output of ca. 500 mW. The signal was detected with an extended S-20 photomultiplier and amplified in a photon counting system. The uncertainties in the measured Raman shifts due to the instruments were ±2 cm^{-1}.

General Considerations

The nomenclature used in this work is the same as used in previous publications.[2,3,13,14] The initial molar amount of one of the added substances (in the present work NaCl, $AlCl_3$, $SeCl_4$, and Na_2O) dissolved in 1 L of melt is defined as its formality, C'. The excess formality of NaCl or $AlCl_3$ is defined as the difference in formality between NaCl and $AlCl_3$ or $AlCl_3$ and NaCl, respectively. The compositions of the melts are given either in mole fractions such as X_{NaCl}, X_{AlCl_3}, X_{SeCl_4}, and X_{Na_2O} or in the notation NaCl/$AlCl_3$/$SeCl_4$/Na_2O. The NaCl/$AlCl_3$/$SeCl_4$/Na_2O notation is used to indicate the molar ratios of NaCl, $AlCl_3$, $SeCl_4$, and Na_2O which were weighed. These ratios might or might not correspond to the actual molar ratios which prevail in the melt. This is so because in some melts precipitates occur which affect the relative amounts of the weighed substances. The densities necessary to calculate the formalities of the mixtures of $SeCl_4$ and NaCl–$AlCl_3$ were calculated as described previously.[15] It was assumed that the density of the melt did not change by additions of Na_2O. This assumption will only give rise to a small error as the amount of Na_2O added was small compared to the NaCl–$AlCl_3$ present. All NaCl–$AlCl_3$ melts with less than 50 mol % NaCl are called acidic and similarily all melts with more than 50 mol % NaCl are called basic. When solutes are present the acidity/basicity of the melts is determined by the pCl of the melt with the use of the NaCl–$AlCl_3$ solvent at the same temperature as a reference. Thus for the NaCl–$AlCl_3$ solvent at 175 °C, an acidic melt is characterized by pCl >2.58 whereas a basic melt is characterized by pCl <2.58.

It has previously[2,13] been shown that close to the 1:1 composition in the KCl–$AlCl_3$ system (from 47 to about 52 mol % KCl) the potential of a chlorine/chloride concentration cell is within the experimental uncertainity given by eq 1 where

$$pCl_I = -(F/(RT \ln 10))\Delta E + pCl_{II} \qquad (1)$$

pCl_I and pCl_{II} are the negative logarithms of the concentration in cell compartments I and II, respectively, and II refers to the reference compartment saturated with KCl. In the present work it is assumed that eq 1 is correct also for the NaCl–$AlCl_3$ system in about the same concentration range (i.e., from 48 to 50 mol % NaCl). The average experimental coordination number of chloride, $\bar{n}$, for Se(IV) is calculated as $(C'_{NaCl} + 3C'_{AlCl_3} + 4C'_{SeCl_4} - [Cl^-] - 4[AlCl_4^-] - 7[Al_2Cl_7^-] - 10[Al_3Cl_{10}^-] - 6[Al_2Cl_6])/C'_{SeCl_4}$. The average chloride–oxide exchange number is defined as the average number of moles of chloride ions released each time 1 mol of oxide ions is added to the melt. With the technique used thus, values are obtained not at constant pCl but within a pCl range, which, however, is kept rather small.

Results and Discussion

Determination of the Solubility of NaCl in $NaAlCl_4$ and Model Equilibria of the NaCl–$AlCl_3$ System at 175 °C. The results of several potentiometric investigations of the NaCl–$AlCl_3$ system at 175 °C were already available in the literature[8-11] when the present examination was started. As will be seen later the main reason for a reinvestigation of the NaCl–$AlCl_3$ system was that an unexpected deviation was found for the value of $\bar{n}$ calculated for Se(IV) in the NaCl–$AlCl_3$–$SeCl_4$ system. An examination of the pure system was therefore undertaken to make sure that this deviation was not due to errors in the constants used in the description of the solvent.

In order to determine the pCl of the saturated reference melt in the electrochemical cell, it was necessary to determine the solubility of NaCl in $NaAlCl_4$. This was done in the same way as for the analogous KCl–$KAlCl_4$ system.[13,16] If $-(F/$

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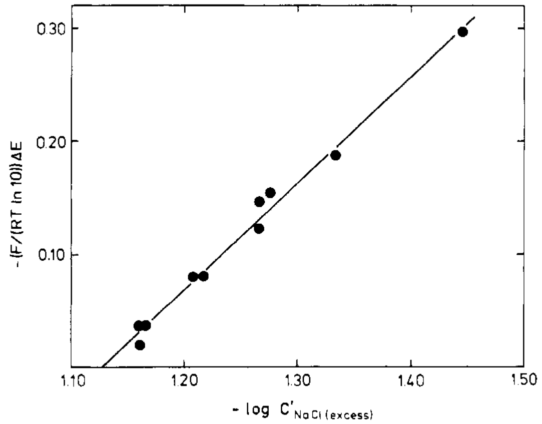

Figure 1. Plot used to obtain pCl for the $NaCl-AlCl_3$ melt saturated with NaCl at 175 °C.

