THE COORDINATION CHEMISTRY OF 3d TRANSITION METAL IONS IN FUSED SALT SOLUTIONS*

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INTRODUCTION

A renewed scientific interest in fused salts has arisen in the last decade owing in part to the rapidly expanding technological importance of these substances.

Historically, the recognition of fused salts as a class of highly ionic liquids may be traced to the classic experiments of Michael Faraday in 1834 which led to the establishment of the law of equivalent conductance. Following Faraday's work, fused salts became important for the electrowinning of the alkaline earth metals, for the large scale production of aluminium in 1866 and, in more recent years, for the preparation of many newly useful metals like titanium and plutonium. Today, the applications of fused salts have proliferated greatly and include areas as diverse as fuel cells and high temperature nuclear reactors.

The elucidation of the constitution and structure of fused salts has been an intriguing problem since the days of Faraday. A large number of detailed studies of thermodynamic and transport properties of fused salts has been carried out and has given us an understanding of many aspects of the nature of these ionic liquids. Of particular importance from the viewpoint of the present work is the extensive evidence which has been accumulated pointing to the existence of complex ions in melts. In fact, complex ions are very often invoked to rationalize a large number of phenomena involving fused salts.

However, many important questions remain which cannot be answered by having recourse to the classical kinds of experiments already mentioned. Questions concerning the stoicheiometry, structure and stability of complex ions require a better understanding particularly since such information can be expected to aid in the development of new and more adequate theories of melt structure. One can anticipate that spectroscopic studies will make an important contribution towards the solution of problems of this sort, and it is fortunate that in recent years techniques have become available for measuring the u.v., visible, infra-red and Raman spectra of fused salts.

The work to be described here deals with one phase of this effort—the crystal field spectra of 3d transition metal ions in chloride melts. As will be

seen, these studies bear not only on the coordination chemistry of the transition metal ions and complex ionic species in melts, but also on the structural properties of the melts themselves.

CHARACTERISTICS OF CRYSTAL FIELD SPECTRA OF 3d METAL IONS AT HIGH TEMPERATURES IN CHLORIDE MELTS

The familiar colours of the transition metal ions in crystals and in solutions are due to absorption bands which have their origins in electronic transitions within the $3d$ shell. The electric field of the nearest neighbour anions splits the energy levels of the unpaired d electrons and electronic transitions between these split energy levels give rise to the observed " crystal field " spectra.

The spectra of transition metal ions in chloride melts at high temperatures present certain novel features which will be discussed first in a general way with reference to the spectra of Ti^{3+} and Co^{2+}. Later, the spectra of tripositive V and Cr and of dipositive V, Cr, Mn, Fe, Ni and Cu will be discussed in detail. Finally, the results will be correlated with crystal field stabilization energies competing primarily against electrostatic interactions to determine the nature of the complexes.

To gain an over-all perspective, it is convenient to group the spectra of the $3d$ metal ions into two classes based on the effect of temperature on the positions of the absorption bands. Ions in the first class are characterized by changes of thousands of wavenumbers in the positions of band maxima in the range 400–1000°. By contrast, the band maxima of ions in the second class undergo changes of the order of only a few hundred wavenumbers in the same temperature interval.

As will become apparent, ions in the first category are those which undergo a change in the number of coordinating chloride ions or in the configuration of a particular chlorocomplex with temperature. Ions in the second class preserve both their coordination number and the geometrical arrangement of the surrounding chloride ions as a function of temperature.

An example of an ion in the first category is Ti^{3+} (d^1), while an example of an ion in the second is Co^{2+} (d^7). By focusing attention on these two ions the manner in which the positions, widths and intensities of the absorption bands are affected by temperature will become clear. It will also become apparent how these spectral changes can be interpreted in terms of changes in the stoicheiometry and structure of complexes formed by the transition metal ions with chloride ions of the melt.

The spectrum of Co^{2+} [d^7, ^4F] in chloride melts

The Co^{2+} ion in LiCl–KCl eutectic (*Figure 1*) has as the most prominent feature in its spectrum a band with complex structure in the region 13,000–17,000 cm⁻¹. The location and structure of this band in the melt spectrum is very similar to the room temperature crystal spectrum of Co^{2+} substituted isomorphously for Zn^{2+} in the Cs_2ZnCl_4 lattice (curve I). In this compound, the M^{2+} ions are surrounded by four chloride ions in a tetrahedral arrangement. The similarity of the solution and the crystal spectra strongly suggests that the melt spectra are due to the tetrahedral $CoCl_4^{2-}$ ion[1, 2]. An

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entirely different spectrum, having a single maximum at 17,000 cm^{-1} reminiscent of Co^{2+} in aqueous solutions and hydrated crystals, is found when Co^{2+} is isomorphously substituted for Cd^{2+} in the CsCdCl$_3$ lattice where the M^{2+} ion is surrounded by six chlorides in an octahedral arrangement.
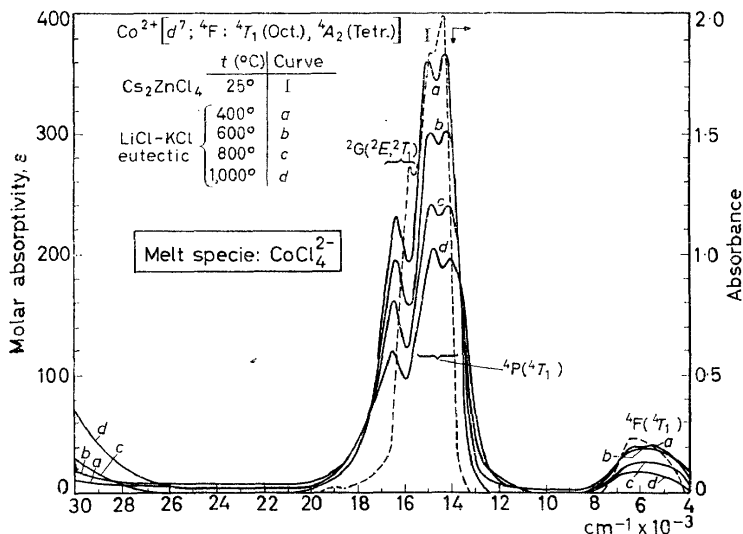

Figure 1. Absorption spectra of Co^{2+} in chloride media

The visible band of CoCl$_4^{2-}$ can be resolved into three components at room temperature which may be ascribed to transitions from the $^4A_2$ ground state to the excited ^{2}G(^2E, $^2T_1$) and ^{4}P($^4T_1$) states[3-5]. It is of interest to note that the three band structure observed at room temperature is still clearly resolved in the melt spectra and that the general appearance of the band does not change appreciably on raising the temperature from 400 to 1,000°.

