with a straightforward naive application of the back-bonding model, which would predict the exchange rate of the title compound to be in between those of $Ru(H_2O)_6^{2+}$ (1.8×10^{-2} s^{-1} [12]) and $Ru(H_2O)_6^{3+}$ (3.5×10^{-6} s^{-1} [12]). The fast water exchange cannot be attributed to a significant shift of the Ru–O distances either.[29] $Ru(H_2O)_6^{2+}$ and $Ru(\eta^6\text{-}C_6H_6)(H_2O)_3^{2+}$ have very similar thermally corrected (295 K) average metal–oxygen bond lengths of 2.131 (9)[13a] and 2.127 (12) Å, respectively. The very facile substitution of the water ligands in $M(\eta^6\text{-}C_6H_6)(H_2O)_3^{2+}$ should thus be ascribed to transition-state properties rather than to those of the electronic ground state. A similar trans effect in the transition state without corresponding manifestations in structural parameters of the ground state has been discussed for substitution reactions of square-planar platinum(II) complexes.[30]

Activation parameters for the substitution reaction of the two ruthenium aqua ions[12] and the mixed benzene–water complexes are summarized in Table VII. The broad variation of ΔS^* in particular is indicative of distinctively different pathways for the water substitution in the various complex ions. The same conclusion follows from ΔV^*. An interchange mechanism (I) with approximately equal contributions of bond breaking and bond making applies for $Ru(H_2O)_6^{2+}$, the activation volume ΔV^* being -0.4 ± 0.7 cm^3 mol^{-1}. The significantly negative value of ΔV^* (-8.3 ± 2.1 cm^3 mol^{-1}) for $Ru(H_2O)_6^{3+}$ is fully compatible with an associative pathway (I_a).[12] The small positive ΔV^*'s for the two $M(\eta^6\text{-}C_6H_6)(H_2O)_3^{2+}$ complex ions are accepted as evidence for an interchange mechanism in which bond breaking is slightly ahead of bond making. The water-exchange mechanism for these arene–aqua ions is characterized by a strong trans-labilizing effect of the aromatic ligand on coordinated water.

Acknowledgment. We thank CIBA-GEIGY for performing the microanalyses. This work was supported by the Swiss National Science Foundation (Grant No. 2.430-0.84).

Registry No. $Ru(H_2O)_6(tos)_2$, 15694-44-7; $[Ru(\eta^6\text{-}C_6H_6)(H_2O)_3](tos)_2$, 96826-82-3; $[RuCl_2(\eta^6\text{-}C_6H_6)]_2$, 37366-09-9; $[Ru(\eta^6\text{-}C_6H_6)(H_2O)_3]SO_4$, 113221-14-0; $[Os(\eta^6\text{-}C_6H_6)(H_2O)_3](tos)_2$, 113221-15-1; $[OsCl_2(\eta^6\text{-}C_6H_6)]_2$, 69462-16-4; 1,3-cyclohexadiene, 592-57-4; 1,4-cyclohexadiene, 628-41-1.

Supplementary Material Available: Tables SI and SII, listing thermal parameters, Table SIII, listing atomic positional parameters for the 295 K structure, and Table SIV, listing interatomic distances and angles, together with hydrogen bond lengths for the sulfate anion, and Figure 4, the packing diagram of the unit cell (5 pages); tables of calculated and observed structure factors (24 pages). Ordering information is given on any current masthead page.

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Coordination Chemistry of UO_2^{2+} and VO^{2+} in KSCN–KF Ionic Melts

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The stepwise complexation of fluoride ions with UO_2^{2+} and VO^{2+} in molten KSCN has been investigated at 185 °C. Fluoride activities were measured in systems (K^+, UO_2^{2+})–(SCN^-, F^-) and (K^+, VO^{2+})–(SCN^-, F^-) by a recently developed potentiometric method utilizing a fluoride-selective membrane electrode. Average ligand numbers from 0 to 4.9 and from 0 to 3.8 were established for the uranyl(VI) and vanadyl(IV) systems, respectively. Higher ligand numbers cannot be achieved due to precipitation of $K_3UO_2F_5$ and K_3VOF_5. Stability constants for five consecutive steps for uranyl(VI) and four consecutive steps for vanadyl(IV) have been determined. A specific interaction energy parameter, ΔA_j, for each step of ligand exchange of thiocyanate for fluoride is determined. For VO^{2+} the overall fluoride complexation is well described by one single parameter: $\Delta A = -39.6$ kJ·mol^{-1}, independent of j for $1 \leq j \leq 4$. For UO_2^{2+} a slight increase in ΔA_j with increasing j is ascribed to increasing electrostatic repulsion in the equatorial plane of the O–U–O moiety. Changes in hard-sphere Coulomb interaction energies can qualitatively explain the stability sequence $Co^{2+} < Cr^{3+} < VO^{2+} < UO_2^{2+}$ for fluoride complexes in molten KSCN only if formal charges higher than +3.0 and +3.5 are assigned to V and U in VO^{2+} and UO_2^{2+}, respectively. Differences in standard free energy change for the substitution of SCN^- and F^- between aqueous solution (298 K) and KSCN–KF melt (458 K) for these four acceptors are found to be remarkably constant, 29 kJ·(mol F)$^{-1}$, irrespective of central ion and j for $j = 1$ and 2.

