

The reaction amounts to the linking up of two 1,3-diaza-2-phosphacyclopentane units by an N,N'-dimethylethylenediamine bridge. It is of interest that V could also be obtained by the reaction of IV (R = C₆H₅) with the twofold molar amount of N,N'-dimethylethylenediamine, as demonstrated by a comparison of the nmr spectra of both products.

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The Solubility of Silver Chloride and Silver Bromide in Molten Lithium Nitrate–Potassium Nitrate Eutectic Mixture

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The solubilities of AgCl and AgBr in molten LiNO₃–KNO₃ eutectic mixture were measured as a function of temperature and halide ion concentration. The temperature was varied between 150 and 200° and the concentration of halide ion was varied between 1 × 10⁻³ and 2 × 10⁻¹ *m*. The solubility products of the silver halides and the stability constants of the halide complexes were evaluated. The dependence on temperature of the stability constants follows the generalized quasi-lattice model developed by Blander.

Measurements of the distribution of AgCl₂⁻ between an LiNO₃–KNO₃ molten salt mixture and an organic solution of tetraheptylammonium nitrate in polyphenyl diluent as a function of chloride concentration made possible the evaluation of the stability constants of the silver chloride complexes AgCl and AgCl₂⁻.² In the present work, another independent method, solubility measurements, is used to extend the study to silver bromide complexes and to introduce the temperature as a variable.

Experimental Section

The characteristics and the preparation of the eutectic LiNO₃–KNO₃ molten salt mixture were described previously.² The solubility of AgCl(s) and AgBr(s) in the molten nitrate mixture containing (Li,K)Cl and (Li,K)Br, respectively, was measured in the temperature range 150–200° using the radioactive tracer method. The 260-day ^{110m}Ag radiotracer in the form of AgNO₃ in nitric acid solution with a specific activity of 17.4 mCi/mg of Ag was obtained from the New England Nuclear Corp. The solubility of silver halide was expressed in molality: *S* = moles of Ag(I)/1000 g of (Li,K)NO₃ mixture.

For each run approximately 100 g of a melt 10⁻³ *m* in AgNO₃ containing ^{110m}Ag was prepared and aliquots of 9–10 g were poured into glass test tubes and weighed. Known amounts of

KCl or KBr and LiNO₃ were added to cover a concentration range of halide between 2 × 10⁻³ and 4 × 10⁻¹ *m* and to keep the mole ratio of K to Li constant at 1.38. The specific radioactivity of the melt in each tube was determined before the addition of the halide salt and expressed as counting rate per gram of (Li,K)NO₃ mixture. The tubes were stoppered and kept in an oven at desired temperature (±1°) for 24 hr so the AgX(s) would settle to the bottom of the tubes. The exposure of tubes to light was minimized. Aliquots of approximately 0.2 g of clear melt were taken every day for 4 days with preheated disposable glass pipets into vials, weighed, dissolved in 6 *M* NH₃, and counted with a well-type scintillation counter. These measurements showed that equilibrium was reached in less than 24 hr. The equilibrium concentration of Ag(I) was calculated from the decrease of radioactivity of the melt and the concentration of X⁻ assuming that the precipitate formed was AgX(s).

Results

The solubilities of AgCl and AgBr in molten LiNO₃–KNO₃ eutectic mixture were measured as a function of temperature and halide ion concentration. In all of the experiments the mole ratio of K⁺ to Li⁺ was kept constant at 1.38, which is the eutectic ratio for LiNO₃ and KNO₃. The nitrate and halides containing this proportion of alkali ions will be denoted MNO₃ and MX, respectively.

The concentration of MCl was varied between 4 × 10⁻³ and 2 × 10⁻¹ *m* and the temperature was varied

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between 150 and 200°. The data obtained are given in Figure 1. The concentration of MBr was varied between 1.2×10^{-3} and $1.0 \times 10^{-1} m$ and the temperature was varied between 150 and 190°. The data obtained are given in Figure 2.

