2. Alkali-Metal Hexachloroniobates and Hexachlorotantalates. The Raman spectra of the molten alkali-metal hexachloroniobates and hexachlorotantalates are shown in Figures 3 and 4, respectively. The scale factors within this set are identical except for those of the $KTaCl_6$ spectra. The characteristics of these spectra are given in Table II, which also includes results from the literature.

Mamantov et al.[15] have measured the Raman spectra of $KTaCl_6$ at 693 K. The results obtained in this work are in excellent agreement given the small differences in specimen composition and temperature in the two studies. For $CsNbCl_6$ there is good agreement between the results obtained in this work and those of Øye et al.[17] However, in this work it was not possible to detect the weak band in the vicinity of 280 cm^{-1} or to resolve the peak at 178 cm^{-1} into the reported components.[17]

As for Cs_2ZrCl_6 and Cs_2HfCl_6 mentioned above, the existence of the octahedrally coordinated NCl_6^- ion has been proposed on the basis of spectral measurements of solid $CsNbCl_6$,[17] $KTaCl_6$[15] and $CsTaCl_6$.[14]

As was the case in Table I, in Table II there appears to be a small shift in the position of the ν_1 peak with a change in alkali-metal cation, where ν_1 decreases as the size of the cation increases. In contrast to Table I, Table II shows that for a given alkali metal, there is a shift in the position of the ν_1 peak with a change in refractory metal, where ν_1 increases with atomic number. This demonstrates that the similarity in the chemical behaviors of niobium and tantalum is not as pronounced as is the case for zirconium and hafnium.

3. General Observations. The refractory-metal compounds studied in this work exhibited behavior in conformity with the existence of octahedrally coordinated species of the O_h point group symmetry, although the constituent refractory-metal chlorides possess different symmetries. In fact, group 4 chlorides are of a symmetry different from that of the group 5 chlorides. $ZrCl_4$ and $HfCl_4$ have T_d symmetry, while $NbCl_5$ and $TaCl_5$ have D_{3h} symmetry.[19-21]

Comparison of Tables I and II reveals that it may be possible on the basis of the Raman spectrum to detect changes in valency of refractory-metal species in these melts. Specifically, the ν_1 peaks of K_2ZrCl_6 and K_2HfCl_6 lie at ~325 cm^{-1} while the corresponding peaks of $KNbCl_6$ and $KTaCl_6$ lie at 370–390 cm^{-1}. This represents a shift of approximately 55 cm^{-1} in changing from the analogous group 4 to group 5 compounds. In an investigation of chlorotitanates, a shift of 30 cm^{-1} was noted on going from Ti^{4+} to Ti^{3+}.[17] Because these shifts are easily detectable in the Raman spectra of these melts, it should be possible to conduct spectroreducibility studies.

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Registry No. Na_2ZrCl_6, 18346-98-0; K_2ZrCl_6, 18346-99-1; Cs_2ZrCl_6, 16918-86-8; Li_2HfCl_6, 18346-97-9; Na_2HfCl_6, 12016-11-4; K_2HfCl_6, 19381-63-6; Cs_2HfCl_6, 16918-87-9; $KNbCl_6$, 16919-88-3; $CsNbCl_6$, 16921-14-5; $NaTaCl_6$, 16920-14-2; $KTaCl_6$, 16918-73-3; $CsTaCl_6$, 16921-15-6.

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Desolvation Energies for Rare-Earth-Metal Perchlorate, Chloride, and Nitrate Electrolytes from 0.1 *m* to Saturation

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Work of desolvation values for rare-earth-metal perchlorate, chloride, and nitrate electrolytes across the rare-earth-metal series from 0.1 to 1 *m* are relatively uniform and are in the sequence of perchlorates > chlorides > nitrates. Changes in $T\Delta S$ in this region are in the sequence of perchlorates > nitrates > chlorides and reveal a geometric anion obstruction factor that depends on anion size and complexity. Desolvation energies for 0.2 *m* increments for the region of 1 *m* to saturation show that negative values of $T\Delta S$ persist to saturation for the perchlorate series but $T\Delta S$ values for chlorides all change from negative to positive near saturation. For the nitrate series at saturation, incremental values of $T\Delta S$ are negative for lanthanum through gadolinium, near zero for terbium, dysprosium, holmium, and erbium, and positive for thulium, ytterbium, and lutetium. Zero crossing of incremental $T\Delta S$ is interpreted to be an indicator that outer-sphere ion pairing is complete, and positive $T\Delta S$ is the result of ion compression of inner-sphere cation water and electrolyte destructuring on formation of inner-sphere ion pairs by water displacement.