The half-width of the band increases markedly from 2,200 cm^{-1} at room temperature in the crystal to 3,300 cm^{-1} at 400° and 4,100 cm^{-1} at 1,000° in the melt. This temperature broadening may be ascribed to the increasing vibrational amplitudes of the chlorides since the CoCl$_4^{2-}$ complex will be in excited higher vibrational levels at the higher temperatures. The mechanism of the temperature broadening presumably involves the cubic crystal field splitting parameter Dq which, on the point charge model, is proportional to R^{-5} and, therefore, very sensitive to changes in R, the metal–ligand internuclear distance. Since the $^4A_2$–$^4T_1$ separation[6] depends very strongly on Dq, increasing the fluctuation in Dq by raising the CoCl$_4^{2-}$ complex to higher vibrational states can be expected to result in appreciable temperature broadening.

The effect of temperature on the integrated band intensity in the range 13,000–17,000 cm^{-1} is given in *Table 1*. It can be seen that the oscillator strength

$$f = 4 \cdot 32 \times 10^{-9} \int e_\nu \mathrm{d}\nu \qquad (1)$$

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decreases with temperature by 25 per cent in the 400–1,000° region. In order to understand this effect, it is necessary to consider the mechanisms responsible for the intensities of inner shell $d \rightarrow d$ transitions. In the free ion, such transitions are highly forbidden but when the ion is in solution or in a crystal, the selection rule prohibition is removed by the mixing of orbitals of

Table 1. Oscillator strength, f, and degree of ionicity, α, of the $CoCl_4^{2-}$ complex as a function of temperature

$t(°C)$	$f \times 10^3$	α
25	6·0*	0·63†
400	4·5	0·74
600	4·3	0·76
800	3·5	0·81
1,000	3·2	0·83

* Ref. 4.
† Ref. 11

opposite parity. Van Vleck[7] first pointed out that such mixing can occur because the crystal field surrounding the ion lacks a centre of symmetry or by removal of the centre, if it exists, through an appropriate molecular vibration.

The observed intensity decrease of the $CoCl_4^{2-}$ spectrum rules out the vibronic mechanism which would lead to an increase of intensity with temperature of the form[8]

$$f = f_0 \left[1 + \exp \left(-\theta / T \right) \right] \qquad (2)$$

where θ is the frequency of the non-totally symmetric vibration in temperature units $(\theta / 1·44 = \omega \; cm^{-1})$, and f_0 is the value of the oscillator strength at 0°K. A detailed discussion of the vibronic mechanism for octahedrally coordinated $3d$ ions has recently been given[9, 10].

In the case of the tetrahedral $CoCl_4^{2-}$ ion, the non-centrosymmetric electric field can produce intensity by mixing $3d$ and $4p$ wave functions of the metal or by mixing $3d$ and ligand wave functions. Ballhausen and Liehr, in order to account for the intense bands of tetrahedral complexes, have had to assume $3d$-ligand orbital mixing[11]. Their equation for $CoCl_4^{2-}$ takes the form

$$f[^4A_2 \rightarrow \; ^4T_1(P)] = \frac{256}{15} \cdot \frac{1 - \alpha^2}{1 - 2S\alpha(1 - \alpha^2)^{\frac{1}{2}}} \; A^2 \cdot 1·085 \times 10^{11}$$

$$\cdot \; \nu(^4A_2 \rightarrow \; ^4T(P) \; cm^{-1}) \qquad (3)$$

where A is the ligand coupling integral; S, the overlap integral; and α the degree of ionicity of the complex. With the values $A = -5·19 \times 10^{-10}$, $S = -2·0 \times 10^{-1}$, α takes the value 0·63 to obtain the experimental value $f[^4A_2 \rightarrow \; ^4T_1(P)] = 6 \times 10^{-3}$ for $CoCl_4^{2-}$ at room temperature[4]. In deriving the f-values given in Table 1, the integration was performed over the entire region 13,000–17,000 cm^{-1} thus including the area under the highest energy

component of the band. This component is presumably a transition to a doublet state[12] which borrows most of its intensity from the lower energy ^4P states[13] through the spin–orbit coupling interaction.

Assuming that the ligand coupling integral A remains constant with temperature (small changes in S, the overlap integral, will not affect the intensity appreciably according to equation (3)), the values of α required to account for the intensity decrease of the band are listed in *Table 1*. On this picture, and bearing in mind the severe approximations used in deriving equation (3) and applying it to the present situation, the intensity decrease may be thought of as due to an increasing ionicity of the Co—Cl bond with increasing temperature. This particular way of explaining the intensity decrease may ultimately have to be modified by a more refined theoretical treatment*. However, one can be reasonably certain that the observed intensity decrease is in fact real, since induced emission which would lead to a similar effect has been shown[14] to introduce less than 1 per cent error in an absorbance measurement at $\sim$1,000° for all energies larger than 4,000 cm^{-1}.

The increase in ionicity of the Co—Cl bond observed spectroscopically should be reflected in the thermodynamic properties of the melt. Thus, one may expect that the more ionic the bond character, the closer will be the approach to a statistical anion–cation distribution and to ideal thermodynamic behaviour of solutions of Co^{2+} in alkali halide melts.

The positions of the three maxima of the CoCl$_4^{2-}$ band exhibit small temperature variations in that the two lowest energy maxima shift to lower energies (from 14,080 to 14,000 cm^{-1} and 14,930 to 14,800 cm^{-1} respectively) while the highest energy maximum shifts to higher energies (from 16,400 to 16,500 cm^{-1}) on raising the temperature from 400 to 1,000°. It is likely that these relatively small shifts are entirely due to band broadening. At any rate, it seems unprofitable at this stage to attempt an interpretation in terms of changes in the equilibrium metal–chlorine distance and the effects such changes would have on the positions of the bands.

The conclusions to be drawn from the study of the Co^{2+} spectrum in LiCl–KCl eutectic are that (*i*) the ion exists in the form of the tetrahedral CoCl$_4^{2-}$ complex over the entire temperature region accessible to measurement, and (*ii*) the observed intensity decrease can be (tentatively) explained on the basis of an increasing ionicity of the Co—Cl bond with temperature.

The spectrum of Ti^{3+} [d^1, ^{2}D] in chloride melts

The Ti^{3+} spectrum in chloride melts is characterized by very large changes in band positions and intensities both as a function of temperature and of Cl$^-$ activity of the melt (*Figure 2*). The spectrum of Ti^{3+} in LiCl–KCl eutectic at 400° is characterized by a broad absorption band in the region 8,000–15,000 cm^{-1}. The band has a shoulder at 10,000 cm^{-1} and a maximum[15] at 13,000 cm^{-1}. As the temperature is increased, a new band develops with a maximum at $\sim$7,000 cm^{-1}. It will be noted that, contrary to the situation in the case of Co^{2+}, the intensity of the Ti^{3+} spectrum increases

* *Footnote added in proof*: In a private communication to D.M.G., Dr Liehr has re-emphasized that caution must be exercised in the interpretation of α in equation (3). He has considered the problem from an alternative theoretical point of view which he feels accounts for the observed intensity decrease of the CoCl$_4^{2-}$ spectrum in a better way.

markedly with temperature. In a solvent composed of an equimolar mixture of CsCl and $GaCl_3$ the spectrum is greatly intensified and shifted to longer wavelengths. The Ti^{3+} spectrum is indeed so vastly different in this solvent at temperatures above 500° as to bear no resemblance to the spectrum in LiCl–KCl eutectic at 400°.