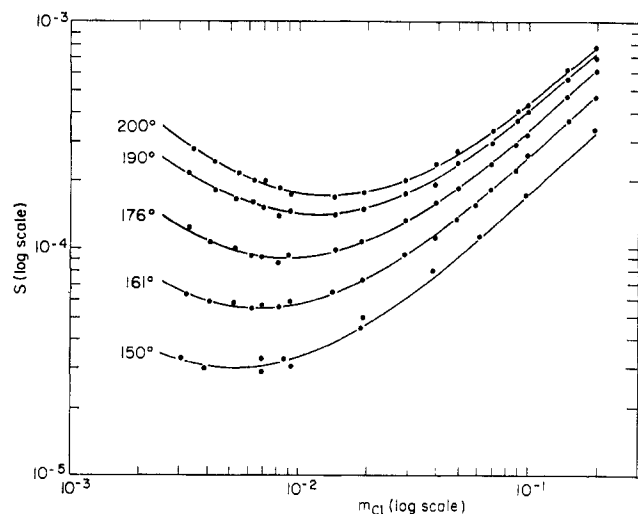


Figure 1.—Solubility of AgCl vs. MCl concentration at several temperatures.

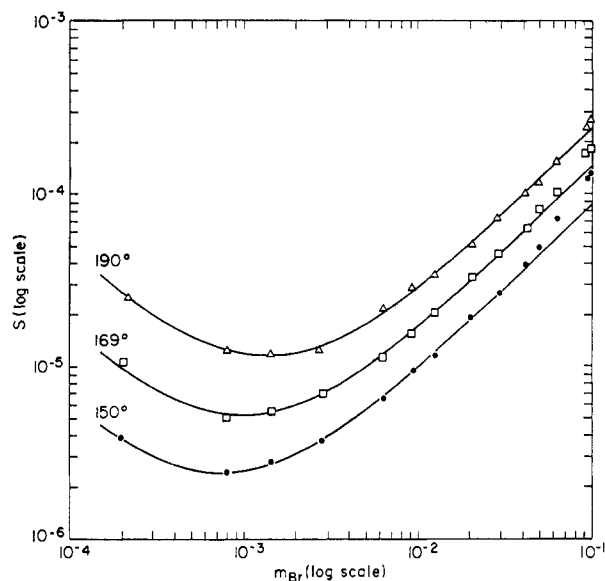


Figure 2.—Solubility of AgBr vs. MBr concentration at several temperatures.

Attempts were made to measure the solubility of AgI in this melt, but at concentrations of MI higher than $5 \times 10^{-3} m$ evolution of $I_2(g)$ was observed. Evolution of $Br_2(g)$ was also observed for concentrations of MBr higher than $5 \times 10^{-1} m$ and temperatures higher than 200°. This behavior of the halides is consistent with the findings of Topol, *et al.*,^{3a} and may explain the observed decrease in reproducibility of the electromotive force^{3b} data with increase of the atomic weight of the halide.

All the experiments were carried out in such a way

(3) (a) L. E. Topol, R. A. Osteryoung, and J. H. Christie, *J. Phys. Chem.*, **70**, 2857 (1966); (b) A. Alvarez-Funes, J. Braunstein, and M. Blander, *J. Am. Chem. Soc.*, **84**, 1538 (1962).

that the equilibrium concentration of the halide ion in the melt was at least five times the concentration of silver remaining in solution. Under these conditions it is assumed that the solubility of $AgX(s)$ is given by the expression

$$S = [Ag^+] + [AgX] + [AgX_2^-] \quad (1)$$

and the equilibrium concentration of the halide ion by

$$[X^-] \approx [MX]^i - [AgNO_3]^i + S \quad (2)$$

where the superscript i denotes initial concentration.