Introduction

In recent investigations of fluoride complexation with Cr(III) and Co(II) in molten KSCN, it has been demonstrated that the substitution of SCN^- for the harder ligand F^- in the coordination sphere of the central ion proceeds in a stepwise manner.[1,2] Application of simple quasi-lattice formalism[3] has shown that the specific interaction energy parameters for the ligand-exchange reactions, schematically written as

$$M\text{–}NCS + F^- \rightarrow M\text{–}F + SCN^- \qquad (1)$$

are remarkably constant, i.e. independent of the number of fluoride ions already coordinated to M.

The total complexation from $Cr(NCS)_6^{3-}$ to $Cr(NCS)_2F_4^{3-}$ could thus be modeled by use of one single interaction energy ΔA, once the overall coordination number for the hard acceptor ion Cr(III) was known. These findings of course raise a number of further questions pertaining to complex formation in systems of acceptor–donor pairs of essentially hard–hard character in a fairly soft solvent melt like KSCN. Such questions are as follows: (a) To what extent does F^- associate with other polyvalent metal ions in consecutive steps, which can be described by use of one single quasi-lattice interaction energy parameter? (b) Can observed interaction energies for different acceptor–donor systems be related to estimated changes in hard sphere Coulomb interaction energies in a straightforward way? (c) Is there any relation between thermodynamic parameters for complex formation for hard–hard acceptor–donor pairs in aqueous solution on one hand and molten salts on the other?

In this paper we have extended studies of fluoride systems in KSCN melts to the oxycations UO_2^{2+} and VO^{2+}. These ions have been chosen in order that features in the complexation thermodynamics which may be due to restrictions on the SCN^-/F^- coordination geometry may be detected. UO_2^{2+} and VO^{2+} are probably the two most widely studied oxycations. They are stable in a variety of solvents and give a large number of coordination compounds in the solid state. The complex formation reactions with SCN^- and F^- in aqueous solution are well documented.[4] It

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has been concluded that the main contribution to the standard free energy change for the association between UO_2^{2+} or VO^{2+} and the hard ligand F^- in aqueous solution is a large entropy gain due to desolvation of donor and acceptor ions. Positive ΔH° values for the stepwise formation processes, involving substitution of coordinated water molecules for fluoride, have been interpreted as due to the pronounced electrostatic character of the metal–fluoride bonds in the resulting complexes.[5-7]

The stability of UO_2^{2+} in molten salts has been inferred from the close similarities between absorption spectra obtained in molten alkali-metal fluoride, chloride, and nitrate media on one hand and those recorded in aqueous solution on the other.[8,9] We recorded the spectrum of $K_3UO_2(NCS)_5$ dissolved in molten KSCN at 185 °C in order to confirm the existence of UO_2^{2+}. In KSCN melts as well as in LiCl–KCl melts the band due to intramolecular electronic transitions of the uranyl(VI) ion is partially covered by a charge-transfer band. The appearance of the spectrum in KSCN is, however, very similar to the one obtained in LiCl–KCl eutectic at 400 °C, although slightly shifted toward higher energies. It is thus concluded that U(VI) retains the oxygen coordination in KSCN melts as well.

The reactions of a series of vanadium compounds in molten KSCN have shown that oxidation state IV is the most stable one.[10] The stability of VO^{2+} in thiocyanate melts has been inferred from the close resemblance of spectra of $K_2VO(NCS)_4$ in molten KSCN at 200[10] and 185 °C[11] and spectra of VO^{2+} obtained in concentrated aqueous thiocyanate solutions.[12,13]

One previous study of complex formation in mixed-anion melts has demonstrated the strong affinity of uranyl(VI) for fluoride ions in an alkali-metal chloride–fluoride melt,[14] and the fluoride complexation in KSCN has recently been demonstrated qualitatively by us.[15] In the present work we have utilized the same experimental technique for potentiometric determination of fluoride activities in molten salt mixtures that was used in the previous study of chromium(III) fluoride complexation in the same solvent.[1]

Experimental Section

Chemicals. KSCN and KF were treated prior to use as described previously.[1,15]

$K_3UO_2(NCS)_5\cdot 2H_2O$ was prepared by mixing hot aqueous solutions of $UO_2SO_4\cdot 3.5H_2O$, $Ba(SCN)_2\cdot 2H_2O$, and KSCN in a molar ratio of 1:1:3.[16] The mixture was stirred for 15 min at 60 °C. The precipitated $BaSO_4$ was removed by filtration, and the solution was evaporated to almost dryness. The deep red crystals obtained were dissolved in a minimum of ethyl acetate, the solution was filtered, and the solvent was removed by heating. The resulting crystals were ground and dried under vacuum at 40 °C for several hours until no further weight loss could be detected. A spectrophotometric method utilizing the strong absorption of the uranyl(VI) thioglycolate complex at 380 nm[17] was used to analyze the orange dehydrated salt. The uranium content found was 40.5%, in good agreement with the theoretical value of 39.8% for $K_3UO_2(NCS)_5$.

