metal, K_1 in acetone exceeds that in ethanol, in agreement with spectral evidence for slightly greater stabilization by acetone. Also, since, in general, the values of K_1 are less than 6, both ethanol and acetone are seen to provide slightly less ligand field stabilization than does water. This is also in agreement with the spectral shifts.

Statistically K_2 values should be either 2 or $^1/_2$, depending on whether the complex formed is the *cis* isomer or the *trans* isomer. Of the two possible forms, the latter might be expected to be favored because of steric hindrance at the *cis* sites. However, the K_2 values are small even as compared to the *trans* value of $^1/_2$. Two causes for the low values can be imagined. One would be a thermodynamic *trans* effect; that is induced dipoles tending to favor two different ligands at the *trans* positions. A second contributing cause could be a solvent effect. The second substitution occurs in solutions where the solvent is predominantly organic. Therefore, the reaction which requires separation from the charged ion of the H_2O molecule which is more polar than the entering solvent molecule will be inhibited by the low dielectric constant of the predominantly organic solvent. Whatever the detailed explanation, its nature must be such as not to depend markedly on the identity of the metal ion, since the values of K_2 in Table V are remarkably free from trends.

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Cobalt(II) Species in Fused Chloride Solvents[1]

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Absorption spectra in the range 4000–34,000 cm.$^{-1}$ of Co(II) in molten KCl–$AlCl_3$ mixtures have been studied as a function of melt composition. The Co(II) spectra in melts varying from 0 to 42 mole % KCl are interpreted as due to $Co(Al_2Cl_7)_2$ species with Co(II) in octahedral coordination. In the region 42–49.9 mole % KCl, the spectral data and mathematical analysis of the equilibrium indicate the formation of the mixed complex $Co(Al_2Cl_7)(AlCl_4)$ with Co(II) in a severely distorted octahedral environment of chlorides. The spectrum of this species is characterized by a splitting of the ^4P band into three components with an over-all separation of 3400 cm.$^{-1}$. At 300°, the equilibrium constant for the reaction $Co(Al_2Cl_7)_2 + AlCl_4^- = Co(Al_2Cl_7)(AlCl_4) + Al_2Cl_7^-$ is found to be $K = 3.5 \times 10^{-2}$. The solid phase in equilibrium with the mixed complex is $CoCl_2$. The solubility of $CoCl_2$ at 300° decreases to values less than 8×10^{-4} *M* as the KCl:$AlCl_3$ ratio approaches 1. In melts with KCl:$AlCl_3$ ratios larger than 1 as well as in molten alkali chlorides, $MgCl_2$, $CdCl_2$, and $PbCl_2$, the Co(II) spectra are characteristic of the $CoCl_4^{2-}$ species. The degree of distortion of the $CoCl_4^{2-}$ species and the oscillator strength of the ^4P band transitions are correlated with the ionic potential of the melt cations. The Co(II) spectrum in solid and liquid $MgCl_2$ is discussed with reference to the structure of molten $MgCl_2$.

Introduction

The dipositive 3d transition metal ions have been shown to occur as markedly different ionic species in the highly dissociated alkali chloride melts compared with the nondissociated aluminum chloride melt.[2,3] It is therefore of interest to study the equilibria between the various species in mixtures of the alkali chlorides with aluminum chloride.

The different ionic species are in all probability correlated with changes in the thermodynamic activity coefficients of the 3d ions. This expectation is made plausible by a consideration of ion polarizabilities. Thus, in alkali chloride melts, the dipositive 3d ions tend to polarize the chloride ions more strongly than do the solvent alkali cations, while in aluminum chloride melts the reverse situation occurs with the solvent Al(III) ions exerting the stronger polarizing force. On this basis, the activity coefficients of the 3d ions are expected to be smaller in alkali chloride than in aluminum chloride rich melts.

We have chosen to study the equilibria between Co(II) species in the KCl–$AlCl_3$ binary system in order to gain further insight into the forces governing the behavior and stability of such species as a function of the ionic nature of the melt. Clearly, such information is important to a basic understanding of the thermodynamics of a large class of metal ions in molten salt systems.

In the LiCl–KCl eutectic melt the absorption spectrum of Co(II) is that of the tetrahedral $CoCl_4^{2-}$ species.[2] The occurrence of the $CoCl_4^{2-}$ rather than the $CoCl_6^{4-}$ species in this highly ionic melt can be rationalized in terms of large (~30 kcal.) electrostatic repulsion energies favoring the four- over the six-coordinated form.[2] In the covalent $AlCl_3$ melt, however,

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(1) Work performed under the auspices of the U. S. Atomic Energy Commission.

(2) D. M. Gruen and R. L. McBeth, *Pure Appl. Chem.*, **6**, 23 (1963).

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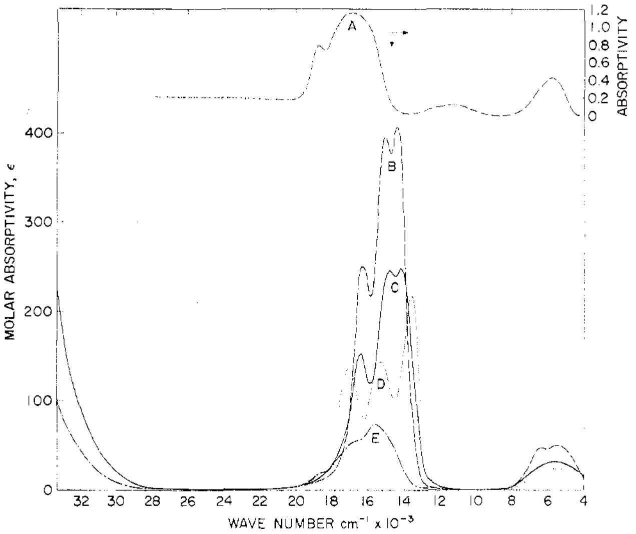

Figure 1.—Spectra of Co(II) in chloride surroundings: A, crystalline $Co(AlCl_4)_2$ at 25°; B, 50.3 mole % KCl, 49.7 mole % $AlCl_3$ at 300°; C, 100.0 mole % KCl at 800°; D, 49.9 mole % KCl, 50.1 mole % $AlCl_3$ at 300°; E, 35.5 mole % KCl, 64.5 mole % $AlCl_3$ at 300°.

the electrostatic repulsion energies between chloride ions are decreased, resulting in the formation of octahedrally coordinated cobalt species.[3]

The present investigation concerns itself with a study of the structures, stoichiometries, and equilibria among the various Co(II) species in melts ranging from purely molecular ($AlCl_3$) to essentially completely ionic (KCl). This paper also presents data on Co(II) spectra in a variety of other fused chloride solvents which are correlated closely with the results obtained on the KCl–$AlCl_3$ system.