If the concentration of silver and halide are low, *i.e.*, $S < 10^{-3} m$ and $[X^-] < 3 \times 10^{-2} m$, the activity coefficients of all of the species in the melt can be assumed equal to unity. The activity coefficient of MCl in the (Li,K)NO₃ eutectic melt at 150° for $[MCl] = 3 \times 10^{-2} m$ was calculated to be equal to 0.992.² Equation 1 can then be written

$$S = K_{sp}(1 + K_1[X^-] + K_1K_2[X^-]^2)/[X^-] \quad (3)$$

where K_1 and K_2 are the formation constants² of the complexes AgX and AgX_2^- , respectively, and K_{sp} is the solubility product of $AgX(s)$. These constants were evaluated using the curve-fitting methods described by Rossotti and Rossotti⁴ and the values obtained are given in Tables I and II. The curves in Figure 1 were drawn using the constants given in Table I and the activity coefficients for MCl determined previously² for concentrations of MCl higher than $3 \times 10^{-2} m$. The points shown are experimental. The curves in Figure 2 were drawn using only the constants in Table II since no data on activity coefficients for MBr are available. They give a good description of the data up to a concentration of MBr of $4 \times 10^{-2} m$. At higher concentrations of MBr positive deviations are observed that increase as the temperature decreases. This behavior can be attributed to the formation of higher complexes. However, to evaluate the stability constants of these higher bromide complexes, it will be necessary to determine the activity coefficient of the bromide salt in the melt.

The dependence of the constants on temperature is shown in Figure 3. The values of K_{sp} for AgCl and AgBr obtained by Tien and Harrington^{5a} are also shown, and with the exception of the value for AgCl at 148° a good agreement was obtained. The values of ΔH for the different equilibria involved are shown in Table III together with some values determined by other workers.

Tien and Harrington reported a value for the association constant of AgCl at 225° in the lithium nitrate-potassium nitrate eutectic.^{5b} This value was corrected in a later note.^{5c} Braunstein, *et al.*,^{5d} confirmed the corrected value and reported another value at 240° in a 70-30 mol % potassium nitrate-lithium nitrate melt. A line through these two points

(4) F. J. C. Rossotti and H. Rossotti, "The Determination of Stability Constants," McGraw-Hill Book Co., Inc., New York, N. Y., 1961.

(5) (a) H. T. Tien and G. W. Harrington, *Inorg. Chem.*, **2**, 369 (1963); (b) H. T. Tien and G. W. Harrington, *ibid.*, **3**, 215 (1964); (c) G. W. Harrington and H. T. Tien, *ibid.*, **3**, 1333 (1964); (d) J. Braunstein, H. Braunstein, and H. S. Minano, *ibid.*, **3**, 1334 (1964).

TABLE I

EQUILIBRIUM CONSTANTS FOR THE SYSTEM Ag(I)-Cl

Temp, °C	$10^7 K_{sp}$, m	$10^{-2} K_1$, m	$10^{-1} K_2$, m	$10^{-2} K_1$, mol fraction	$10^{-2} K_2$, mol fraction	$-\Delta A$, kcal/mol
150	0.44 ± 0.02	3.00 ± 0.20	12.0 ± 0.10	3.43 ± 0.23	13.7 ± 0.11	5.49
161	1.03 ± 0.04	2.38 ± 0.12	9.30 ± 0.07	2.72 ± 0.14	10.6 ± 0.88	5.43
176	2.27 ± 0.06	1.79 ± 0.08	7.00 ± 0.06	2.04 ± 0.09	8.00 ± 0.07	5.37
190	4.65 ± 0.07	1.35 ± 0.06	5.30 ± 0.04	1.54 ± 0.07	6.05 ± 0.05	5.28
200	6.80 ± 0.07	1.15 ± 0.05	4.51 ± 0.03	1.31 ± 0.06	5.10 ± 0.03	5.24

