# Stability and Thermodynamics of Thermochromic Cobalt(II) Chloride Complexes in Low-Melting Phase Change Materials[†]

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The well-known fact that cobalt(II) halide complexes in various media undergo changes in coordination, absorbance, and color with increasing temperature was combined with the high latent heat of fusion of new materials suitable for simultaneous control of temperature, light intensity, and heat storage. Hence, the increase in absorbance with temperature acts as an autoregulated shading protection from overheating. Several binary mixtures of calcium nitrate tetrahydrate and ammonium nitrate, $x\mathrm{Ca(NO_3)_2 \cdot 4H_2O} + (1 - x)\mathrm{NH_4NO_3}$, with low melting points were studied as suitable solvents for the formation of cobalt(II) chloride complexes. The temperature dependence of the densities of these melts has been measured. Absorption spectra in the visible spectral range [(400 to 800) nm] have also been investigated. The overall stability constants of $[\mathrm{Co(NO_3)_4}]^{2-}$, $[\mathrm{Co(NO_3)_2Cl_2}]^{2-}$, and $[\mathrm{CoCl_4}]^{2-}$ complexes at different temperatures were calculated using a nonlinear regression program. On the basis of these stability constants, the thermodynamic data (i.e., enthalpy, entropy, and free-energy changes) were calculated for the corresponding complexation reactions. Also, the dependence of the enthalpy and entropy changes on the solvent composition has been analyzed.

## Introduction

A large number of passive solar agricultural greenhouses use latent heat storage materials undergoing a solid/liquid phase change.[1] They have been extensively used in the past three decades in order to increase plant quality and productivity and decrease consumption of fossil fuels for heating. Research work in this area involves studies of new materials and their optical properties upon addition of some thermochromic complex compounds. The thermochromic substance is usually a transition-metal complex with mixed ligands that undergoes reversible changes in optical properties in response to a change in temperature and thus acts as a self-regulating shading.[2]

Studies of ionic association (complex formation) at an early stage have mainly been restricted to inorganic salt hydrates and most concentrated aqueous solutions (so-called hydrous melts) as reaction media. The most commonly used inorganic salt for this purpose is certainly calcium nitrate tetrahydrate. This salt, either pure or mixed with another inorganic component or organic solvent, has a high latent heat of fusion and a low melting point and has been considered as a good phase change material (PCM) for thermal energy storage.[3] It has also been proposed for simultaneous control of temperature and insulation in solar heat storage systems to protect the solar-heated greenhouses from overheating.[2,4] The PCM should be transparent in the molten state. At the same time, the metal complex compound should exhibit low absorbance in the visible spectral range.

The formation of thermochromic cobalt(II) halide complexes has been studied in various anhydrous and aqueous melts.[5−9] In these melts, formation of the complexes $[\mathrm{Co(NO_3)_4}]^{2-}$, $[\mathrm{Co(NO_3)_2X_2}]^{2-}$, and $[\mathrm{CoX_4}]^{2-}$ (X = Cl, Br) has been postulated. The corresponding geometries are octahedral for the nitrate complexes, severely distorted octahedral for the mixed nitrate/halide complexes, and tetrahedral in the case of the pure halide complexes. Changing of the melt color from pale-pink to dark-blue follows this change of geometry. Hence, additional chemical energy can be stored in such a system.

**Table 1. Temperature and Chloride Molality Dependence of the Density (*d*) of Different $x\mathrm{Ca(NO_3)_2 \cdot 4H_2O} + (1 - x)\mathrm{NH_4NO_3}$ Melts**

| $x$ | $d/\mathrm{g \cdot cm^{-3}}$ |
|---|---|
| 0.3 | $d = 1.869 - 7.30 \cdot 10^{-4} \cdot T - (0.0373 - 7.3 \cdot 10^{-5} \cdot T) \cdot m(\mathrm{Cl^-})$ |
| 0.4 | $d = 1.965 - 8.30 \cdot 10^{-4} \cdot T - (0.0859 - 1.6 \cdot 10^{-4} \cdot T) \cdot m(\mathrm{Cl^-})$ |
| 0.5 | $d = 1.959 - 8.09 \cdot 10^{-4} \cdot T - (0.0676 - 1.2 \cdot 10^{-4} \cdot T) \cdot m(\mathrm{Cl^-})$ |
| 0.6 | $d = 1.909 - 8.38 \cdot 10^{-4} \cdot T - (0.0999 - 2.4 \cdot 10^{-4} \cdot T) \cdot m(\mathrm{Cl^-})$ |
| 0.7 | $d = 1.979 - 8.32 \cdot 10^{-4} \cdot T - (0.0889 - 1.9 \cdot 10^{-4} \cdot T) \cdot m(\mathrm{Cl^-})$ |