Introduction

In a previous paper we used a desolvation method to calculate crystallization energies of rare-earth-metal perchlorates, chlorides, and nitrates.[1] Gibbs energy changes were calculated from solvent activity data of Spedding and co-workers,[2-4] Rard and Spedding,[5,6] and Rard, Miller, and Spedding.[7] Inverse heat of dilution data[8-11] were combined with ΔG values in the second law of thermody-

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namics to give entropy changes. Several cation and anion size effects were revealed. In this paper we extend the method to include desolvation of electrolytes in the concentration range of 0.1 *m* to saturation.

Several electrolytes at smaller concentrations have been evaluated by Debye–Hückel parameters by Spedding and coworkers,[3,4,12] and activity coefficients have been calculated for wide concentration ranges.[2-7] Pitzer, Peterson, and Sylvester have given a theoretical treatment of chloride, nitrate, and perchlorate electrolytes.[13] Parameters for Pitzer's equation have been evaluated by Rard and Spedding[5,6] and Rard, Miller, and Spedding.[7]

In this paper we evaluate desolvation energies of rare-earth-metal perchlorates, chlorides, and nitrates at intermediate and high concentrations. Work and heat requirements are of interest in thermochemical water-splitting cycles for hydrogen production, which have a common need of efficient reagent recycle. Virtually all of the experimentally verified cycles to date require a solution chemistry step that is followed by water removal.[14] The rare-earth-metal series is ideal for evaluation of both cation and anion effects with the aid of the second law of thermodynamics.

Method

The reversible work or Gibbs energy change for desolvation of an electrolyte and condensing pure water is the work of compressing the vapor over the electrolyte to the pressure of the vapor over pure liquid water at the specified temperature. For small increments an average value of the log of pressure or log of water activity can be used for the computation. If the variation of activity with molality is known, the exact integral can be employed.

The work of removal of 1 mol of water from a rare-earth-metal electrolyte and condensing it as pure water is, $\Delta G = -RT \ln (Ae/1)$ where *Ae* is the activity of solvent water and the activity of pure water is 1. When 1 mol of rare-earth-metal perchlorate, chloride, or nitrate is dissolved in water at molality *m*, the water to rare-earth-metal ratio is $55.508/m$. Removal of water will change this ratio to give a larger value of *m*, and the activity of water will decrease. Data in the literature on rare-earth-metal electrolyte water activities are recorded primarily as osmotic coefficients that are proportional to ln (*Ae*): $\phi = -55.508 \ln (Ae/4m)$.[2] The number 4 is the sum of the rare-earth-metal cation plus 3 anions, and *m* is the molality. When *m* has a value of m_1 that increases to m_2 by desolvation, the water removed from the electrolyte is $55.508 \cdot (1/m_1 - 1/m_2)$. The mean value of $m\phi$ is $0.5(m_1\phi_1 + m_2\phi_2)$. Combining the equation for ϕ with the equation for ΔG for the process gives as a very good approximation for incremental desolvation:

$$\Delta G_{1,2} = 2RT(m_1\phi_1 + m_2\phi_2)(1/m_1 - 1/m_2) \text{ cal mol}^{-1} \qquad (1)$$

Equation 1 allows use of experimental incremental data points. The variation of ϕ with *m* has been evaluated for most rare-earth-metal electrolytes,[2-7] and the exact equation for the Gibbs energy change of desolvation is

$$\Delta G_{1,2} = 4RT \int_{m_1}^{m_2} \phi \, \mathrm{d}(\ln m) \text{ cal mol}^{-1} \qquad (2)$$

For reversible desolvation the enthalpy of desolvation is the thermodynamic inverse of the enthalpy of solvation, or inverse heat of dilution. The second law of thermodynamics gives the energy content of entropy change as $T\Delta S$.

