components. In addition there was no evidence of the characteristic water absorption.[21]

These results indicate that some of the chromate ions in the latter compound find themselves in surroundings different from that provided solely by the crystal field of the solid.

Discussion

The data we have presented can be represented by the reaction scheme

$$[Co(NH_3)_5H_2O]^{+3} + HCrO_4^- = [Co(NH_3)_5H_2O]^{+3}\cdot CrO_4^{-2} + H^+ \quad (6)$$

$$[Co(NH_3)_5H_2O]^{+3}\cdot CrO_4^{-2} = [Co(NH_3)_5CrO_4]^+ + H_2O \quad (7)$$

but it should be emphasized that the tabulated values of the equilibrium constant refer to reaction 1.

At 25°, we combine the value obtained for K_0 with the enthalpy change obtained at an ionic strength of 1×10^{-2} to compute $\Delta F° = 1.37$ kcal./mole, $\Delta H° = -1.96$ kcal./mole, and $\Delta S° = -11.2$ e.u. for reaction 1.

To compare the affinities of sulfate and chromate ions for the aquopentaamminecobalt(III) ion we write eq. 1 as in eq. 8.

$$Co(NH_3)_5H_2O^{+3} + CrO_4^{-2} = C \quad (8)$$

From the value of 3.20×10^{-7} for the dissociation constant of $HCrO_4^-$,[22] combined with the value of $\Delta H° = -0.7$ kcal./mole[23] for that process, we find (for reaction 9 at 25°) $\Delta F° = -7.48$ kcal./mole, $\Delta H° = -1.3$ kcal./mole, and $\Delta S° = 20.9$ e.u.

The value obtained by Taube and Posey[3] for the outer-sphere association between aquopentaamminecobalt(III) and sulfate ion is 1.89×10^3. Since the value reported here for the association between that cation and chromate is 3.07×10^5, it is evident that the latter complex is more stable by a factor of *ca.* 10^2.

This result is qualitatively consistent with the arguments previously cited.[4] It is, however, interesting to note (although not amenable to quantitative rationalization) that in a similar comparison between $CeCrO_4^{+2}$ and $CeSO_4^{+2}$, Tong and King[4] found the chromate complex to be more stable by a factor of 10^7.

Acknowledgment.—We wish to express our appreciation to Dr. J. Ferraro for allowing us to quote the results of the infrared studies. Conversations with Professors H. Taube and E. L. King during the course of this investigation have been stimulating.

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(21) The spectra were recorded with a Perkin-Elmer Model 14. The samples were dried at 100° overnight prior to pressing in a KBr pellet.

(22) J. D. Neuss and W. Rieman, *J. Am. Chem. Soc.*, **56**, 2238 (1934).

(23) L. G. Hepler, *ibid.*, **80**, 6181 (1958).

CONTRIBUTION FROM THE CHEMISTRY DIVISION,
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Octahedral Absorption Spectra of the Dipositive 3d Metal Ions in Molten Aluminum Chloride[1]

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The absorption spectra of dipositive Ti, V, Cr, Mn, Fe, Co, Ni, and Cu in molten $AlCl_3$ were measured in the wave number range 4000–34,000 cm.$^{-1}$ at 227° and 5.6 atm. All the spectra which were obtained using the $AlCl_3$ solvent can be interpreted on the basis of octahedral configurations of chlorides about the central transition metal ions. These observations are in contradistinction to the situation in alkali chloride melts where, with the exception of V^{2+}, the dipositive 3d ions display fourfold coordination. A discussion of the possible reasons for the different coordination behavior in various chloride solvent systems is presented.

Introduction

The coordination chemistry of the di- and tripositive 3d metal ions in alkali chloride melts was discussed in a recent paper.[2] Briefly, the situation in alkali chloride melts appears to be the following: the di- and tripositive 3d ions can exist in either a four- or a six-coordinated form with a mobile equilibrium between the two forms. It was postulated that for each ion, the equilibrium constant of the octahedral–tetrahedral (O–T) transformation in alkali chloride melts is determined primarily by two factors: the octahedral site stabilization energy [o.s.s.e. (M^{n+})] depending on the number of unpaired electrons in the 3d shell and an electrostatic factor [E^{n+}] depending on the charge of the 3d ion. (Entropy changes were found to be small, the $T\Delta S$ terms being of the order 1–2 kcal./mole, and were neglected.)

Only for the ions Ti^{3+}, V^{3+}, and V^{2+} was it possible experimentally to study the O–T transformation. For all the other 3d ions, the equilibrium constants in alkali chloride melts favor either the six- or the four-coordinate form so strongly that the energetically unstable form is present in amounts too small to be measured using presently available techniques.