Results and Discussion

(1) Dipositive Cobalt Species in KCl–$AlCl_3$ Melts.—Pure molten aluminum chloride consists of Al_2Cl_6 molecules. It was suggested that $CoCl_2$ dissolves in this melt according to the equation[3]

$$CoCl_2 + 2Al_2Cl_6 = Co(Al_2Cl_7)_2 \qquad (1)$$

A plausible structure for this complex is one in which Co(II) is octahedrally surrounded by six chlorides belonging to two $Al_2Cl_7^-$ groups, the $Al_2Cl_7^-$ group in turn having a structure based on two $AlCl_4$ tetrahedra sharing one corner. The neutral $M(Al_2Cl_7)_2$ complex would provide an octahedral chloride environment for Co(II) in molten $AlCl_3$ without requiring the high concentration of negative charge which tends to destabilize octahedral $CoCl_6^{4-}$ complexes in the ionic KCl melt.

A brief review of the KCl–$AlCl_3$ phase diagram is in order.[4–6] There are two eutectics, at 49 mole % $AlCl_3$ (250°) and at 67 mole % $AlCl_3$ (128°). The compound $KAlCl_4$ melts congruently at 256°. A liquid immiscibility gap extends from 99.6 to 81.8 mole % $AlCl_3$.

The spectrum (Figure 1, curve E) of a solution of $CoCl_2$ in an $AlCl_3$ melt with 35.5 mole % KCl, close to the composition KAl_2Cl_7, is practically identical with the spectrum in pure $AlCl_3$, indicating that the postulated $Co(Al_2Cl_7)_2$ complex is the only light-absorbing species present in the composition range 0–35.5 mole % KCl. Successive additions of KCl to the 35.5 mole % KCl melt resulted in only minor spectral changes until a composition of ~42 mole % KCl was reached. Upon further addition of KCl, the $Co(Al_2Cl_7)_2$ spectrum characteristic of octahedral coordination gradually transformed into a new spectrum.

The spectrum at the composition 49.9 mole % KCl (Figure 1, curve D) is that of the new species and is characterized by three widely spaced components with maxima at 13,600, 15,400, and 17,000 cm.$^{-1}$.

Addition of KCl to a melt containing 49.3 mole % KCl resulted in partial precipitation of Co(II) and the formation of a blue precipitate which chemical and X-ray analysis showed to be $CoCl_2$. The dichloride was found to have a solubility less than 8×10^{-4} *M* in the composition range 49.9–50.0 mole % KCl at 300°. Instead of $CoCl_2$, one might have expected $Co(AlCl_4)_2$ to precipitate, but this compound has a melting point below 225° (*cf.* the preparation of this compound in the Experimental section).

Addition of KCl to a melt whose KCl:$AlCl_3$ ratio was exactly equal to 1 caused the $CoCl_2$ precipitate to redissolve completely with only a few times more than the stoichiometric amount of KCl needed to form $CoCl_4^{2-}$. The soluble species in melts with KCl:$AlCl_3$ greater than 1 have the characteristic tetrahedral Co(II) spectrum as illustrated, for example, by the spectrum of a solution containing 50.3 mole % KCl (Figure 1, curve B). The tetahedral species is probably $CoCl_4^{2-}$, but the spectrum of a $CoCl_3AlCl_4^{2-}$ complex might differ in only minor ways from the observed spectrum.

The spectrum of the cobalt species formed in the composition range 42–49 mole % KCl with its three widely spaced maxima (Figure 1, curve D) suggests a severely distorted octahedral arrangement of chlorides about the cobalt.

Under certain conditions cobalt is known to form the compound $Co(AlCl_4)_2$,[7,8] and the possibility has to be considered that the spectrum of the octahedrally distorted species is due to a soluble $Co(AlCl_4)_2$ complex formed by replacing two $Al_2Cl_7^-$ groups by two $AlCl_4^-$ groups. The crystal structure of $Co(AlCl_4)_2$, determined by Ibers,[8] may be described in terms of cobalt and aluminum atoms situated in octahedral and tetrahedral holes, respectively, of a nearly close-packed chlorine lattice. Although the Co–Cl distances in the $CoCl_6$ octahedron are not significantly different from one another, the octahedron is somewhat distorted.[8]

We have prepared $Co(AlCl_4)_2$ by allowing $CoCl_2$ and $AlCl_3$ to react in stoichiometric proportions and have observed the room temperature spectrum of this compound on a thin layer of the polycrystalline solid (Figure 1, curve A). The spectrum of $Co(AlCl_4)_2$ is remarkably

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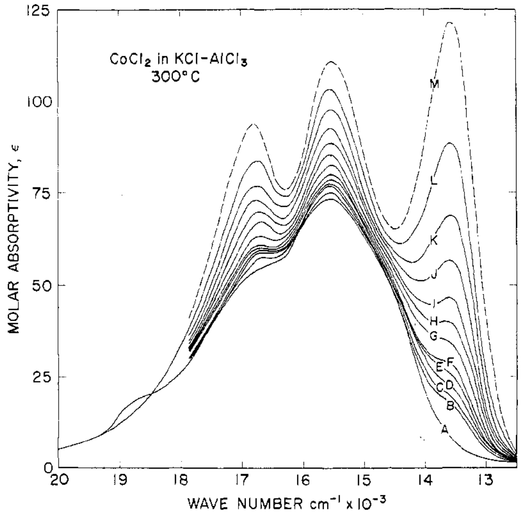

Figure 2.—Spectra of Co(II) in molten KCl–AlCl$_3$ mixtures. The letters identifying the curves refer to specific mole percentages of KCl listed in Table I.

similar with respect to the relative intensities of the bands and the location of the band maxima to the room temperature CoCl$_2$ crystal spectrum studied by Ferguson, Wood, and Knox.[9] The similarity between these two spectra indicates that the degree of distortion of the CoCl$_6$ octahedra in Co(AlCl$_4$)$_2$ and in CoCl$_2$[10] is about equal but is not sufficiently severe to cause the large splitting seen in the solution spectrum of the distorted Co(II) species. It should be pointed out, however, that, in solid Co(AlCl$_4$)$_2$, Co(II) is surrounded by four AlCl$_4^-$ groups, while in solution this number might well be different. The three components of the distorted Co(II) species (Figure 1, curve D) may be identified with transitions from the ground state to the split ligand field components of the excited ^{4}P state. On the basis of the above considerations, the large over-all splitting of 3400 cm.$^{-1}$ is very likely caused by unequal Co–Cl distances in the CoCl$_6$ octahedra. In a mixed complex such as Co(Al$_2$Cl$_7$)(AlCl$_4$) two sets of Co–Cl distances might be expected. It will be shown below that the formation of a mixed complex is consistent with the stoichiometric analysis of the chemical equilibrium leading to the formation of the new species.