Extensive heat of dilution measurements of perchlorates, chlorides, and nitrates have been made by Spedding, Mohs, Derer, and Habenschuss,[8] Spedding, DeKock, Pepple, and Habenschuss,[9] and Spedding, Derer, Mohs, and Rard.[11] Comprehensive treatments of data have been given. In this paper, the raw data of heat of dilution are used with appropriate interpolations and extrapolations to yield the necessary enthalpy of desolvation data (by inversion) for specific molality regions.

Table I. Precision of Eq 1 vs. Eq 2 for Calculation of $\Delta G_{1,2}$ for Lanthanum Nitrate

m_1, mol kg^{-1}	m_2, mol kg^{-1}	$\Delta G_{1,2}$(eq 2), cal mol^{-1}	$\Delta G_{1,2}$(eq 1) − $\Delta G_{1,2}$(eq 2), cal mol^{-1}	$\Delta G_{1,2}$(eq 1)/ $\Delta G_{1,2}$(eq 2)
0.1	0.1001	1.7736	−0.0001	0.9999
0.1	0.11	169.00	0.26	1.002
0.1	0.12	323.14	1.82	1.006
0.1	0.2	1228.5	104.2	1.085
1.0	1.001	2.034	0.010	1.005
1.0	1.1	196.65	0.57	1.002
2.0	2.001	1.250	−0.025	0.979
2.0	2.2	237.6	0.60	1.003
3.0	3.001	0.936	0.026	1.027
3.0	3.2	188.89	0.25	1.001
4.0	4.001	0.866	−0.038	0.956
4.0	4.2	163.50	0.07	1.0004
4.602	4.603[a]	0.836	0.065	1.076

[a] Saturation at 298.2 K.[11]

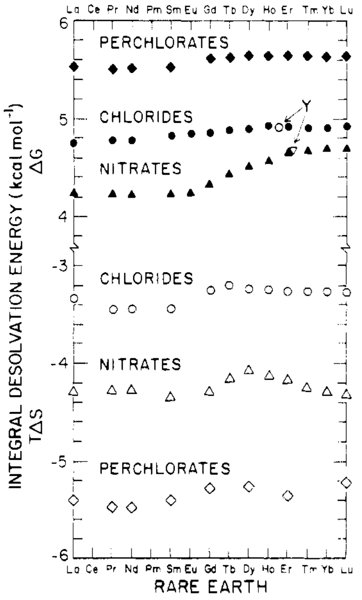

Figure 1. Integral desolvation ΔG and $T\Delta S$ from 0.1 to 1 *m*. Precision of calculations is better than ± 15 cal mol^{-1} for ΔG and ± 25 cal mol^{-1} for $T\Delta S$. Heat of dilution data have a standard deviation of less than 10 cal mol^{-1}. For La, Pr, Nd, and Sm perchlorates, ΔG is 5523 ± 11 cal mol^{-1}, and for Gd–Lu perchlorates, ΔG is 5644 ± 18 cal mol^{-1}. For Y, Er, Tm, Yb, and Lu chlorides, ΔG is 4908 ± 8 cal mol^{-1}. For La, Pr, Nd, Sm, and Eu nitrates, ΔG is 4229 ± 12 cal mol^{-1}, and ΔG is 4670 ± 21 cal mol^{-1} for Y, E, Tm, Yb, and Lu nitrates. The slope of the chloride plot from La to Ho (allowing for Ce and Pm) is 16 cal mol^{-1} per element. The slope of the nitrate plot from Eu to Er is 83 cal mol^{-1} per element. The separation in $T\Delta S$ between chlorides and nitrates is −932 ± 72 cal mol^{-1} with the minimum separation at Pr and the maximum separation at Lu. The separation in $T\Delta S$ between chlorides and perchlorates for eight data points is −2020 ± 40 cal mol^{-1} with the minimum separation at Sm and the maximum separation at Er. Data are from ref 2–11, 16, and 23.