Table I. Values of Cell Potential and Composition for the $NaCl-AlCl_3$ System at 175 °C

X_{NaCl}	X_{AlCl_3}	$-\Delta E$, mV	X_{NaCl}	X_{AlCl_3}	$-\Delta E$, mV
0.4801_9	0.5198_1	347.3	0.5010_1	0.4989_9	26.4
0.4837_9	0.5162_1	339.3	0.5013_0	0.4987_0	16.7
0.4869_2	0.5130_8	330.0	0.5014_9	0.4985_1	13.7
0.4869_7	0.5130_3	329.8	0.5015_2	0.4984_8	13.0
0.4901_4	0.5098_6	318.9	0.5015_3	0.4987_7	10.9
0.4903_1	0.5096_9	318.4	0.5017_0	0.4983_0	7.2
0.4937_6	0.5062_4	300.2	0.5017_4	0.4982_6	7.1
0.4938_7	0.5061_3	300.0	0.5019_3	0.4980_7	3.3
0.4967_8	0.5032_2	274.8	0.5019_4	0.4980_6	3.3
0.4969_7	0.5030_3	272.6	0.5019_4	0.4980_6	1.8
0.4985_0	0.5015_0	245.2			

$(RT \ln 10))\Delta E$ for the measurements obtained at mole fractions of NaCl higher than 0.500 is plotted against the negative logarithm of the excess formality of NaCl, straight lines with a slope of unity are obtained. The intercept at the abscissa (where $-\Delta E = 0$) will give pCl_{II}. Such a plot is shown in Figure 1 (for the data given in Table I). Here the straight line is drawn on the basis of a least-squares method with the slope fixed at unity. However, if the slope is allowed to vary, one obtains also a slope close to unity, in this case 0.94 (4). The intercept at the abscissa gives a pCl value of 1.128 (6) or, given in mole fraction of NaCl, $X_{NaCl} = 0.50209$ (5). These values are somewhat different from other figures—also with pCl on molar basis—obtainable (respectively) from the literature: Trēmillon and Letisse,[8] 1.080 (20) and 0.5023 (1); Torsi and Mamantov,[9] 1.174 and 0.5019 (taken from the authors diagram); Fannin et al.,[10] 1.17 (2) and 0.5019 (1); Boxall et al.,[11] 1.051 and 0.5025.

By comparison with the analogous $KCl-AlCl_3$ system,[16] three models were proposed for the equilibria in this system to account for the pCl behavior in the acidic (and basic) range: model 1, $2AlCl_4^- \rightleftarrows Al_2Cl_7^- + Cl^-$, $Al_2Cl_7^- \rightleftarrows Al_2Cl_6(soln) + Cl^-$ (with equilibrium constants K_1 and K_2); model 2, $2AlCl_4^- \rightleftarrows Al_2Cl_7^- + Cl^-$, $3Al_2Cl_7^- \rightleftarrows 2Al_3Cl_{10}^- + Cl^-$ (with equilibrium constants K_1 and K_3); model 3, $2AlCl_4^- \rightleftarrows Al_2Cl_7^- + Cl^-$, $3Al_2Cl_7^- \rightleftarrows 2Al_3Cl_{10}^- + Cl^-$, $2Al_3Cl_{10}^- \rightleftarrows 3Al_2Cl_6(soln) + 2Cl^-$ (with equilibrium constants K_1, K_3, and K_4). In the case of the $KCl-AlCl_3$ system on the basis of Raman spectra and calculations on vapor pressure measurements model 3 was found to give the best fit.

Assuming arbitrary values for the equilibrium constants for models 1,2, and 3 and varying these systematically so that the smallest deviation (least squares) is obtained between measured and calculated results, it is possible to obtain the pK values as given in Table II (calculated for all measurements with X_{NaCl} lower than 0.5000). As in the case of the $KCl-AlCl_3$ system,[16] model 3 is assumed to give the best description of the solvent. It should be noted that the uncertainties for pK_3 and pK_4 in model 3 are (unrealistic) large; however, measurements on the $NaCl-AlCl_3$ system at higher temperatures than 175 °C[17] show a gradual decrease of the value of pK_3 and pK_4 as the temperature is increased, indicating that this model could well be a close approximation to the reality. Also calculations using the found pK value for model 3 and based on the assumption that the vapor pressure above the melt[18] is proportional to the species fraction of Al_2Cl_6 present in the melt (Raoult's law extended over the whole range for the $AlCl_3-NaAlCl_4$ system) give a much better agreement with model 3 than with model 1. Model 2 will of course only give rise to insignificant vapor pressures. Unfortunately, more accurate measurements are needed in order to use Henry's law which would be the correct law to use under the given circumstances.[16]

Table II. Model Equilibria for the $NaCl-AlCl_3$ System at 175 °C[a]

reactions	model no.	pK
$2AlCl_4^- \rightleftarrows Al_2Cl_7^- + Cl^-$	1	7.046 (3)[b]
$Al_2Cl_7^- \rightleftarrows Al_2Cl_6 + Cl^-$		6.095 (25)
$2AlCl_4^- \rightleftarrows Al_2Cl_7^- + Cl^-$	2	7.053 (3)
$3Al_2Cl_7^- \rightleftarrows 2Al_3Cl_{10}^- + Cl^-$		6.77 (11)
$2AlCl_4^- \rightleftarrows Al_2Cl_7^- + Cl^-$	3	7.052 (7)
$3Al_2Cl_7^- \rightleftarrows 2Al_3Cl_{10}^- + Cl^-$		6.9[c]
$2Al_3Cl_{10}^- \rightleftarrows 3Al_2Cl_6 + 2Cl^-$		14[c]

[a] Calculations are based on the 11 measurements in the pCl range 3.885–5.034. [b] I.e., 7.046 ± 0.003. [c] Large uncertainties in values (see text).

