The spectral differences between basic and acidic melts at cation frequencies could reflect a difference in the cation–anion interactions or simply be a result of packing constraints. The importance to physical properties of the nature of the anion can be considerable and the acidic ($Al_2Cl_7^-$ containing) system is liquid at far lower temperatures than the basic melts. For $C_5D_5N^+CH_3$, the asymmetric CH_3 bending band at 1452 cm^{-1} broadens in aqueous solution, thereby satisfying the criterion for a low barrier to alkyl-group rotation.[15] In general, the spectra of the melts seem to be more similar to that of the solid chloride salt and the rotational freedom may be restricted by a quasi-crystalline lattice type of solvent structure. Detailed IR studies, which include band assignments from isotropic studies, could aid in answering questions as to how the rotational and molecular entropy factors are related to the low liquidus temperatures of these melt systems.

Additional applications of infrared studies on solutes in these systems will be forthcoming.[16]

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Experimental Section

Preparation of chemicals and melts have been described previously.[2] Liquid IR cells were filled and sealed with Teflon stoppers in a drybox containing a purified argon atmosphere. Spectra in the 200–650-cm^{-1} regions for the 2:1 and 1:1 melts were recorded on a Beckman IR 12 spectrometer with 0.045-in. polyethylene windows and a 0.003-in. Teflon spacer. Although an attempt was made to eliminate the polyethylene spectra by matching cells in the double-beam mode, this approach was not particularly successful. Cancellation of the window contribution to the spectra by digitalization of the data and computer subtraction methods might be more fruitful. The window material showed no visible sign of interaction with these molten salts. A conventional NaCl liquid cell (Fisher Scientific) was used for the 4000–650-cm^{-1} experiments.

The purple solid $Te_4(Al_2Cl_7)_2$ compound was prepared according the the procedure of Couch et al.[13] and its IR spectrum obtained in a Nujol mull between polythylene plates. An attempt to record its Raman spectrum was unsuccessful.

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Stability and Species Spectra of Cobalt(II) Halide Complexes in Molten Eutectic (K,Li)NO₃ at 160 °C

S. HEMMINGSSON and B. HOLMBERG*

The stepwise formation of halide complexes of Co(II) in molten eutectic (K,Li)NO₃ at 160 °C has been followed by a spectrophotometric technique. Stability constants for $CoCl_j^{2-j}$ and $CoBr_j^{2-j}$ ($0 \leq j \leq 4$) and the corresponding resolved species spectra for all complexes are reported. In particular, it is shown that a spectrum of only CoX_4^{2-} is experimentally unobtainable in (K,Li)NO₃ in this temperature region. No definite conclusions on the coordination geometry of intermediate species between dodecahedral $Co(NO_3)_4^{2-}$ and tetrahedral CoX_4^{2-} can be drawn from the resolved spectra. No fluoride complexes can be detected. The order of decreasing complex stability is Cl⁻ > Br⁻ ≫ F⁻, which is in sharp contrast to the sequence F⁻ > Cl⁻ > Br⁻ for aqueous solution. This shift in F⁻ position is an obvious consequence of the presence of high-field Li⁺ cations in the solvent.

Introduction

A typical a–a association in molecular solvents is thought of as being energetically favored mainly by a large gain in configurational entropy due to desolvation of donor and acceptor ions, whereas the predominantly electrostatic donor–acceptor bonds yield small negative or even positive enthalpy contributions to the free energy of complexation.[1] Such arguments are unlikely to hold in ionic melts. In typical ionic liquids with an inherent short-range order, complex association is generally considered to be due to nonionic interaction between central ion and ligand. Therefore, it is of great interest to obtain a more detailed knowledge of the coordination chemistry of potential class a acceptors in ionic model solvents of rather "hard" character, such as alkali nitrate melts.

From the sequence of stability of halide complexes in aqueous solution, F > Cl > Br,[2-4] Co(II) may be classified as a class a acceptor.[5] The ability of Co(II) to form halide complexes in nitrate melts is well-known from several studies,[6-10] predominantly on chloride systems. It appears, however, that attempts of quantitative characterization of the stepwise complex formation have yielded largely conflicting and incomplete results.

The moderate tendency for precipitation of Co_3O_4 from halide-containing nitrate melts below 200 °C[11] makes such systems accessible to investigation by visible spectrophotometry. Gruen and co-workers[12,13] and later Tananaev and

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Dzhurinskii[14,15] have qualitatively explained the changes in Co(II) spectra in molten alkali nitrates upon partial substitution of NO_3^- for halide ions by assuming successive formation of halide complexes. Similar qualitative observations have been made by Barkatt and Angell[16] for Co^{2+}- and Cl^--doped glasses of KNO_3–$Ca(NO_3)_2$.