In our previous papers, calculated species spectra for each cobalt(II) halide complex and their spectral behavior have been investigated.[8,9] In this work, our research has been extended to cobalt(II) chloride complexes formed in $x\mathrm{Ca(NO_3)_2 \cdot 4H_2O} + (1 - x)\mathrm{NH_4NO_3}$ melts with $x = 0.40$ and 0.60, and the standard thermodynamic functions for formation of the cobalt(II) chloride complexes in the calcium nitrate tetrahydrate + ammonium nitrate melts have also been estimated. Thus, additional data on metal complex formation in mixed low-temperature inorganic solvents can be provided.

## Experimental Section

The absorption spectra of melts with variable chloride and cobalt(II) concentrations were recorded over the wavelength range (400 to 800) nm on a Secomam Anthelie Advanced 2 spectrophotometer with thermostatted cell compartments. The temperature was kept constant to within ± 0.5 K.

All of the chemicals were reagent-grade products. The solvent melt was prepared by melting together appropriate amounts of

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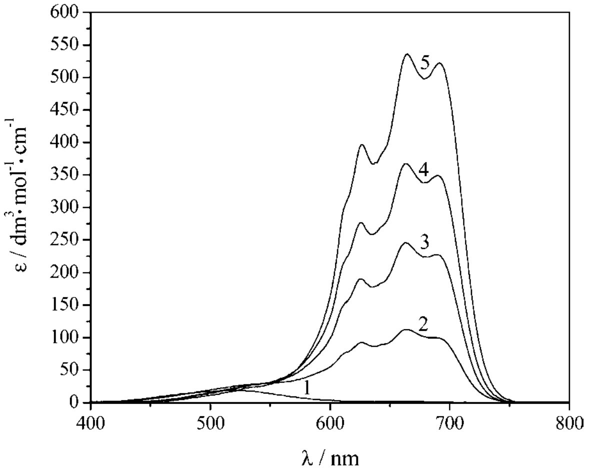

**Figure 1.** Representative set of spectra for five different chloride concentrations at 328.15 K in a $0.4Ca(NO_3)_2 \cdot 4H_2O + 0.6NH_4NO_3$ melt. The corresponding melt compositions are as follows: $m(Co^{2+})$/mol·kg$^{-1}$: (1) 0.008692; (2) 0.008457; (3) 0.003442; (4) 0.003405; (5) 0.003351. $m(Cl^-)$/mol·kg$^{-1}$: (1) 0; (2) 0.5161; (3) 0.7101; (4) 0.9137; (5) 1.2224.

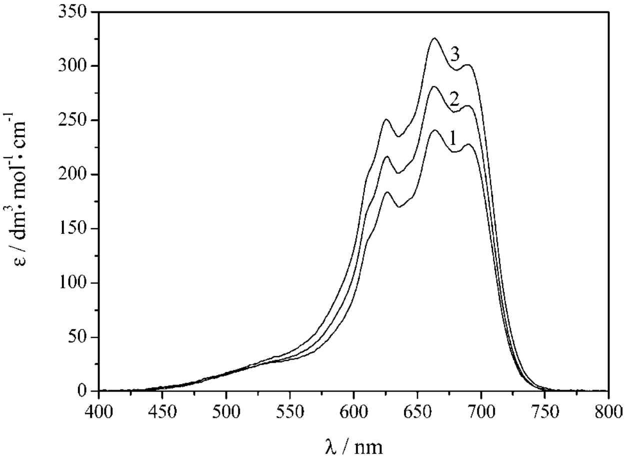

**Figure 2.** Variation of the spectra of cobalt(II) with temperature for the $0.4Ca(NO_3)_2 \cdot 4H_2O + 0.6NH_4NO_3$ system: (1) 318.15 K; (2) 328.15 K; (3) 338.15 K. $m(Co^{2+}) = 0.003430$ mol·kg$^{-1}$; $m(Cl^-) = 0.7752$ mol·kg$^{-1}$.

calcium nitrate tetrahydrate (Merck) and ammonium nitrate (Merck). The water/calcium nitrate molar ratio was adjusted to 4.00 by drying or addition of water. Five different $xCa(NO_3)_2 \cdot 4H_2O + (1 - x)NH_4NO_3$ mixtures (with $x = 0.3$, 0.4, 0.5, 0.6, and 0.7) were investigated. Mixures with $x = 0.1$ and 0.2 were not investigated because of their inmiscibility.

