Contribution from the Faculty of Science, University of Belgrade, 11001 Belgrade, Yugoslavia,
and the Boris Kidrič Institute, 11001 Belgrade, Yugoslavia

Cadmium Chloride Complexes in Anhydrous Calcium Nitrate–Potassium Nitrate Melts

IVAN J. GAL,* DRAGICA STOJIĆ, and RUŽICA M. NIKOLIĆ

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The formation constants of $CdCl^+$ and $CdCl_2$ in anhydrous melts of $xKNO_3$–$(1-x)Ca(NO_3)_2$ (x = 1–0.44) at selected temperatures (450–670 K) have been determined from emf measurements in suitable concentration cells with Ag/AgCl electrodes. The results are discussed in terms of quasi-lattice models which predict the thermodynamic data for $CdCl^+$ formation as functions of the melt composition and temperature.

Ionic association and particularly formation of metal halide complexes in anhydrous nitrate melts have been investigated mainly in 1:1 salts and their mixtures. Only few papers are devoted to complex formation in charge-unsymmetrical nitrate melts as, for example, in mixtures of $Ca(NO_3)_2$–KNO_3.[1–3] One reason for this lack of data is probably the fact that charge-unsymmetrical molten salts are from a theoretical standpoint poorly understood. Whereas ionic association in charge-symmetrical melts can be successfully interpreted in terms of Blander's general quasi-lattice model[4,5] or its extension to quaternary charge-symmetrical salt mixtures,[6] no suitable models are proposed, so far, for charge-unsymmetrical quaternary melt systems.

The present work investigates the ionic associations $Cd^{2+} + Cl^-$ and $[CdCl]^+ + Cl^-$ in molten salt mixtures of $xKNO_3$–$(1-x)Ca(NO_3)_2$, at various temperatures. Thus, our system is a charge-unsymmetrical quaternary melt, with KNO_3 and $Ca(NO_3)_2$ as major components and $Cd(NO_3)_2$ and KCl as minor components. The purpose of the investigation is twofold: to provide some new information on chemical equilibria in such systems and to propose a simple model for the ionic association leading to $[CdCl]^+$ formation.

Experimental Section

The formation constants of cadmium chloride complexes have been derived from emf measurements of a concentration cell of the following type:

$$\text{Ag, AgCl}\left|\begin{array}{l} x\text{KNO}_3 \\ (1-x)\text{Ca(NO}_3)_2 \\ \text{KCl }(n_{\text{Cl}}) \\ \text{Cd(NO}_3)_2\ (n_{\text{Cd}}) \end{array}\right\|\begin{array}{l} x\text{KNO}_3 \\ (1-x)\text{Ca(NO}_3)_2 \\ \text{KCl }(n_{\text{Cl}}) \\ \end{array}\left|\text{Ag, AgCl}\right.$$

Here (Ag, AgCl) refers to the silver–silver chloride electrode, x and $(1-x)$ are the mole fractions of components KNO_3 and $Ca(NO_3)_2$ of the solvent, and n_{Cl} and n_{Cd} are the total concentrations of Cl^- and Cd^{2+} solutes, expressed in Temkin's ion fractions.[7] The chloride concentration, n_{Cl}, is kept equal in both half-cells. The electrodes were prepared as described elsewhere.[8,9] The measuring cell consisted of a Pyrex glass vessel divided by a sintered glass disk in two cell compartments. It has been provided with openings for electrodes, for thermocouples, and for addition of salts. The complete cell was placed in a specially constructed and thermoregulated oven which served as a thermostat, so that any desired temperature of the cell (in the range 100–400 °C) could be kept constant within ±0.5 °C. The emf of the cell was measured with a Beckman Model 1019 research pH meter, operated as a null-balance millivoltmeter. The accuracy of the measurements was ±0.1 mV.

Melts of desired composition were prepared from known weights of carefully dried salts. Calcium nitrate was dried by prolonged heating at 220 °C in a dry atmosphere.

The Nernst slope of the concentration cell was tested at different temperatures and salt composition, in the absence of cadmium nitrate. In one half-cell the concentration of KCl was kept constant; in the other half-cell the concentration was varied. In all tests the theoretical Nernst slope was obtained within ±2%, which indicates that the solutions behave ideally in the concentration range tested (up to 5×10^{-2} m KCl) and justifies the neglect of the liquid-junction potential.