Results

Work of desolvation from eq 1 vs. eq 2 was calculated for lanthanum nitrate by using the osmotic coefficient polynomial developed by Rard, Miller, and Spedding.[7] These results for specific molality increments are listed in Table I and are representative of the three anion series. Equation 2 is the preferred equation since it is exact when the osmotic coefficient is known as a function of molality. Rard, Miller, and Spedding quoted a standard deviation of 0.0013 for the fit of the lanthanum nitrate osmotic coefficient polynomial.[7] Consequently, for eq 1 to be useful when osmotic coefficient data are used, it should agree with eq 2 within the precision desired for ΔG. Table I shows that, for a precision of 1 cal mol^{-1}, the increment of molality for eq 1 at 0.1 *m* should be 0.01. At 1 *m* it should be 0.05, and above 2 *m*

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Table II. Calculated and Extrapolated Solvent/Cation Ratios for Zero Crossing of $T\Delta S$ for Incremental Changes of 0.2 in Molality and Integral $T\Delta S$ (cal mol^{-1}) from Saturation Molalities to Molalities of Zero $T\Delta S$

	solvent/cation ratio								
	perchlorate[a]		nitrate[b]		chloride[c]		integral $T\Delta S$ from satn to zero $T\Delta S$		
RE	satn	zero $T\Delta S$	satn	zero $T\Delta S$	satn	zero $T\Delta S$	perchlorate	nitrate	chloride
La	11.62	10.5[d]	12.05	9.5[d]	14.25	20.6	-55[d]	-150[d]	365
Pr	11.76	10.5[d]	11.12	9.5[d]	14.24	19.5	-30[d]	-80[d]	330
Nd	11.86	10.0[d]	12.11	9.0[d]	14.12	18.6	-120[d]	-215[d]	335
Sm	11.91	10.0[d]	12.98	11.5[d]	15.24	18.9	-130[d]	-70[a]	45
Eu	11.98		12.99		15.49	19.7			140
Gd	12.01	9.0[d]	12.70	9.5[d]	15.46	19.4	-405[d]	-125[d]	140
Tb	12.02		12.25	12.0[d]	15.53	20.3		-10	175
Dy	12.06	8.0[d]	11.72	12.3[d]	15.29	20.1	-505[d]	10	145
Ho	11.99		11.04	11.2	15.01	19.8		0	225
Er	12.01	8.0[d]	10.17	12.3	14.67	19.0	-660[d]	0	210
Tm	12.01		9.32	14.2	14.30	17.7		300	125
Yb	11.96		8.35	15.4	13.87	17.7		360	95
Lu	11.99	8.0[d]	8.17	15.6	13.46	17.3	-730[d]	580	70

[a] Data from ref 2 and 8. [b] Data from ref 4–7, 11, 16, and 23. [c] Data from ref 3, 9, and 10. [d] Extrapolated into the supersaturation region.

it could be as large as 0.2. Since heat of dilution data are reliable to better than 10 cal mol^{-1},[8,9,11] values of ΔG are reported in this paper to the nearest 1 cal mol^{-1} to minimize rounding errors. The calculated values of ΔG will be as reliable as the combined standard deviation of the osmotic coefficients (0.2%) and molality (0.1%).

Integral desolvation values of ΔG and $T\Delta S$ for water removal from 0.1 to 1 *m* are plotted in Figure 1 for the three anion series. In this concentration range there are similarities and differences in ΔG, which are pointed out in the figure caption. Anion work requirements are in the sequence of perchlorates > chlorides > nitrates. Yttrium chloride falls between holmium and erbium chlorides, and yttrium nitrate falls at erbium nitrate.

Energy requirements for $T\Delta S$ in Figure 1 are in the sequence of perchlorates > nitrates > chlorides. Differences across the rare-earth-metal series for the three anions are relatively uniform and are related to anion size and complexity.

Figure 2 shows that the least variation in ΔG for water removal from 1 *m* to saturation is in the perchlorate series where there is a break at gadolinium and a maximum at lutetium. The chloride plot shows a minimum at europium and a maximum at lutetium, and yttrium chloride falls between thulium chloride and ytterbium chloride. The nitrate series has a minimum at lanthanum, a maximum at lutetium, and a crossing of the chloride series at thulium. This crossing is a manifestation of the increasing solubility of thulium, ytterbium, and lutetium nitrates with respect to the chlorides.