Table III. Values of Cell Potential and Composition for the $NaCl-AlCl_3-SeCl_4$ System at 175 °C[a]

0.1 F $SeCl_4$			0.2 F $SeCl_4$		
X_{NaCl}	X_{AlCl_3}	$-\Delta E$, mV	X_{NaCl}	X_{AlCl_3}	$-\Delta E$, mV
0.4878_4	0.5065_5	310.6	0.4831_5	0.5055_8	294.8
0.4913_9	0.5029_5	269.7	0.4872_5	0.5013_8	241.4
0.4925_3	0.5018_9	254.9	0.4885_5	0.5000_4	168.7
0.4937_1	0.5006_1	211.6	0.4888_2	0.4998_0	150.2
0.4940_1	0.5003_9	201.1	0.4889_5	0.4996_5	118.9
0.4945_1	0.4998_1	126.2	0.4891_4	0.4995_0	95.8
0.4947_6	0.4997_0	101.1	0.4907_9	0.4977_1	4.9
0.4954_5	0.4988_4	32.8			
0.4960_2	0.4984_3	24.0			

[a] Corrections have not been made for the oxide impurity present in the melt.

From Table II it can be seen that the equilibrium constant for the first equilibrium (i.e., pK_1) is rather independent of the model considered. It is therefore reasonable to compare pK_1 (or K_1) with values given in the literature even if the second equilibria differ. At 175 °C the following values of K_1 have been obtained: Trēmillon and Letisse,[8] 13.3 (15) × 10^{-8}; Torsi and Mamantov,[9] 7.9 (18) × 10^{-8}; Fannin et al.,[10] 7.8 (6) × 10^{-8}; Boxall et al.,[11] 10.6 (2) × 10^{-8}; the present work (model 1), 9.00 (6) × 10^{-8}. It can be seen that the latter result is not far from the average of the literature values.

Potentiometric Measurements for the $NaCl-AlCl_3-SeCl_4$, the $NaCl-AlCl_3-Na_2O$, and the $NaCl-AlCl_3-SeCl_4-Na_2O$ Systems at 175 °C. In Table III are shown for the $NaCl-AlCl_3-SeCl_4$ system the values of $-\Delta E$ as a function of X_{NaCl}

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Table IV. Values of Cell Potential and Composition for the NaCl-$AlCl_3$-Na_2O and NaCl-$AlCl_3$-$SeCl_4$-Na_2O Systems at 175 °C[a]

X_{NaCl}	X_{AlCl_3}	X_{Na_2O}	$-\Delta E$, mV	X_{NaCl}	X_{AlCl_3}	X_{SeCl_4}	X_{Na_2O}	$-\Delta E$, mV
0.5008_4	0.4991_6		34.6^b	0.4900_8	0.4990_5	0.0108_6		59.6^d
0.4987_9	0.4997_0	0.0015_0	14.6^b	0.4887_1	0.4990_4	0.0108_3	0.0014_2	32.8^d
0.4895_9	0.5089_1	0.0015_0	307.5^c	0.4869_7	0.4994_5	0.0107_9	0.0027_8	26.7^d
				0.4895_3	0.5088_2	0.0109_2	0.0016_4	305.8^e

[a] Footnote citations *b–e* indicate measurements made by addition to the same potentiometric cell.

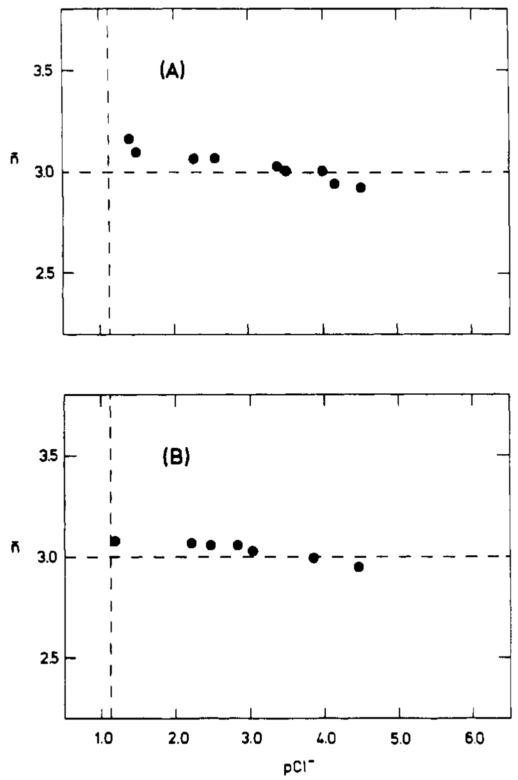

Figure 2. Average experimental coordination number ($\bar{n}$) for Se(IV) in NaCl–$AlCl_3$ at 175 °C as a function of pCl: A, 0.10 F Se(IV); B, 0.20 F Se(IV). The vertical dashed lines show the limiting pCl, due to saturation with NaCl. No corrections for the oxide impurity present have been made.

and X_{AlCl_3} (for 0.10 and 0.20 F $SeCl_4$). A plot of the average experimental coordination number ($\bar{n}$) for Se(IV) as a function of the pCl calculated from Table III is shown in Figure 2.