(2) **Equilibria in KCl–AlCl$_3$ Mixtures.**—The spectral changes observed on successive additions of KCl to a 42 mole % KCl melt are shown in Figure 2. Melt compositions for twelve KCl additions are listed in column 2 of Table I. Corresponding to each of these additions, the molar absorptivities at 13.6, 15.6, and 16.8 × 10^3 cm.$^{-1}$ are given in columns 5, 4, and 3. The molar absorptivities were calculated using the concentration of Co(II) determined by chemical analysis together with the densities of the melts. The densities were obtained by linear interpolation between experimentally determined values of $\rho_{300°} = 1.55$ and 1.64 g./cc. at 40.6 and 50 mole % KCl, respectively. Densities were measured in calibrated and thermostated pycnometers.

TABLE I

MOLAR ABSORPTIVITIES OF Co AT SELECTED WAVE LENGTHS IN MELTS WITH VARYING KCl:AlCl$_3$ RATIOS AT 300°

Curve designation (Figure 2)	Mole % KCl	Molar absorptivities (ε), l./mole cm. 16,800 cm.$^{-1}$	15,600 cm.$^{-1}$	13,600 cm.$^{-1}$	% CoAl$_2$Cl$_7$-AlCl$_4$
A	35.45	54.0	73.1	9.4	0.7
B	42.27	56.7	74.8	18.2	5.8
C	42.95	58.4	77.0	19.9	6.7
D	43.68	59.0	77.2	22.7	8.0
E	44.35	59.6	78.4	25.9	9.4
F	45.03	60.3	80.0	28.4	11.1
G	45.67	62.9	82.2	34.3	13.1
H	46.31	66.5	84.9	40.0	15.7
I	46.96	69.6	88.2	46.5	19.2
J	47.59	72.7	92.1	56.5	23.9
K	48.17	76.5	97.3	68.5	30.1
L	48.74	83.3	103.1	88.1	39.4
M^a	49.32	92.8	110.7	121.2	55.5
Fig. 1, curve D^b	49.90	137.2	145.0	218.0	100.0

^{a} Small amounts (≈15%) of CoCl$_2$ had precipitated so that the concentration of CoCl$_2$ in solution was not exactly known. The concentration was calculated by extrapolating the molar absorptivity at 16,300 cm.$^{-1}$ where the change in molar absorptivity with composition had a minimum. The molar absorptivities for the three peaks were then calculated. ^{b} At 49.9 mole % KCl so much CoCl$_2$ (≈80%) had precipitated that an extrapolation procedure for calculating the molar absorptivity was not considered reliable. The molar absorptivity at 13,600 cm.$^{-1}$ was estimated using the least-square analysis of Figure 3 assuming 100% Co(Al$_2$Cl$_7$)(AlCl$_4$). The calculated concentration was then used for determining the molar absorptivities for the two other peaks.

The molar absorptivities at 13,600 cm.$^{-1}$ were used to obtain information on the stoichiometry of the equilibrium. The bulk melt was considered to consist only of the species K$^+$, Al$_2$Cl$_7^-$, and AlCl$_4^-$. In the concentration range 33.3–50 mole % KCl, the concentration of each of these species is determined by the equilibrium

$$\mathrm{Al_2Cl_7^-} + \mathrm{Cl^-} = 2\mathrm{AlCl_4^-} \qquad (2)$$

According to all available evidence this equilibrium lies far to the right.[3,11] The moles of Al$_2$Cl$_7^-$ and AlCl$_4^-$ for $N_{\mathrm{KCl\ total}} + N_{\mathrm{AlCl_3\ total}} = 1$ are given by

$$N_{\mathrm{Al_2Cl_7^-}} = 1 - 2N_{\mathrm{KCl}} \qquad (3)$$

$$N_{\mathrm{AlCl_4^-}} = 3N_{\mathrm{KCl}} - 1 \qquad (4)$$

In solution, Co(II) is presumably surrounded either by Al$_2$Cl$_7^-$ or by AlCl$_4^-$ groups. The equilibrium between the octahedral Co(Al$_2$Cl$_7$)$_2$ complex and the distorted complex can be written in the general form

$$\mathrm{Co(Al_2Cl_7)_2} + n_1\mathrm{AlCl_4^-} = \mathrm{Co(Al_2Cl_7)_{2-n_2}(AlCl_4)_{n_1}}^{n_2-n_1} + n_2\mathrm{Al_2Cl_7^-} \qquad (5)$$

The equilibrium quotient, K, for reaction 5 is given by

$$K = \frac{[\mathrm{Co(Al_2Cl_7)_{2-n_2}(AlCl_4)_{n_1}}^{n_2-n_1}][\mathrm{Al_2Cl_7^-}]^{n_2}}{[\mathrm{Co(Al_2Cl_7)_2}][\mathrm{AlCl_4^-}]^{n_1}} \qquad (6)$$

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(9) J. Ferguson, D. L. Wood, and K. Knox, *J. Chem. Phys.*, **39**, 881 (1963).