Integral desolvation values of $T\Delta S$ for the region of 1 *m* to saturation are plotted in Figure 3. The variation for chlorides across the series is much the same as for perchlorates. Nitrates are quite different, with the plot showing a positive slope and close approach to the chloride plot at lutetium.

Incremental desolvation energies for relatively small increases in molality in Figure 4 show considerably more detail of the changes in ΔG and $T\Delta S$ as water is removed from 0.4 *m* to saturation. Lanthanum, gadolinium, dysprosium, and lutetium are typical for the series. Plots of ΔG are linear near 1 *m* to saturation. There are notable differences in $T\Delta S$ for the anion series. Chloride plots cross zero $T\Delta S$, and all go positive before saturation. None of the perchlorate plots cross zero $T\Delta S$, and only thulium, ytterbium, and lutetium nitrate plots cross to give positive $T\Delta S$. Data points for terbium, dysprosium, holmium, and erbium nitrates terminate at saturation on the zero $T\Delta S$ line within the precision of the data.

Perchlorates of dysprosium, erbium, and lutetium and all nitrates show two different $T\Delta S$ slopes with the slope changes at solvent/cation ratios of 18–27. Erbium, thulium, ytterbium, and lutetium nitrates have a third $T\Delta S$ slope that is near zero from solvent/cation ratios of 13–15 to the respective saturation ratio.

Additional treatment of desolvation energy data included identification of solvent/cation ratios at zero values of $T\Delta S$ on changing molality by increments of 0.2. Some of the data were

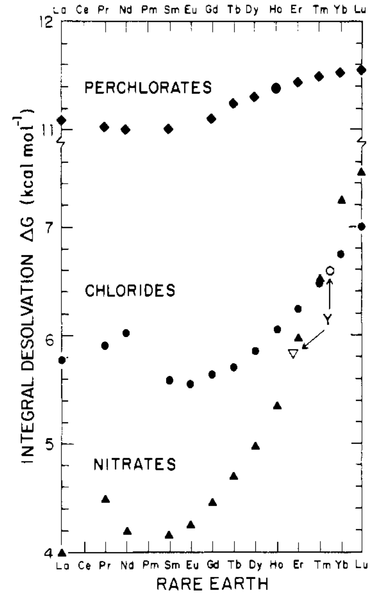

Figure 2. Plots of integral desolvation ΔG from 1 *m* to saturation. Precision of data is ±0.3% of calculated ΔG values. The mean value for La, Pr, Nd, Sm, and Gd perchlorates is 11 045 ± 42 cal mol^{-1}.

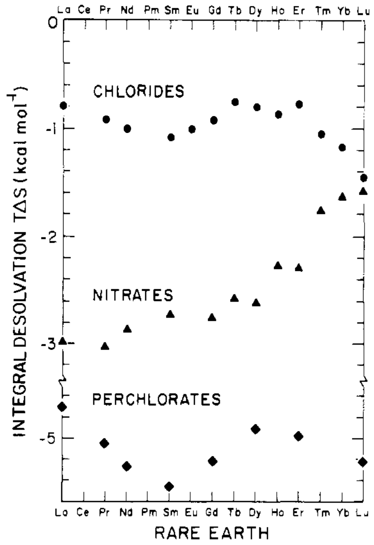

Figure 3. Plots of integral desolvation $T\Delta S$ from 1 *m* to saturation. Precision of data is ±20 cal mol^{-1} for chlorides and ±30 cal mol^{-1} for nitrates and perchlorates. The separation in chlorides and perchlorates is −4130 ± 202 cal mol^{-1} with the minimum separation at Lu and the maximum separation at Sm for the eight perchlorate points and corresponding chloride points.