A stock solution of cobalt(II) nitrate was prepared by dissolving $Ca(NO_3)_2 \cdot 4H_2O$ in a known amount of the solvent melt. Anhydrous ammonium chloride (Merck) was added into an appropriate amount of the solvent melt to obtain the desired cobalt(II)/chloride ion ratio in the solution.

In order to calculate the molar absorption coefficients, stability constants, and thermodynamic functions, all of the concentrations were expressed in units of molarity (mol·dm$^{-3}$). The densities of the melt solutions, which are required for conversion of molalities onto the molarity scale, were determined picnometrically at different temperatures and ammonium chloride concentrations for all of the investigated melts. The densities of the mixtures were determined using a pycnometer having a bulb volume of 10 cm$^3$. The volume of the pycnometer was calibrated as a function of temperature using distilled water at various temperatures. The pycnometer filled with liquid was kept in a thermostatically controlled and well-stirred water bath maintained at a constant temperature to within ± 0.5 K for (15 to 20) min to attain thermal equilibrium. The density measurements were carried out at temperatures of (308.15, 318.15, 328.15, 338.15, and 343.15) K. Each experimental density value is the average of at least three measurements.

Our experimental density data have been deposited at the editorial office and can be obtained upon request from the authors. Repeated experimental measurements showed reproducibility within 1 %, and an average value was used in further calculations. The best linear fit of our experimental data yielded the equations given in Table 1 for the dependence of the melt density on temperature ($T$) over the range (313 to 343) K and the ammonium chloride molality [$m(Cl^-)$] up to 1.4 mol·kg$^{-1}$. The uncertainties in the chloride molality and the temperature were less than ± 0.0001 mol·kg$^{-1}$ and ± 0.05 K, respectively.

## Results and Discussion

***Absorption Spectra.*** This paper reports results derived from spectra of 30 solutions with different cobalt(II) and chloride concentrations at three temperatures [(318.15, 328.15, and 338.15) K]. A reduced set of spectra is presented here as an

**Table 2. Values of log[$\beta_{mn}$/(mol$^{-1}$·dm$^3$)$^4$] for $[Co(NO_3)_mCl_n]^{2-m-n}$ in Molten $xCa(NO_3)_2 \cdot 4H_2O + (1 - x)NH_4NO_3$**

| $T$/K | $[Co(NO_3)_4]^{2-}$ | $[Co(NO_3)_2Cl_2]^{2-}$ | $[CoCl_4]^{2-}$ | source |
|---|---|---|---|---|
| | | $0.7Ca(NO_3)_2 \cdot 4H_2O + 0.3NH_4NO_3$ | | |
| 318.15 | 2.77 ± 0.03 | 4.86 ± 0.02 | 6.77 ± 0.02 | |
| 328.15 | 2.95 ± 0.03 | 5.01 ± 0.01 | 7.08 ± 0.01 | ref 9 |
| 338.15 | 3.32 ± 0.03 | 5.30 ± 0.01 | 7.53 ± 0.01 | |
| | | $0.6Ca(NO_3)_2 \cdot 4H_2O + 0.4NH_4NO_3$ | | |
| 318.15 | 2.75 ± 0.05 | 5.19 ± 0.05 | 6.96 ± 0.03 | |
| 328.15 | 2.86 ± 0.02 | 5.21 ± 0.01 | 7.11 ± 0.00 | this work |
| 338.15 | 3.07 ± 0.02 | 5.51 ± 0.01 | 7.48 ± 0.00 | |
| | | $0.5Ca(NO_3)_2 \cdot 4H_2O + 0.5NH_4NO_3$ | | |
| 318.15 | 2.22 ± 0.04 | 4.69 ± 0.03 | 6.82 ± 0.03 | |
| 328.15 | 2.44 ± 0.03 | 4.94 ± 0.02 | 7.15 ± 0.01 | ref 9 |
| 338.15 | 2.70 ± 0.04 | 5.40 ± 0.05 | 7.70 ± 0.02 | |
| | | $0.4Ca(NO_3)_2 \cdot 4H_2O + 0.6NH_4NO_3$ | | |
| 318.15 | 2.38 ± 0.03 | 4.68 ± 0.04 | 6.79 ± 0.03 | |
| 328.15 | 2.68 ± 0.07 | 4.86 ± 0.02 | 7.10 ± 0.06 | this work |
| 338.15 | 3.15 ± 0.06 | 5.33 ± 0.01 | 7.41 ± 0.02 | |
| | | $0.3Ca(NO_3)_2 \cdot 4H_2O + 0.7NH_4NO_3$ | | |
| 318.15 | 2.32 ± 0.02 | 4.61 ± 0.04 | 6.78 ± 0.01 | |
| 328.15 | 2.67 ± 0.02 | 4.66 ± 0.03 | 7.07 ± 0.02 | ref 9 |
| 338.15 | 2.80 ± 0.07 | 5.03 ± 0.06 | 7.49 ± 0.04 | |