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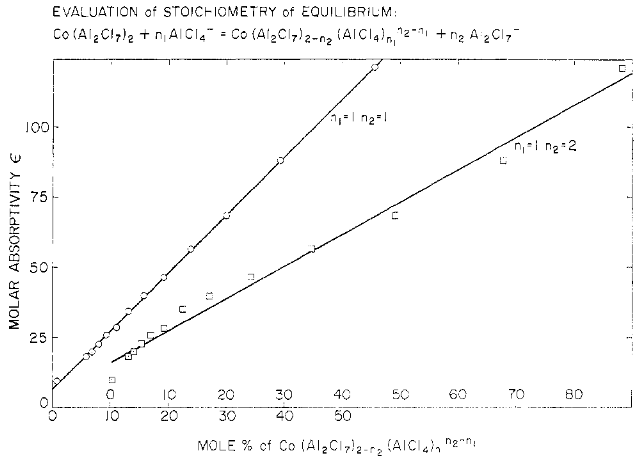

Figure 3.—Plot of molar absorptivity ε *vs.* mole % $Co(Al_2Cl_7)_{2-n_2}(AlCl_4)_{n_1}^{n_2-n_1}$ for $n_1 = 1$, $n_2 = 1$ and $n_1 = 1$, $n_2 = 2$.

Setting $[Co(Al_2Cl_7)_{2-n_2}(AlCl_4)_{n_1}^{n_2-n_1}] = X$ and $[Co(Al_2Cl_7)_2] = 1 - X$ one obtains

$$K = \frac{X(1 - 2N_{KCl})^{n_2}}{(1 - X)(3N_{KCl} - 1)^{n_1}} \tag{7a}$$

$$X = \frac{1}{1 + [(1 - 2N_{KCl})^{n_2}/K(3N_{KCl}) - 1)^{n_1}]} \tag{7b}$$

The effect of Co(II) on $Al_2Cl_7^-$ and $AlCl_4^-$ mole fractions has not been explicitly taken into account in this treatment. This approximation is valid since the Co(II) concentrations were very low, $\sim 10^{-2}$ *M*. In equilibrium 5 involving two optically absorbing species with molar absorptivities $\epsilon_1^{\lambda_i}$ and $\epsilon_2^{\lambda_i}$, respectively, at any wave length λ_i, the measured molar absorptivity ε at any wave length λ_i is given by

$$\epsilon^{\lambda_i} = (1 - X)\epsilon_1^{\lambda_i} + X\epsilon_2^{\lambda_i} \tag{8}$$

$$\epsilon^{\lambda_i} = \epsilon_1^{\lambda_i} + (\epsilon_2^{\lambda_i} - \epsilon_1^{\lambda_i})X \tag{9}$$

Equation 9 shows ϵ^{λ_i} to be a linear function of *X*. Different values of n_1, n_2, and *K* were chosen to give the best fit to a straight line calculated by means of a least-squares computer program. Figure 3 gives the results of the calculation for $n_1 = 1$, $n_2 = 1$ and for $n_1 = 1$, $n_2 = 2$ using only the ε values at 13,600 cm.$^{-1}$. A fit with a standard deviation of 0.6 l./mole cm. is obtained for $n_1 = n_2 = 1$ while $n_1 = 1$, $n_2 = 2$ gives a systematic deviation from a straight line and the standard deviation is 3.5 l./mole cm. The calculation is not sensitive enough to distinguish between $n_1 = 1$ and $n_1 = 2$.

A calculation using molar absorptivities at the three wave lengths 13.6, 15.6, and 16.8 × 10^3 cm.$^{-1}$ gives a standard deviation of 1.1 l./mole cm. for $n_1 = 1$, $n_2 = 1$ and 2.5 l./mole cm. for $n_1 = 1$, $n_2 = 2$. In the absence of evidence to the contrary, we assume that the simplest situation with $n_1 = 1$, $n_2 = 1$ occurs. The equilibrium between the octahedral and the distorted complex is then given by

$$Co(Al_2Cl_7)_2 + AlCl_4^- = Co(Al_2Cl_7)(AlCl_4) + Al_2Cl_7^- \tag{10}$$

The best fit of the data was obtained with $K = 3.54 \times 10^{-2}$ for the equilibrium quotient characterizing eq. 10 at 300°. The calculated mole % of the distorted complex is given in the last column in Table I. The small value of *K* is a reflection of the fact that $AlCl_4^-$ forms weaker complexes with Co(II) compared with $Al_2Cl_7^-$. It is reasonable to postulate two different Co–Cl distances in a mixed complex: one set of three Co–Cl distances to the $Al_2Cl_7^-$ group; another set of three to the $AlCl_4^-$ group. Stronger bonding to the $Al_2Cl_7^-$ group would make this set of distances somewhat shorter than the Co–Cl distances to the $AlCl_4^-$ group. The considerable distortion of the complex revealed by its spectrum is seen to arise naturally from a structure for the complex suggested by an analysis of the ionic equilibrium occurring in this system.

One ought, however, to point out that although the mathematical analysis gives strong indication of the formation of a $Co(Al_2Cl_7)(AlCl_4)$ complex, one cannot completely exclude other possibilities. For example, the complex might be a mixed complex such as $CoCl_2(Al_2Cl_7)^-$. The analysis given here is based on the assumption that for $N_{KCl} < 0.5$ all Cl^- is bound to Al^{3+} and the two Al^{3+} species constitute an ideal anion solution. Activity measurements of Cl^- and Al_2Cl_6 in KCl-$AlCl_3$ mixtures, solubility measurements of $CoCl_2$, and spectral and thermodynamic studies of the system $AlCl_3$–$CoCl_2$ would be very desirable to obtain further insight into the nature of the ionic species and their equilibria in melts of this type.

(3) Solubility of $CoCl_2$ in KCl–$AlCl_3$ Mixtures.—The solubility of $CoCl_2$ was found to be 3.3 × 10^{-3} *M* in a melt with 49.3 mole % KCl at 300°. Upon further addition of KCl, the solubility decreased. The solubility of $CoCl_2$ was estimated to be 0.8 × 10^{-3} *M* in a melt with 49.9 mole % KCl (Table I, footnote *b*).

Low solubilities of transition metal chlorides in melts with KCl:$AlCl_3$ ratios slightly less than 1 appear to be quite generally encountered. We have observed very low solubilities for VCl_3 and $NiCl_2$, and other workers[11,12] have made similar observations on UCl_3.

When the KCl:$AlCl_3$ ratio exceeds 1 by an amount corresponding to only a few times the quantity of KCl required for the reaction

$$CoCl_2 + 2Cl^- = CoCl_4^{2-} \tag{11}$$

the precipitated $CoCl_2$ redissolves as already mentioned.