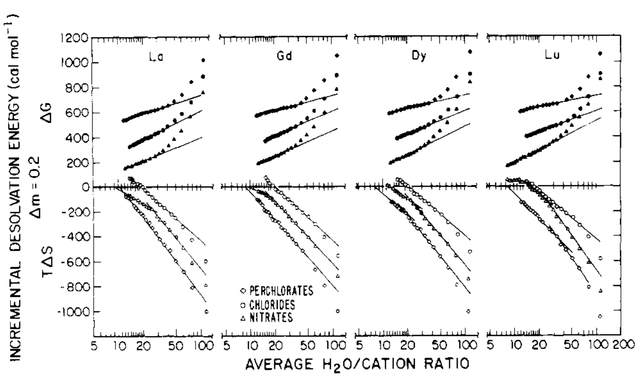

Figure 4. Desolvation energies for removal of water in 0.2 *m* increments from 0.4 *m* to saturation. Precision of ΔG is ±0.3%, and heat of dilution data for calculating $T\Delta S$ are reliable to better than 10 cal mol^{-1}.[8,9,11] At zero $T\Delta S$, solvent/cation ratios are reliable to about ±0.5, and extrapolated values are no better than ±1.

extrapolated into supersaturation regions to a zero intersection as shown in Figure 4 and Table II. Regions of positive $T\Delta S$ are also listed in Table II.

Discussion

Isothermal desolvation of electrolytes is a work consumptive process, so ΔG is never zero. However, the enthalpy change can be zero, for which the work and $T\Delta S$ are equivalent. Small enthalpy changes are shown by perchlorates and nitrates on desolvation in the region of 0.1–1 *m*, but all chloride electrolytes absorb significantly more heat on desolvation. This difference results in an anion effect on $T\Delta S$ across the rare-earth-metal series as shown in Figure 1, where geometric and obstructive differences in anions create more disorder for solvent movement in the sequence chloride < nitrate < perchlorate. This effect prevails to saturation (Figure 3), but with considerable attenuation in the nitrate series for thulium, ytterbium, and lutetium.

Figure 4 and Table II show regions of zero $T\Delta S$, which signal the end of entropic reordering in the electrolyte prior to crystallization. For the condition of zero $T\Delta S$, work is equivalent to heat absorption, and outer-sphere ion pairing should be complete. Inner-sphere anion penetration can start. Near zero $T\Delta S$ values at saturation are shown by terbium, dysprosium, holmium, and erbium nitrates, but lanthanum, praseodymium, neodymium, samarium, and gadolinium nitrates still have negative $T\Delta S$ values at saturation. Extrapolation of $T\Delta S$ data of lanthanum–gadolinium nitrates to zero $T\Delta S$ gives reasonable inner-sphere cation water numbers. The precision of extrapolations is no better than ±1 water.

Perchlorates also show zero $T\Delta S$ by extrapolations through the supersaturation regions. This behavior can be explained by the lack of propensity by perchlorate ion for inner-sphere cation water replacement in aqueous media, which has been demonstrated by optical,[15,17] NMR,[18] thermodynamic,[19] and excited state studies[20,21] and by X-ray diffraction studies of crystals.[22] Outer-sphere ion pairing should be complete at incipient crystal hydrate formation. The extrapolation for dysprosium perchlorate is coincident with the crystal hydrate number 8, and erbium perchlorate and lutetium perchlorate also give this number. The stable hydrate of the perchlorate series at 298 K is the 8-hydrate.[8] Saturated dysprosium perchlorate electrolyte is the only rare-earth-metal electrolyte evaluated by this desolvation method that gives a $T\Delta S$ value near zero for crystal hydrate formation.[1]

There is a trend for $T\Delta S$ of nitrate to approach $T\Delta S$ of chloride with the trend perceptible at holmium and becoming most prominent at lutetium as shown in Figure 4. The $T\Delta S$ plots of erbium, thulium, ytterbium, and lutetium nitrates have linear sections that progressively approach the chloride plots and parallel them at high molalities prior to the zero $T\Delta S$ crossings. The effect of nitrate approaches the lesser effect of chloride, where chloride complexing is outer sphere.[15] There may be replication by nitrate of the monodentate nature of chloride.

The small values of positive $T\Delta S$ for all chlorides and for thulium, ytterbium, and lutetium nitrates in Table II seem to represent a destructuring process (or processes) for the electrolyte that is necessary prior to crystal hydrate formation in following crystallization reactions that yield relatively large negative $T\Delta S$ values.[1] This process may be destruction of polymeric electrolyte hydrogen bonds (rather than polymeric solvent hydrogen bonds) by ion compression when several water molecules are removed by vaporization. Table II shows that the positive $T\Delta S$ values are calculated for removal of >3 to <8 mol of solvent prior to saturation. Inner-sphere, monodentate penetration of chloride or nitrate in this region is not precluded, since it may be fractionally small to give small changes in $T\Delta S$.[24] Solvent water would be partially replaced from the inner-sphere reaction. Thus, entropic reordering with respect to electrolyte crystallization could be accompanied by electrolyte destructuring, which would require excess energy compared to normal solvent destructuring.