This work was undertaken in order to get a more complete quantitative picture of the Co(II) complexation with bromide, chloride, and fluoride. We have also aimed at a resolution of spectra into components for the various complex species. The solvent chosen is eutectic (K,Li)NO₃ at 160 °C.

Experimental Section

Spectra were recorded with a Unicam SP 700 spectrophotometer. The furnace compartment for the optical cells is an electrically heated aluminum block with vulcan asbestos insulation, inserted in a water-cooled jacket. The holes for the cells in the aluminum core are stoppered with heavy vulcan asbestos plugs running through the top insulation. The lower part of these plugs consists of aluminum disks. These metal disks cap the cells and are in good thermal contact with the heated Al block, thus largely eliminating vertical temperature gradients in the cells.

Thermostating is effected by a Eurotherm proportional temperature regulator, CR/DHS/PID/SCR, using a Pt-resistance sensor. The temperature of the furnace block is separately measured by another Pt sensor connected to a Knauer DC bridge fitted with an external resistance comparison arm. Absolute calibration was made with a standard Pt-resistance thermometer (National Physical Laboratory, Teddington), immersed in a filled cell under operating conditions. The temperature of the water in the outer jacket is kept at 30 °C by means of a separate circulation thermostat. Typical short-term temperature variations in the melts, recorded under these conditions, amount to some hundredths of a degree.

The wavelength calibration was checked intermittently by use of the 656.1-nm emission line of the deuterium lamp.

All commercial chemicals were of p.a. grade and were separately predried at 120–130 °C. The pure eutectic solvent and stock melts containing halide were prepared from weighed amounts of LiNO₃ and potassium salts with a K:Li ratio of 57:43. The salt mixtures were fused under vacuum and purged with dry nitrogen at 350 °C to remove traces of water. After filtration through a glass frit the melts were quenched and stored in dry atmosphere prior to use.

Melts containing predetermined amounts of Co(II) could not be prepared due to small but significant losses of Co as oxide precipitate prior to the final filtration at the cell filling. Dehydrated cobalt(II) halides were used as source of cobalt ions. Since the complexation in the studied systems is weak, the presence of halide in small amounts introduced in this way does not present any difficulties in the data evaluation for the stepwise association.

Weighed amounts of solidified melts were fused at 160 °C under vacuum on a glass frit and purged with dry nitrogen flowing with a low pressure through the frit from below. By reversal of the nitrogen flow the melt was forced through the frit into the silica cell. The pressure was reduced again to remove spurious gas bubbles and then raised to atmospheric pressure with nitrogen.

Spectra were as a rule recorded with 10-mm cells between 350 and 750 nm vs. pure (K,Li)NO₃ melt as reference. For each melt several spectra were recorded repeatedly with intervals ranging from 15 min to many hours. In this way it was ascertained that no changes in the spectra due to oxide formation occurred within 24 h. This paper reports results derived from spectra of 62 melts, distributed on various halide systems as follows: Cl (40), Br (17), and F (5). The compositions of the fluoride-containing melts are listed in Table I. For the chloride- and bromide-containing melts, the compositions are given as supplementary material (Tables V and VI).

Variations in refractive index of the nitrate melts upon partial substitution of NO_3^- for halide are known to be negligible in the actual composition range.[17] The variations in mass density were checked

Table I. The Composition of Melts Co,K,Li–NO₃,Br,F of Which Spectra Have Been Recorded for Determination of Cobalt(II) Fluoride Complexes

melt	C_{Co}/ mol kg⁻¹	C_{Br}/ mol kg⁻¹	C_F/ mol kg⁻¹
A	0.004 72	0.009 44	0.0194
B	0.004 31	0.008 62	0.0249
C	0.003 25	0.006 50	0.0211
D	0.004 08	0.177 2	0.0284
E	0.000 75	0.170 5	0.0262

by absorbance measurements at 370 nm on K₂CrO₄-containing melts with different halide concentrations, 0–0.5 mol kg⁻¹. No significant density variations could be detected, and a constant value of $\rho = 1.98 \times 10^3$ kg m⁻³ [18] has been used.

Analyses for Co(II) and halide were performed on aqueous solutions of solidified aliquots of the melts after the spectrophotometric measurements.