example of the changing geometry and coordination of cobalt(II) in these systems.

The overall molar absorption coefficient $\varepsilon$ is defined as:

$$\varepsilon = Al^{-1}c_{\mathrm{M}}^{-1} \tag{1}$$

where $A$ is absorbance, $l$ is the light pathway length, and $c_{\mathrm{M}}$ is the total metal ion concentration. The position of the absorption maximum (519 nm) and the value of the overall molar absorption coefficient ($\varepsilon_{\max}/\mathrm{dm^3 \cdot mol^{-1} \cdot cm^{-1}} = 18.9$ at 328.15 K) for the spectra without chloride ions added in the melts indicate octahedral coordination of cobalt(II) (Figure 1, trace 1).

Addition of ammonium chloride caused a pronounced shift of the absorption band toward lower energies and a large increase of the overall molar absorption coefficient with increasing chloride concentration, indicating a change from octahedral to tetrahedral coordination of cobalt(II) and a change of the melt color from pale-pink to dark-blue. The spectra show three maxima, at (626, 662, and 690) nm. The shape and the positions of these maxima are similar for the two investigated $x\mathrm{Ca(NO_3)_2 \cdot 4H_2O} + (1-x)\mathrm{NH_4NO_3}$ mixtures ($x = 0.4$ and 0.6).

An increase in temperature also caused an increase in the overall molar absorption coefficients in the chloride-containing melts (Figure 2). Figure 2 illustrates the changes in the spectra with increasing temperature for the system $0.4\mathrm{Ca(NO_3)_2 \cdot 4H_2O} + 0.6\mathrm{NH_4NO_3}$. Very similar changes with increasing temperature were obtained for the $x = 0.6$ system.

***Stability Constants and Thermodynamic Functions.*** The complex-formation equilibria in a mixed-ligand system,

$$\mathrm{M} + m\mathrm{A} + n\mathrm{B} \rightleftarrows \mathrm{MA}_m\mathrm{B}_n \tag{2}$$

can be characterized by a set of stability constants:

$$\beta_{mn} = \frac{[\mathrm{MA}_m\mathrm{B}_n]}{[\mathrm{M}][\mathrm{A}]^m[\mathrm{B}]^n} \tag{3}$$

On the basis of the cobalt(II) coordination by halide ions in other solvents, we assumed that the complexes were mononuclear in cobalt(II) and that the maximum ligand coordination number for cobalt(II) was 4.

For the computation of the stability constants $\beta_{mn}$ and species spectra $\varepsilon_{mn}(\lambda)$, the nonlinear regression program STAR developed by Beltrán et al.[10] was used. Part of the program is STAR/FA, which is used for determination of the number of absorbing species by factor analysis. From a large number of trials to determine the most relevant complex species, it was concluded that the following complexes were formed: $[\mathrm{Co(NO_3)_4}]^{2-}$, $[\mathrm{Co(NO_3)_2Cl_2}]^{2-}$, and $[\mathrm{CoCl_4}]^{2-}$. The results are given in Table 2.