Av 5.36 ± 0.13

TABLE II

EQUILIBRIUM CONSTANTS FOR THE SYSTEM Ag(I)-Br

Temp, °C	$10^3 K_{sp}$, m	$10^{-2} K_1$, m	$10^{-2} K_2$, m	$10^{-4} K_1$, mol fraction	$10^{-2} K_2$, mol fraction	$-\Delta A$, kcal/mol
150	0.52 ± 0.02	2.06 ± 0.08	8.22 ± 0.30	2.35 ± 0.09	9.39 ± 0.34	7.11
169	1.48 ± 0.05	1.57 ± 0.06	6.62 ± 0.25	1.79 ± 0.07	7.15 ± 0.28	7.19
190	4.40 ± 0.07	1.16 ± 0.06	4.62 ± 0.20	1.32 ± 0.07	5.28 ± 0.23	7.25

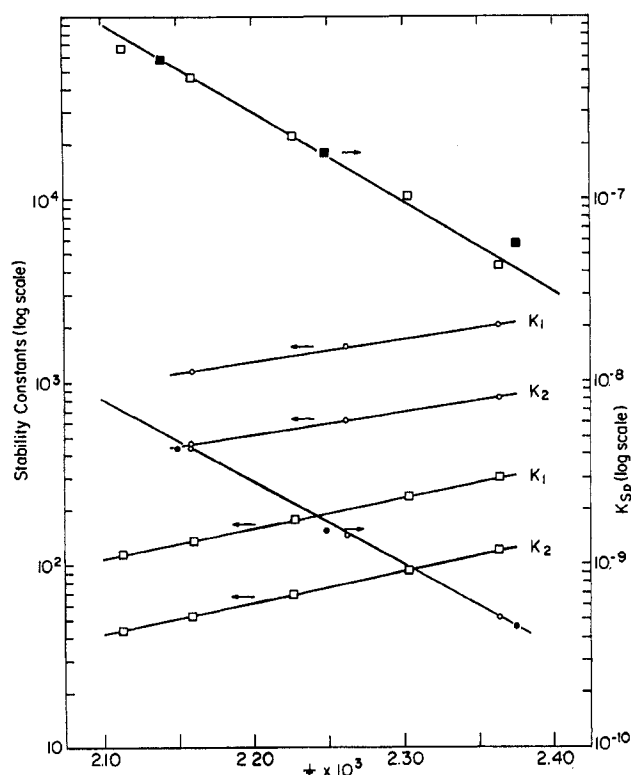
Av 7.18 ± 0.07 

Figure 3.—Temperature dependence of equilibrium constants: □, Ag(I)-Cl system; ○, Ag(I)-Br system. Solubility products from ref 5a: ■, AgCl; ●, AgBr.

TABLE III
VALUES OF ΔH

Change in state	ΔH , kcal/mol		
	a	b	c
AgCl(s) = Ag ⁺ + Cl ⁻	22.2 ± 1.2	18.9 ± 0.9	19.5
AgBr(s) = Ag ⁺ + Br ⁻	22.0 ± 0.4	26.1 ± 0.7	23.2
Ag ⁺ + Cl ⁻ = AgCl and AgCl + Cl ⁻ = AgCl ₂ ⁻	-1.69 ± 0.02
Ag ⁺ + Br ⁻ = AgBr and AgBr + Br ⁻ = AgBr ₂ ⁻	-1.25 ± 0.02

^a This work. ^b J. Jordan, J. Meier, E. J. Billingham, and J. Pendergrast, *Nature*, **187**, 318 (1960). ^c See ref 5a.

has the same slope as the corresponding curve in Figure 3, but it lies about 25% higher than our extrapolated curve. The second association constant for AgCl₂⁻

TABLE IV

VALUES OF ΔA_1 FOR AgX ASSOCIATION IN VARIOUS MELTS

Melt	$-\Delta A_1$, kcal/mole	Temp range, °C	Ref
Ag ⁺ Cl ⁻			
0.42 LiNO ₃ + 0.58 KNO ₃	5.36	150-200	a
0.33 LiNO ₃ + 0.67 KNO ₃	5.7	391	b
KNO ₃	5.64	350-436	c, d, e
LiNO ₃	4.97	...	f
NaNO ₃	4.59	300-500	g
CsNO ₃	6.29	440	b
Ag ⁺ Br ⁻			
0.42 LiNO ₃ + 0.58 KNO ₃	7.18	150-190	a
KNO ₃	6.87	403-500	c
LiNO ₃	7.44	...	f
NaNO ₃	6.23	402-500	h