With the experimental setup described, emf measurements up to about 400 °C could be carried out. For measurements in pure calcium nitrate solvent, temperatures above 560 °C are required. Such temperatures are too high for reliable measurements of emf in nitrate melts. (For the phase diagram of $xKNO_3$–$(1-x)Ca(NO_3)_2$, see ref 10.)

Results

Our experimental data (i.e., the emf values as functions of solvent composition x, solute concentrations n_{Cl} and n_{Cd}, and temperature) are too extensive to be listed here. They are available as supplementary material. The consecutive association constants

$$K_1 = [CdCl^+]/[Cd^{2+}][Cl^-]$$

$$K_2 = [CdCl_2]/[CdCl^+][Cl^-]$$

have been determined according to the method of Braunstein et al.,[11] modified for unsymmetrical charge distribution.[12] For the present case, the basic equation is

$$\exp\left(-\frac{F(\Delta E)}{RT}\right) - 1 = \frac{1}{2-x}K_1 n_{Cd} - \frac{1}{2-x}(K_1^2 - 2K_1K_2)n_{Cd}n_{Cl} + \ldots \quad (1)$$

Here, F is the Faraday constant, R the gas constant, and ΔE the emf. From this equation one obtains

$$\lim_{\substack{n_{Cd}\to 0\\ n_{Cl}\to 0}} \frac{\partial}{\partial n_{Cd}}\left[\exp\left(-\frac{F(\Delta E)}{RT}\right) - 1\right] = \frac{1}{2-x}K_1 \quad (2)$$

$$\lim_{\substack{n_{Cd}\to 0\\ n_{Cl}\to 0}} \frac{\partial^2}{\partial n_{Cd}\partial n_{Cl}}\left[\exp\left(-\frac{F(\Delta E)}{RT}\right) - 1\right] = \frac{1}{2-x}(2K_1K_2 - K_1^2) \quad (3)$$

By plotting $[\exp(-F(\Delta E)/RT) - 1]$ against n_{Cd} at constant x, T, and chloride concentration n_{Cl}, a practically straight line is obtained whose slope at $n_{Cd} \to 0$ can be easily determined. The slopes of such lines for different chloride concentration are then plotted against n_{Cl}, giving again a straight line whose intercept equals $[1/(2-x)]K_1$ and whose slope equals $[1/(2-x)](2K_1K_2 - K_1^2)$. The slopes and intercepts have been obtained by linear regression analysis of the data. Figure 1 illustrates the procedure for the solvent 0.67 KNO_3–0.33 $Ca(NO_3)_2$ at 573 K. The method is simple and ensures that K_1 and K_2 are true thermodynamic constants (they refer to infinite dilution of $Cd(NO_3)_2$ and KCl). The association constants are listed in Table I. Since the K_1 values will be used to test some models, the standard deviation of each K_1 value (obtained by linear regression analysis) is also listed in Table I.

Discussion

Let us consider the simplest ionic association, i.e., the formation of $CdCl^+$ species, in terms of the quasi-crystal concept of molten salts, as outlined in Blander's association model.[4] We start first with the association reaction in the pure KNO_3 solvent (x = 1), i.e., in a ternary mixture of KNO_3,

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* To whom correspondence should be addressed at the University of Belgrade.

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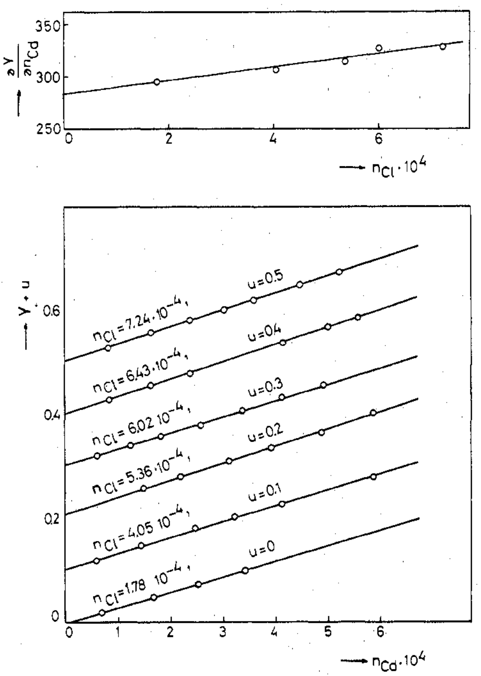