Spectral changes as profound as those encountered with Ti^{3+} can be expected to be reflections of fundamental changes in the physical situation in which the ion finds itself in the melt.
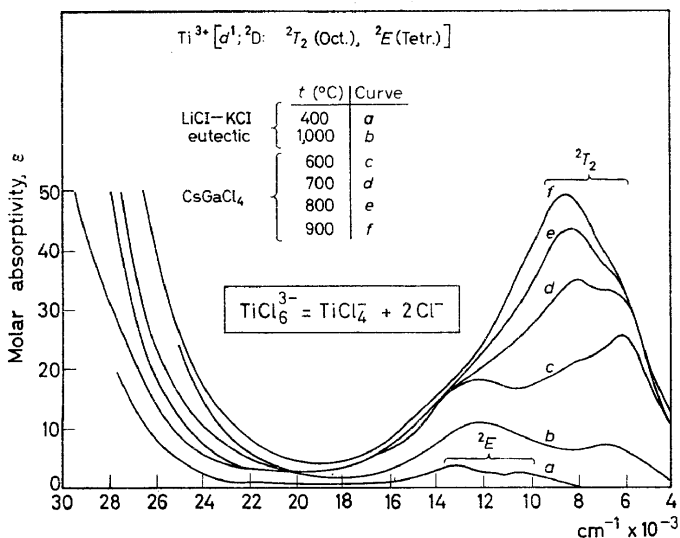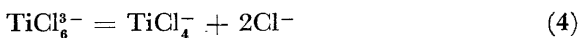

Figure 2. Absorption spectra of Ti^{3+} in chloride media

The nature of the spectral changes are best understood on the basis of the octahedral–tetrahedral equilibrium

$$TiCl_6^{3-} = TiCl_4^- + 2Cl^- \qquad (4)$$

The transformation from six-coordinated $TiCl_6^{3-}$ to four-coordinated $TiCl_4^-$ can be expected to result in two important spectral changes. First, on the point charge model, $Dq_{,\text{ tetrahedral}} = |4/9|\ Dq_{,\text{ octahedral}}$, and, therefore, the optical transition should be strongly shifted to lower energies. Second, the intensity would be expected to increase in going from an (approximately) octahedral to an (approximately) tetrahedral species lacking a centre of inversion symmetry and displaying an appreciable degree of covalent bonding[11].

The spectral observations fulfill both theoretical predictions in a qualitative fashion. Thus, the intensity of the spectrum in the region 4,000–17,000 cm^{-1} increases from $f = 0·1 \times 10^{-3}$ in LiCl–KCl eutectic at 400° to $f = 1·5 \times 10^{-3}$ in $CsGaCl_4$ at 900°, a ratio of 15·0. Furthermore, the energy of the transition shifts from a band system centred at ~12,000 cm^{-1} in LiCl–KCl eutectic at 400°C to a band system centred at ~8,000 cm^{-1} in $CsGaCl_4$ at 900°C.

Purely chemical considerations lend further support to the octahedral–tetrahedral transformation hypothesis. Comparing spectra in LiCl–KCl eutectic and $CsGaCl_4$ at equal temperatures, the equilibrium (4) lies further on the side of $TiCl_4^-$ in the latter than in the former solvent. The stability of $GaCl_4^-$ lowers the Cl^- activity in $CsGaCl_4$ melts compared with alkali halide melts and provides the driving mechanism for displacing the equilibrium. It is obvious that Ti^{3+} could, with appropriate precautions, serve as a " colour indicator " for Cl^- activity in melts.

An examination of *Figure 2* shows that the absorption bands both of $TiCl_6^{3-}$ and $TiCl_4^-$ have a complex structure indicative of a splitting of energy levels. One mechanism capable of producing such splittings is distortion from octahedral or tetrahedral symmetry and it seems reasonable to interpret the spectroscopic results on chlorocomplexes of Ti^{3+} and of a number of the other 3d ions on this basis.

Anticipating results derived from the spectral work on the other 3d ions, one can say that:

(*i*) the spectra of the di- and tripositive 3d metal ions in chloride melts can be interpreted on the basis of hexa- and tetrachloro-complexes;

(*ii*) for some 3d ions an equilibrium between the two forms exists which depends, among other factors, on the temperature and Cl^- activity of the melt;

(*iii*) distortions from octahedral and tetrahedral symmetry occur frequently;

(*iv*) coordination numbers and configurations are strongly influenced by crystal field stabilization energies.

INTERPRETATION OF THE SPECTRA OF CHLOROCOMPLEXES OF 3d METAL IONS

The preceding discussion of the spectra of Co^{2+} and Ti^{3+} in chloride melts has shown that the results can be interpreted using crystal field theory as well as direct comparisons of melt with crystal spectra.

In this section, those elements of crystal field theory bearing on the interpretation of the spectra will be reviewed, and the criteria for selection of suitable host crystal lattices will be given together with the available structural information.

Crystal field theory

A complete and rigorous theory of the chlorocomplexes of the 3d metal ions would have to include effects due to spin–orbit coupling and σ bonding. The point charge model employed here neglects these effects, thus giving energy level spacings which are, and can only be, in qualitative agreement with the experimental results. A more refined treatment is beyond the scope of the present study.

The Hund ground states of the free ions of the 3d series together with the states in weak octahedral and tetrahedral fields are given in *Table 2*. The octahedral site stabilization energies are also listed. Except for Mn^{2+} (d^5) which has a ^6S ground state, the other ions of the 3d series possess either D or F ground states.