From this figure it can be seeen that $\bar{n}$ for all of the measurements is in the neighborhood of 3, indicating formation of $SeCl_3^+$. It is also clear that there is a larger deviation from the ideal value of 3.00 than would be expected from other measurements of similar systems.[13,19,20] Furthermore, the $\bar{n}$ values seem to decrease a little as the pCl is increased, but it will be seen later in connection with the Raman spectra that there is no indication of other Se(IV) complexes than $SeCl_3^+$ even if much higher pCl values than given in Figure 2 are attained. Furthermore, there is no reason to expect the deviation to be due to errors in the constats used in the description of the solvent. The best way to explain the above deviation is therefore that Se(IV) reacts with an impurity in the melt and the most probable impurity is oxide. It was therefore decided to investigate the influence of adding oxide to the melt.

In these experiments the potential of the melt was measured with glassy carbon electrodes in a common electrode cell[2,13] where both chambers contained Cl_2 gas at the same pressure (0.8 atm at 175 °C). The values of the measured cell potentials and the compositions are given in Table IV. From Table IV it is possible to calculate average oxide–chloride exchange numbers by using as references $-\Delta E$ values calculated from the self-dissociation constants for the solvent, assuming Se(IV) to be present as $SeCl_3^+$ in the NaCl–$AlCl_3$–$SeCl_4$ system. In the NaCl–$AlCl_3$–Na_2O system this exchange number was found to be 2.51 as an average value for the pCl range 1.29–1.52 (i.e., in basic melts), and 2.90 as an average value for the pCl range 4.59–4.70 (i.e., in acidic melts). These values are close to the η values given by Gilbert and Osteryoung[21] at comparable pCl values (i.e., pCl values based on molar units). However, in contrast to the present exchange numbers these numbers were obtained with aluminum electrodes, and the pCl is readjusted to its orginial value after the oxide addition by coulometric anodization of the electrode. Furthermore, the oxide addition is made by $BaCO_3$ (which decomposes to BaO + CO_2(g)). According to this latter work the correct η value at a pCl (molar units) of 3.2 is 3.0, and it approaches 2.0 as the melt becomes increasingly basic. It should also in this connection be mentioned that Trêmillon and Letisse[8] found an exchange number of 3.2 as an average value for the pCl range 2.6–3.9 (also based on molar units and calculated from the authors diagram).

On the basis of the measurements on the NaCl–$AlCl_3$–$SeCl_4$–Na_2O system (given in Table IV), average exchange numbers of 1.84 and 1.62 in the pCl ranges 1.43–1.50 and 1.50–1.80 (i.e., basic melts) were obtained, respectively. It can be seen that these exchange numbers are about one unit (as an average 0.78 unit) lower than the value obtained in basic melts without Se(IV) present. In the pCl range 4.57–4.71 (i.e., in acidic melts) the average exchange number with Se(IV) present was found to be 3.14. This value is rather close to the value (i.e., 3.0) found for acidic melts with no Se(IV) present. Therefore, it seems likely that $SeCl_3^+$ reacts with aluminum oxychlorides consuming approximately one chloride ion at low pCl values (i.e., in basic melts) while there is no reaction—or it reacts without change in chloride activity—at high pCl values (i.e., in acidic melts).

Raman Spectra of NaCl–$AlCl_3$–$SeCl_4$ and NaCl–$AlCl_3$–$SeCl_4$–Na_2O Melts at 175 °C. In Figures 3 and 4 are shown a series of Raman spectra of 0.2 and 0.5 F $SeCl_4$ dissolved in different NaCl–$AlCl_3$ melts with increasing acidity. For comparison, the spectrum of an acidic NaCl–$AlCl_3$ melt with no $SeCl_4$ added is shown in Figure 3. It is obvious from these figures that the formed Se(IV) species is independent of the chloride activity of the melt. It should be noted that the melts giving rise to spectra A in Figures 3 and 4 were saturated with respect to NaCl. The only change in the spectra is due to formation of $Al_2Cl_7^-$, indicated by the development of a band at 313 cm^{-1} as the melt is made more acidic.[22,23] It is furthermore clear that the relative height of the strong polarized band due to Se(IV) (located at 420 cm^{-1}) compared with the main band due to $AlCl_4^-$ (located at 349 cm^{-1}) increases proportionally with the concentration of Se(IV). This does

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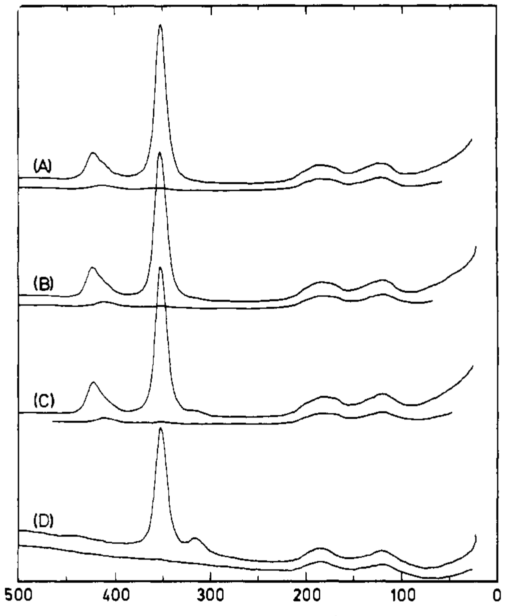