$K_2VO(NCS)_4\cdot 5H_2O$ was prepared from $VOSO_4\cdot 5H_2O$, $Ba(SCN)_2\cdot 2H_2O$, and KSCN in a molar ratio of 1:1:2. The procedure of synthesis and drying was the same as for the uranyl(VI) compound. The crystals obtained were bright blue, and the dehydrated product was a gray-blue powder. The substance was analyzed spectrophotometrically for VO^{2+} in aqueous solution with a large excess of thiocyanate (1 M).[12] ϵ_{760} was determined to be 57.7 ± 0.8 $M^{-1}\ cm^{-1}$ in separate calibration experiments. The vanadium content found was 17.9% (calculated for $K_2VO(NCS)_4$ 17.7%).

$K_3UO_2(NCS)_5$, $K_2VO(NCS)_4$, and chemicals containing fluoride were weighed and handled under a dry N_2 atmosphere in a glovebox.

Stability of the Melts. Melts of $K_3UO_2(NCS)_5$ in KSCN or in KSCN–KF mixtures were exposed to laboratory air in a preliminary study. In fluoride-free systems small amounts of a black precipitate, probably UO_2, could be observed. This observation is in agreement with previous results reported by Yanagi and Ikeda.[18,19] This compound was not formed, however, in melts containing KF. Instead, a gray-white solid precipitated. X-ray powder diffraction analysis showed that the main product was $K_2U_2O_7$. Since uranate formation does not occur in fluoride-free melts, it is concluded that fluoride mediates the formation of $K_2U_2O_7$ when the melt is in contact with the laboratory atmosphere containing H_2O (cf. ref 20 and 21). A possible reaction scheme may be

$$2K^+ + 2UO_2^{2+} + 6F^- + 3H_2O \rightarrow K_2U_2O_7(s) + 6HF$$

Emf Measurements. All potentiometric measurements were performed under a flow of dry nitrogen in order to prevent precipitation reactions of the kind described above.

A fluoride-selective membrane electrode, developed by us for work in molten salts up to 200 °C, was used to measure fluoride activities. The electrode design and treatment have been described previously.[1,15] The cell employed was

$$\begin{array}{c|l||l|c|l|c} & \text{KSCN(l)} & \text{KSCN(l)} & & \text{KSCN(l)} & \\ & & \text{KF} & \text{LaF}_3 & & \\ \text{Ag} & \text{Ag}_2\text{SO}_4\text{(satd)} & \text{K}_3\text{UO}_2\text{(NCS)}_5\text{ or} & \text{membrane} & \text{KF(satd)} & \text{Ag} \\ & & \text{K}_2\text{VO(NCS)}_4 & & \text{Ag}_2\text{SO}_4\text{(satd)} & \end{array}$$

Further details on furnaces, temperature control, cell construction, and measurements have been described elsewhere.[1,22-24]

The compositions of the test melts were varied by additions of $K_3UO_2(NCS)_5$ or $K_2VO(NCS)_4$ and solidified stock melts of KF + KSCN. Stable emf readings could then be obtained within 0.5 h after the melt composition had been changed.

The ranges of total concentrations covered in the uranyl(VI) system were $5.2 \times 10^{-4} \le C_U/(\text{mol}\cdot\text{kg}^{-1}) \le 8.0 \times 10^{-3}$ and $1.0 \times 10^{-3} \le C_F/(\text{mol}\cdot\text{kg}^{-1}) \le 2.3 \times 10^{-2}$ and the free fluoride concentration was in the range $6.0 \times 10^{-6} \le [F^-]/(\text{mol}\cdot\text{kg}^{-1}) \le 1.9 \times 10^{-2}$. Corresponding figures for the vanadyl(IV) system were $4.4 \times 10^{-4} \le C_V/(\text{mol}\cdot\text{kg}^{-1}) \le 3.4 \times 10^{-3}$, $8.5 \times 10^{-4} \le C_F/(\text{mol}\cdot\text{kg}^{-1}) \le 1.1 \times 10^{-2}$ and $3.8 \times 10^{-5} \le [F^-]/(\text{mol}\cdot\text{kg}^{-1}) \le 5.2 \times 10^{-3}$.