Table 2. States and energies in weak octahedral and tetrahedral fields (Dq units)

Ions	Configurations and ground states of free ions	Octahedral and tetrahedral states and energies*	Octahedral site stabilization energies†
Ti³⁺, Fe²⁺	$d^{1,6}$: ^{2,5}D	$^{2,5}T_{2g}(\mp 4)$, $^{2,5}E_g(\pm 6)$	1·3
Cr²⁺, Cu²⁺	$d^{4,9}$: ^{2,5}D	$^{2,5}E_g(\mp 6)$, $^{2,5}T_{2g}(\pm 4)$	4·2
Mn²⁺	d^5 : ^{6}S	$^6A_{1g}(0)$	0
V³⁺, Co²⁺	$d^{2,7}$: ^{3,4}F	$^{3,4}T_{1g}(\mp 6)$, $^{3,4}T_{2g}(\pm 2)$, $^{3,4}A_{2g}(\pm 12)$	0·7
V²⁺, Cr³⁺, Ni²⁺	$d^{3,8}$: ^{4,3}F	$^{4,3}A_{2g}(\mp 12)$, $^{4,3}T_{2g}(\mp 2)$, $^{4,3}T_{1g}(\pm 6)$	9·3
		$A_{1g} = \Gamma_1$: $A_{2g} = \Gamma_2$; $E_g = \Gamma_3$; $T_{1g} = \Gamma_4$; $T_{2g} = \Gamma_5$	

* The lowest lying state in a crystal field is the one with the largest negative energy value. Take upper sign of energy value for octahedral and lower sign for tetrahedral fields.
† It can be shown that the stabilization energies in Dq units are (*i*) in octahedral fields: 4 for $d^{1,6}$; 6 for $d^{2,4,7,9}$; 12 for $d^{3,8}$; (*ii*) in tetrahedral fields: ¼ for $d^{4,9}$; 3 for $d^{1,3,6,8}$; 12 for $d^{2,7}$. The figures in this column of the tables were obtained by multiplying the tetrahedral stabilization energies by 4 9 and subtracting this product from the corresponding octahedral site stabilization energies. A discussion of these and other related matters may be found in two important papers[16,17].

In a cubic (octahedral or tetrahedral) field, a D-state is split into two levels designated by T_{2g} and E_g and separated by an energy 10 Dq (*Figure 3*). In the case of d^1 and d^9, these are the only levels arising from the d-configurations. In the free ion d^4 and d^6 configurations, there are upper triplet H, P, F and G multiplets spaced in the region 22,000–28,000 cm⁻¹.
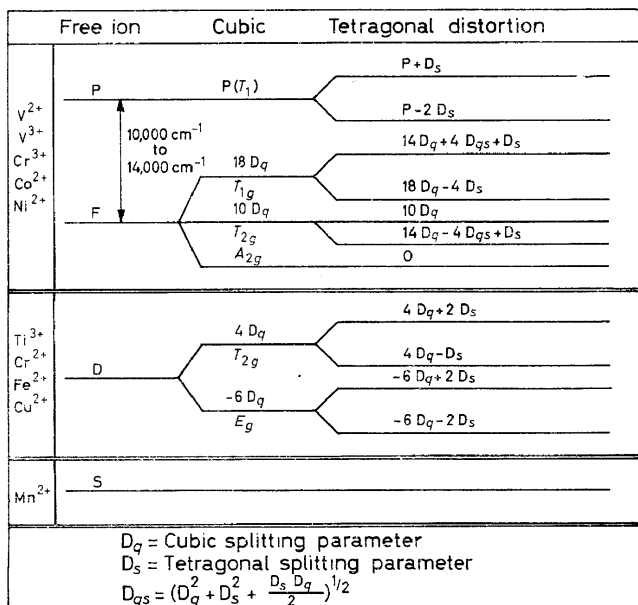

Figure 3. Energy levels of P, F, D and S states in crystal fields of cubic and tetragonal symmetry

Transitions from the quintet ground states to these excited triplet multiplets can be expected to be of low intensity. Because of their relatively high energy,

they would occur very near the intense charge transfer bands and would in all likelihood be masked by them. For these reasons, the D-state ions in chloride melts would be expected to display as the most prominent feature in their spectrum a single absorption band due to the $T_{2g} \rightleftharpoons E_g$ transition.

An F-state in an electric field of cubic symmetry is split into three energy levels designated by T_{1g}, T_{2g} and A_{2g} where the T_{1g}–T_{2g} separation is 8 Dq and the T_{2g}–A_{2g} separation is 10 Dq. In addition to ^{3}F and ^{4}F ground states, there are ^{3}P and ^{4}P excited states spaced in the region 10,000–14,000 cm^{-1} in the free ion configurations $d^{2, \, 3, \, 7, \, 8}$. Transitions from the F-ground states to the P(T_1) excited states are intense because no change in spin-multiplicity is involved. The P(T_1) states are not split by a cubic crystal field. For d^2 and d^7 configurations in octahedral fields and d^3 and d^8 configurations in tetrahedral fields, the A_{2g}(F) and T_1(P) states cross at Dq $\approx$ 1,000 cm^{-1}, so that at larger Dq values the T_1(P) state lies below the A_{2g}(F) state. In any event, the spectra of ions possessing F-ground states can be expected to have more than one band in the region accessible to measurement in chloride melts. One is likely to observe three bands corresponding to transitions from the lowest F-state component to the upper two components and in addition a transition to the P-multiplet.

The ^{6}S ground state of the Mn^{2+} ion is not split in a crystal field and transitions to upper ^{4}G, ^{4}P and ^{4}D state would be expected to occur in the region 20,000–35,000 cm^{-1}.

A general characteristic of the melt spectra is that the transitions occur at lower energies compared with analogous transitions in aqueous solutions or hydrated crystals. The reason is to be found in the observation that the ligand field due to an octahedron of chloride ions is only about 75 per cent as large as that due to an octahedron of water dipoles. An illustration of this fact is provided by the $^4A_{2g} \rightarrow \, ^4T_{2g}$ transition of Cr^{3+}, separated by 10 Dq, which occurs at 17,600 cm^{-1} in aqueous solution and at 12,500 cm^{-1} in LiCl–KCl eutectic at 400°. The ratio of Dq's, 1,250/1,760 = 0·71, is in agreement with the earlier observations on chlorocomplexes in aqueous solutions[18].

A further shift of a transition to lower energies occurs whenever a change from hexa- to tetracoordination takes place. The shift in energy is due to the smaller value of Dq for tetrahedral versus octahedral configuration. A detailed examination of the $3d$ ion spectra in chloride melts shows that they possess more components than can be accounted for considering only fields of cubic symmetry. Most of the absorption bands are complex; they are skew shaped, or possess shoulders and subsidiary maxima. Frequently, the individual components are not completely resolved at the melt temperatures. A comparison with theoretical calculations, therefore, involves assumptions as to the shape of the components giving rise to the structure of the band envelope. Nevertheless, it will be instructive to examine the effect of distortions from cubic symmetry on the number and spacing of the energy levels and to correlate the calculated energies of transitions with the observed spectra insofar as is possible.