Figure 1. Graphical determination of K_1 and K_2 in a 0.67 KNO_3–0.33 $Ca(NO_3)_2$ melt at 573 K. $Y = \exp[-(F(\Delta E)/RT)] - 1$. For the sake of clarity the lines are shifted along the ordinate by an amount of u.

Table I. Equilibrium Constants (Ion Fraction Scale)

x^a	T/K	K_1	K_2
1.000	623	281 (±12)^b	215
0.902	573	320 (±10)	430
0.791	513	598 (±19)	461
	573	348 (±25)	199
0.670	453	1260 (±25)	639
	473	962 (±20)	518
	493	791 (±14)	409
	573	377 (±12)	302
0.600	573	276 (±14)	388
0.500	593	247 (±12)	244
	613	195 (±10)	199
	633	192 (±14)	101
0.440	663	152 (±16)	173

^{a} Mole fraction of KNO_3. ^{b} Standard deviations are given in parentheses.

$Cd(NO_3)$, and KCl. The association reaction can be described by eq 4.

$$Cd(NO_3)_{Z_2} + KCl(NO_3)_{Z_1-1} = CdCl(NO_3)_{Z_2-1} + K(NO_3)_{Z_1} \quad (4)$$

We assume that the divalent Cd^{2+} has an average coordination number Z_2 (number of nearest anion neighbors), whereas K^+ has a coordination number Z_1. For the sake of simplicity, charges are omitted. Equation 4 is in fact an exchange of anions in the anionic "sublattice": Cl^- ion, initially in the coordination sphere of K^+, exchanges its site with a NO_3^- ion, initially in the coordination sphere of Cd^{2+}. (The reaction $Cd^{2+} + Cl^- = CdCl^+$ is a shorthand notation of eq 4.) Let us define the energy change associated with this reaction in terms of pairwise bond energies ϵ_{i-j} (per mole):

$$\Delta E_1 = \epsilon_{Cd-Cl} + \epsilon_{K-NO_3} - \epsilon_{Cd-NO_3} - \epsilon_{K-Cl} = E_{Cd-Cl} - E_{K-Cl} \quad (5)$$

where $E_{Cd-Cl} = \epsilon_{Cd-Cl} - \epsilon_{Cd-NO_3}$ and $E_{K-Cl} = \epsilon_{K-Cl} - \epsilon_{K-NO_3}$ (we can also set arbitrarily for pure nitrate salts $\epsilon_{Cd-NO_3} = 0$ and $\epsilon_{K-NO_3} = 0$).

For the entropy change of the reaction, as in Blander's model,[4] we take into account only the change in configurational entropy, and we neglect the internal entropy contributions (assuming that the difference in vibrational entropy when NO_3^- and Cl^- exchange their sites is negligible). A chloride ion can occupy any of the Z_2 sites around Cd^{2+}; thus the configurational entropy change is

$$\Delta S_1 = R \ln Z_2 \quad (6)$$

Since no noticeable volume change takes place, eq 5 and 6 give the standard free energy change for the association reaction eq 4:

$$\Delta G_1° = \Delta A_1° = \Delta E_1 - RT \ln Z_2 \quad (7)$$

This equation is in agreement with Blander's[4] expression $K_1 = Z[\exp(-\Delta E_1/RT) - 1]$, if $K_1 >> Z$ (which is the usual case). The energy parameter ΔE_1 is assumed to be temperature independent.