Figure 3. Series of Raman spectra (parallel and perpendicular polarizations) of Se(IV) in $NaAlCl_4$ at 175 °C (A–C). For comparison a spectrum of $NaAlCl_4$ (D) with an excess of $AlCl_3$ is given. The formal concentrations of added $SeCl_4$ and excess $AlCl_3$ and the mole ratios of $NaCl/AlCl_3/SeCl_4$ were as follows: A, 0.20 F $SeCl_4$, 0.00 F $AlCl_3$, 0.4944/0.4944/0.0112; B, 0.20 F $SeCl_4$, 0.20 F $AlCl_3$, 0.4884/0.5004/0.0112; C, 0.20 F $SeCl_4$, 0.43 F $AlCl_3$, 0.4819/0.5063/0.0118; D, 0.00 F $SeCl_4$, 0.97 F $AlCl_3$, 0.4719/0.5218/0.0000. The melt giving rise to spectrum A was saturated with NaCl.

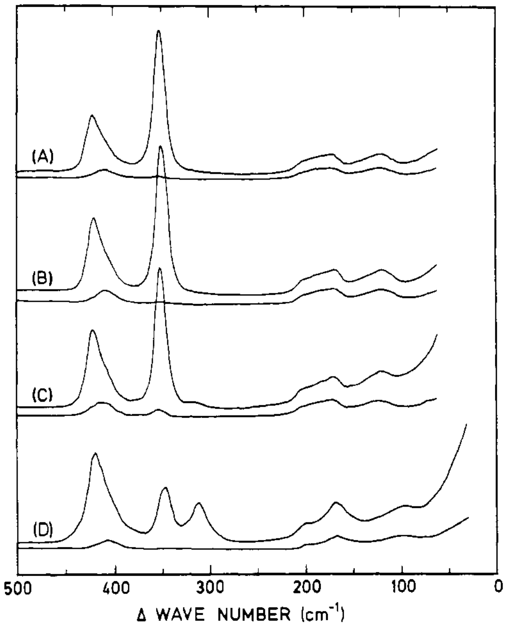

Figure 4. Series of Raman spectra (parallel and perpendicular polarizations) of Se(IV) in $NaAlCl_4$ at 175 °C. The formal concentrations of added $SeCl_4$ and excess $AlCl_3$ and the total mole fractions of NaCl and $AlCl_3$ were as follows: A 0.50 F $SeCl_4$, 0.00 F $AlCl_3$, 0.4865/0.4850/0.0285; B, 0.48 F $SeCl_4$, 0.51, F $AlCl_3$, 0.4714/0.5009/0.0277; C, 0.52 F $SeCl_4$, 0.92 F $AlCl_3$, 0.4576/0.5118/0.0306; D, 0.63 F $SeCl_4$, 3.78 F $AlCl_3$, 0.3535/0.6032/0.0433. The melt giving rise to spectrum A was saturated with NaCl.

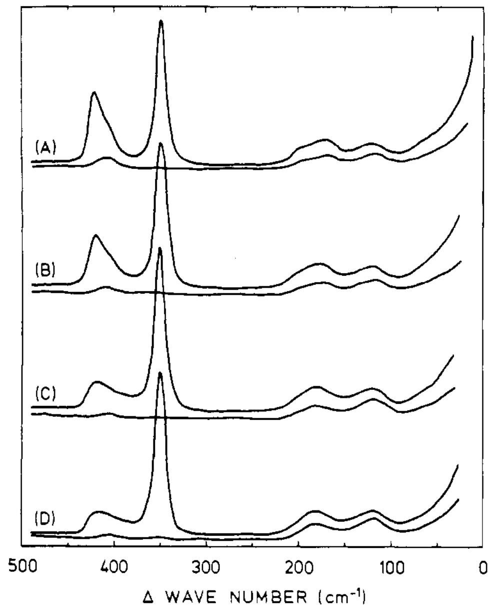

Figure 5. Series of Raman spectra (parallel and perpendicular polarizations) of $SeCl_4$ and Na_2O in NaCl–$NaAlCl_4$ (basic melt) at 175 °C. The formal concentration of $SeCl_4$ and mole ratios of $NaCl/AlCl_3/SeCl_4/Na_2O$ were as follows: A, 0.48 F $SeCl_4$, 0.4712/0.5006/0.0281/0.0000; B, 0.48 F $SeCl_4$, 0.4634/0.5005/0.0277/0.0084; C, 0.45 F $SeCl_4$, 0.4445/0.5053/0.0265/0.0237; D, 0.45 F $SeCl_4$, 0.4378/0.5080/0.0216/0.0326. The melts giving rise to spectra B–D were saturated with NaCl.

of course not apply to spectrum D in Figure 4, where the melt is so acidic that the concentration of $AlCl_4^-$ has decreased considerably. All these results combined with the observation obtained by the potentiometric method indicates formation of only one Se(IV) species, namely, $SeCl_3^+$.