It would clearly be of importance to find conditions

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(1) Based on 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).

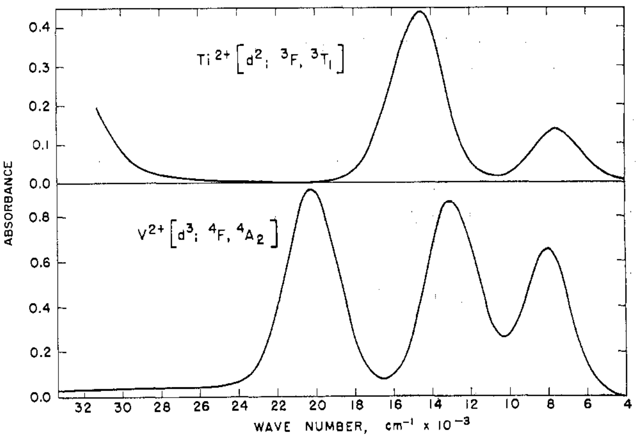

Fig. 1.—Absorption spectra of $TiCl_2$ and VCl_2 in molten $AlCl_3$ at 227° and 5.6 atm.

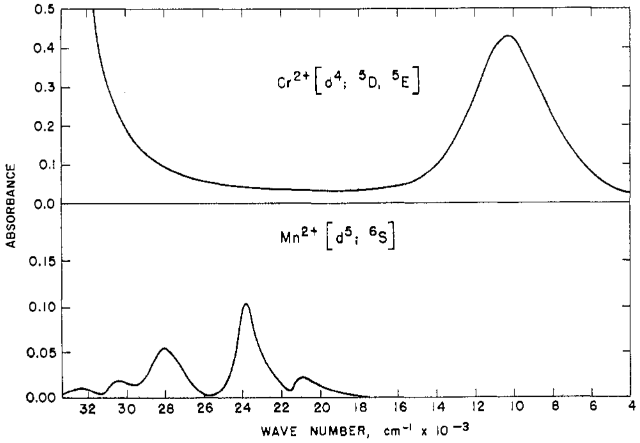

Fig. 2.—Absorption spectra of $CrCl_2$ and $MnCl_2$ in molten $AlCl_3$ at 227° and 5.6 atm.

under which one could extend the studies of O–T transformations to a large number of other ions. Of particular interest would be a study of coordination number equilibria for a series of ions of the same charge type. The relative importance on the energetics of the equilibria

$$MCl_6^{4-} = MCl_4^{2-} + 2Cl^- \qquad (1)$$

of factors other than site stabilization energies, factors such as ion sizes and bonding effects, could then be evaluated.

In the series of dipositive ions Ti^{2+}–Cu^{2+}, in alkali chloride melts, only V^{2+}, the ion with the largest octahedral site stabilization energy (o.s.s.e. = 19 kcal./mole) occurs in octahedral coordination. Thus V^{2+} is the only dipositive ion which can successfully overcome the large electrostatic factor ($E^{2+} = -30$kcal./mole) tending to destabilize the octahedral form in highly ionic melts.[3]

We have recently observed that in the covalent melt of $AlCl_3$ all the dipositive 3d ions occur in octahedral coordination. The present paper presents and discusses the results of this study. It appears that $AlCl_3$ can be used as a component in a solvent system which will make possible detailed studies of coordination number equilibria of several of the dipositive 3d ions. Investigations with this aim in view are currently in progress and will form the subject of a subsequent paper.

Results and Discussion

(A) The Spectra of the Dipositive 3d Ions in Liquid $AlCl_3$.—The spectra of dilute solutions of dipositive 3d metal ions in molten $AlCl_3$ are given in Fig. 1–4. The concentrations (*M*) were $TiCl_2$ (1.50×10^{-2}), VCl_2 (8.68×10^{-2}), $CrCl_2$ (not known), $MnCl_2$ (0.534), $FeCl_2$ (5.23×10^{-2}), $CoCl_2$ (2.97×10^{-3}), $NiCl_2$ (5.00×10^{-2}), and $CuCl_2$ (1.66×10^{-2}). The concentrations were calculated from the measured volume of the solution and the known amount of MCl_2 weighed out (see Experimental section). The locations of the absorption maxima, the half-widths of the bands, and their molar absorptivities in molten $AlCl_3$ are listed in Table I. Also given in Table I are the locations of the absorption maxima for the dipositive 3d ions (with the exception of Ti^{2+}) in dilute solid solutions in crystalline $CsCdCl_3$. The crystal spectra of the 3d ions in $CsCdCl_3$ had been investigated previously and interpreted in terms of the splitting of the d electron energy levels by an electric field of octahedral symmetry.[2] This theoretical interpretation is consistent with the physical situation in these solid solutions, where 3d ions substitutionally replace cadmium ions which are octahedrally surrounded by six chlorides.