We have, however, obtained preliminary evidence from $NiCl_2$ dissolution experiments showing that the primary dissolution step on the KCl-rich involves the formation of a mixed complex, $NiCl_3AlCl_4^{2-}$. ($NiCl_2$ dissolves as a tetrahedral complex, but the dissolution is proportional to the *first* power in added KCl.) The same situation in the $CoCl_2$ case would result in the dissolution reaction

$$CoCl_2 + Cl^- + AlCl_4^- = CoCl_3AlCl_4^{2-} \tag{12}$$

followed, on further addition of Cl^-, by the equilibrium

$$CoCl_3AlCl_4^{2-} + Cl^- = CoCl_4^{2-} + AlCl_4^- \tag{13}$$

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(12) R. H. Moore, *Inorg. Chem.*, **3**, 1738 (1964).

TABLE II

ABSORPTION MAXIMA, MOLAR ABSORPTIVITIES, AND OSCILLATOR STRENGTHS OF THE ^{4}P BAND OF Co(II) IN FUSED CHLORIDE SOLVENTS

2	3	4	5	6	7	8
Substance	Temp., °C.	Absorption maxima, cm.$^{-1}$ × 10^{-3} (molar absorptivities, l./mole cm.) I	II	III	$\Delta_{\text{III-I}}$	Oscillator strength × 10^3
Tetrahedral and Distorted Tetrahedral Coordination						
Pyridinium chloride	150	14.3 (630)	14.9 (570)	15.9 (360)	1.5	5.42
KCl–$AlCl_3$ (50.3 mole % KCl)	300	14.4 (406)	15.1 (395)	16.3 (250)	1.9	4.48
CsCl	800	14.2 (292)	14.8 (289)	16.4 (176)	2.2	3.82
KCl	800	14.2 (249)	14.8 (245)	16.4 (152)	2.2	3.35
NaCl	820	14.2 (223)	15.0 (223)	16.5 (140)	2.3	3.25
LiCl	800	14.3 (173)	15.1 (179)	16.7 (117)	2.4	2.89
$CdCl_2$	650	14.2 (173)	15.0 (176)	16.6 (121)	2.4	2.83
$MgCl_2$	800	14.4 (154)	15.1 (156)	16.8 (101)	2.4	2.54
$PbCl_2$	600	14.0	14.8	16.3	2.3	
Octahedral Coordination						
$AlCl_3$	227	~14.8	15.7 (76)	~16.7		0.97
$GaCl_3$	150	~14.8	15.8 (58)	~16.7		0.78
KCl–$AlCl_3$ (35.5 mole % KCl)	300	~14.6	15.8 (73)	~16.7		1.05
Strongly Distorted Octahedral Coordination						
$HgCl_2$	350	13.6 (228)	15.4 (197)	16.8 (188)	3.2	3.8
KCl–$AlCl_3$ (49.9 mole % KCl)	300	13.6 (218)	15.4 (145)	17.0 (137)	3.4	3.0

A $CoCl_3AlCl_4^{2-}$ species would have to possess a nearly regular tetrahedral configuration as spectrum B, Figure 1 does not give evidence of a severely distorted structure.

Further work on the solubility of metal chlorides in KCl–$AlCl_3$ is needed to help clarify the interesting equilibria encountered in these systems.

These phenomena can be discussed from the point of view of generalized acid–base concepts. In molten Al_2Cl_6, $CoCl_2$ behaves as a base with respect to the acid Al_2Cl_6. We suggest that $CoCl_2$ reacts to form the complex $Co(Al_2Cl_7)_2$. With addition of KCl, Al_2Cl_6 forms stepwise the bases $Al_2Cl_7^-$ and $AlCl_4^-$. The increasing $AlCl_4^-:Al_2Cl_7^-$ ratio displaces equilibrium 10 to the right and appears to result in the formation of a mixed complex above 42 mole % KCl. The precipitation reaction which occurs at very low $Al_2Cl_7^-$ concentrations may be formally written as

$$Co(Al_2Cl_7)(AlCl_4) + 3AlCl_4^- = CoCl_2 + 3Al_2Cl_7^- \quad (14)$$

Further addition of KCl converts $Al_2Cl_7^-$ to $AlCl_4^-$ and, thereupon, excess KCl forms the soluble Co(II) species in accordance with eq. 11 and 12. In the composition region KCl:$AlCl_3$ > 1, $CoCl_2$ behaves as an acid relative to the base KCl.

It is significant that precipitation occurs on the $AlCl_3$-rich side over a KCl composition range which is larger by a factor of 10–100 than the corresponding dissolution reaction on the KCl-rich side. This implies that the equilibrium quotient for equilibrium 11 is larger than for equilibrium 1. The greater stability of the $CoCl_4^{2-}$ complex relative to the $Co(Al_2Cl_7)_2$ complex is a reflection of chloride ion affinities which according to the present work appear to be in the order $KCl \ll CoCl_2 < Al_2Cl_6$.

The results of this study show that the $AlCl_4^-$ group, being coordinatively saturated and of low polarizability, has very poor solvent properties for those metal chlorides which have basic properties with respect to Al_2Cl_6 and acidic properties with respect to KCl. Dissolution of metal chlorides on the $AlCl_3$-rich side apparently occurs only when the $Al_2Cl_7^-$ activity becomes large enough to form a complex containing at least one such solubilizing group.

(4) **Absorption Maxima and Oscillator Strengths of the ^{4}P Band of Co(II) in Fused Chlorides.**—The profound spectral changes of Co(II) in the KCl–$AlCl_4$ system have been discussed in the previous sections of the paper in terms of changing numbers, geometrical arrangements, and bonding properties of the chloride nearest neighbors. The sensitivity of the Co(II) spectrum to these parameters suggests the use of the Co(II) probe ion as a promising tool for the investigation of the structural properties of fused salts. Toward this end, Co(II) spectra have been measured in a variety of molten chloride systems and the results are given in summary form in Table II. Listed are the absorption maxima and molar absorptivities (in parentheses) of the components of the ^{4}P band for each solvent and solvent temperature together with the integrated oscillator strength ($f = 4.32 \times 10^{-9} \int \epsilon_\nu \partial\nu$) over the range 10,000–20,000 cm.$^{-1}$. This region includes all components of the ^{4}P absorption band.