In pure $Ca(NO_3)_2$ solvent (when $x = 0$), the association reaction is

$$Cd(NO_3)_{Z_2} + CaCl(NO_3)_{Z_2-1} = CdCl(NO_3)_{Z_2-1} + Ca(NO_3)_{Z_2} \quad (8)$$

Here we assume that the divalent Cd^{2+} and Ca^{2+} ions have the same coordination number Z_2. As previously, we define

$$\Delta E_2 = E_{Cd-Cl} - E_{Ca-Cl} \quad (9)$$

$$\Delta S_2 = R \ln Z_2 \quad (10)$$

$$\Delta G_2° = \Delta A_2° = \Delta E_2 - RT \ln Z_2 \quad (11)$$

Again, the parameter ΔE_2 should not depend on temperature.[4]

In mixtures of $xKNO_3$–$(1 - x)Ca(NO_3)_2$, both reactions, eq 4 and 8, contribute to the formation of $[CdCl]^+$ species. Since the energies ΔE_1 and ΔE_2 are based on pairwise ion interactions (which neglect the influence of surrounding), we assume that the standard free energy change $\Delta G_x°$ in the above solvent mixture can be expressed in terms of $\Delta G_1°$ and $\Delta G_2°$, which refer to pure KNO_3 and $Ca(NO_3)_2$ solvent, respectively. Thus

$$\begin{aligned}\Delta G_x° &= -RT \ln K_{1(x)} = n(\Delta G_1°) + (1 - n)\Delta G_2° \\ &= n(\Delta E_1) + (1 - n)\Delta E_2 - RT \ln Z_2 \end{aligned} \quad (12)$$

Here $K_{1(x)}$ is the formation constant of $[CdCl]^+$ in the solvent of composition x, whereas n and $(1 - n)$ are probabilities ($0 \leq n \leq 1$) of the two possible reaction paths. A simple solution would be to equate $n = x$, which gives the well-known Flood equation[13]

$$\Delta G_x° = x(\Delta E_1) + (1 - x)\Delta E_2 - RT \ln Z_2 \quad (13)$$

Equation 13 is often valid in charge-symmetrical mixtures when ΔE_1 and ΔE_2 are not too different. A theoretically more sound approach would be to derive n by statistical mechanical calculations, assuming, quite generally, a function of the type $n = n(x,T,\Delta E_1,\Delta E_2,Z_2,...)$.

Since the probabilities of the two possible reaction paths depend on how the chloride ligand is distributed between the coordination spheres of K^+ and Ca^{2+}, let us assume that n is proportional to the number of K^+–Cl^- ion pairs established at equilibrium and that $1 - n$ is proportional to the corresponding number of Ca^{2+}–Cl^- ion pairs. Since the system is very dilute in Cl^-, we exclude the possibility that Cl^-–K^+–Cl^- or Cl^-–Ca^{2+}–Cl^- is formed. For the sake of simplicity, let us calculate the equilibrium distribution of Cl^- in the ternary system $Ca(NO_3)_2$–KNO_3–KCl, when cadmium is absent.

If the number of K^+ ions is N_1, their average coordination number Z_1, the number of Ca^{2+} ions N_2, and the corresponding coordination number Z_2, then the number of anion sites around K^+ and Ca^{2+} ions are Z_1N_1 and Z_2N_2, respectively. Let the fractions y_1 and y_2 of these anion sites be occupied by Cl^- ions, so that $(1 - y_1)$ and $(1 - y_2)$ are the fractions occupied by NO_3^- ions. Hence, the number of K^+–Cl^- pairs is $y_1N_1Z_1$, and the

Table II. Comparison of Experimental and Calculated $\Delta G_x°$ Values[a]

		$-\Delta G_x°/\text{kJ mol}^{-1} = RT \ln K_1$					
			calcd with				
x (mole fraction of KNO_3)	T/K	exptl (Table I)	eq 23			eq 24 $Z = 6$	eq 13 $Z = 6$
			$\varphi = 1, Z_2 = 6$	$\varphi = 0.67, Z_2 = 6$	$\varphi = 1.5, Z_2 = 4$		
1.000	623	29.2	29.3	29.3	29.2	29.3	29.3
0.902	573	27.5	28.2	28.1	28.4	28.3	28.3
0.791	513	27.3	27.0	26.9	27.4	27.1	27.2
0.791	573	27.9	28.0	27.8	28.1	28.0	28.1
0.670	453	26.8	25.8	25.6	26.4	26.0	26.1
0.670	473	27.0	26.1	26.0	26.6	26.2	26.4
0.670	493	27.3	26.5	26.3	26.9	26.6	26.7
0.670	573	28.2	27.7	27.5	27.9	27.8	27.8
0.600	573	26.7	27.5	27.3	27.7	27.6	27.7
0.500	593	27.2	27.6	27.4	27.7	27.7	27.8
0.500	613	26.9	27.9	27.7	27.9	28.0	28.1
0.500	633	27.7	28.2	28.0	28.2	28.3	28.4
0.440	663	27.7	28.6	28.4	28.4	28.7	28.8
0.000	850		30.7	30.7	30.6	30.7	30.7