The total time for a run, calibration of the electrode, and the complex formation study was 1 day. During this time a maximum of data points were collected as described recently.[1]

Electronic Absorption Spectra. The spectra referred to in the Introduction were recorded with a Unicam SP 700 instrument, modified for high-temperature work. The design and temperature control of the furnace compartement have been described earlier.[25] $K_3UO_2(NCS)_5$ mixed with KSCN was melted, stirred, and transferred into 10-mm fused-silica cells. Spectra were recorded between 350 and 700 nm with pure KSCN as reference.

Results and Discussion

Fluoride activities can be measured accurately by use of a modified fluoride-selective membrane electrode in molten salts up to 200 °C. The electrode has been shown to give a linear relationship between the emf, E, and log $[F^-]$

$$E = E_0 - k \log([F^-]/(\text{mol}\cdot\text{kg}^{-1})) \qquad (2)$$

in molten KSCN in the concentration range $3 \times 10^{-4} \le C_F/(\text{mol}\cdot\text{kg}^{-1}) \le 5 \times 10^{-1}$.[15]

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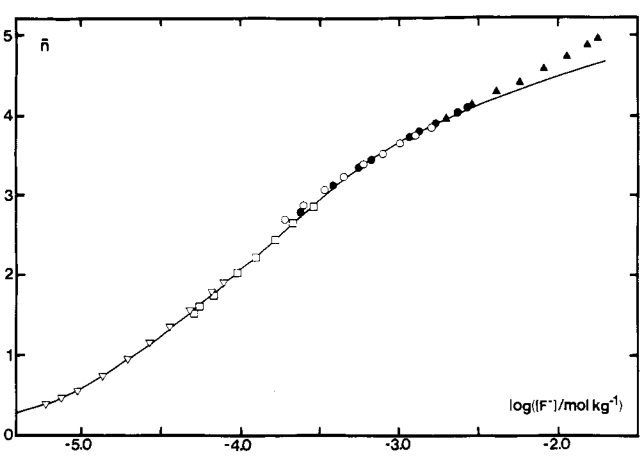

Figure 1. Typical experimental results from emf measurements of the fluoride activity in KSCN–KF melts containing UO_2^{2+} at 185 °C. Experimentally determined $\bar{n}$ from different series are displayed, and the full-drawn curve is constructed by use of the stability constants β_j in Table I. The experimental data are chosen to illustrate the typical spread in results and the extent of overlapping by different series.

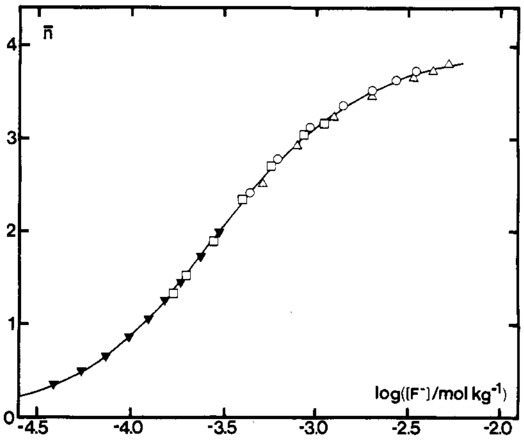

Figure 2. Results as in Figure 1 for the VO^{2+} system.

The experimental emf data were used to derive $[F^-]$ from eq 2, and average ligand numbers, $\bar{n}$, were thus obtained from

$$\bar{n} = (C_F - [F^-])/C_M \qquad (3)$$

C_M is the total concentration of uranyl(VI), C_U, or vanadyl(IV), C_V.

Experimental results from different series of measurements are displayed with different marker symbols in Figures 1 and 2. The experimentally determined ligand numbers are apparently independent of C_M in both systems. This primarily indicates that only mononuclear complexes have to be taken into account in the data analysis. Indirectly, it also provides evidence that the oxygen ligands in fact remain coordinated to the central ions as the fluoride complexation proceeds.

The measurements were limited by precipitation reactions when high average ligand numbers were reached (i.e. ~4.9 for uranyl(VI) and ~3.8 for vanadyl(IV)). X-ray powder diffraction analysis indicated the compounds $K_3UO_2F_5$ and K_3VOF_5.[26] The precipitation of these compounds gives further support for our assumption that the UO_2 and VO moieties are intact when SCN^- is substituted for F^- in the complexation reactions. A conditional solubility product, K_s', for these compounds can be calculated according to

$$K_s' = [M^{2+}][F^-]^5 \qquad (4)$$

K_s' was estimated at 185 °C to be $(4 \pm 1) \times 10^{-22}$ $mol^6 \cdot kg^{-6}$ for $K_3UO_2F_5$ and $(5 \pm 1) \times 10^{-20}$ $mol^6 \cdot kg^{-6}$ for K_3VOF_5. These estimates are based on knowledge of the association constants from Table I and visual observations of precipitation of the fluoride compounds in the test melts.