The intensities of the 3d ion spectra with the exception of Ni^{2+} in $AlCl_3$ melts are lower by factors of 5–10 than those of similar spectra in alkali halide melts where the 3d ions are known to be tetrahedrally coordinated. For example, the intensity of the ground state to $T_1(P)$ transition of Co^{2+} has a molar absorptivity of 76 in molten $AlCl_3$ as compared with 370 in LiCl–KCl eutectic at 400°.[2] The intensities of d–d transitions in an octahedral field are quite generally lower than in a tetrahedral field since the former possess a center of symmetry which the latter lacks.

The low spectral intensities, together with the similarity in the location of the band maxima in molten $AlCl_3$ and in solid $CsCdCl_3$, strongly suggest that the dipositive 3d ions are octahedrally coordinated in molten $AlCl_3$.

The coordination behavior in $AlCl_3$ melts is in contradistinction, as has already been pointed out, to the situation in alkali chloride melts. There, with the exception of V^{2+}, the dipositive 3d ions display fourfold coordination. The profound differences in behavior in the two solvent systems will be discussed in terms of a solvation model to be presented in a later section of this paper. Values for the octahedral splitting parameter *Dq* are listed in Table I for the 3d ions in $AlCl_3$ melts and in $CsCdCl_3$ solid solutions. For ions with D ground states, the *Dq* values were obtained by dividing the energy of the lowest lying

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[3] The E^{3+} factor for tripositive ions is only about −10 kcal./mole and the tripositive ions Ti^{3+}, V^{3+}, and Cr^{3+} are sixfold coordinated in LiCl–KCl eutectic at 400°.

TABLE I

SPECTRAL CHARACTERISTICS OF THE DIVALENT 3d METALS IN MOLTEN $AlCl_3$ AT 227°

Corresponding values in $CsCdCl_3$ crystal at room temperature given in parentheses

Ion	Absorption max., cm.$^{-1}$ × 10^{-3}	Half-width, cm.$^{-1}$ × 10^{-3}	Molar absorptivity, l./mole cm.	Transition	*Dq*, cm.$^{-1}$
Ti^{2+}	7.6	3.0	9.1	$T_1 \rightarrow T_2(F)$	700
$3d^2$	14.5	3.2	29.4	$T_1 \rightarrow A_2(F) + T_1(P)$	
V^{2+}	8.0 (7.6)	3.0	7.6	$A_2 \rightarrow T_1(F)$	800 (700)
$3d^3$	13.1 (12.1)	3.3	10.1	$A_2 \rightarrow T_2(F)$	
	20.3 (20.0)	3.2	10.7	$A_2 \rightarrow T_1(P)$	
Cr^{2+}	10.2 (9.3)	4.7	*a*	$E \rightarrow T_2$	1020 (930)
$3d^4$					
Mn^{2+}	21.0 (19.6)	1.7	0.043		...
$3d^5$	23.8 (23.9)	1.2	0.197	$^6S \rightarrow {}^4G$	
	... (27.2)				
	28.1 (28.1)	1.9	0.103	$^6S \rightarrow {}^4D + {}^4P$	
	30.5 (30.0)	1.0[b]	0.037		
	32.3 (...)	1.5	0.021		
Fe^{2+}	7.1 (6.7)	2.1[b]	4.6	$T_2 \rightarrow E$	710 (670)
$3d^6$	24.1	4.5	11.0	$T_2 \rightarrow P + H + F$	
Co^{2+}	... (11.8)			$T_1 \rightarrow A_2$	500 (500)
$3d^7$	15.8 (16.3)	3.4	75.7	$T_1 \rightarrow T_1(P)$	
Ni^{2+}	6.4 (5.9)	2.4[b]	6.2	$A_2 \rightarrow T_2$	640 (600)
$3d^8$	10.8 (10.1)	3.0	10.3	$A_2 \rightarrow T_1$	
	21.0 {(19.3) (20.6)	2.7	51.6	$A_2 \rightarrow T_1(P)$	
Cu^{2+}	11.6 (12.5)	5.3	11.7	$E \rightarrow T_2$	1160 (1250)
$3d^9$					

[a] Exploded while trying to drive the reaction $2CrCl_3 + Cr = 3CrCl_2$ to completion. [b] Measured as twice the width of the narrowest half of the band.

absorption band by 10. For ions with F ground states, the *Dq* values were obtained by matching the observed spectra to energy level diagrams given by Liehr and Ballhausen[4] and by Liehr.[5] It can be seen that the values in the melt are higher than in the crystal except in the case of Cu^{2+}. We will return to this point when discussing possible coordination models in $AlCl_3$ melts.