There have been many studies that demonstrate outer-sphere complexing of chloride and nitrate. Choppin and co-workers have shown by spectroscopic and NMR measurements and by thermodynamic methods[15,25,26] that chloride complexes of the rare-earth-metal series are predominately outer sphere except at high chloride concentrations. Habenschuss and Spedding showed by X-ray diffraction that chloride ion is outer sphere in concentrated solutions (anion/cation ratio = 3),[27-29] corresponding to molalities slightly smaller than the molalities where $T\Delta S$ is positive (Table II). There are other verifications of outer-sphere chloride complexing[30] and identification of conditions for inner-sphere chloride penetration.[21,30]

Nitrate complexing of rare-earth-metal cations in aqueous electrolytes at equilibrium is similar to that of chloride,[15,31,32] but somewhat stronger.[15] Inner-sphere nitrate complexing also is known from spectral, NMR, and laser excitation measurements.[11,17,18,20,21,33] The ground-state, anhydrous, inner-sphere terbium trinitrate in acetonitrile is stable to hydration in mixed solvent with water/cation ratios less than 10.[34]

The different $T\Delta S$ behavior in the nitrate series seems to be a manifestation of both the lanthanide contraction and bonding of nitrate when inner-sphere water is replaced. In the crystal hydrates three bidentate nitrates occupy coordination sites of four inner-sphere waters,[35-40] based on electrolyte cation hydration numbers of 8–9.[27-29,41,42] Chloride ion site occupancy in the crystal hydrates is nearly one ion for one inner-sphere electrolyte cation

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water.[27-29] One mechanism for inner-sphere nitrate penetration in electrolytes could involve one monodentate oxygen bond of nitrate by replacement of one inner-sphere water.[18] Then, subsequent bidentate bonding could occur on crystallization by displacement of three inner-sphere waters by two nitrates.

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Registry No. $La(ClO_4)_3$, 14017-46-0; $LaCl_3$, 10099-58-8; $La(NO_3)_3$, 10099-59-9; $Pr(ClO_4)_3$, 13498-07-2; $PrCl_3$, 10361-79-2; $Pr(NO_3)_3$, 10361-80-5; $Nd(ClO_4)_3$, 13498-06-1; $NdCl_3$, 10024-93-8; $Nd(NO_3)_3$, 10045-95-1; $Sm(ClO_4)_3$, 13569-60-3; $SmCl_3$, 10361-82-7; $Sm(NO_3)_3$, 10361-83-8; $EuCl_3$, 10025-76-0; $Eu(NO_3)_3$, 10138-01-9; $Gd(ClO_4)_3$, 14017-52-8; $GdCl_3$, 10138-52-0; $Gd(NO_3)_3$, 10168-81-7; $Tb(ClO_4)_3$, 14014-09-6; $TbCl_3$, 10042-88-3; $Tb(NO_3)_3$, 10043-27-3; $Dy(ClO_4)_3$, 14017-53-9; $DyCl_3$, 10025-74-8; $Dy(NO_3)_3$, 10143-38-1; $Ho(ClO_4)_3$, 14017-54-0; $HoCl_3$, 10138-62-2; $Ho(NO_3)_3$, 10168-82-8; $Er(ClO_4)_3$, 14017-55-1; $ErCl_3$, 10138-41-7; $Er(NO_3)_3$, 10168-80-6; $Tm(ClO_4)_3$, 14014-10-9; $TmCl_3$, 13537-18-3; $Tm(NO_3)_3$, 14985-19-4; $Yb(ClO_4)_3$, 13498-08-3; $YbCl_3$, 10361-91-8; $Yb(NO_3)_3$, 13768-67-7; $Lu(ClO_4)_3$, 14646-29-8; $LuCl_3$, 10099-66-8; $Lu(NO_3)_3$, 10099-67-9; YCl_3, 10361-92-9; $Y(NO_3)_3$, 10361-93-0.