In Figure 5(A) is shown a Raman spectrum of 0.5 F $SeCl_4$ dissolved in a basic NaCl–$AlCl_3$ melt, and in Figure 5(B–D) are shown the changes in the spectra as increasing amounts of Na_2O is added. From this figure it is clear that the bands due to $SeCl_3^+$ (located at 420, 409, 202, and 170 cm^{-1}) decrease in intensity as the amount of Na_2O is increased. Furthermore, a new and polarized band appears around 390 cm^{-1}. A more quantitative examination of the spectra reveals that the change from spectra 5(A) to 5(B) is best described as a one-to-one reaction between $SeCl_3^+$ and oxide but that the reaction thereafter is less complete (spectra 5(C) and 5(D)); this behavior is consistent with an equilibrium constant for the oxide reaction of the order of 1. It should be mentioned that all melts containing Na_2O were saturated with respect to NaCl.

In Figure 6 is shown a similar series of Raman spectra starting with the spectrum of a ca. 0.4 F $SeCl_4$ in an acidic NaCl–$AlCl_3$ melt at 175 °C and followed by spectra of acidic melts with increasing amounts of Na_2O added. From this figure it is clear that in this case there is little or no reaction between $SeCl_3^+$ and oxides added. For comparison the spectrum of an acidic NaCl–$AlCl_3$ melt to which only Na_2O has been added is also given. From this spectrum (6(D)) it is clear that the oxochloro complex of Al(III) formed has no bands which at the given concentration will interfere with bands due to the Se(IV) complexes. It should be mentioned that in the melts containing Na_2O a precipitate was formed. However, the concentration of $SeCl_3^+$ did not decrease by addition of Na_2O, and since the precipitate increased with increasing additions of Na_2O, it is clear that there is no selenium present in the precipitate. According to the work by Trêmillon et al.,[24] Al_2O_3 has a minimum solubility around a pCl value of 4.8 (molar units) in a NaCl–$AlCl_3$ melt at 210 °C. The formal oxide concentration at this temperature and

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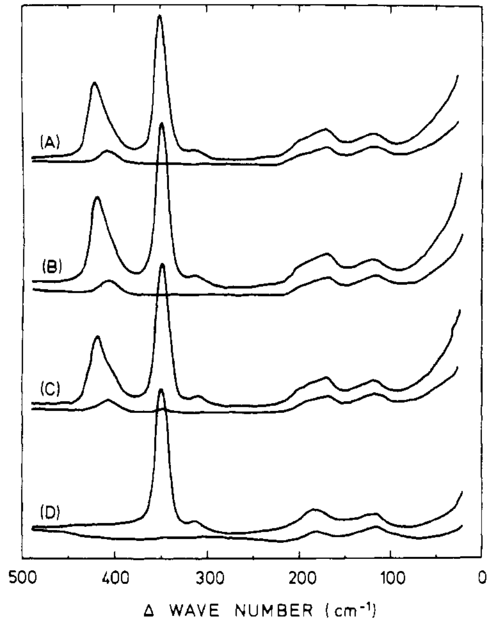

Figure 6. Series of Raman spectra (parallel and perpendicular polarizations) of $SeCl_4$ and Na_2O in $NaAlCl_4$-$AlCl_3$ (acid melt) at 175 °C (A–C). For comparison a spectrum of $NaAlCl_4$ (D) with an excess of $AlCl_3$ and added Na_2O is given. The formal concentrations of $SeCl_4$ and the mole ratios of $NaCl/AlCl_3/SeCl_4/Na_2O$ were as follows: A, 0.45 F $SeCl_4$, 0.4582/0.5144/0.0274/0.0000; B, 0.44 F $SeCl_4$, 0.4432/0.5221/0.0267/0.0080; C, 0.41 F $SeCl_4$, 0.4135/0.5353/0.0246/0.0266; D, 0.00 F $SeCl_4$, 0.4691/0.5222/0.0000/0.0087. The melts giving rise to spectra B–D were saturated with respect to aluminum oxide.

pCl is 0.07 F; a lower solubility is to be expected at 175 °C. The pCl in the melts of interest (see Figure 6(B–D)) are not far from 4.8, and it can be seen from the work by Trêmillon et al.[24] that the solubility will not differ much from the minimum value. Since the added amounts of Na_2O correspond to calculated oxide concentrations of 0.13, 0.45, and 0.15 F, respectively, it is clear that the melts must be saturated with respect to Al_2O_3.