Table I. Overall and Stepwise Stability Constants and Total Interaction Energy Parameters, ΔA_j, for $UO_2F_j^{2-j}$ and VOF_j^{2-j} in Molten KSCN at 185 °C[a]

	j	β_j/ $(mol^{-j} \cdot kg^j)$	K_j/ $(mol^{-1} \cdot kg)$	$-\Delta A_j$/ $(kJ \cdot mol^{-1})$	β_j^*/ $(mol^{-j} \cdot kg^j)$
UO_2^{2+}	1	$(7.8 \pm 0.4) \times 10^4$	7.8×10^4	45.7 ± 0.2	3.9×10^4
	2	$(1.8 \pm 0.1) \times 10^9$	2.2×10^4	44.4 ± 0.3	6.0×10^8
	3	$(8.2 \pm 0.7) \times 10^{12}$	4.7×10^3	41.1 ± 0.4	4.7×10^{12}
	4	$(1.8 \pm 0.1) \times 10^{16}$	2.2×10^3	40.8 ± 0.4	1.8×10^{16}
	5	$(1.9 \pm 0.4) \times 10^{18}$	1.1×10^2	32.8 ± 0.8	
VO^{2+}	1	$(8.7 \pm 0.5) \times 10^3$	8.7×10^3	38.2 ± 0.2	1.3×10^4
	2	$(4.4 \pm 0.3) \times 10^7$	5.1×10^3	39.8 ± 0.3	6.1×10^7
	3	$(1.2 \pm 0.1) \times 10^{11}$	2.6×10^3	40.4 ± 0.3	1.3×10^{11}
	4	$(9.7 \pm 0.4) \times 10^{13}$	8.3×10^2	39.8 ± 0.3	1.0×10^{14}

[a] The error limits define a 95% confidence level. The parameters β_j^* are obtained from model calculations (eq 8) with $\Delta A = -43.0$ $kJ \cdot mol^{-1}$ for the uranyl(VI) system (steps 1–4) and $\Delta A = -39.6$ $kJ \cdot mol^{-1}$ for the vanadyl(IV) system.

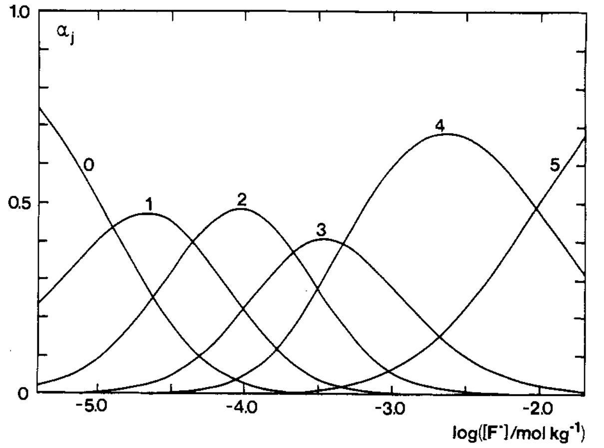

Figure 3. Fraction α_j of U in different complexes $UO_2(NCS)_{5-j}F_j^{3-}$ in molten KSCN–KF at 185 °C. j is indicated on the curves.

The complex formation can be described by a set of overall equilibria

$$M^{2+} + jF^- \rightleftharpoons MF_j^{2-j} \qquad (5)$$

where coordinated SCN^- ions have been omitted for the sake of clarity. The cumulative and stepwise stability constants β_j and K_j are defined in the conventional way.[1]

The stability constants were calculated by a recently described least-squares procedure, minimizing the sum $\sum(E_{exptl} - E_{calcd})^2$.[1] The number of experimental data points (C_M, C_F, E_{exptl}) was 188 for uranyl(VI) and 108 for vanadyl(IV). Four and five consecutive complexation steps can be unambiguously identified for VO^{2+} and UO_2^{2+}, respectively. The stability constants are collected in Table I. Figures 1 and 2 show that the fit to experimental data is good except for the highest fluoride concentrations in the uranyl(VI) system. This discrepancy is due not to anomalously large errors $|E_{exptl} - E_{calcd}|$ but rather to the fact that C_F and $[F^-]$ are of almost equal magnitudes. The reason for this is that C_U has to be kept as low as possible in order to prevent precipitation of $K_3UO_2F_5$. However, one can of course not exclude the possibility that the systematic deviation from the complex formation curve might be due to precipitation of the fluoride compound in amounts that could not be observed by visual inspection of the cell.