Calculations and Results

In the conventional way of analyzing data the stepwise formation of complexes ML_j are described by a set of overall equilibria.

$$M + jL \rightleftharpoons ML_j \tag{1}$$

In sufficiently dilute systems the cumulative and stepwise stability constants β_j and K_j are expressed as

$$\beta_j = [ML_j][M]^{-1}[L]^{-j} \qquad K_j = [ML_j][ML_{j-1}]^{-1}[L]^{-1} \tag{2}$$

with $0 \leq j \leq N$, N being the maximum ligand coordination number. The basic equations to be used are

$$C_L = [L] + [M] \sum_{j=0}^{N} j\beta_j[L]^j \tag{3}$$

$$C_M = [M]\sum_{j=0}^{N} \beta_j[L]^j \tag{4}$$

$$\epsilon = (\sum_{j=0}^{N} \epsilon_j\beta_j[L]^j)(\sum_{j=0}^{N} \beta_j[L]^j)^{-1} \tag{5}$$

with $\beta_0 = 1$. The overall molar absorption coefficient is

$$\epsilon = Al^{-1}C_M^{-1} \tag{6}$$

which is experimentally determined from the absorbance A, pathway of light l, and total concentration of central ion C_M. The specific molar absorption coefficients ϵ_j are defined through

$$A = l\sum_{j=0}^{N} \epsilon_j[ML_j] \tag{7}$$

if, as is the case in the present study, L does not absorb light.

The Chloride System. The data analysis will be described in some detail for the chloride system, which has been subject to the most thorough investigation. The calculations were performed by use of both molalities, mole fractions, and concentrations in eq 2–5 in order to produce a basis for comparison of the effect of various activity approximations on the results.

For the final computation of stability constants β_j and species spectra $\epsilon_j(\lambda)$ the least-squares program LETAGROP-SPEFO[19] was utilized. Due to the large extent of overlapping of species spectra and the fact that several different complexes are present in comparable amounts in most melts, the final calculations had to be supported by good estimates of starting values of several parameters in order to achieve a proper

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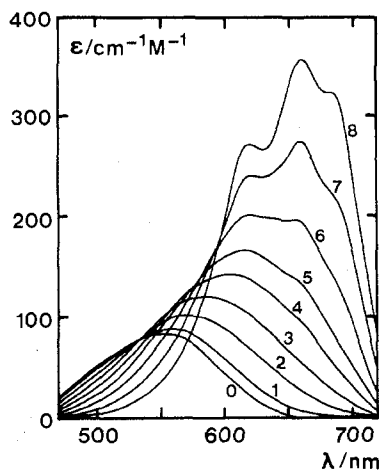(19) Sillén, L. G.; Warnqvist, B. *Ark. Kemi* **1969**, *31*, 377.

Figure 1. The reduced set of spectra for nine different [Cl⁻], obtained by extrapolation to $C_{Co} = 0$ of experimental spectra for Co,K,Li-NO₃,Cl melts at 160 °C. [Cl⁻]/mol kg⁻¹: 0 (0), 0.00999 (1), 0.0299 (2), 0.0498 (3), 0.0746 (4), 0.0993 (5), 0.1483 (6), 0.245 (7), 0.482 (8).

convergence toward minimum in the error square sum. These estimates were derived from a reduced data set of nine spectra, representing different values of [Cl⁻], obtained by extrapolation of experimental ϵ at various wavelengths (470–720 nm) to C_{Co} = 0 (Figure 1). In this way $\epsilon_0(\lambda)$, i.e., the spectrum of solvent coordinated cobalt ion, Co²⁺, is immediately obtained.

From eq 5

$$\frac{d \ln \epsilon}{d \ln [L]} = (\sum_{j=0}^{N} j\epsilon_j\beta_j[L]^j)/(\sum_{j=0}^{N} \epsilon_j\beta_j[L]^j) -$$

$$(\sum_{j=0}^{N} j\beta_j[L]^j)/(\sum_{j=0}^{N} \beta_j[L]^j) \quad (8)$$

By substitution of the two terms in the right-hand member, eq 8 can be rewritten as

$$\frac{d \ln \epsilon}{d \ln [L]} = \bar{n}_\epsilon - \bar{n} \quad (9)$$

where $\bar{n}$ is the average ligand number and $\bar{n}_\epsilon$ analogously describes the average partition of absorbance on different complexes. Clearly

$$N \geq |\bar{n}_\epsilon - \bar{n}| \quad (10)$$

and, for two different wavelengths λ_1 and λ_2

$$N \geq |(\bar{n}_\epsilon(\lambda_1) - \bar{n}) - (\bar{n}_\epsilon(\lambda_2) - \bar{n})| \quad (11)$$

An analysis of data according to eq 9 and 11 at 490 and 700 nm yields $N \geq 2.8$. Furthermore, there is a nonlinear relation between the ϵ values at 470 and 490 nm. This indicates the existence of at least two absorbing species in this wavelength region, so $\bar{n}_\epsilon(490) \neq 0$ for some [Cl⁻]. Hence $N > 3$ is a very reasonable estimate.