The splittings of P, D and F states in fields of cubic symmetry and tetragonal symmetry are given in *Figure 3*. The sequence of energy levels as

given in the figure is correct for $d^{1, 2, 6, 7}$ in tetrahedral and $d^{3, 4, 8, 9}$ in octahedral symmetry. An inverted sequence applies for changes to octahedral and tetrahedral symmetry of the respective configurations as indicated in *Table 2*. In the energy level expressions given in *Figure 3*, Dq is the cubic field splitting parameter, Ds is the tetragonal field splitting parameter for the second degree terms of the tetragonal potential[19] and $Dqs = (Dq^2 + Ds^2 + DsDq/2)^{\frac{1}{2}}$. The parameter Dt for the fourth degree tetragonal potential term has been neglected in these expressions, and has in fact been found to be much smaller than Ds for a number of ions[20, 21]. Furthermore, trigonal distortions have not been considered.

In effect, a tetragonal distortion removes degeneracy thus increasing the number of energy levels: the P-state splits into two levels; the D-state into four levels and the F-state into five levels. The magnitude of Ds, the tetragonal splitting parameter can, in some cases, be deduced from the observed melt spectra.

Host crystal lattices

Although crystal field theory provides a powerful tool for the interpretation of the melt spectra, a need was felt for a direct experimental approach to help establish the nature of the chlorocomplexes. For this purpose comparison studies of melt spectra with spectra of isomorphously substituted crystals were employed.

Reasonably close solid state analogues of the dilute solutions of $3d$ ions in melts were found in the form of equally dilute solid solutions of these ions in double chloride matrices. The problem was one of finding suitable crystal lattices in which the coloured di- and tripositive $3d$ ions can isomorphously replace colourless ions situated on lattice sites surrounded by four or six chloride ions. Those double chlorides in which the di- and tripositive metal ions are surrounded by *isolated* octahedral or tetrahedra of chloride ions were felt to represent a closer physical approach to the melt situation than compounds in which corners, edges or faces are shared. Furthermore, it was desirable, in most cases, to prepare single crystals from melts (rather than from aqueous solutions) in order to obtain anhydrous substances. Double salts useful for this purpose have to be congruently melting and must not exhibit a phase transition in going from the melting point to room temperature.

Bearing these criteria in mind, the double chlorides selected as most suitable for our work were Cs_2ZnCl_4 and $CsAlCl_4$ with tetrahedral arrangement of Cl^- and $CsCdCl_3$ and Cs_3ScCl_6 with octahedral arrangement of Cl^- about the central metal ions[22]. Since up to this time most of the work with these double salts has been done with the dipositive ions, only the structures of Cs_2ZnCl_4 and $CsCdCl_3$ will be discussed here in any detail.

The structure of Cs_2ZnCl_4 is $Pnam/D_{2h}^{16}$, isomorphous with the well-known compound Cs_2CoCl_4[23, 24]. In these compounds, the central metal ion is surrounded by an almost regular tetrahedron of Cl^-.

The compound $CsCdCl_3$ occurs in cubic and hexagonal modifications. The cubic form is of the perovskite type[25]. Only the hexagonal form is obtained from the melt. This phase has been found to be isostructural with hexagonal $BaTiO_3$[26] by Dr Stanley Siegel, Argonne National Laboratory[27].

The space group of the hexagonal form is C6/mmc-D_{6h}^4. One third of the $CdCl_6^{4-}$ octahedra are of type I, each chlorine corner being shared by a neighbouring octahedron. The remaining $CdCl_6^{4-}$ octahedra are of type II, each octahedron sharing a face with another and three corners with octahedra of type I.

CRYSTAL FIELD SPECTRA OF V^{3+}, V^{2+}, Cr^{3+}, Cr^{2+}, Mn^{2+}, Fe^{2+}, Ni^{2+}, AND Cu^{2+} IN CHLORIDE MELTS

The spectrum of V^{3+}, $[d^2, {}^3F]$ in chloride melts

The spectrum of V^{3+} (*Figure 4*) in chloride melts has been studied by a number of workers[2, 28, 29]. Harrington and Sundheim interpreted the
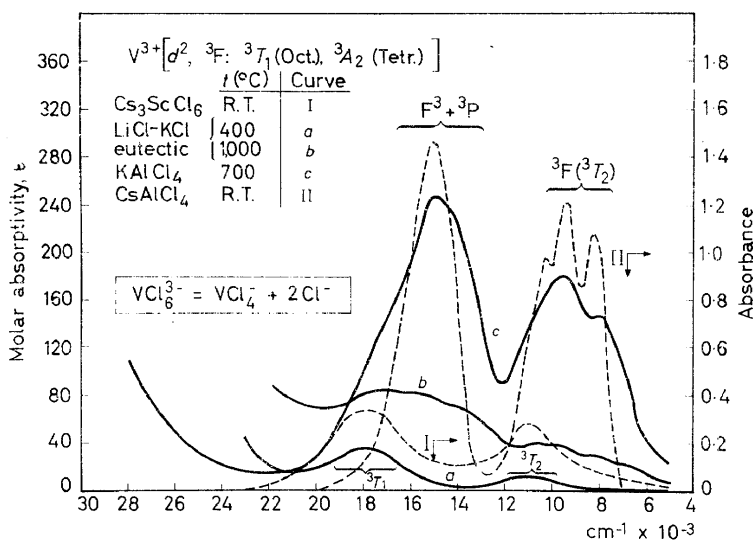
Figure 4. Absorption spectra of V^{3+} in chloride media

spectrum in LiCl–KCl eutectic at ~400° as due to the octahedral VCl_6^{3-} species. At higher temperatures, a marked increase in the intensity of the spectrum was observed by Gruen and McBeth[29] as well as shifts of the absorption bands to longer wavelengths. This behaviour was interpreted[29] as due to an octahedral–tetrahedral transformation equilibrium of the form

$$VCl_6^{3-} = VCl_4^- + 2Cl^- \tag{5}$$

Spectral changes of this sort were still being observed at 1,000°, the highest temperature at which measurements could be carried out. This indicated that the equilibrium (5) was still shifted to the left even at 1,000°. In order to obtain the spectrum and extinction coefficient of the VCl_4^- species, VCl_3 was dissolved in a melt of $KAlCl_4$ where the low Cl^- activity due to the formation of $AlCl_4^-$ complexes could be expected to assist temperature in driving the equilibrium (5) to the right[30]. Finally, a single crystal of $CsAlCl_4$

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was grown with a small concentration of V^{3+} substituted for Al^{3+} in the crystal lattice[31]. The crystal spectrum and the high temperature melt spectrum in $KAlCl_4$ were very similar, confirming the earlier interpretation[29] of the high temperature melt spectra as due to the VCl_4^- species.

A very detailed study of the octahedral–tetrahedral transformation equilibrium of V^{3+} was undertaken by Dr R. Gut in 1960–61 while he was a Resident Research Associate at Argonne on a year's leave of absence from the ETH, Zurich, Switzerland. This work will be reported in a separate publication.