The fraction α_j of different species is defined as

$$\alpha_j = [MF_j^{2-j}]/C_M \qquad (6)$$

Here α_0 is the fraction of "free" central ion, i.e. UO_2^{2+} and VO^{2+} coordinated to SCN^- only. Figures 3 and 4 show the species distribution in the concentration ranges investigated. The stability domains of different complexes overlap considerably, and no single

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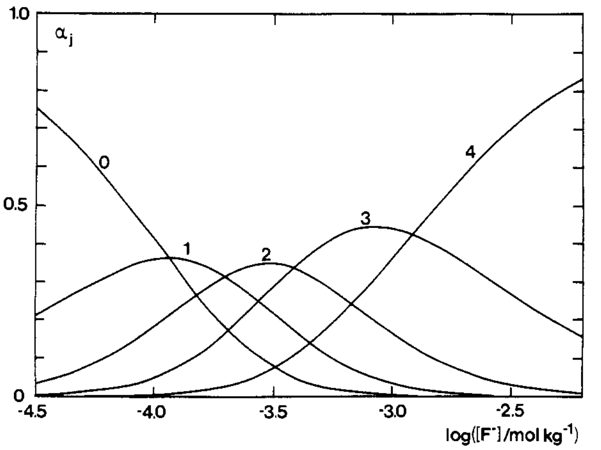

Figure 4. Fraction α_j of V in different complexes $VO(NCS)_{4-j}F_j^{2-}$ in molten KSCN–KF at 185 °C. *j* is indicated on the curves.

species dominates at any free ligand concentration.

The smoothness of the complex formation and distribution curves suggests that the fluoride complexation mainly occurs as the simple ligand-exchange process (1) in every step. The configurational entropy change for an ionic redistribution process like (1) in molten salts is largely determined by the short-range ordering imposed by the requirement of charge alternation in the melt, and is—in contrast to assumptions made for aqueous solutions[5-7]—unlikely to be a major driving force for association between hard acceptor ions and F^- in ionic melts. Hence, it is anticipated that the strength of fluoride complexation with these central ions in liquid KSCN might—at least qualitatively or semiquantitatively—be predicted mainly from estimated changes in Coulomb interaction energies and ideal configuration entropy changes for the ligand-exchange process (1) in very step *j*. According to the quasi-lattice theory for complex formation in reciprocal molten-salt systems,[3] the specific interaction energy ΔA_j for the *j*th step can be calculated as

$$\Delta A_j = RT \ln \left[(Z - j + 1) j^{-1} K_j^{-1}\right] \qquad (7)$$

provided the complexation is strong, i.e. $\exp(-\Delta A_j/RT) \gg 1$. The stepwise association constants K_j are expressed in mole fraction units, and Z is the quasi-lattice coordination number. When calculated in this way, ΔA_j may be regarded as the change in total acceptor–donor interaction energy including free energy contributions from changes in vibrational and rotational degrees of freedom for the thiocyanate ion. It seems justified to use a coordination number of 5 for uranyl(VI) since solid compounds, i.e., $K_3UO_2F_5$,[27] $(NH_4)_3UO_2F_5$,[28,29] and $Cs_3UO_2(NCS)_5$,[30] contain discrete anions with five monodentate ligands coordinated in the equatorial plane of the uranyl(VI) ion, giving a pentagonal-bipyramidal structure for $UO_2L_5^{3-}$. For the coordination of vanadyl(IV), things are less clearcut, but irrespective of whether the coordination is described as square pyramidal[31] or quasi-octahedral,[32] the number of equally attractive coordination sites must be 4, and this number is thus used as Z for VO^{2+}.

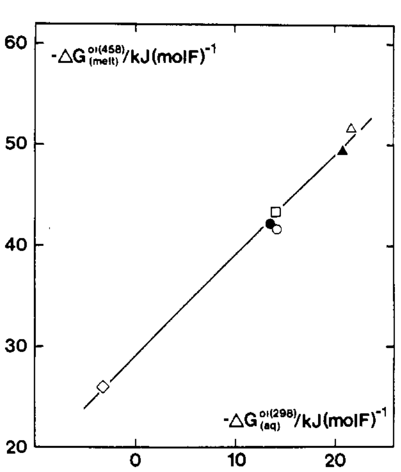

Figure 5. $\Delta G_{melt}{}^{\circ\prime}{}_{458}$ versus $\Delta G_{aq}{}^{\circ\prime}{}_{298}$ for processes 10 and 9, respectively. Symbols: Co^{2+} (j = 1), ◇; Cr^{3+} (j = 1), ○; Cr^{3+} (j = 2), ●; VO^{2+} (j = 1), □; UO_2^{2+} (j = 1), △; UO_2^{2+} (j = 2), ▲.