A spectrum of CoCl$_N^{2-N}$ cannot be obtained experimentally due to the limited solubility of alkali chloride. A fairly good estimate of ϵ_N is obtained by extrapolation of ϵ to [Cl⁻]⁻¹ = 0. This procedure generates a spectrum which is very similar to those which have been ascribed to CoCl₄²⁻ in the solid state,[20] concentrated aqueous HCl solution[21] and molten chlorides[12,13,22,23] (species spectra from the final computations are given in Figure 2), so N is assumed to be 4.
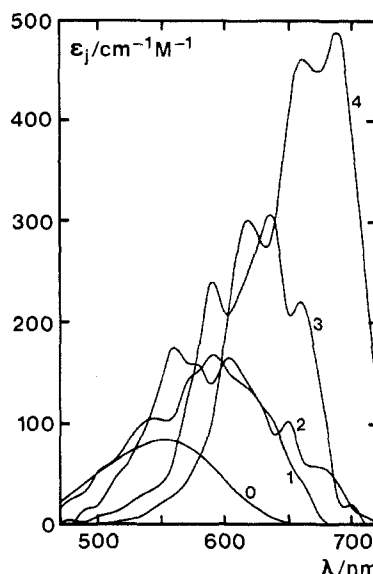

Figure 2. Resolved species spectra for CoCl$_j^{2-j}$ in eutectic (K,Li)NO₃ at 160 °C. j is printed on the curves.

Table II. Stability Constants β_j for CoCl$_j^{2-j}$ Calculated in Molalities (A), Concentrations (B), and Ionic Mole Fractions (C)[a]

j	A β_j/mol^j kg^{-j}	B β_j/1.98^j M^j	C β_j/11.45^{-j}
1	11.7 ± 2.4	11.9 ± 2.4	12.0 ± 2.4
2	240 ± 21	246 ± 21	247 ± 21
3	1720 ± 180	1680 ± 180	1670 ± 170
4	7960 ± 920	8240 ± 950	8310 ± 950
U_{min}	0.1666	0.1667	0.1666

[a] The constants according to alternatives B and C are normalized with solvent density and molality numbers to be directly comparable with A. U_{min} is the minimum error square sum obtained for each set of constants.

Table III. Overall and Stepwise Stability Constants for CoCl$_j^{2-j}$ and CoBr$_j^{2-j}$ in Fused (K,Li)NO₃ Eutectic at 160 °C

	j 1	2	3	4
Cl⁻: β_j/mol^j kg^{-j}	11.7 ± 2.4	240 ± 21	1720 ± 180	7960 ± 920
Br⁻: β_j/mol^j kg^{-j}	6.2 ± 2.4	98 ± 27	520 ± 200	1940 ± 430
Cl⁻: K_j/mol kg^{-1}	11.7 ± 2.4	20.5 ± 4.6	7.2 ± 1.0	4.62 ± 0.72
Br⁻: K_j/mol kg^{-1}	6.2 ± 2.4	15.6 ± 7.5	5.4 ± 2.5	3.73 ± 0.74

As ϵ_0 and ϵ_4 are known, a reasonable basis for the starting estimates of β_j values can be obtained from equations derived by series expansion of ϵ or ϵ^{-1} in powers of [Cl⁻] or [Cl⁻]⁻¹. From

$$\frac{\epsilon_0 - \epsilon}{\epsilon_0[L]} = \left(1 - \frac{\epsilon_1}{\epsilon_0}\right)\beta_1 +$$

$$\left[\left(1 - \frac{\epsilon_2}{\epsilon_0}\right)\beta_2 - \left(1 - \frac{\epsilon_1}{\epsilon_0}\right)\beta_1^2\right][L] + \ldots \quad (12)$$

and a set of analogous expressions, the conditions $\beta_1 \geq 13$ mol⁻¹ kg, $\beta_2 \geq 107$ mol⁻² kg², $(\beta_2/\beta_4) \geq 0.032$ mol² kg⁻², and $(\beta_3/\beta_4) \geq 0.20$ mol kg⁻¹ are obtained.