The spectrum of Ti^{2+} has apparently not been observed before. Using the energy level diagram of Liehr and Ballhausen[4] for the isoelectronic V^{3+} ion, the two bands in the Ti^{2+} spectrum at 7600 and 14,500 cm.$^{-1}$ can be assigned to the transitions $T_1 \rightarrow T_2(F)$ and $T_1 \rightarrow A_2(F) + T_1(P)$, respectively, with a *Dq* value of 700 cm.$^{-1}$. An interesting situation exists with respect to the $A_2(F)$ and $T_1(P)$ levels which are just at the cross-over point in the Ti^{2+} spectrum, whereas $A_2(F)$ lies some 5000 cm.$^{-1}$ above $T_1(P)$ in the V^{3+} spectrum.

The band in the Fe^{2+} spectrum with maximum at 24,100 cm.$^{-1}$ is presumably due to intercombination transitions between the T_2 component of the split ^5D ground state and excited triplet P, H, and F states. It is of interest to note that the ratio of intensities of the intercombination bands at 24,100 cm.$^{-1}$ to the crystal field band at 7100 cm.$^{-1}$ is ~2, whereas the analogous ratio for the spectrum of Fe^{2+} in aqueous sulfuric acid solutions is ~0.1.[6]

(B) Structure and Properties of Liquid $AlCl_3$.—The instability of the octahedral 3d chloro complexes MCl_6^{4-} in ionic melts may be due to the excessive accumulation of negative charge, leading to strong anion repulsions. Effective means of reducing the charge on the complexes can therefore be expected to stabilize octahedral coordination in chloride media. The existence of the dipositive 3d ions in octahedral coordination in liquid $AlCl_3$ indicates that markedly different complex species are present in this solvent medium than are encountered in alkali chloride solvents. The following discussion will attempt to clarify the nature of the transition metal chloro complexes in molten $AlCl_3$.

Solid $AlCl_3$ has an ionic layer structure.[7] On melting, however, the volume increases 83%[8] compared to an increase of ~25% for the alkali halides and ~4% for the alkaline earth halides. The equivalent conductance of $AlCl_3$ decreases at the melting point and is only 1.9 × 10^{-5} cm.^{2}/ohm equiv. at 200°.[9]

It is by now well recognized that these drastic changes are due to the formation of the molecular Al_2Cl_6 species in the melt.[10] The structure of the molecules has been determined by X-ray diffraction studies of the melt and can be described as two $AlCl_4$ tetrahedra sharing an edge. The double tetrahedron is somewhat distorted, making the common edge the shortest Cl–Cl distance.

The question that arises in connection with the

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(4) A. D. Liehr and C. J. Ballhausen, *Ann. Phys.* (N. Y.), **6**, 134 (1959).

(5) A. D. Liehr, in the Symposium on Molecular Structure and Spectroscopy, June 12–16, 1961, Ohio State University, Columbus, Ohio.

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(7) J. A. A. Ketelaar, C. H. MacGillavry, and P. A. Renes, *Rec. trav. chim.*, **66**, 501 (1947).

(8) H. Schinke and F. Sauerwald, *Z. anorg. allgem. Chem.*, **287**, 313 (1956).

(9) W. Biltz and W. Klemm, *ibid.*, **152**, 267 (1926).

(10) R. L. Harris, R. E. Wood, and H. L. Ritter, *J. Am. Chem. Soc.*, **73**, 3151 (1951).

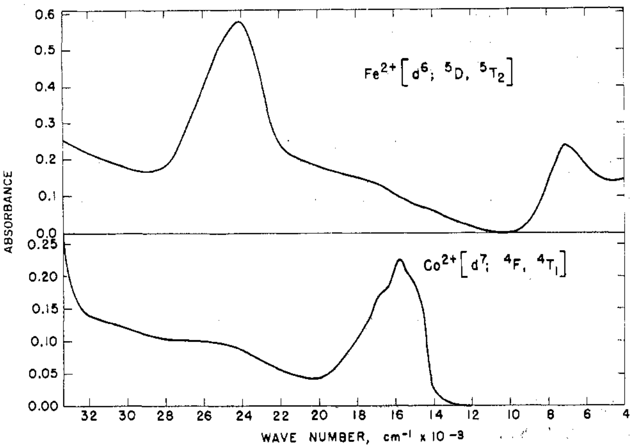

Fig. 3.—Absorption spectra of $FeCl_2$ and $CoCl_2$ in molten $AlCl_3$ at 227° and 5.6 atm.

present study concerns the molecular and ionic species which are formed on dissolution of 3d metal dichlorides in molten $AlCl_3$.