The low temperature melt spectra of V^{3+} can be interpreted as arising from an octahedral VCl_6^{3-} complex as indicated earlier. With an energy level diagram which includes spin–orbit coupling effects[32], one obtains good agreement of calculated with observed transitions for $Dq = 1,200$ cm^{-1}. The observed bands at 11,000 cm^{-1} and 18,020 cm^{-1} are, on this picture, to be identified with transitions from the $^3T_1$ ground state to $^3T_2(^3F)$ and $^3T_1(^3P)$ excited states respectively.

The spectrum of VCl_4^- cannot be interpreted on the basis of an undistorted tetrahedral species since one would expect to observe only three bands due to transitions from the $^3A_2(^3F)$ ground state to $^3T_2(^3F)$, $^3T_1(^3F)$, and $^3T_1(^3P)$ excited states. In fact, the spectrum consists of at least five and possibly six overlapping absorbing bands. A tetragonal distortion of the tetrahedron is probably the major perturbation giving rise to the larger number of levels. Preliminary calculations of the energy levels as a function of the tetragonal splitting parameter Ds give reasonable agreement for $Dq = -500$ cm^{-1}, $Ds = -300$ cm^{-1}.

The larger intensity of the VCl_4^- spectrum indicates that σ-bonding may be important in this complex and points to the necessity of molecular orbital type calculations.

The spectrum of V^{2+} (d^3, ^4F) in chloride melts

The spectrum of V^{2+} in LiCl–KCl eutectic was studied as a function of temperature in the range 400–1,000°[29]. Marked intensity changes and shifts in band positions were noted in this temperature interval and were interpreted as due to the octahedral–tetrahedral transformation equilibrium

$$VCl_6^{4-} = VCl_4^{2-} + 2Cl^- \tag{6}$$
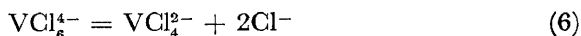
Since the first report of these studies, additional work has confirmed the interpretation of the low temperature ($\sim$400°) melt spectrum as due to an octahedral VCl_6^{4-} species and of the high temperature ($\sim$1,000°) melt spectrum as due to a VCl_4^{2-} species. Recently, we have incorporated V^{2+} into the $CsCdCl_3$ structure by isomorphously replacing a small amount of Cd^{2+}. The crystal spectrum (*Figure 5*, I) was found to be essentially identical with the 400° melt spectrum. The three absorption bands at 7,200 cm^{-1}, 12,020 cm^{-1} and 19,050 cm^{-1} can be fitted to a theoretical energy level diagram which includes spin–orbit coupling[33] with $Dq = 700$ cm^{-1}. The observed bands are to be identified with transitions from the $^4A_2$ ground state to $^4T_2(^4F)$, $^4T_1(^4F)$ and $^4T_1(^4P)$ excited states respectively.

In order to displace the equilibrium (6) strongly to the right, VCl_2 was

dissolved in molten Cs_2ZnCl_4 to give a blue solution. The Cl^- activity of this melt can be expected to be quite low because of the formation of $ZnCl_4^{2-}$. The spectrum of V^{2+} at 900° in this solvent (Figure 5, c) may be interpreted in terms of a very strongly distorted VCl_4^{2-} species. Under the conditions of this experiment, all of the V^{2+} is presumed to be present in the form of VCl_4^{2-}.
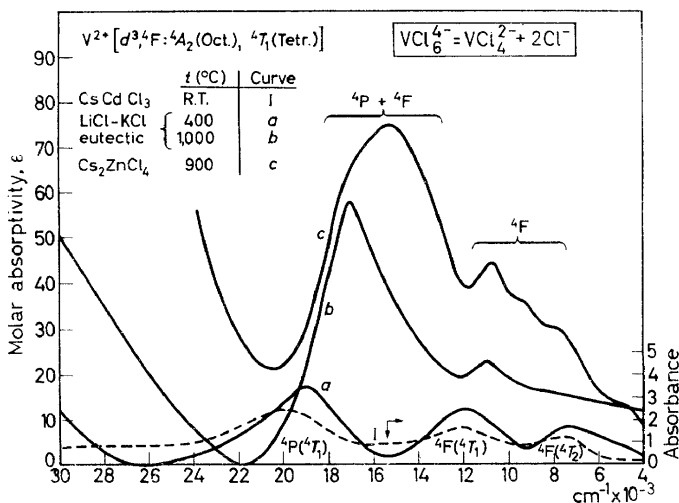

Figure 5. Absorption spectra of V^{2+} in chloride media

It does not appear to be possible to incorporate V^{2+} in the Cs_2ZnCl_4 crystal lattice for the following reasons: the compound $CsVCl_3$ is extremely stable[34] (m.p. 1,090°), has a low solubility in Cs_2ZnCl_4 at its melting point 601°, and appears to crystallize out, even when present in very low concentration, on solidification of the melt. Comparison of melt and crystal spectra in the case of VCl_4^{2-} have, therefore, not yet been carried out for lack of a suitable host crystal lattice.

The spectrum of Cr^{3+} (d^3, ^4F) in chloride melts

The spectrum of Cr^{3+} in LiCl–KCl eutectic (Figure 6) is characterized by two broad bands with maxima at 12,500 cm^{-1} and 18,500 cm^{-1}. The Cr^{3+} spectrum was first observed in this melt by Harrington and Sundheim[2] and interpreted by them as due to the octahedral $CrCl_6^{3-}$ complex. These workers found only negligible spectral changes in the range 392–444°. We have extended the temperature range to 1,000° and find that, even at the highest temperatures, the spectrum is interpretable on the basis of a $CrCl_6^{3-}$ species, with no indication of an octahedral–tetrahedral equilibrium in the LiCl–KCl eutectic.

Our assignment of the 12,500 cm^{-1} and 18,500 cm^{-1} bands to the transitions $^4A_2 \rightarrow {}^4T_2(^4F)$ and $^4A_2 \rightarrow {}^4T_1(^4F)$ is identical to that given before[2]

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with $Dq = 1,250$ cm^{-1}. The transition $^4A_2 \rightarrow {}^4T_1(^4P)$ is not observed in the melt as it is presumably hidden by the intense charge transfer band.
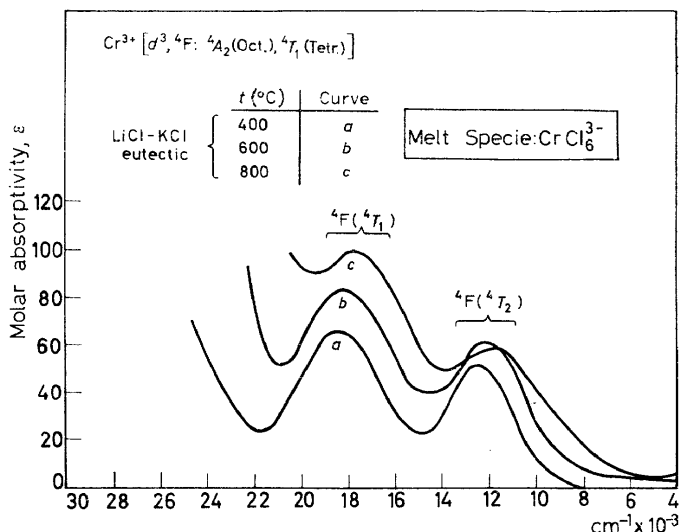