Before proceeding with a detailed discussion of these results, a brief review of the theory of the Co(II) spectrum is in order. The Co(II) ion has a d^7 electronic configuration outside the argon core. This configuration gives rise to the free ion ground term ^{4}F and the excited states ^{4}P, ^{2}G, ^{2}P, ^{2}H, ^{2}D, ^{2}F. Octahedral or tetrahedral crystalline electric fields split the ^{4}F state into three states designated $^4A_2$, $^4T_2$, and $^4T_1$. The $^4P(^4T_1)$ state is split only by fields of symmetry lower than cubic and has at most three Stark components. On the point charge model, $Dq_{\text{tetrahedral}} = -{}^4/_9 Dq_{\text{octahedral}}$ so that in general a coordination number change involving one kind of ligand will result in shifts of band maxima which can be of the order of several thousand wave numbers.

Electronic transitions within the d-shell are Laporte forbidden and coupling of electronic with vibrational motions of the ligands is a frequently invoked mechanism by means of which these transitions become somewhat allowed in electric fields possessing a center of symmetry. The intensities of d–d transitions in tetrahedral fields are generally larger by a factor of 5–10 than in octahedral fields since the former lack a center of inversion symmetry. However, the oscillator strength of the $CoCl_4^{2-}$ complex ion appears to be too large by an order of magnitude to be accounted for by the vibronic mechanism even taking into account the absence of inversion symmetry. A "covalency" mechanism involving metal–ligand overlap has therefore been proposed by Ballhausen and Liehr,[13] to account for the increased intensity.

The present study restricts itself to a consideration of the most prominent feature of the Co(II) absorption spectrum in crystals and solutions which is due to transitions from the ground state to components of the ^4P state. It turns out that the ^2G level is close to ^4P in energy so that overlap of energy levels occurs in this region of the spectrum. The contribution of ^2G to the intensity of the $^4P + {}^2G$ absorption band is estimated to be about 10% since transitions to ^2G are spin forbidden. To a first approximation then, the observed intensity is due to the ^4P state.

In the free Co(II) ion, the ^4P levels lie in the energy range 15,000 to 16,000 cm.$^{-1}$. However, it is well-known that the interelectronic repulsion energies are decreased on complex formation so that the term splittings are reduced from the free ion values. With the Racah parameter B = 760 cm.$^{-1}$ and C/B = 4.6, the ^4P state lies between 11,000 and 12,000 cm.$^{-1}$ in the absence of a crystal field.[9,14,15] Crystal field splitting raises the energy of the ^4P state. The ^4F–^4P transition is found in the region 14,000 to 20,000 cm.$^{-1}$ in ionic solids and liquids, depending on the magnitude of Dq, the crystal field splitting parameter.

An examination of the spectra in Figure 1 shows that the ^4P bands are composite. Depending on the medium and on temperature, the bands are more or less completely resolved into three components. The maxima of absorption of the three components are listed in Table II, columns 4, 5, and 6. Following each wave length entry, the molar absorptivity at the wave length of the maximum is given in parentheses. In column 7, the separation between the lowest and highest wave length component is listed. The oscillator strengths over all three components are listed in the final column of Table II.

The structure of the ^4P band of Co(II) can be caused either by spin–orbit interaction or by crystal field splitting. An over-all separation of ~1000 cm.$^{-1}$ is expected for ζ = 400 cm.$^{-1}$, which is a reasonable value of the spin–orbit coupling parameter according to Ferguson.[14] However, splittings of 1500–3400 cm.$^{-1}$ are in fact observed (Table II, column 7). The situation in the chloride melts therefore appears to be one in which the crystal field splitting of the Co(II) energy levels due to low symmetry fields is large compared to the spin–orbit coupling interaction. The over-all splittings, given by the Δ_{III-I} numbers, are then a qualitative measure of the degree of distortion of the octahedral or tetrahedral Co(II) species in the various chloride melts. The spectra of Co(II) studied in the present investigation can be broadly divided into three groups reflecting different numbers and arrangements of chlorides around Co(II).

The first group of spectra with oscillator strengths of 5.4–2.5 × 10^{-3} appears to involve Co(II) in a four-coordinated site. Two recognizable subdivisions occur within this group: (a) In molten pyridinium chloride and in KCl–$AlCl_3$, 50.3 mole % KCl, the $CoCl_4^{2-}$ ion appears to be least distorted with Δ_{III-I} = 1500 and 1900 cm.$^{-1}$, respectively. (b) In the molten alkali chlorides and in molten $CdCl_2$, $MgCl_2$, and $PbCl_2$, the splitting of the ^4P band varies from 2200 to 2400 cm.$^{-1}$, pointing to larger distortions from tetrahedral symmetry than found in group (a).

Examination of Table II reveals that the degree of distortion as measured by the parameter Δ_{III-I} increases slowly with increasing ionic potential of the melt cations. The ionic potential, e/r, which increases from 0.6 for Cs(I) to 3.1 for Mg(II) also has a pronounced effect on the oscillator strength, which decreases from the value 3.82 × 10^{-3} in molten CsCl to 2.54 × 10^{-3} in $MgCl_2$.

The degree of distortion of the $CoCl_4^{2-}$ and the intensity of the ^4P band are apparently affected in opposite directions by an increase in the ionic potential of the melt cations. The higher the ionic potential of the solvent cations, the more effectively they can neutralize the charge on the $CoCl_4^{2-}$ complex, thus lowering the chlorine–chlorine repulsion energies. The four-coordination of the $CoCl_4^{2-}$ complex is a result of competition between chlorine repulsion energies which favor the tetrahedral configuration and crystal field stabilization energies which favor a distorted arrangement. On the other hand, a high ionic potential implies a high polarizing power. The chloride ions are strongly polarized by small, highly charged melt cations, thus tending to decrease the covalent "overlap" between the chlorines and Co(II). The intensity of the ^4P band would therefore be expected to decrease strongly with increasing polarizing power of the melt cations if the "covalency" mechanism of intensity proposed by Ballhausen and Liehr is operative.[13] Observations are in agreement with this expectation.

A second group of spectra with oscillator strengths of ~1 × 10^{-3} is found in molten $AlCl_3$, $GaCl_3$, and KCl–$AlCl_3$ mixtures up to the composition ~42 mole % KCl. The low intensity of the ^4P band, the higher energy of the central component of the band, and the similarity of the spectrum with those of $CoCl_2$ and Co-$(AlCl_4)_2$ leaves little doubt that Co(II) is octahedrally coordinated in these solvents. The magnitude of the

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[13] C. J. Ballhausen and A. D. Liehr, *J. Mol. Spectry.*, **2**, 342 (1958); Errata, *ibid.*, **4**, 190 (1960).