Discussion of the $NaCl$-$AlCl_3$-$SeCl_4$ and $NaCl$-$AlCl_3$-$SeCl_4$-Na_2O Systems. It is now possible to say something more definite about the reactions which take place in the melt. It is well-known from the literature[25] that by heating SeO_2 and $SeCl_4$, $SeOCl_2$ is formed. $SeOCl_2$ is known to have bands at 161, 255, 279, 347, 388, and 955 cm^{-1}.[26] Unfortunately, in the present investigation due to other absorptions, only one band can be seen clearly, namely, the polarized band found at 390 cm^{-1}. This band could be the polarized band given in the literature (at 388 cm^{-1}). A possible formulation for the oxochloro complex formed in basic $NaCl$-$AlCl_3$ melts is "$AlOCl_2^-$".[21,24] The reaction between $SeCl_3^+$ and the oxide impurity may therefore be eq 2. This reaction explains the

$$\text{"}AlOCl_2^{-}\text{"} + SeCl_3^+ + Cl^- \rightleftarrows SeOCl_2 + AlCl_4^- \qquad (2)$$

observations so far. It is a one-to-one reaction between $SeCl_3^+$ and oxide; one chloride ion is consumed each time one $SeCl_3^+$ ion reacts with oxide. Furthermore, since a chloride ion is involved in the reaction it is dependent on the acidity of the melt and in such a way that a decrease in chloride activity will favour formation of $SeCl_3^+$ which implies that $SeCl_3^+$ is unaffected by oxide in acidic melts. The effect of this reaction on the apparent chloride coordination number, $\bar{n}$, for Se(IV) is that $\bar{n}$ will increase with increasing oxide impurity in basic melts but remain unchanged in acidic melts.

Table V. Raman Shifts (cm^{-1}) and Assignments of Bands Present in the Observed Spectra[a]

this work	assignt	other investigations
420 vs, p	ν_1 (A_1) $SeCl_3^+$ str	419 s, p, [$SeCl_3^+$, $AlCl_4^-$][6]
409 m, dp	ν_3 (E) $SeCl_3^+$ str	397 m, dp, [$SeCl_3^+$, $AlCl_4^-$][6]
390 m, p	ν_1 (A_1) $SeOCl_2$ str, (?)	388 s, p, $SeOCl_2$[26]
349 vs, p	ν_1 (A_1) $AlCl_4^-$ str	351 vs, p, $AlCl_4^-$ [22]
313 s, p	ν_1 (A_{1g}) $Al_2Cl_7^-$ str	312 vs, p, $Al_2Cl_7^-$ [23]
202 m, p?	ν_2 (A_1) $SeCl_3^+$ bend	
183 s, dp	ν_4 (F_2) $AlCl_4^-$ bend	186 s, dp, $AlCl_4^-$ [22]
170 m, dp	ν_4 (E) $SeCl_3^+$ bend	
165 s, dp	ν_5 (E_g) $Al_2Cl_7^-$ bend	164 s, dp, $Al_2Cl_7^-$ [23]
120 s, dp	ν_2 (E) $AlCl_4^-$ bend	121 s, dp, $AlCl_4^-$ [22]
97 s, dp	ν_6 (E_g) $Al_2Cl_7^-$ bend	99 s, dp, $Al_2Cl_7^-$ [23]

[a] Key: m, medium; s, strong; v, very; dp, depolarized; p, polarized.

A correction based on a formal oxide impurity of 0.01 M (or ca. 0.1 mol %) would bring the measured points (shown in Figure 2) down to ca. 3.00 in the basic region. There is one more reason to believe that this in fact is the level for the oxide impurity. Previously[2,13,15,19] we have found that the equimolar mixture of KCl and $AlCl_3$ that we prepare as the basis melt nearly always appears to contain an excess of KCl (up to 0.1 mol %). The excess is calculated from the electrode potential of the equimolar mixture which we routinely measure in order to check the composition. This apparent basicity of the equimolar melt is consistent with the presence of a small impurity of aluminum oxychloride in the used aluminum chloride since aluminum oxychloride does not act as an acid for pCl >ca. 2 (indicated by η values of 3 for these higher pCl values[21]).

In Table V are given assignments of all the measured bands compared with literature values. As one can see a rather good agreement is obtained for $SeCl_3^+$. If one compares the band positions found for the $SeCl_3^+$ ion with the ones found for the $TeCl_3^+$ ion,[3] it is clear that all the band positions for the same type of vibrations are found at higher frequencies for the $SeCl_3^+$ ion than for the $TeCl_3^+$. This can be explained by the higher mass of the tellurium atom compared with the selenium atom and the expected stronger bonding in $SeCl_3^+$ than in $TeCl_3^+$.

The conclusion is that only one Se(IV) complex, namely, $SeCl_3^+$, is formed in the $NaCl$-$AlCl_3$-$SeCl_4$ system at 175 °C. $SeCl_4$ therefore reacts with the $NaCl$-$AlCl_3$ solvent in the same way as NaCl, contributing with 1 mol of Cl^- for each mole of added $SeCl_4$. This is in contrast to reaction 3 proposed by

$$SeCl_5^- + Cl^- \rightleftarrows SeCl_6^{2-} \qquad (3)$$

Robinson and Osteryoung[7] to explain their results obtained with a rotating-disk electrode. It is, however, evident that there are some similarities between eq 2 and 3. In both cases a Se(IV) complex reacts with one chloride ion forming another Se(IV) complex. The best explanation of the data obtained by Robinson and Osteryoung[7] is probably therefore that the oxide impurity level in the melt was so high and the concentration of dissolved Se(IV) so low (ca. 1/100 of the present concentration) that all Se(IV) in the basic region was converted to the oxochloro complex instead of the proposed $SeCl_6^{2-}$ ion, whereas in the acidic region it was present as the $SeCl_3^+$ ion (instead of as the $SeCl_5^-$ ion).