There is considerable evidence that addition of chloride ion to molten $AlCl_3$ is a stepwise process characterized by the two equilibria

$$Al_2Cl_6 + Cl^- = Al_2Cl_7^- \qquad (2)$$

$$Al_2Cl_7^- + Cl^- = 2AlCl_4^- \qquad (3)$$

with equilibrium quotients

$$K_1 = \frac{N_{Al_2Cl_7^-}}{(N_{Al_2Cl_6})(N_{Cl^-})} \qquad (4)$$

$$K_2 = \frac{(N_{AlCl_4^-})^2}{(N_{Al_2Cl_7^-})(N_{Cl^-})} \qquad (5)$$

The existence of $AlCl_4^-$ is firmly established. This complex ion has been shown to occur, for example, as a stable tetrahedral species in crystals such as $NaAlCl_4$ [11a] and $Co(AlCl_4)_2$.[11b] The properties of $Al_2Cl_7^-$, however, remain to be explored. The phase diagram work of Kendall, Crittenden, and Miller[12] has revealed stable compounds, however, of the type MAl_2X_7 such as $TlAl_2Cl_7$ and $NaAl_2Br_7$.

The importance of eq. 4 is perhaps best illustrated by a consideration of the vapor pressure data of Dewing[13] on the $AlCl_3$–NaCl system in the range 100–49.5 mole % $AlCl_3$. From these data, the calculated $AlCl_3$ activities in the melt at 190° are as shown below.

Mole % $AlCl_3$	100	65.8	64.0	58.1	53.6
Activity of $AlCl_3$ in the NaCl–$AlCl_3$ melt	1	1.7×10^{-1}	1.1×10^{-1}	2.1×10^{-2}	4.0×10^{-3}

The decrease of the $AlCl_3$ activity is of course too pronounced to be described in terms of a regular solution of $AlCl_3$ and NaCl and suggests that complex formation is involved. Furthermore, the 50-fold decrease in activity between 100 and 58 mole % $AlCl_3$ is most easily rationalized by assuming the formation of a complex ion such as $Al_2Cl_7^-$.

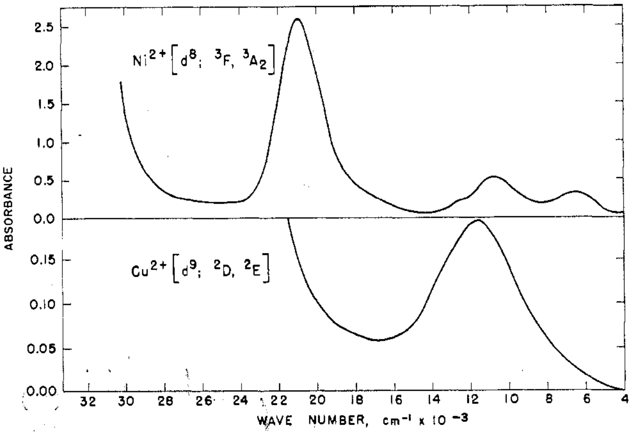

Fig. 4.—Absorption spectra of $NiCl_2$ and $CuCl_2$ in molten $AlCl_3$ at 227° and 5.6 atm.

Assuming the species in the melt to be Al_2Cl_6, $Al_2Cl_7^-$, $AlCl_4^-$, Cl^-, and Na^+ the following two relations are obtained.

$$N = N_{Cl^-} + N_{Al_2Cl_7^-} + N_{AlCl_4^-} \qquad (6)$$

$$1 - N = 2N_{Al_2Cl_6} + 2N_{Al_2Cl_7^-} + N_{AlCl_4^-} \qquad (7)$$

where N = mole fraction of NaCl. Furthermore, by assuming ideal mixing of the species and by neglecting N_{Cl^-} in eq. 6, the following equation is obtained by combination of eq. 4, 5, 6, and 7.