In Table I interaction energies, ΔA_j, for all steps are collected. The closeness of all ΔA_j's in the vanadyl(IV) system implies that the complexation over all four steps can be described by one single interaction parameter ΔA independent of the number of fluoride ligands already attached to the VO^{2+} ion. In this respect the VO^{2+}–F^-/SCN^- system bears close resemblance to the Cr^{3+}–F^-/SCN^- system, and the four overall stability constants might thus be estimated as[1]

$$\beta_j^* = (\exp(-j\Delta A/RT)) \prod_{n=1}^{j} ((Z - n + 1)/n) \qquad (8)$$

In Table I the set of β_j^* values calculated with the best fitting value $\Delta A = -39.6$ kJ·mol⁻¹ for $Z = 4$ are included for comparison. The agreement with experimentally determined β values is very good.

In the UO_2^{2+} system there is a trend toward lower gain in energy on going from j = 1 to 5. This is most probably due to increasing electrostatic repulsion between the ligands as the smaller fluoride ions replace thiocyanate, the ligands being confined to the equatorial plane perpendicular to the O–U–O axis. Hence, this feature also supports our assumption that the O–U–O configuration remains intact as the fluoride complexation proceeds.

The values of ΔA_j for the four first steps in the UO_2^{2+} system are still reasonably close, so an average value $\Delta A = -43.0$ kJ·mol⁻¹ will be used for comparison with other systems, notably the Cr^{3+} and Co^{2+} systems, in which the corresponding average values of ΔA are −36.4 and −21.3 kJ·mol⁻¹, respectively.[1,2] The concept of Coulomb complexing was introduced by Blander and coworkers[33,34] to describe an association process in which the complex formation energy largely arises from changes in Coulomb ionic interactions. It has been demonstrated earlier that such a model applies to the association of Ca^{2+} with IO_3^- in $(K,Na)NO_3$ melts,[35] and the model might—to a first approximation—also be applied to fluoride complexation with polyvalent acceptor ions in molten KSCN, where the Coulomb effects are expected to be of major importance. For the +2 ions the observed stability sequence $Co^{2+} < VO^{2+} < UO_2^{2+}$ can be qualitatively accounted for by expressing ΔA for the various systems as a change in Coulomb interaction on changing SCN^- for F^- according to the reaction scheme (1), using fixed charges located on V and U and interatomic bond distances from crystal structure data. This would require formal charges of at least +2.1 on V and +2.5 on U in VO^{2+} and UO_2^{2+}, which seems reasonable in view of results from recent calculations of the charge distribution within the oxycations.[36,37] If the Cr^{3+} system is included in the comparison, however, the observed sequence $Co^{2+} < Cr^{3+} < VO^{2+} < UO_2^{2+}$ would require charges higher than +3.0 on V and +3.5 on U in order to be reproduced by a Coulomb model only. For vanadium in particular, the

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estimated minimum charge seems unrealistically high. Covalent interactions to various extents—especially between the polyvalent acceptor ions and SCN^-—are most probably of some importance in determining the magnitude of ΔA. A more quantitative treatment, including a mapping of Coulomb and non-Coulomb effects, must wait, however, until further systems in mixed KSCN–KF melts have been investigated.

An instructive comparison with aqueous solution data can be made. For the four systems investigated in KSCN–KF melts by us, there are reliable data on the stability of the first complexes of Co^{2+}, Cr^{3+}, VO^{2+}, and UO_2^{2+} with SCN^- and F^- as well as the second complexes of Cr^{3+} and UO_2^{2+} in water at 298 K and $I = 1.0$ or 0.5 M.[4] Hence, the standard free energy change $\Delta G_{aq}{}^{\circ\prime}{}_{298}$ for

$$(1/j)\mathrm{M(NCS)}_j{}^{q+}(\mathrm{aq}) + \mathrm{F}^-(\mathrm{aq}) \rightarrow (1/j)\mathrm{MF}_j{}^{q+}(\mathrm{aq}) + \mathrm{SCN}^-(\mathrm{aq}) \quad (9)$$

can be calculated and directly compared with $\Delta G_{melt}{}^{\circ\prime}{}_{458}$ for

$$(1/j)\mathrm{M(NCS)}_Z{}^{p-} + \mathrm{F}^- \rightarrow (1/j)\mathrm{MF}_j\mathrm{(NCS)}_{Z-j}{}^{p-} + \mathrm{SCN}^- \quad (10)$$

in KSCN–KF melts at 458 K for $j = 1$ and 2. The quantities so obtained all refer to the exchange of *one* SCN^- for F^-. Figure 5 shows the surprisingly good correlation between $\Delta G_{melt}{}^{\circ\prime}{}_{458}$ and $\Delta G_{aq}{}^{\circ\prime}{}_{298}$. The best fitting straight line

$$\Delta G_{melt}{}^{\circ\prime}{}_{458} = k_1 \Delta G_{aq}{}^{\circ\prime}{}_{298} + k_2 \quad (11)$$

is obtained with the parameter $k_1 = 1.00 \pm 0.05$ and $k_2 = -28.9 \pm 0.8$ kJ·(mol F)$^{-1}$. The value of k_1 is of course fortuitous, but the result is nevertheless remarkable. The ligand-exchange reaction (1) obviously occurs with a gain in free energy that is 29 kJ·(mol F)$^{-1}$ larger in the molten-salt systems at 458 K *irrespective* of central ion and actual step of complexation. The underlying reason for this is of course unclear at the present stage, although it seems that the difference in free energy of transfer of the complex ions between water and molten salt largely depends on the structure of the outer coordination shell only.