^a This work. ^b C. Thomas and J. Braunstein, *J. Phys. Chem.*, **68**, 957 (1964). ^c See ref 3b. ^d F. R. Duke and H. M. Garfinkel, *J. Phys. Chem.*, **65**, 461 (1961). ^e See ref 8. ^f Calculated from eq 6. ^g D. G. Hill, J. Braunstein, and M. Blander, *J. Phys. Chem.*, **64**, 1038 (1960). ^h D. L. Manning, R. C. Bansal, J. Braunstein, and M. Blander, *J. Am. Chem. Soc.*, **84**, 2028 (1962).

reported by Tien and Harrington^{5c} is lower than our extrapolated value but just within the large limit of error reported.

The generalized calculations for the quasi-lattice model developed by Blander⁶ lead to expressions for K_1 and K_2

$$K_1 = Z(\beta_1 - 1) \quad (4)$$

$$K_1 K_2 = Z(Z - 1)(\beta_1 \beta_2 - 2\beta_1 + 1)/2 \quad (5)$$

where Z is the quasi-lattice coordination number, $\beta_j = \exp(-\Delta A_j/RT)$, and ΔA_j is the specific molar Helmholtz free energy change for the formation of the j th bond. The temperature dependences of the constants K_1 and K_2 obtained in this work are correctly predicted by eq 4 and 5 with a value of $Z = 5$ and $\beta_1 = \beta_2$. The values of ΔA given in Tables I and II were calculated using the values of K_1 and K_2 on the mole fraction scale. These values of ΔA show a monotonic change with temperature but the total change is smaller than the experimental error of the solubility measurements.

(6) M. Blander, *J. Chem. Phys.*, **34**, 432 (1961).

Calculations were also carried out with $Z = 6$ and the values of ΔA obtained are about 3.5% smaller.

Within the experimental errors the values of ΔA_1 in mixtures of two nitrates (a and b) obey the linear relation⁷

$$\Delta A_1(\text{mixture}) = x_a \Delta A_1(\text{in pure a}) + x_b \Delta A_1(\text{in pure b}) \quad (6)$$

where x is the mole fraction of the nitrates. This equation was found to be followed by the Cl^- and Br^- complexes of $\text{Ag}(\text{I})$ in NaNO_3 and KNO_3 mixtures. In spite of the large difference between the ionic radii of Li^+ and K^+ this relation was used to calculate the value of ΔA_1 for the Cl^- and Br^- complexes of $\text{Ag}(\text{I})$ in pure LiNO_3 melt using the values of ΔA_1 for pure KNO_3 obtained by Manning, *et al.*,⁸ and assuming that they are independent of temperature. The values found are given in Table IV together with the values for other melts. The values of $-\Delta A_1$ for the pure LiNO_3 melt seem large

(7) M. Blander in "Molten Salt Chemistry," M. Blander, Ed., Interscience Publishers, New York, N. Y., 1964, p 127 ff.

(8) D. L. Manning, J. Braunstein, and M. Blander, *J. Phys. Chem.*, **66**, 2069 (1962).

when compared with those for pure NaNO_3 or KNO_3 . This type of anomalous behavior of the melts containing LiNO_3 has also been observed in the formation of CdBr^+ and CdBr_2^0 and AgCl^{10} complexes in LiNO_3 - KNO_3 mixtures. In these systems the values of $-\Delta A_i$ become larger as the mole fraction of LiNO_3 increases and the values are larger than in the corresponding NaNO_3 - KNO_3 mixtures. These anomalous effects have been explained on the basis of a smaller effective radius of the nitrate ion in lithium-containing melts.⁹⁻¹¹ Thomas and Braunstein¹⁰ have pointed out some of the difficulties of emf measurements at high lithium nitrate concentration and the solubility method reported here may be more effective for exploring high lithium systems.