[a] Parameters: (1) for $Z_2 = 6$, $\Delta E_1 = -20.0$ and $\Delta E_2 = -18.0$ kJ mol^{-1}; (2) for $Z_2 = 4$, $\Delta E_1 = -22.0$ and $\Delta E_2 = -19.8$ kJ mol^{-1}.

number of Ca^{2+}–Cl^- pairs is $y_2N_2Z_2$. The sum of these pairs is, of course, equal to the number of cationic sites around the Cl^- ions:

$$Z_1N_1y_1 + Z_2N_2y_2 = Z_3N_3 \tag{14}$$

where N_3 is the number of Cl^- ions and Z_3 is their average number of cation neighbors. The energy of the system is

$$E = (Z_1N_1y_1E_{\text{K-Cl}} + Z_2N_2y_2E_{\text{Ca-Cl}})N_A^{-1} \tag{15}$$

where N_A is Avogadro's number. The number of configurations Ω of the ternary ionic melt is

$$\Omega = (\Omega^+)(\Omega^-) = (\Omega_1^-)(\Omega_2^-)(\Omega^+) \tag{16}$$

where Ω^+ refers to the distribution of cations on cation sites and Ω^- of anions on anion sites. The latter is equal to the product of numbers of anion configurations around the K^+ ions (Ω_1^-) and Ca^{2+} ions (Ω_2^-). If we assume a random mixing of K^+ and Ca^{2+} on the cation sites, Ω^+ is independent of y_1 and y_2. The numbers of configurations of anions are

$$\Omega_1^- = \frac{(Z_1N_1)!}{(Z_1N_1y_1)![Z_1N_1(1-y_1)]!} \tag{17}$$

$$\Omega_2^- = \frac{(Z_2N_2)!}{(Z_2N_2y_2)![Z_2N_2(1-y_2)]!} = \frac{(Z_2N_2)!}{(Z_3N_3 - Z_1N_1y_1)!(Z_2N_2 - Z_3N_3 + Z_1N_1y_1)!} \tag{18}$$

The most probable values of y_1 and y_2 are obtained by maximizing the expression $\ln [\Omega \exp(-E/kT)]$, using the Stirling approximation $\ln N! = N \ln N - N$, and taking into account that, if y_1 is the independent variable, y_2 can be expressed in terms of y_1 by eq 14. Thus, from

$$\frac{d}{dy_1} \ln [\Omega \exp(-E/kT)] = 0$$

one obtains

$$\frac{y_1}{y_2} = \frac{1-y_1}{1-y_2} \exp[-(E_{\text{K-Cl}} - E_{\text{Ca-Cl}})/RT]$$

or

$$\frac{y_1}{y_2} = \frac{1-y_1}{1-y_2} \exp\left[\frac{(E_{\text{Cd-Cl}} - E_{\text{K-Cl}}) - (E_{\text{Cd-Cl}} - E_{\text{Ca-Cl}})}{RT}\right] = \frac{1-y_1}{1-y_2} \exp[(\Delta E_1 - \Delta E_2)/RT] \tag{19}$$