In the final computations the error square sum $U = \sum w^2(\epsilon - \epsilon_{calcd})^2$ was minimized for 560 points in the (ϵ, C_{Co}, C_{Cl}) space from the original set of experimental spectra of 40 melts. The weight function w was ϵ^{-1} for $\epsilon > \epsilon^*$ and $(\epsilon^*)^{-1}$ for $\epsilon \leq \epsilon^*$. The

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Table IV. Review of Stability Constants for $CoCl_j^{2-j}$ in Molten Alkali Nitrate Media around 160 °C (Literature Data)

| | | | β_j/mol^j kg^{-j} | | | | |
solvent	temp/°C	method	$j = 1$	$j = 2$	$j = 3$	$j = 4$	ref
(Li,K)NO₃	160	distrib (various evaluation methods)	13	104	251		
			14	100	346	141	
			19	161	200	4000	6
(Li,K)NO₃	160	distrib	17	220	1040	12640	7
(Li,K,Na)NO₃	161	emf	20	58			8
(Li,K,Na)NO₃	158	polarogr	47				9
(Li,K)NO₃	160	spectr	12	50	200		10

limiting value ϵ^* was set to 50 cm^{-1} M^{-1} in order to ensure that contributions to U from different wavelengths are of the same order of magnitude in the whole spectral range. The computed stability constants are given in Table II.

The final set of species spectra was calculated from the experimental spectra of nine selected melts, covering the whole wavelength and composition range studied. A total of 234 points in the experimental $(\epsilon, C_{Co}, C_{Cl})$ space were used, and ϵ_j was calculated at every tenth nanometer from a minimization of U, using fixed values of β_j as given in Table II. Figure 2 displays the species spectra of $CoCl_j^{2-j}$ with $j = 0$–4.

The Bromide System. The computations of the stability constants were made analogously to the procedure used for the chloride melts, but the calculations were performed with β_j in molality units only. Table III gives the overall and stepwise stability constants for both bromide and chloride complexes for the sake of comparison.

Species spectra for $CoBr_j^{2-j}$ are given in Figure 3. They have been drawn by use of values for ϵ_j obtained in the simultaneous least-squares fit of both β_j and ϵ_j to the total $(\epsilon, C_{Co}, C_{Br})$ material using 238 experimental points at 14 wavelengths.

The Fluoride System. No quantitative calculations pertaining to CoF_j^{2-j} complexes were made. The results for the fluoride systems will be described and discussed in the next section.

Discussion

In the present study of chloride association it has been necessary to extend the measurements to melts which are almost saturated in LiCl in order to achieve reliable information on the higher complexes $CoCl_3^-$ and $CoCl_4^{2-}$. At most about 5% of the solvent nitrate ions have been exchanged for Cl⁻ in the most concentrated solutions, and the choice of activity approximating quantities in the equilibrium constant expressions might be of crucial importance for the analysis of data in terms of thermodynamic stabilities—at least for the formally negatively charged complexes. However, the numerical values of the β_j constants in Table II clearly indicate that this choice is of no practical importance. The same conclusion can be drawn from a comparison of U_{min} according to the three alternatives A, B, and C.

Holmberg[24] has demonstrated the effects of changes in solvent activity on the interpretation in terms of apparent stabilities of complex species in minor amounts as the fraction of solute ions becomes large in ionic melts. In the present case the reaction scheme (eq 1) is an obvious oversimplification. A better description might be

$$Co(NO_3)_z + jCl^- \rightleftharpoons CoCl_j(NO_3)_{z-j} + jNO_3^- \quad (13)$$
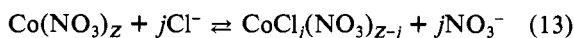
The difference between models (1) and (13) can be readily accounted for by substituting [L][NO₃⁻]⁻¹ for [L] in eq 2–5. It can be shown quite easily, however, that a thermodynamic analysis according to the "realistic" model (13) using ionic fractions for [L] and [NO₃⁻], which seems reasonable, is quite

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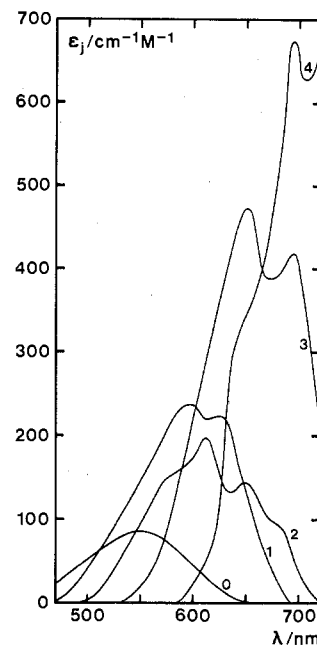

Figure 3. Resolved species spectra for $CoBr_j^{2-j}$ in eutectic (K,Li)NO₃ at 160 °C. j is printed on the curves.

analogous to the calculation process according to the simplified model (1) by use of molalities for all solute species (alternative A in Table II). Hence, the data of Table II also demonstrate that the schematic model (1) is a quite sufficient basis for quantitative calculations.