$$X^3 + (3N - 1 - K)X^2 + [K(1 - 2N) + 0.25(1 - 3N)^2]X - 0.25K(1 - 2N)^2 = 0 \qquad (8)$$

where $X = N_{Al_2Cl_6}$ and $K = K_2/K_1$. It should be pointed out that eq. 8 is valid only for $N < 0.5$. In this concentration range neglecting N_{Cl^-} in eq. 8 is justifiable on the reasonable assumption that the product K_1K_2 is a large number. It is seen from eq. 8 that the activity of $AlCl_3$ is determined only by the ratio K_2/K_1 and not by the magnitude of the constants themselves. Equation 8 fits Dewing's results well in the region 65.8–53.6 mole % $AlCl_3$ with $K = 10^{-2}$. Recently, Moore, Morrey, and Voiland [14,15] published a study of uranium distribution between $KAlCl_4$ melts and aluminum metal. These workers postulated the occurrence of equilibria according to eq. 2 and 3 and obtained the value $K \sim 3 \times 10^{-11}$ as a best fit to their data. The difference in K values for the NaCl–$AlCl_3$ and KCl–$AlCl_3$ is greater than one would expect and points to the need for further work in defining the equilibrium constants for the formation of chloroaluminate complexes. Both the vapor pressure study of Dewing and the distribution experiments of Moore, *et al.*, however, point to the existence of $Al_2Cl_7^-$ ions in these melts and to the preponderance of this ion relative to $AlCl_4^-$ in dilute solutions of alkali chlorides in $AlCl_3$.

(C) Solvation Model for the Dipositive 3d Ions in Liquid $AlCl_3$.—In view of the strong tendency toward $Al_2Cl_7^-$ complex formation in $AlCl_3$–alkali chloride melts, it is likely that the same species exists in mixtures

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[11] (a) N. C. Baenziger, *Acta Cryst.*, **4**, 216 (1951); (b) J. A. Ibers, *ibid.*, **15**, 967 (1962).

[12] J. Kendall, E. D. Crittenden, and H. K. Miller, *J. Am. Chem. Soc.*, **45**, 963 (1923).

[13] E. W. Dewing, *ibid.*, **77**, 2639 (1955).

[14] R. H. Moore, J. R. Morrey, and E. E. Voiland, *J. Phys. Chem.*, **67**, 744 (1963).

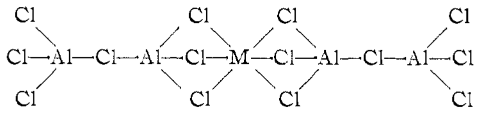
[15] J. R. Morrey and R. H. Moore, *ibid.*, **67**, 748 (1963).

with divalent chlorides. Appropriate activity data have not yet been obtained, however.

We wish to suggest that the 3d metal dichlorides dissolve in molten $AlCl_3$ according to the equation

$$MCl_2 + 2Al_2Cl_6 = M(Al_2Cl_7)_2 \qquad (9)$$

The dielectric constant of molten $AlCl_3$ is not known, but is expected to be small. (Compare $\epsilon = 2.9$ for molten $AlBr_3$.[16]) One therefore expects the ion $Al_2Cl_7^-$ to be linked directly to M^{2+}, leading to the following model for the structure of the complex


(10)

In this model, the M^{2+} ion is octahedrally surrounded by six chlorides belonging to two $Al_2Cl_7^-$ groups, the $Al_2Cl_7^-$ group in turn having a structure of two $AlCl_4$ tetrahedra sharing one corner. The structure of the $Al_2Cl_7^-$ ion has not yet been elucidated by means of X-ray or spectroscopic studies, and the model for the structure of the complex presented here may have to be modified in the light of such studies. To gain further insight into this problem, Raman spectra of $AlCl_3$–alkali chloride mixtures are to be studied in this laboratory. The $M(Al_2Cl_7)_2$ complex is neutral and furnishes an octahedral chloride environment for the M^{2+} ions without requiring excessive charge fluctuations in the local melt environment.

It was noted earlier that the spectral Dq values are about 10% larger in $AlCl_3$ melts than in $CsCdCl_3$ solid solutions. This may be taken as an indication of smaller M–Cl distances in the melt than in the $CsCdCl_3$ crystal. In the crystal, the small 3d ion ($r \sim 0.8$ Å.) replaces the larger Cd^{2+} ion ($r = 0.92$ Å.) and the M–Cl distance is determined almost completely by the dimensions of the crystal lattice. Interestingly enough, in the one case for which data are available, Dq of Ni^{2+} in molten $AlCl_3$ is the same as that of $NiCl_2$ isomorphously substituted in the compound $CsMgCl_3$.[17] It would appear therefore that the Ni–Cl bonds for dilute solutions of Ni^{2+} in $AlCl_3$ melts have properties similar to those of $CsMgCl_3$ insofar as internuclear distances and degree of ionic character are concerned.