Figure 6. Absorption spectra of Cr^{3+} in chloride media

The spectrum of Cr^{2+} (d^4, ^{5}D) in chloride melts

A recent study[15] of the spectrum of Cr^{2+} in LiCl–KCl eutectic revealed the presence of a broad band (*Figure 7*) with maximum at 9,800 cm^{-1} presumably due to the transition $^5T_2 \rightarrow {}^5E$. The position of the band maximum
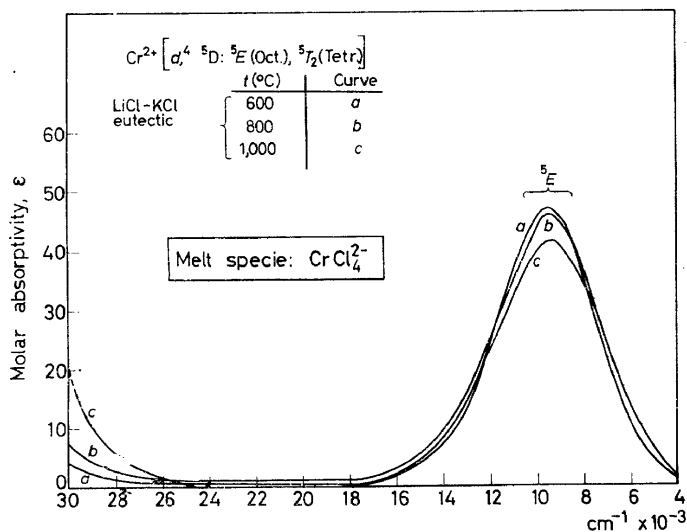

Figure 7. Absorption spectra of Cr^{2+} in chloride media

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remains essentially unchanged in the temperature range 400–1,000°. One is led to conclude that the spectrum is due to a single ionic species over the temperature region accessible to measurement, and it seems reasonable to assign the formula $CrCl_4^{2-}$ to the complex present in the melt. Crystal spectra of Cr^{2+} in the host lattices $CsCdCl_3$ and Cs_2ZnCl_4 have been obtained. Absorption bands in the vicinity of 9,800 cm^{-1} were observed in both lattices although one would have expected the band maximum in the former to occur at a higher wavenumber than in the latter crystal. Assuming that the $CrCl_4^{2-}$ complex is very strongly distorted in the melt and also that the Cr^{2+} ion is able to induce local distortions in its nearest neighbour chlorides in the crystal lattices, the coincidence of the melt and crystal spectra can be explained on the basis of tetragonal distortions in both media. However, a more detailed and satisfying description of the configuration of this complex is required; it awaits on the one hand further data obtained on more carefully grown crystals and on the other, detailed theoretical calculations.

The spectrum of Mn^{2+} (d^5, ^{6}S) in chloride melts

The spectra of Mn^{2+} in LiCl–KCl eutectic at 400 and 1,000° are presented in *Figure 8*, together with crystal spectra of $CsCd_{1-x}(Mn_x)Cl_3$ and Cs_2Zn_{1-x}

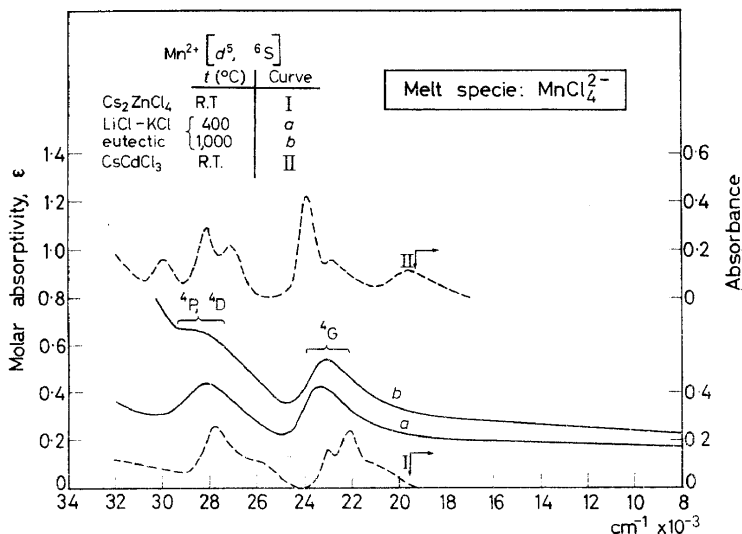*Figure 8.* Absorption spectra of Mn^{2+} in chloride media

$(Mn_x)Cl_4$ taken at room temperature. The spectra are characterized by two absorption bands at $\sim$22,000 cm^{-1} and $\sim$28,000 cm^{-1} presumably due to spin-forbidden transitions from the ^{6}S ground state to upper ^{4}G, ^{4}P and ^{4}D states.

The melt spectra presented here are in good agreement with similar spectra reported by Sundheim and Kukk[35] at a temperature of 436°. The Mn^{2+} spectrum in chloride surroundings has been studied by numerous

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workers in both crystals, aqueous and low temperature non-aqueous solvents[36]. Most pertinent to the present work is the discussion of spectral intensities given by Sundheim and Kukk. These workers argue that the oscillator strength of the tetrahedral $MnCl_4^{2-}$ spectrum would be expected to be a factor of 10 greater than that of Mn^{2+} in aqueous solution, where one is presumably dealing with the octahedral hexa-aquo manganous ion. In fact, the intensity of the Mn^{2+} spectrum in LiCl–KCl eutectic found by Sundheim and Kukk, and also in our work, falls in the range expected for a tetrahedral $MnCl_4^{2-}$ complex, thus lending strong support to the argument in favour of a four- rather than a six-coordinate complex.

The reason one must resort to an intensity argument to decide on the stoicheiometry of the complex is due to the fact that Mn^{2+} is in an S ground state. Since there is no first order crystal field splitting of a spectroscopic S state, the effect on the spectrum due to a change from octahedral to tetrahedral coordination can be expected to be negligible particularly at melt temperatures where the bands are considerably broadened. Indeed, an examination of the crystal spectra of Mn^{2+} (*Figure 8*) in octahedral $CsCdCl_3$ and tetrahedral Cs_2ZnCl_4, reveals only small differences in the two spectra even at room temperature.