An explanation must be found why $SeCl_6^{2-}$ and $SeCl_5^-$, in contrast to $TeCl_6^{2-}$ and $TeCl_5^-$, are not formed in solution under the present circumstances. In this connection it should be noted that the Se^{4+} ion is considerable smaller than the Te^{4+} ion. Even if a coordination number of 6 can be obtained in some crystals,[4] a coordination number of 4 is to be expected based on a simple model using the ionic radii[27] (i.e., with a

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coordination number of 4, contact is obtained between the Se^{4+} ion and Cl$^-$ ions in contrast to the case when the coordination number is 6). The formation of SeCl$_3^+$ rather than SeCl$_4$ is probably due to the presence of the stereochemically active lone pair.[28]

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Registry No. AlCl$_3$, 7446-70-0; NaCl, 7647-14-5; SeCl$_4$, 10026-03-6; Na$_2$O, 1313-59-3; SeCl$_3^+$, 21687-08-1; SeOCl$_2$, 7791-23-3; AlCl$_4^-$, 17611-22-2; Al$_2$Cl$_7^-$, 27893-52-3.

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Resonance Raman Spectra of Iron Tetraphenylporphyrin Complexes: Characterization of Structure and Bonding Sensitive Bands

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Resonance Raman spectra of iron–TPP complexes of general formula Fe^n(TPP)(L)(L′) with n = II or III are reported. The use of two different exciting lines allows the observation of totally and non totally symmetric modes. The frequencies of four structurally significant Raman bands, A (ca. 1360 cm^{-1}, p), B (ca. 1375 cm^{-1}, dp), C (ca. 1520 cm^{-1}, ap), and D (ca. 1560 cm^{-1}, p), are discussed: all of them are dependent on the spin of the iron atom. Among the non totally symmetric modes the occurrence of band B is characteristic of pentacoordinated derivatives, and the frequency of band C which appears as equivalent to band IV of physiological porphyrins is a sensitive spin indicator. Within the low-spin Fe^{II} derivatives, the frequencies of the totally symmetric modes A and D are both sensitive to dπ(Fe)–π^*(TPP) interactions: band A frequency is more specifically dependent on the π acidity of the axial ligand, and band D frequency reflects the stereochemistry around the iron atom. Finally, the vibrational pattern of pentacoordinated complexes is very distinctive.

During the last years, resonance Raman (RR) spectroscopy has been increasingly used to characterize hemoproteins and physiological porphyrin derivatives.[1] Correlations have been established between the frequencies of some prominent Raman bands and the spin and oxidation states of the iron atom in protoporphyrin IX and in mesoporphyrin: for example band I is considered as an oxidation-state marker band, while band IV is a spin marker band (nomenclature according to ref 2). Meanwhile, due to the convenient synthesis of iron tetraphenylprophyrin (hereafter TPP), a great number of Fe(TPP) derivatives have been prepared, as models for various hemoproteins complexes.[3,4] Usually X-ray structural studies have been carried out, and some of the data have been used to get a better insight into the heme structure, as the measurements on the proteins are of much lower accuracy. As far as the optical properties are concerned, the comparisons between Fe(TPP) complexes and hemoproteins derivatives have not been carried out to such an extent. And indeed significant differences exist in the visible spectra of Fe(TPP) derivatives compared to that of physiological porphyrins such as shifts on band positions and absence of $\alpha\beta$ splittings.[5] Recently a resonance Raman study has been devoted to some Fe(TPP) derivatives, showing a vibrational pattern poorer than that of physiological porphyrins: with use of blue excitation, only totally symmetric modes were observed, and three prominent bands were characterized, whose frequencies are altogether dependent on both the spin and oxidation states of the iron.[6]

As new derivatives have been described and structurally characterized,[7–9] including pentacoordinated low-spin Fe^{II} complexes, we think it worthwhile to investigate their Raman spectra, using both Soret and β excitations, and reinvestigate some of the previously examined derivatives, with β excitation. Thus the frequency changes of the totally symmetric modes, already described in ref 6, have been studied as a function of various electronic and structural parameters; non totally symmetric modes have been characterized, mainly band B (dp, ca. 1370 cm^{-1}) which only occurs in pentaccordinated species and band C (ap, ca. 1500–1550 cm^{-1}), whose frequency is dependent on the spin state of the iron and thus appears as the equivalent of band IV of physiological porphyrins. Finally a vibrational pattern characteristic of pentacoordination is proposed.

Experimental Section

In the Fe^{III} series, the complex [Fe(TPP)(Me$_2$SO)$_2$]$^+$[10] was obtained by dissolution in Me$_2$SO of [Fe(TPP)(C$_2$H$_5$OH)$_2$]BF$_4$, which was

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[10] Abbreviations: Me$_2$SO = dimethyl sulfoxide; Im = imidazole; py = pyridine; pip = piperidine; *i*-PrNO = isopropylnitroso; TPP = dianion of tetraphenylporphyrin; TpClPP = diianion of tetrakis(*p*-chlorophenyl)porphyrin; TpivPP = dianion of *meso*-5,5,5,5-tetrakis(*o*-(pivaloylamido)phenyl)porphyrin; MS = dianion of mesoporphyrin; PP$_{IX}$ = dianion of protoporphyrin IX; Hb = hemoglobin.

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