In Table IV we have collected a number of stability constants for $CoCl_j^{2-j}$ in molten alkali nitrates around 160 °C obtained by various authors with different methods. The spread is considerable. Our result is, however, in fairly good agreement with those obtained by distribution experiments by Vittori and Porthault.[7] The discrepancies in β_3 and β_4 might in part be due to the fact that the interpretation of distribution data is dependent on assumptions about the nature of extractable species. The results from emf measurements of the chloride activity obtained by Pacák and Sláma[8] cannot be directly compared with ours, since they refer to a somewhat different cation composition of the solvent as does β_1 obtained by polarography.[9] Qualitatively, however, the larger values of β_1 in these melts are in accordance with the lower content of Li⁺. The apparently low stability of CoCl₂, reported by Pacák and Sláma, is probably caused by the fact that ligand activity measurements are a blunt instrument for studying higher complexes in these rather weak systems.

Figure 4 displays the fraction α_j of Co(II) present in different complexes $CoCl_j^{2-j}$ as a function of log ([Cl⁻] mol⁻¹ kg). The curves have been drawn from the smallest [Cl⁻] used in this study to a maximum value close to the saturation concentration of alkali chloride. In Figure 5 the corresponding plots for the Co(II)–Br system are given. A comparison with the chloride complexation in aqueous solution, which has recently been thoroughly investigated by Bjerrum and co-
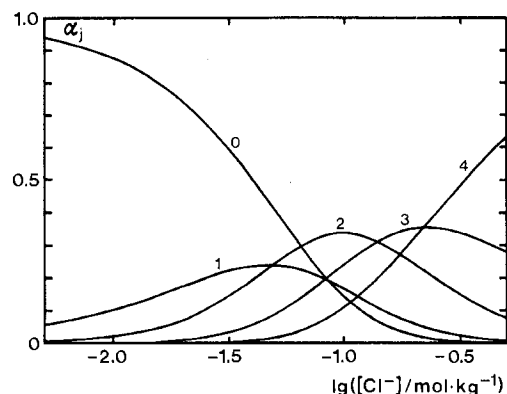
Figure 4. The fraction α_j of Co(II) in different complexes $CoCl_j^{2-j}$ in eutectic $(K,Li)NO_3$ at 160 °C. j is indicated on the curves.

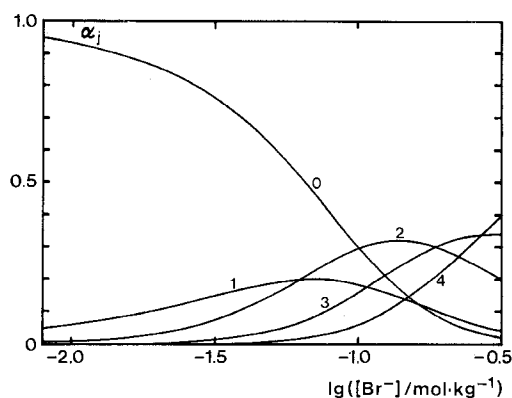**Figure 5.** The fraction α_j of Co(II) in different complexes $CoBr_j^{2-j}$ in eutectic $(K,Li)NO_3$ at 160 °C. j is indicated on the curves.

workers,[25] shows that the intermediate species $CoCl_2$ and $CoCl_3^-$ are much more prominent in nitrate melts. The magnitudes of the stepwise constants K_1-K_4 in aqueous solution indicate that the change in coordination geometry from octahedral (in the hexasolvate $Co(H_2O)_6^{2+}$) to tetrahedral (in $CoCl_4^{2-}$) probably occurs with the formation of $CoCl_2$.

In nitrate melts the situation is different. The resolved spectrum for $CoCl_4^{2-}$ in molten $(K,Li)NO_3$ (Figure 2) agrees excellently with those reported for tetrahedral $CoCl_4^{2-}$ in solid Cs_2CoCl_4,[20] in 12 M aqueous HCl solution,[21] and in melts of $CoCl_2$ and pyridine hydrochloride[12] and alkali chloride such as eutectic $(K,Li)Cl$[13] and $CsCl$.[22] Hence, it is highly probable that the 1:4 chloride species in nitrate melts is a tetrahedral anion $CoCl_4^{2-}$ with no oxygen from NO_3^- coordinated to Co(II).