With the constants in Table 2, the standard thermodynamic functions for complex formation in $x\mathrm{Ca(NO_3)_2 \cdot 4H_2O} + (1 - x)\mathrm{NH_4NO_3}$ could be calculated. The standard enthalpy and entropy changes $\Delta H^\circ_{mn}$ and $\Delta S^\circ_{mn}$ were estimated from the temperature variation of $\Delta G^\circ_{mn}$, which is related to $\beta_{mn}$ through the expression

$$\Delta G^\circ_{mn} = -RT \ln \beta_{mn} \tag{4}$$

Figure 3 shows that $\Delta G^\circ_{mn}$ is a good linear function of temperature. Thus, the thermodynamic parameters were estimated by linear regression analysis as temperature-independent constants over the studied temperature range. The same trend was observed in different $x\mathrm{Ca(NO_3)_2 \cdot 4H_2O} + (1 - x)\mathrm{NH_4NO_3}$ melts for each complex species (Figure 4).

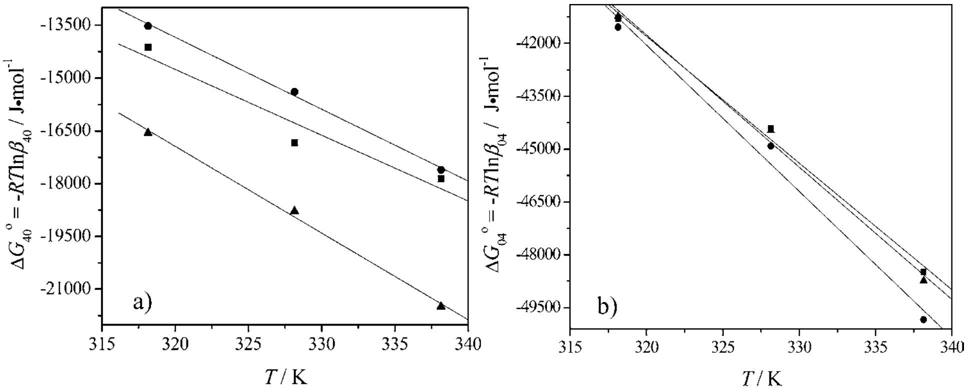

**Figure 3.** Temperature dependence of $\Delta G^\circ_{mn} = -RT \ln \beta_{mn}$ in three different $x\mathrm{Ca(NO_3)_2 \cdot 4H_2O} + (1 - x)\mathrm{NH_4NO_3}$ melts for (a) $[\mathrm{Co(NO_3)_4}]^{2-}$ and (b) $[\mathrm{CoCl_4}]^{2-}$: ■, $x = 0.3$; ●, $x = 0.5$; ▲, $x = 0.7$.

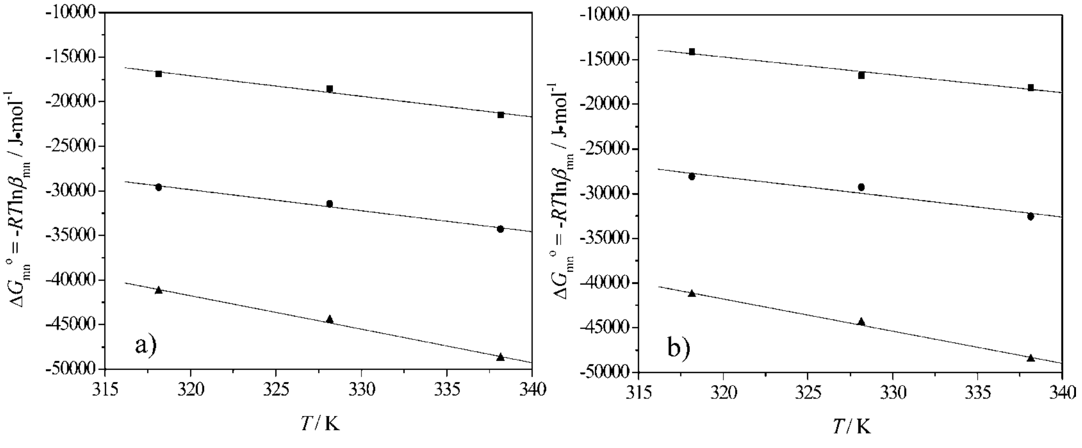

**Figure 4.** Temperature dependence of $\Delta G^\circ_{mn} = -RT \ln \beta_{mn}$ in $x\mathrm{Ca(NO_3)_2 \cdot 4H_2O} + (1 - x)\mathrm{NH_4NO_3}$ melts with (a) $x = 0.7$ and (b) $x = 0.3$ for different chloride complexes: ■, $[\mathrm{Co(NO_3)_4}]^{2-}$; ●, $[\mathrm{Co(NO_3)_2Cl_2}]^{2-}$; ▲, $[\mathrm{CoCl_4}]^{2-}$.