Equation 19 is also obtained by a more elaborate calculation when cadmium is present and Cd^{2+}–Cl^- pairs are formed. Since the thermodynamic data refer to an infinite dilution of solutes, $y_1 << 1$ and $y_2 << 1$, so that eq 19 is reduced to

$$y_1/y_2 \simeq \exp[(\Delta E_1 - \Delta E_2)/RT] \tag{20}$$

In accordance with the assumption that the probabilities n and $(1 - n)$ of eq 12 are proportional to the equilibrium number of K^+–Cl^- and Ca^{2+}–Cl^- ion pairs, respectively, we define

$$n = k\frac{Z_1N_1y_1}{Z_1N_1y_1 + Z_2N_2y_2} \qquad 1 - n = k\frac{Z_2N_2y_2}{Z_1N_1y_1 + Z_2N_2y_2} \tag{21}$$

Here, k is a constant. Equations 20 and 21 give

$$\frac{n}{1-n} = \varphi\frac{x}{1-x} \exp[(\Delta E_1 - \Delta E_2)/RT]$$

or

$$n = \frac{(x\varphi) \exp[(\Delta E_1 - \Delta E_2)/RT]}{1 - x + (x\varphi) \exp[(\Delta E_1 - \Delta E_2)/RT]} \tag{22}$$

where $\varphi = Z_1/Z_2$ and $x = N_1/(N_1 + N_2)$ is the mole fraction of KNO_3 in the mixture xKNO$_3$–$(1 - x)$Ca(NO$_3$)$_2$. Combining eq 12 and 22 one obtains

$$\Delta G_x° = -RT \ln K_{1(x)} = \Delta E_2 + (\Delta E_1 - \Delta E_2)\frac{(x\varphi) \exp[(\Delta E_1 - \Delta E_2)/RT]}{1 - x + (x\varphi) \exp[(\Delta E_1 - \Delta E_2)/RT]} - RT \ln Z_2 \tag{23}$$

The last equation represents a thermodynamic model for the association reaction which leads to $[CdCl]^+$ formation. It predicts the dependence of K_1 (and $\Delta G_x°$, $\Delta H_x°$, and $\Delta S_x°$) on the salt composition and temperature. Equation 23 is, in fact, a two-variable (x, T) four-parameter (ΔE_1, ΔE_2, φ, Z_2) function. At $x = 1$ and $x = 0$, it is reduced to eq 7 and 11, respectively. If $\varphi \rightarrow 1$ and $\exp[(\Delta E_1 - \Delta E_2)/RT] \rightarrow 1$, eq 13 is obtained. The four parameters can be determined, in principle, independently, and all have definite physical meaning (they are not adjustable parameters). Thus, ΔE_1 and ΔE_2 are obtained by eq 7 and 11 if the thermodynamic constant K_1 is determined in pure KNO_3 and $Ca(NO_3)_2$ melt, at whatever temperature (since these parameters should be temperature independent). The average coordination numbers Z_1 and Z_2 can be deduced from radial distribution functions, and they are usually between 4 and 6.[5] Incidentally, eq 23 is not sensitive toward φ since its value appears in the numerator and denominator of the expression on the right-hand side of the equation.

In Table II we have compared the experimental values of $\Delta G_x°$ with the values obtained by our model (eq 23). In pure KNO_3 melt the bond-energy parameter ΔE_1 for $Z_2 = 6$ is -20.0 kJ mol^{3-1}, and for $Z_2 = 4$ it is -22.0 kJ mol^{-1}. (Since $\Delta G_1°$ is obtained experimentally, the value of ΔE_1 depends on the coordination number Z_2 adopted. This is also true for ΔE_2 (eq 11 and 7).) Since direct measurements in pure $Ca(NO_3)_2$ were not feasible, we use a value of ΔE_2 based on measurements in $Ca(NO_3)_2$–xH_2O melts, extrapolated to $x = 0$ (i.e., to anhydrous melt).[3] This value is -18.8 ± 0.8 kJ mol^{-1} for $Z_2 = 6$, and we have tested several values between -18.0 and -19.6 kJ mol^{-1}. Since higher values gave somewhat better fits, we adopted the value -18.0 kJ mol^{-1} for $Z_2 = 6$. The model was tested with $Z_2 = 6$ and 4 and $Z_1 = 6$ and 4. For the sake of comparison, in Table II are also listed the data obtained by Flood's equation (eq 13) and by the model of Bombi and Sacchetto.[6] The last model refers to charge-symmetrical melts, but it could be applied to the present system under the assumptions that $Ca(NO_3)_2$ in the melt behaves as a 1:1 salt, i.e., as $Ca(NO_3)^+ + NO_3^-$, and $Z_2 = Z_1 = Z$. According to that model

$$\Delta G_x° = RT \ln [x \exp(\Delta E_1/RT) + (1 - x) \exp(\Delta E_2/RT)] - RT \ln Z \quad (24)$$