From Figure 5 it can be seen that $CoBr_4^{2-}$ amounts to at most 40% of the total Co(II) content at the limit $[Br^-] = 0.3$ mol kg^{-1} which is set by the solubility of alkali bromide. Nevertheless a fairly good resolved spectrum for $CoBr_4^{2-}$ can be obtained. As might be expected, all bromide complexes absorb light at somewhat lower energies than the analogous chloride complexes. Hence, all details of ϵ_4 for $CoBr_4^{2-}$ are not reproduced in Figure 3 since part of the spectrum falls outside the wavelength range covered. Figure 3 reveals, however, a shoulder around 660 nm, a maximum approximately at 695 nm and probably another one for $\lambda \geq 720$ nm. These features are in good agreement with spectra that have been assigned to tetrahedral $CoBr_4^{2-}$ in various solvents[26] and pure bromide melts,[27] including eutectic $(K,Li)Br$.[28] It is thus

concluded that $CoBr_4^{2-}$ has a configuration quite analogous to that of $CoCl_4^{2-}$ in the fused nitrate solvent.

The spectrum $\epsilon_0(\lambda)$ in Figures 2 and 3, derived from halide-containing nitrate melts, agrees with those reported from halide-free glasses $KNO_3-Ca(NO_3)_2$,[16,29] melts $(K,Li)NO_3$,[30] and the solid $(R_4As)_2Co(NO_3)_4$.[31] As pointed out by Duffy and Ingram,[29] this spectrum probably arises from $Co(NO_3)_4^{2-}$ with four bidentate nitrates, giving a dodecahedral oxygen coordination to Co(II) as derived from X-ray diffraction data for $(R_4As)_2Co(NO_3)_4$.[32]

Judging from the species spectra in Figures 2 and 3 one might be inclined to suggest that the main transition to tetrahedral geometry occurs on building up CoX_3^- from CoX_2. No definite structural information can be gained, however, from the shape of the spectra of CoX^+, CoX_2, and CoX_3^-. The uncertainties in the ϵ_j values are as a rule on the order of 10–20 cm^{-1} M^{-1} for the chloride system, so the finer details of the spectra are almost certainly artifacts. In the bromide system the corresponding uncertainties are somewhat larger, 10–30 cm^{-1} M^{-1}, mainly because of the "tight" coexistence of all species (Figure 5) in almost the whole composition range where changes in experimental spectra occur.

The structural rearrangements, leading to tetrahedral CoX_4^{2-}, might involve changes in nitrate coordination modes from bidentate to monodentate to yield a mixed halide–oxygen configuration with a reduced number of coordinating atoms as compared to the original dodecahedral $Co(NO_3)_4^{2-}$. At present, however, the experimental evidence is insufficient for further detailed speculations about coordination changes.

To the knowledge of the present authors, no previous quantitative investigation of cobalt bromide complexation in nitrate melts has been published, except for the emf study by Pacák and Sláma.[8] They found $\beta_1 = 12$ mol^{-1} kg, which—for reasons already discussed—compares badly with our results.

Figure 5 shows that the building up of complexes $CoBr_j^{2-j}$ proceeds qualitatively very similarly to the chloride complexation. Thermodynamically, however, all bromide complexes are undoubtedly weaker than the corresponding chloride species. This finding is in contrast to previous statements by Tananaev and Dzhurinskii[15] and later by Inman and co-workers[33] but confirms the assumption by Frouzanfar and Kerridge[11] based on observations of Co_3O_4 precipitation rates in mixed nitrate–halide melts.

Here it may be appropriate to make an important remark on the general spectral behavior and complex compositions of the $NO_3^--Cl^-$ and $NO_3^--Br^-$ melts. From Figures 1–5 it is evident that the only Co(II) single species spectrum that can be obtained by direct measurements to a reasonably good degree of approximation is that of $Co(NO_3)_4^{2-}$. In particular, the spectra of $CoCl_4^{2-}$ and $CoBr_4^{2-}$ cannot be experimentally recorded. For instance, in the classical work by Gruen and co-workers[13] and in the later study by Tananaev and Dzhurinskii[14] the spectra reported for the most halide-rich melts actually refer to rather composite systems with Co(II) mainly distributed over three species, $CoCl_4^{2-}$ (~60%), $CoCl_3^-$ (~30%), and $CoCl_2$ (~10%) (Figure 4). Thorough ligand field calculations for $CoCl_4^{2-}$[34] have most probably been performed by use of spectra of a complex mixture of the same kind.

Correspondingly, Co(II) spectra from $(K,Li)(NO_3,Br)$ melts, which (for unclear reasons) have been attributed to

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species such as $CoBr_3^{3-}$ and $CoBr_6^{4-}$ at 160 °C,[15] most certainly originate from melts with an approximate Co(II) distribution of $CoBr_4^{2-}$ (~40%), $CoBr_3^-$ (~35%), $CoBr_2$ (~20%), and $CoBr^+$ (~5%) (Figure 5).