In only one case, that of Cu^{2+}, is Dq lower in $AlCl_3$ melts than in $CsCdCl_3$. It is possible that because of the large octahedral "hole" available to the Cu^{2+} in $CsCdCl_3$, considerable distortion of the octahedron occurs, leading to splitting of energy levels and increased values of Dq.

Experimental

Anhydrous $MnCl_2$, $FeCl_2$, $NiCl_2$, and $CuCl_2$ were obtained by dehydration of the hydrated analytical grade crystals in a stream of dry HCl gas. The anhydrous double salt Cs_2CoCl_4 was prepared by crystallization from aqueous solutions and used as a source of $CoCl_2$. The compound VCl_2 was prepared by treating V metal with HCl gas at 950°.[18]

A 1-cm. path length optical quartz cell (Fisher-Porter) was sealed to one end of the bar of a quartz T, the sections of the T being 10 mm. i.d. × 20 cm. The other end of the bar was fitted with a tube filled with Drierite. A weighed amount of anhydrous salt was rapidly transferred to the optical cell to minimize contact with moist air. In the case of VCl_2, $MnCl_2$, and $FeCl_2$, a small piece of V, Mn, or Fe metal was added to prevent possible oxidation. It was assumed that V, Fe, or Mn metal does not react according to the equation

$$3M + 2AlCl_3 = 3MCl_2 + 2Al \qquad (11)$$

The potentials of these metals relative to Al metal are not known in molten $AlCl_3$. However, in LiCl–KCl eutectic the $V–V^{2+}$ and $Fe–Fe^{2+}$ potentials are considerably more positive[19,20] while the $Mn–Mn^{2+}$ potential is somewhat more negative than the $Al–Al^{3+}$ potential. A study of electrode potentials in molten $NaAlCl_4$[21] shows, however, that in this medium $Mn–Mn^{2+}$ is also more positive than $Al–Al^{3+}$. Experimentally, dissolution of the solid metal piece did not appear to occur in the spectral cells and it is, therefore, believed that none of the transition metals reduced $AlCl_3$ to Al metal.

Approximately 2 g. of analytical grade Al wire was placed in the remaining section of the T between two quartz wool plugs. The horizontal section containing the Al wire was then connected to an HCl generator and dry HCl was allowed to flow through the system for 10 min. During this period, the quartz apparatus containing the salt was warmed gently to remove the last traces of adsorbed water. The Al metal was heated to its melting point, at which temperature the reaction with HCl gas to form $AlCl_3$ proceeded at a convenient rate. The $AlCl_3$ was sublimed through the quartz wool plug and was collected in the optical cell. When ~4 g. of $AlCl_3$ had been collected, the cell assembly was removed from the HCl generator, connected to a vacuum line, and evacuated after taking off the Drierite tube. The cell was then sealed off under vacuum ~2 cm. above the optically flat portion. The $AlCl_3$ was melted under its own pressure by heating the cell in a furnace constructed of a Nichrome-wound Vycor tube. At a temperature of about 230°, the chlorides of the the divalent 3d metals dissolved readily in the $AlCl_3$ melt.

Solutions of all of the 3d metal dichlorides were prepared as described above with the exception of solutions of $TiCl_2$ and $CrCl_2$ which had to be prepared *in situ* in the cell. Solutions of divalent Ti were obtained by allowing excess Ti metal to react with a solution of $PbCl_2$ in molten $AlCl_3$, according to the equation

$$PbCl_2 + Ti = TiCl_2 + Pb \qquad (12)$$

$PbCl_2$ and Ti were sealed in the optical cell together with $AlCl_3$ using the procedure already described. The cell containing the mixture was heated to about 230°. At the beginning of the reaction, in addition to Ti metal, two liquids were present revealing liquid–liquid immiscibility similar to that observed in the $AlCl_3$–$SnCl_2$ system, for example.[12] In the latter system the immiscibility gap extends from 1.5 to 14.3 mole % $SnCl_2$. Liquid immiscibility in systems of this sort appears to be a common phenomenon and has also been observed for mixtures of $AlCl_3$ with NaCl, KCl, NH_4Cl, AgCl, TlCl, and $BaCl_2$.[12] The reaction of Ti with $PbCl_2$ was deemed to have gone to completion when after 3 days at 230° the bottom liquid layer had disappeared and the spectrum characteristic of divalent Ti no longer increased in intensity.