[14] J. Ferguson, *J. Chem. Phys.*, **39**, 116 (1963).

[15] A. D. Liehr, *J. Phys. Chem.*, **67**, 1314 (1963).

splitting, ~2000, indicates that the octahedron of chlorides is somewhat distorted.

A third group of spectra is observed in molten $HgCl_2$ and in KCl–$AlCl_3$ mixtures in the composition region 42–49.9 mole % KCl. These spectra are characterized by a ^4P band oscillator strength of $\sim 3 \times 10^{-3}$ and widely spaced ^4P components with $\Delta_{III-I} = 3200$ cm.$^{-1}$. The over-all splitting is larger than in any Co(II) spectrum known to us and indicates a severely distorted octahedral configuration. We will not propose a definite geometrical arrangement but the strikingly similar absorption spectra indicate the same arrangement in these quite different solvents. Arguments have been presented in an earlier section of the paper to show that the large degree of distortion requires different Co–Cl distances within the six-coordinated complex. From solubility measurements it was concluded that the octahedral complexes are weaker than the $CoCl_4^{2-}$ complex.

(5) **The Structure of Molten Magnesium Chloride.**—Structural studies of molten salts have been carried out primarily by means of X-ray and neutron diffraction measurements.[16-18] Average coordination numbers as well as interatomic distances have been determined for a number of molten alkali and alkaline earth halides. Molten magnesium chloride, however, appears not to have been studied by these techniques.

The application of transition metal ion spectra and in particular of Co(II) spectra to structural studies of fused salts is of interest for certain selected systems. The ideal situation clearly is one in which the Co(II) ion and the solvent cations have virtually identical chemical and physical properties. This ideal situation can be approached, but never realized, by matching the properties of Co(II) as closely as possible to those of the solvent cations. Solid $MgCl_2$ and $CoCl_2$ both crystallize with the $CdCl_2$ layer lattice structure. In this structure, the metal ions occupy one-half of the octahedral holes of an essentially close-packed chloride lattice. The octahedral $MgCl_6$ or $CoCl_6$ coordination groups are linked by sharing edges to form infinite layers. Two adjacent layers of chlorides are held together by van der Waals forces. A third chloride layer follows with the metal ions between the second and third layer. The octahedral ionic radii of Mg(II) and Co(II) are 0.65 and 0.72 Å., respectively; the Mg(II):Cl(I) and Co(II):Cl(I) radius ratios are 0.36 and 0.40, respectively. It will be recalled that for radius ratios less than 0.414, the six octahedrally disposed chlorides are not in contact with the central metal ion Mg(II) or Co(II).

We have isomorphously substituted Co(II) in small concentrations for Mg(II) in solid $MgCl_2$. The solid solution spectrum of Co(II) in $MgCl_2$ is virtually identical with that for pure $CoCl_2$ reported by Ferguson, Wood, and Knox,[9] showing that Co(II) does indeed occupy octahedral positions in the $MgCl_2$ lattice. Striking similarities are found between $MgCl_2$ and $CoCl_2$ as regards some other physical properties important from our point of view. For example, their melting points differ by only about 25° with $MgCl_2$ melting at 715° and $CoCl_2$ melting at 740°. The binary phase diagrams with CsCl display in both cases the 1:1 compounds $CsMCl_3$ with the metal ions in octahedral positions and the 2:1 and 3:1 compounds Cs_2MCl_4 and Cs_3MCl_5 with the metal ions in tetrahedral positions. The cohesive and structural properties of solid magnesium and cobalt chlorides are therefore closely similar.

The $CdCl_2$ structure is retained by $MgCl_2$ between room temperature and its melting point, no phase transformation being reported in the literature. It was of interest then to study the Co(II) spectrum in the solid state up to the melting point. Spectra were obtained on the Co(II) doped $MgCl_2$ crystal at intervals of ~100° between room temperature and 700°. Spectra were then taken at ~10° intervals. Only minor spectral changes were observed compared with the room temperature spectrum even to within 5° of the melting temperature, showing that Co(II) and presumably Mg(II) remain in octahedral sites in the solid.

On melting, the low intensity octahedral spectrum transforms to the intense three-band spectrum characteristic of a somewhat deformed tetrahedrally coordinated Co(II). The maxima of the bands and their oscillator strengths at 800° are listed in Table II, but virtually the same spectrum is observed at 725°, just a few degrees above the melting point of $MgCl_2$.

We wish to suggest that in view of the similarities in the physical properties of $MgCl_2$ and $CoCl_2$, the Co(II) coordination number change from six to four which occurs on melting takes place for the Mg(II) ions of the bulk melt as well. The Mg(II) ions in molten $MgCl_2$ would, therefore, be four-coordinated to chlorides.

Drastic reductions in coordination numbers occur quite generally in going from solid to molten alkali or alkaline earth halides.[16-18] Melting of these ionic crystals is in most cases accompanied by large increases in volume. In the case of $MgCl_2$, the volume increase on melting has been found to be 25% (C. Thalmayer, private communication).

It is of interest to note that a hypothetical solid-state phase transition of $MgCl_2$ from the $CdCl_2$ to the HgI_2 structure would result in a 22% volume increase. This is due to the fact that Mg(II) is too large to fit existing tetrahedral positions in the close-packed $CdCl_2$ lattice. In the HgI_2 structure, one-fourth of the tetrahedral holes are occupied by metal ions and all octahedral holes are empty.

Experimental

Analytical grade chemicals from the following companies were used: Mallinckrodt NaCl, $PbCl_2$, and $HgCl_2$; Baker and Adamson KCl and $NiCl_2 \cdot 6H_2O$; Baker $CoCl_2 \cdot 6H_2O$ and $CdCl_2$; Fisher LiCl. CsCl was obtained as 99% pure from Penn Rare

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[16] H. A. Levy, P. A. Agron, M. A. Bredig, and M. D. Danford, *Ann. N. Y. Acad. Sci.*, **79**, 762 (1960).

[17] J. Zarzycki in "Non-Crystalline Solids," V. D. Fréchette, Ed., John Wiley and Sons, New York, N. Y., 1960, pp. 117–143.

[18] K. Furukawa, *Discussions Faraday Soc.*, **32**, 53 (1961).