Attempts to quantitatively study the fluoride complexes were made by recording spectra of melts with small amounts of $CoBr_2$ (producing essentially Co^{2+} and Br^- in the melt) and KF added up to the solubility limit of LiF (0.03 mol kg⁻¹). No spectral changes at all could be observed, however, after addition of fluoride (melts A–C in Table I). This might be due either to the presence of fluoride complexes with an absorbance in the 550-nm region very similar to that of $Co(NO_3)_4^{2-}$ (cf. ref 35) or to the fact that no fluoride complexes are formed in detectable amounts. In order to discriminate between these two possibilities, we recorded the spectra of melts D and E (Table I) with an approximate fivefold excess of bromide over fluoride. These spectra were identical with those which could be calculated for fluoride-free melts with the same concentrations of cobalt and bromide. Hence, it is concluded that fluoride acts as a considerably weaker ligand than bromide. This conclusion qualitatively agrees with previous observations from conductivity[36] and cryoscopy[37] studies.

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The sequence of decreasing stability of cobalt(II) halide complexes in molten $(K,Li)NO_3$, $Cl^- > Br^- \gg F^-$, is in contrast to the characteristic class a acceptor sequence $F^- > Cl^- > Br^-$ for aqueous solution chemistry of Co(II).[2-4] The reason for this difference is probably to be found in a strong interaction of Li^+ with F^- in the melts. Preliminary measurements[38] indicate that β_1 for LiF in water is about 1.5 M⁻¹ which compares with $\beta_1 = 2.5$ M⁻¹ for CoF^+.[2] If this closeness in affinity for F^- persists in nitrate melts, the large excess of Li^+ over Co(II) effectively reduces the tendency for Co–F complexation.

Correspondingly, there should be a similar although not so pronounced competition between Li^+ and Co(II) for Cl^-. This means that the difference in chloride and bromide affinity for cobalt is actually larger than that indicated by the difference in the corresponding stability constants.

Supplementary Material Available: Tables V and VI, the compositions of Co,K,Li–NO₃,Cl and Co,K,Li–NO₃,Br melts of which spectra have been recorded (2 pages). Ordering information is given on any current masthead page.

(38) Hemmingsson, S., unpublished data.

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Solid Solutions (Ag,Na)₂CrO₄ and Silver Chromate Complexes in (K,Na)NO₃ Melts. A Potentiometric, Spectrophotometric, and Solubility Study

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The complex formation between Ag(I) and CrO_4^{2-} in molten 1:1 $(K,Na)NO_3$ has been studied mainly by emf and solubility measurements. Stability constants β for the rather weak complexes $AgCrO_4^-$, Ag_2CrO_4, and $Ag(CrO_4)_2^{3-}$ have been determined. The emf measurements were performed at five temperatures between 523 and 623 K. The temperature dependence of β_{11} is interpreted in terms of ΔH°_1 and ΔS°_1 for the formal process $Ag^+ + CrO_4^{2-} \rightarrow AgCrO_4^-$, which is favored to about the same extent by ΔH°_1 and $-T\Delta S^\circ_1$ contributions to ΔG°_1 at 553 K. The solubility of a range of solid solutions (Ag,Na)₂CrO₄ has been measured at the reference temperature 553 K in melts with Ag^+ in excess over CrO_4^{2-} and *vice versa*. Stability constants obtained from these measurements agree with those from potentiometric data. The activity of Ag_2CrO_4 in the solids has been determined. A phase transition from solid solutions of Ag_2CrO_4 (I) to a Na-rich phase (II) with $x_{Na} = 0.53 \pm 0.05$ was detected by thermodynamic methods and X-ray powder diffraction techniques. Phase I is close to thermodynamically ideal whereas phase II exhibits large positive deviations from ideality. Absorption spectra of CrO_4^{2-} in melts with various cationic compositions show a remarkable shift of the low-energy band toward lower energies upon association with Ag^+. This is attributed to the occurrence of a considerable d–π back-donation from Ag(I) to CrO_4^{2-}.

Introduction

In previous papers we have reported on the complexation of NO_2^{-1} and IO_3^{-2} with Ag(I) in the molten "standard solvent" equimolar $(K,Na)NO_3$. Although the thermodynamic stability of complexes formed in those systems is comparably low, the silver ion may be considered as a good "probe" metal ion for comparing the complexing ability of various oxoanions, since the Ag(I) activity can be determined conveniently by emf measurements with silver electrodes. A number of emf studies

of Ag(I) association with divalent oxoanions in various molten alkali nitrates have also appeared in the literature,[3-7] but the spread in the data—with respect to temperature, solvent composition, and complex stabilities—is unfortunately too large in most cases to make a meaningful comparison of, e.g., enthalpy and entropy effects on the association in different

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