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Registry No. $UO_2(NCS)_5^{3-}$, 45211-62-9; $VO(NCS)_5^{2-}$, 21136-26-5; KSCN, 333-20-0; KF, 7789-23-3; F_2, 7782-41-4.

Supplementary Material Available: A listing of experimental emf data (6 pages). Ordering information is given on any current masthead page.

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Diantimony Tetraoxides Revisited

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Untwinned crystals of α- and β-Sb_2O_4 have been grown for the first time, and both crystal structures are established from X-ray single-crystal diffraction data. α-Sb_2O_4 is orthorhombic, with $a = 5.434$ (1) Å, $b = 4.8091$ (6) Å, $c = 11.779$ (2) Å, $Z = 4$, and space group $Pna2_1$ (No. 33), and β-Sb_2O_4 is monoclinic, with $a = 12.057$ (1) Å, $b = 4.8352$ (3) Å, $c = 5.384$ (2) Å, $\beta = 104.56$ (1)°, $Z = 4$, and space group $C2/c$ (No. 15). Bond distances and angles are given. In α-Sb_2O_4, $Sb^{V}O_6$ octahedra share vertices forming layers, parallel to the a–b plane, joined by pairs of $Sb^{III}O_4E$ tetragonal pyramids, which share two oxygen atoms. The $Sb^{V}O_6$ octahedra of the β form are more regular and form layers parallel to b–c, with rows of $Sb^{III}O_4E$ pairs along the c direction. In the layers of both forms one interstice exists for every four $Sb^{V}O_6$ octahedra. These interstices have to be viewed through a certain direction in β-Sb_2O_4 to appear identical with those of the α form. For both structures the packing of oxygen atoms is more dense than for cubic or orthorhombic Sb_2O_3. According to bond-valence considerations, ψ-tetragonal-pyramidal coordination of Sb(III) can be considered as octahedral.

The first chemical analysis of Sb_2O_4 was performed in 1845 by Dufrênoy[1] on a sample from Cervantes (Lugo, Spain). Five years later Dana designated this mineral as cervantite.[2] For lack of suitable crystals, in 1938 Dihlström[3] had to infer the structure of synthetic cervantite from that of isomorphous stibiotantalite, $SbTaO_4$, which is orthorhombic, space group $Pna2_1$ (No. 33), $Z = 4$. In 1960 the unit cell dimensions of synthetic cervantite were determined,[4] and 2 years later it was established that the mineral shows the same X-ray diffraction pattern as synthetic cervantite. From crystals obtained by oxidation in air of Sb_2O_3, in 1975 the crystal structure of Sb_2O_4 was refined[5] in space group $Pna2_1$, obtaining an R factor of 0.107. More recently[6] the structure of synthetic Sb_2O_4 has been determined by a profile analysis of powder neutron diffraction data. The refinement in space group $Pna2_1$ converged to $R = 0.0685$ by using isotropic temperature factors, which were negative for Sb atoms.

In 1964, a new form of Sb_2O_4, designated as β-Sb_2O_4, was described.[7] The crystals were monoclinic prisms, elongated along c, with (100) prominent and were polysynthetically twinned on (100) with b and c in common. The structure was refined in space group $C2/c$ (No. 15), $Z = 4$, by using isotropic temperature factors, to $R = 0.066$.

In the course of our studies of Sb oxides, we have repeatedly attempted growing α- and β-Sb_2O_4 crystals under different conditions. At last, we obtained for the first time one crystal of α-Sb_2O_4 and, simultaneously, some nontwinned crystals of β-Sb_2O_4. The work reported here describes both crystal structures, making a comparison between them.

Table I. Coefficients for the Weighting Scheme in α-Sb_2O_4

	a	b		c	d
$\lvert F_o\rvert < 36$	7.55	−0.17	$(\sin\theta)/\lambda < 0.51$ Å^{-1}	2.24	−3.37
$36 < \lvert F_o\rvert < 310$	1.09	0.02	$0.51 < (\sin\theta)/\lambda < 0.71$	−2.11	5.08

Experimental Section

Crystal Growth. Crystals were grown by heating polycrystalline analytical grade α-Sb_2O_4 in evacuated (10^{-3} mmHg) quartz ampules, after three successive treatments at 963, 1073, and 1223 K, each one

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