Solutions of divalent Cr were obtained by allowing excess Cr metal to react with solid $CrCl_3$ in the presence of molten $AlCl_3$. The reaction

$$2CrCl_3 + Cr = 3CrCl_2 \qquad (13)$$

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was very slow, probably due to the insolubility of $CrCl_3$ in $AlCl_3$. The reaction had not gone to completion even after 1 week but had resulted in a concentration of divalent Cr sufficient for measuring the absorption spectrum.

The heights of the solutions in the cells were measured with a cathetometer at 227°. The volumes of the solutions were calculated using this measurement and the known volume of the cell. The cells were then placed in the spectrophotometer furnace. The details of this furnace have been described in a previous publication.[22]

The spectrophotometer used for the present study was a Cary Model 14H spectrophotometer with an optical arrangement having the following sequence: source, chopper, sample, monochromator, detector. This arrangement has the advantage of completely eliminating the black-body radiation from the sample and makes the instrument very useful for high temperature work.

The spectra of the 3d metal ions were determined at 227° where the pressure of $AlCl_3$ is 5.6 atm.[23] The spectrum of pure molten $AlCl_3$ was also obtained at the same temperature and this spectrum was subtracted from the other spectra.

The particular batch of optical cells employed in this work withstood 5.6 atm. of pressure. However, it must be emphasized that since the pressure of $AlCl_3$ increases rapidly with temperature and since the construction of the cells is not uniform it is important to take proper safety precautions. All operations were carried out behind shields and the cells were contained in suitably shielded containers while performing the optical measurements. These precautions are necessary because of the hazardous nature of liquid or gaseous $AlCl_3$.

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Spectral and Magnetic Properties of Chlorocuprates[1a]

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The optical spectra of four-, five-, and six-coordinate chloro complexes of copper(II) are interpreted in terms of the ionic model by using only one set of radial parameters. Magnetic susceptibilities of $[Co(NH_3)_6][CuCl_5]$ and $[Pt(NH_3)_4][CuCl_4]$ are reported.

The chloro complexes of copper(II) provide a unique opportunity to test the applicability of the ionic model for the description of the optical spectra of a series of complexes formed by a particular metal ion and a particular ligand. Probably with no other cation and single ligand do complexes with such a variety of geometries exist. Crystal structure determinations have shown that copper(II) is octahedrally coordinated with a tetragonal distortion in $CuCl_2$[2] and $CsCuCl_3$,[3] present in a trigonal bipyramid in $[Cr(NH_3)_6][CuCl_5]$,[4] constrained in a square coplanar arrangement of chlorides in $[Pt(NH_3)_4][CuCl_4]$,[5] and present in a flattened tetrahedron in Cs_2CuCl_4.[6,7] Some magnetic and spectral investigations of $CsCuCl_3$,[8] Cs_2CuCl_4,[8,9] and $[Co(NH_3)_6][CuCl_5]$[10] have been reported. Gruen and McBeth[11] have measured the spectrum of Cu(II) in the host lattices Cs_2ZnCl_4 and $CsCdCl_3$ and in the LiCl–KCl eutectic, and recently Furlani and Morpurgo[12] have studied the spectra of some tetrahalogenocuprates in solution. We now wish to show that the spectral data for all these compounds can be interpreted in a consistent manner by the ionic model with the use of only one set of radial parameters.

Magnetic susceptibilities of powdered $[Pt(NH_3)_4][CuCl_4]$ and $[Co(NH_3)_6][CuCl_5]$, which is isomorphous with $[Cr(NH_3)_6][CuCl_5]$,[4] are reported.

Experimental

The compounds used in the studies were prepared by conventional methods and were analyzed for nitrogen, hydrogen, and/or chloride before use. The analytical results indicated that the compounds were pure.

Optical spectra of mineral oil or hexachlorobutadiene mulls as well as those of crystals were obtained at room temperature or at 77°K. with a Cary Model 14 recording spectrophotometer. Reflectance spectra were obtained with a Beckman DU spectrophotometer equipped with the standard reflectance attachment using powdered magnesium oxide as a reflectance standard.

The salt $Rh(NH_3)_6CuCl_5$ was prepared in order to examine the visible spectral region obscured by the $^1A_1 \rightarrow {}^1T_1$ transition of the $Co(NH_3)_6^{+3}$ ion. No electronic transitions of the ion $CuCl_5^{-3}$ were found in this region.

The magnetic susceptibilities were determined by a previously described method[13] using $Hg[Co(CNS)_4]$ as a susceptibility standard.[14] Diamagnetic corrections were estimated from Pascal's constants.[15]

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