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(9) J. Braunstein and A. S. Minano, *Inorg. Chem.*, **3**, 218 (1964).

(10) C. Thomas and J. Braunstein, *J. Phys. Chem.*, **68**, 957 (1964).

(11) S. V. Meschel and O. J. Kleppa, *ibid.*, **68**, 3840 (1964).

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Low-Temperature Far-Infrared Spectra of Hexanitro Complex Salts¹

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Far-infrared spectra of $\text{M}_3[\text{Co}(\text{NO}_2)_6]$ ($\text{M} = \text{Na}, \text{K}, \text{Rb}, \text{and Cs}$) and $\text{M}'_2\text{M}''[\text{Ni}(\text{NO}_2)_6]$ ($\text{M}' = \text{K and Na}; \text{M}'' = \text{Ca and Ba}$) have been measured down to 50 cm^{-1} at room temperature and liquid nitrogen temperature. Lattice vibrations due to the displacements of the outer cations relative to the complex ion are observed below 200 cm^{-1} . Those frequencies change depending upon the mass of the cations and the interionic potential constants. The far-infrared bands due to the lattice vibrations and the intramolecular vibrations in the complex ion were both interpreted for $\text{M}_3[\text{Co}(\text{NO}_2)_6]$ and K_2Ca - and $\text{K}_2\text{Ba}[\text{Ni}(\text{NO}_2)_6]$ by the normal-coordinate analysis of the crystal as a whole, on the basis of the T_h ³ structure determined by the X-ray analysis, only the interaction between the outer cations and the oxygen atoms being taken into account. $\text{Na}_3[\text{Co}(\text{NO}_2)_6]$ reveals quite a different spectrum from those for the other complex salts, in the lattice vibration region as well as in the intramolecular vibration region. This complex spectrum has been interpreted satisfactorily on the basis of the C_{3i} deformed structure.

Introduction

In a previous report we discussed the lattice vibrations of hexanitrocobalt(III) complex salts.³ We also reported that the Na salt revealed a much more complicated spectrum than the K, Rb, and Cs salts.^{3,4} From the viewpoint of the intramolecular vibrations we concluded that the $\text{Co}(\text{NO}_2)_6^{3-}$ ion in the Na salt has C_{3i} (S_6) symmetry instead of T_h symmetry.^{4a}

A far-infrared spectral measurement at liquid nitrogen temperature has recently enabled us to obtain more distinct bands than those at room temperature and we

have obtained well-defined far-infrared spectra in the region down to 50 cm^{-1} at low temperature as well as room temperature for a series of $\text{M}_3[\text{Co}(\text{NO}_2)_6]$ compounds ($\text{M} = \text{Na}, \text{K}, \text{Rb}, \text{and Cs}$). A similar measurement has been extended to the hexanitronickel(II) complex salts such as $\text{K}_2\text{Ca}[\text{Ni}(\text{NO}_2)_6]$, $\text{K}_2\text{Ba}[\text{Ni}(\text{NO}_2)_6]$, and $\text{Na}_2\text{Ba}[\text{Ni}(\text{NO}_2)_6]$.

In the present paper we give the summary of the experimental results and discuss the nature of the lattice vibrations as well as the intramolecular vibrations, on considering the frequency shifts with the lowering of temperature. A normal-coordinate analysis of $\text{Na}_3[\text{Co}(\text{NO}_2)_6]$ has been made on the basis of the structure with the space group C_{3i} , without separating the lattice vibrations and the intramolecular vibrations in the $\text{Co}(\text{NO}_2)_6^{3-}$ ion. These results yield important infor-

(1) Presented before the 10th International Conference on Coordination Chemistry, Nikko, Japan, Sept 1967.

(2) (a) The University of Tokyo; (b) The University of Nagoya.

(3) I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta*, **22**, 1707 (1966).

(4) (a) I. Nakagawa, T. Shimanouchi, and K. Yamasaki, *Inorg. Chem.*, **3**, 772 (1964); (b) I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta*, **23A**, 2099 (1967).