As seen from Table II, the values obtained by the three models are rather close, and the ratio φ of eq 23 has, indeed, only a slight influence. The $\Delta G_x°$ values in Table II differ relatively little. This is partly due to the narrow energy range between ΔE_1 and ΔE_2, so that $\Delta G_x°$ varies slightly with composition, and partly to the fact that an increase of T decreases K_1; hence $\Delta G_x°$ varies only moderately with temperature.

The models reproduce the experimental $\Delta G_x°$ values fairly well if we take into account the uncertainty of the ΔE_2 parameter and the standard deviations of the experimental values (which are 0.1–0.5 kJ mol^{-1}). However, the present system does not allow us to test and compare more precisely the models, since the data are spread in a too narrow energy range: ΔE_1 and ΔE_2 differ only by 2 kJ mol^{-1}. For a precise evaluation of the models more data on systems covering a wider energy range are required, possibly with a difference $|\Delta E_1 - \Delta E_2|$ of at least 4 kJ mol^{-1}.

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Registry No. $CdCl_2$, 10108-64-2; $CdCl^+$, 14457-58-0; KNO_3, 7757-79-1; $Ca(NO_3)_2$, 10124-37-5.

Supplementary Material Available: A linear regression analysis of emf data (see eq 1–3) and tables of emf measurements (3 pages). Ordering information is given on any current masthead page.

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Contribution from Department of Chemistry,
Texas A&M University, College Station, Texas 77843

Mixed Amino Acid–Thiocyanato Complexes of Dimolybdenum(II)

AVI BINO and F. ALBERT COTTON*

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When solutions of $Mo_2(O_2CCH(NH_3)R)_4^{4+}$ and KNCS are mixed, red to red-purple crystalline compounds of composition $Mo_2(O_2CCH(NH_3)R)_2(NCS)_4 \cdot nH_2O$ can be obtained. Two of these, the glycinate (R = H, $n = 1$; **1**) and the L-isoleucinate ($R = CH(CH_3)CH_2CH_3$, $n = 4.5$; **2**), have been investigated in detail by X-ray crystallography. In each one the molecules have a cisoid arrangement of the amino acid groups and the four N-bonded NCS^- ions together with the molybdenum atoms form a sawhorse arrangement. The Mo–Mo distances range from 2.132 (2) to 2.154 (5) Å in the four crystallographically independent molecules. The crystallographic data are as follows. For **1**: space group $P2_1/n$, $a = 20.877$ (7) Å, $b = 8.928$ (3) Å, $c = 24.346$ (6) Å, $\beta = 105.23$ (5)°, $V = 4379$ (2) Å^3, $Z = 8$. For **2**: space group $P2_1$, $a = 9.034$ (3) Å, $b = 23.807$ (6) Å, $c = 14.489$ (3) Å, $\beta = 93.75$ (5)°, $V = 3109$ (2) Å^3, $Z = 4$.

Introduction

It is well-known that carboxylic acid anions, RCO_2^-, have a strong affinity for the quadruply bonded dimolybdenum moiety, Mo_2^{4+}, as well as other such dimetal units such as Cr_2^{4+}, Tc_2^{6+}, and Re_2^{6+}. One class of carboxylic acids of special importance is amino acids, $RHC(NH_3^+)CO_2^-$; these have been shown to bind strongly to Mo_2^{4+} in aqueous solution,[1] and one compound, $Mo_2(O_2CCH_2NH_3)_4(SO_4)_2 \cdot 4H_2O$, has been isolated and its structure determined X-ray crystallographically. This compound has a structure well adapted to single-crystal polarized spectral studies, and these too have been reported.[2]

Further studies of the complexation of amino acids and peptides by the Mo_2^{4+} moiety have been conducted, and we present here the first of several reports on these investigations.

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