Supplementary Material Available: Listings of computer values of integral work of desolvation, enthalpy changes and entropy changes from 0.1 *m* to crystal hydrate formation at 298 K and the BASIC program for eq 2 (5 pages). Ordering information is given on any current masthead page.

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Ferrimagnetism in $MnFeF_5 \cdot 2H_2O$

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The magnetic susceptibility of $MnFeF_5 \cdot 2H_2O$ was measured at temperatures from 5 to 300 K for applied fields of up to 1 kOe with a SQUID susceptometer. A ferrimagnetic phase transition was observed at 38 ± 0.25 K. At temperatures between 200 and 300 K the susceptibility followed a Curie–Weiss law $\chi = C/(T - \Theta)$ with $\Theta = -164$ K and an effective magnetic moment of 7.4 ± 0.1 μ_B. The Mössbauer resonance spectrum gave a quadrupole-split doublet with an isomer shift of 0.483 mm/s relative to α-iron, indicating that all of the iron was Fe^{3+}.

Introduction

Fluoride complexes of the transition metals have been studied extensively in recent years. A large number of compounds $M^{II}M^{III}F_5 \cdot 7H_2O$ are known, where M^{II} is the divalent ion of Mn, Fe, Co, Ni, or Zn and M^{III} is the trivalent ion of Cr, V, Mn, Fe, or Al. The related dihydrates have been formed from the heptahydrates by thermal decomposition[1-5] and by precipitation from solution.[6]

Mössbauer-effect measurements of the mixed-valence iron fluoride dihydrate ($Fe_2F_5 \cdot 2H_2O$) reported by Imbert et al.[7] and by Balcerek et al.[5] along with magnetic susceptibility measurements by Jones and Dawson[8,9] and Walton et al.[10] showed ferrimagnetic ordering below 48.5 K. Susceptibility measurements of the dihydrate $CoFeF_5 \cdot 2H_2O$ by Jones and Dawson[11] showed it also to be ferrimagnetic at temperatures below 27 K. We have investigated the low-temperature magnetic susceptibility of the related dihydrate $MnFeF_5 \cdot 2H_2O$ to determine if it too undergoes similar magnetic ordering. Mössbauer resonance spectra verified the valence state of the iron ions.

Experimental Section

$MnFeF_5 \cdot 2H_2O$ was prepared by mixing HF solutions of Mn(II) and Fe(III). The crystalline product precipitated at 80 °C was the dihydrate;[6] other samples were prepared by crystallization at room temperature and dehydration at 140 °C under vacuum. The identity of the samples was verified by X-ray diffraction patterns,[4] which were completely identified for $MnFeF_5 \cdot 2H_2O$ up to $2\theta = 52°$ and agreed well with the literature for both position and intensity of the lines. No extraneous lines were found; thus the compound was well identified.

The magnetic susceptibility measurements were made with an SHE Model VTS-805 superconducting quantum interference device (SQUID) susceptometer. The polycrystalline powder samples were placed in a fused-quartz container for the magnetic measurements. The measurements were made over the temperature range of 5–300 K at applied fields of up to 1 kOe.

Mössbauer resonance studies were performed at room temperature on a spectrometer operated in the constant-acceleration mode and employing transmission geometry. The samples were sealed in paraffin and mounted on aluminum foil.[5] The source consisted of ^{57}Co diffused into a rhodium matrix. Calibration spectra were made by using an NBS standard absorber of sodium nitroprusside.

Results and Discussion

The temperature dependence of the reciprocal molar susceptibility of $MnFeF_5 \cdot 2H_2O$ is shown in Figure 1 for temperatures between 5 and 300 K at an applied magnetic field of 100 Oe. Measurements at an applied field of 1 kOe gave identical results within experimental uncertainties. The curve displays the characteristic shape of a ferrimagnet and indicates a transition near 38 K. In the molecular field approximation for temperature above the phase transition, the reciprocal susceptibility of a ferrimagnet may be described by[12]

$$\frac{1}{\chi} = \frac{(T - T_c)(T - T_c')}{C(T - \Theta')} \qquad (1)$$

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