Metals, Revere, Pa. LiCl, NaCl, KCl, CsCl, and $PbCl_2$ were dried under vacuum, then melted under vacuum and filtered through a quartz frit. $HgCl_2$ was dried at 120° and 1 atm., then melted and filtered. $CoCl_2$ and $NiCl_2$ were obtained by heating the hydrated crystals in a stream of dry HCl gas. Anhydrous $MgCl_2$ was prepared in the Chemical Engineering Division of this laboratory by vacuum distillation. Small amounts of moisture introduced in transfer operations were removed by keeping $MgCl_2$ molten at 800° for some time, filtering off MgO, and casting the melt into sticks which were kept in sealed quartz tubes until needed for an experiment. Anhydrous pyridinium chloride was obtained by fractional distillation of Eastman Kodak practical grade pyridinium chloride.[19] $CoCl_2$ in $GaCl_3$ was prepared in a similar way as $CoCl_2$ in pure $AlCl_3$.[3] $GaCl_3$ was prepared from analytical grade Ga metal and dry HCl gas and collected in an optical cell. The temperature of the reaction was held below 400°.

A solution of $CoCl_2$ in KCl and $AlCl_3$ was obtained as follows: Weighed amounts of anhydrous KCl and $CoCl_2$ were transferred to the bottom of a quartz tube with a horizontal side arm. A weighed amount of analytical grade Al wire was placed in the side arm, and the side arm was connected to a supply of dry HCl gas. After passing HCl through this apparatus for some time, the Al wire was heated gently until $AlCl_3$ began to form. The $AlCl_3$ was sublimed through the horizontal tube and collected together with the KCl and $CoCl_2$. The mixture was sealed off under vacuum and melted together. The molten mixture was clear except for the presence of a few particles.

The solution of $CoCl_2$ in KCl–$AlCl_3$ was made to contain approximately 33 mole % KCl. The spectrum of Co^{2+} was then studied with successive additions of KCl. To make these measurements, the mixture of KCl, $AlCl_3$, and $CoCl_2$ was transferred after solidification to a Y-shaped quartz and Pyrex apparatus provided at the bottom with a rectangular 1-cm. path length quartz optical cell. One of the branches of the Y contained a quartz frit through which the molten mixture was filtered into the cell. The other branch of the Y was equipped with a Delmar-Urry needle valve stopcock. The valve permitted additions of KCl to be made to the mixture without exposure to the atmosphere.[20] The spectra shown in Figure 2 were obtained starting with 1.5 mg. of $CoCl_2$ in 4.34 g. of KCl–$AlCl_3$ and performing thirteen successive additions of approximately 40 mg. of KCl.

In working with mixtures of KCl and $AlCl_3$, care was taken to avoid exposure to moisture. Apparatus that was to be heated was constructed of quartz and was outgassed at 600° and at a pressure of less than 10^{-5} mm. Valves and stopcocks were warmed with a hair dryer while under vacuum. After outgassing, the apparatus was filled with dry argon gas. Chemicals were transferred in a glove box purged with dry argon. Pieces of KCl weighing ~40 mg. each were heated to 300° at 10^{-5} mm. pressure prior to addition to the KCl–$AlCl_3$ mixture. Essentially no oxide formation was encountered in these experiments. However, in the preparation of KCl and $AlCl_3$ mixtures, it was difficult to avoid formation of carbonaceous matter.[21] These particles were too small to be observed visually and passed through the finest porosity quartz filter disks available. Light scattering in the visible and ultraviolet regions due to these particles gave an apparent increase of optical density of less than 0.14 O.D. unit from 9000 to 5000 Å. Light scattering decreased on addition of KCl, the particles forming a precipitate at the bottom of the cell out of the optical path.

A scattering correction was made as follows: The molar absorptivities of Co at 5000 and 9000 Å. on the high- and low-energy sides of the main absorption band were determined to be 5 and 1 l./mole cm., respectively. These numbers were obtained by making the Co(II) concentration several times larger than in an ordinary experiment in order to minimize the contribution to the total absorption due to scattering. The molar absorptivities at these two wave lengths were found to be independent of concentration in the range 40–50 mole % KCl and were used as fixed points between which a curved background curve was drawn. The background curve was made to have a 2% deflection from a straight line.

$Co(AlCl_4)_2$ was prepared by placing anhydrous $CoCl_2$ and $AlCl_3$ in the ratio 1:2.2 in a quartz tube to which an optical cell was sealed at one end. The tube was sealed under vacuum, and the salts were melted together at 225° in a horizontal glass furnace. The glass furnace was tilted slightly so that the melt collected in the end not containing the optical cell. The other end was kept at a somewhat lower temperature. The glass furnace was then tilted in the opposite direction so that a layer of melt solidified on one of the optically flat sides of the cell. On solidification a portion of the excess $AlCl_3$ vaporized leaving blue needles of $Co(AlCl_4)_2$. The needles were apparently single crystals, some of them attaining a length of 10 mm. After formation of the layer of needles, the furnace was turned to a vertical position. The remaining $AlCl_3$-rich portion solidified in the bottom of the cell separate from the layer of $Co(AlCl_4)_2$ crystals.

The correct crystallization temperature was found by trial and error. It had to be low enough to allow the compound to crystallize but high enough to prevent $AlCl_3$ from crystallizing out of the vapor phase. A procedure similar to the one employed here may facilitate the growth of single crystals of other $M(AlCl_4)_2$ compounds whose preparation has recently been reported.[7]

The spectrophotometer used in this work was a Cary Model 14H with an optical arrangement having the sequence source, chopper, sample, monochromator, detector. This arrangement has the advantage of eliminating the need for making black body radiation corrections. The optical cells were kept at a controlled temperature in a furnace whose design has been described previously.[22]

On completion of the spectral measurements, the salts were allowed to solidify. The solids were dissolved in water, and the Co concentrations as well as the KCl:$AlCl_3$ ratios were determined. Cobalt was analyzed spectrophotometrically to within 2% using Fisher's Nitroso R salt.

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(19) D. M. Gruen and R. L. McBeth, *J. Inorg. Nucl. Chem.*, **9**, 290 (1959).

(20) This apparatus will be described in detail in a forthcoming publication.

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(22) D. M. Gruen and R. L. McBeth, *J. Phys. Chem.*, **66**, 57 (1962).