**Table 3. Standard Enthalpy and Entropy Values for Cobalt(II) Chloride Complex Formation in $x$Ca(NO$_3$)$_2\cdot$4H$_2$O + (1 − $x$)NH$_4$NO$_3$ over the Temperature Range (318.15 to 338.15) K**

| complex | $\Delta H°$/kJ·mol$^{-1}$ | $\Delta S°$/J·mol$^{-1}$·K$^{-1}$ |
|---|---|---|
| 0.7Ca(NO$_3$)$_2\cdot$4H$_2$O + 0.3NH$_4$NO$_3$ | | |
| $[Co(NO_3)_4]^{2-}$ | 54.3 ± 11.3 | 223 ± 34 |
| $[Co(NO_3)_2Cl_2]^{2-}$ | 45.0 ± 8.8 | 234 ± 27 |
| $[CoCl_4]^{2-}$ | 74.1 ± 7.6 | 362 ± 23 |
| 0.6Ca(NO$_3$)$_2\cdot$4H$_2$O + 0.4NH$_4$NO$_3$ | | |
| $[Co(NO_3)_4]^{2-}$ | 32.6 ± 7.1 | 155 ± 22 |
| $[Co(NO_3)_2Cl_2]^{2-}$ | 30.8 ± 15.6 | 195 ± 47 |
| $[CoCl_4]^{2-}$ | 52.4 ± 14.1 | 297 ± 43 |
| 0.5Ca(NO$_3$)$_2\cdot$4H$_2$O + 0.5NH$_4$NO$_3$ | | |
| $[Co(NO_3)_4]^{2-}$ | 49.6 ± 3.2 | 198 ± 10 |
| $[Co(NO_3)_2Cl_2]^{2-}$ | 72.6 ± 14.0 | 317 ± 44 |
| $[CoCl_4]^{2-}$ | 90.5 ± 14.8 | 414 ± 45 |
| 0.4Ca(NO$_3$)$_2\cdot$4H$_2$O + 0.6NH$_4$NO$_3$ | | |
| $[Co(NO_3)_4]^{2-}$ | 80.6 ± 11.1 | 298 ± 34 |
| $[Co(NO_3)_2Cl_2]^{2-}$ | 67.5 ± 17.8 | 301 ± 54 |
| $[CoCl_4]^{2-}$ | 94.0 ± 1.1 | 331 ± 3.3 |
| 0.3Ca(NO$_3$)$_2\cdot$4H$_2$O + 0.7NH$_4$NO$_3$ | | |
| $[Co(NO_3)_4]^{2-}$ | 49.8 ± 12.2 | 202 ± 37 |
| $[Co(NO_3)_2Cl_2]^{2-}$ | 42.5 ± 19.9 | 221 ± 61 |
| $[CoCl_4]^{2-}$ | 73.1 ± 9.1 | 359 ± 28 |

The thermodynamic parameters were calculated from the formation constants expressed on the molarity scale, and these values are presented in Table 3.

It was found in all cases that formation of the complex is endothermic. As molten salts belong to the class of ionic liquids, the major contribution to the total energy change in the complex-forming reactions comes from the reciprocal Coulomb interactions.[11] Accordingly, in the $x$Ca(NO$_3$)$_2\cdot$4H$_2$O + (1 − $x$)NH$_4$NO$_3$ systems, which consist of a small divalent cation (Ca$^{2+}$) and a large univalent cation (NH$_4{}^+$), more positive enthalpy values should be expected in the melts with a larger Ca(NO$_3$)$_2$ mole fraction.[12]

It was also assumed that the enthalpy change is a linear function of $x$. In the case of $[CoCl_4]^{2-}$ formation in the equimolar calcium nitrate tetrahydrate + ammonium nitrate melt, the relative size and polarizability of the smaller chloride ion probably should be taken into account. It should be noticed that the entropy changes are also linear functions of $x$. The octahedral → tetrahedral transformation is strongly favored by an increase in temperature or halide concentration or both. Thermodynamic calculations suggest that octahedral complexes may be easily converted into tetrahedral species if the halide concentration is higher as a result of the greater degree of electrostatic bonding between the cobalt and halide ions.

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