The spectrum of Fe^{2+} (d^6, ^5D) in chloride melts

The spectrum of Fe^{2+} in LiCl–KCl eutectic (*Figure 9*) in the range 400–1,000° is characterized by a single absorption band whose maximum shifts
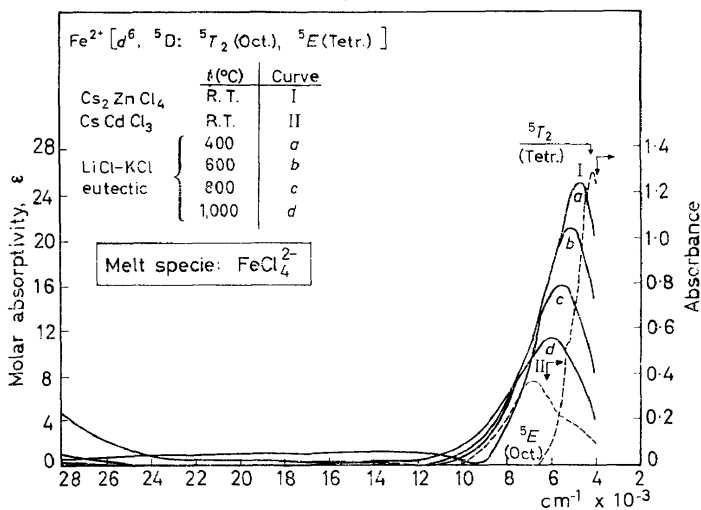

Figure 9. Absorption spectra of Fe^{2+} in chloride media

from 4,800 cm^{-1} at 400° to 6,000 cm^{-1} at 1,000°. The recent assignment[15] of this band to the $FeCl_4^{2-}$ complex receives strong support from studies of the transition in a tetrahedral lattice site $[Cs_2Zn_{1-x}(Fe_x)Cl_4]$ compared with an octahedral site $[CsCd_{1-x}(Fe)_xCl_3]$. The value of $Dq_{,tetra.} = 510$ cm^{-1} for $FeCl_4^{2-}$ may be compared with $Dq_{,tetra.} \cong 300$ cm^{-1} found by Low and

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Weger[37] in the case of Fe^{2+} substituted for Zn^{2+} in the tetrahedral ZnS lattice.

The large molar absorptivity of Fe^{2+} in chloride melts lends further support to assignment of the near i.r. absorption band to a tetrahedral $FeCl_4^{2-}$ species.

The decrease in intensity of the $FeCl_4^{2-}$ spectrum may be accounted for on the assumption of an increasing ionicity of the Fe—Cl bond with increasing temperature analagous to the situation with $CoCl_4^{2-}$. In the latter case, detailed theoretical calculations were available. Similar calculations for $FeCl_4^{2-}$ have not yet been made.

It is to be noted that the band maximum shifts to higher energies with increasing temperature. In contradistinction, the band maxima of the absorption bands of most of the other ions of the 3d group move to lower energies with increasing temperature.

We would like to propose that distortions from tetrahedrality are energetically favoured in the case of the $FeCl_4^{2-}$ complex. Such distortions would lead to larger crystal field splittings and consequent shifting of the band to higher energies with increasing temperature.

Since the configuration of a particular 3d ionic complex is determined by the interplay of a number of subtle factors, which are at present only incompletely understood, one can only speculate as to the reasons for this behaviour. We feel that it is closely connected with the stability of an unsymmetrical vibrational mode of $FeCl_4^{2-}$. The $FeCl_4^{2-}$ complex is in an electronic ground state having E character. It is of interest to note that the only other tetrahedral ion in an E ground state is $TiCl_4^-$ and a similar, though much less pronounced, shift of the band maximum to higher energies was found in this case as well. A satisfying theoretical explanation of these phenomena is however not available at present.

The spectrum of Ni^{2+} (d^8, ^3F) in chloride melts

The spectrum of Ni^{2+} in LiCl–KCl eutectic was first studied by Boston and Smith[38] in 1958. In this pioneering work carried out at temperatures ranging from 364–540° marked spectral changes were observed and interpreted in terms of two light absorbing species. Boston and Smith also noted effects of solvent composition on the relative concentrations of the two species which were substantiated in a later study[39].

Jørgensen[40] interpreted the high temperature spectrum as due to tetrahedral $NiCl_4^{2-}$ which at that time had not previously been observed. The low temperature melt spectrum he interpreted as due to an octahedral nickel complex.

The work of Gruen and McBeth[39] showed in a definitive way that the high temperature spectrum is due to $NiCl_4^{2-}$ by comparing it with a crystal spectrum of $Cs_2Zn_{1-x}(Ni_x)Cl_4$. The low and high temperature melt spectra are given in *Figure 10*, together with crystal spectra obtained at room temperature of $Cs_2Zn_{1-x}(Ni_x)Cl_4$ and $CsCd_{1-x}(Ni_x)Cl_3$*. In their paper, Gruen and McBeth speculated that the low temperature melt spectrum was due

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* These crystals were grown by Dr R. Gut while on leave at Argonne from the ETH, Zurich, Switzerland.

to a tetragonally distorted $NiCl_4^{2-}$ species rather than an octahedrally co-ordinated species. Harrington and Sundheim came to a similar conclusion[2, 41] basing their argument on selection rules between ground and excited states. The crux of the argument turns on the presence at low melt temperatures of an absorption band at $\sim$19,500 cm^{-1} and its gradual disappearance as the temperature is raised. That the low temperature melt spectrum is definitely not due to an octahedral chlorocomplex of Ni^{2+} is shown very clearly by a comparison with the spectrum of Ni^{2+} in an octahedral site as in $CsCdCl_3$.
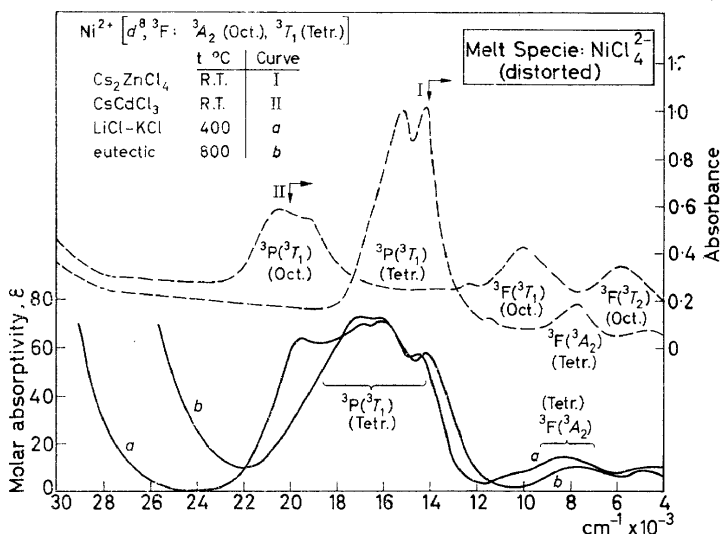

Figure 10. Absorption spectra of Ni^{2+} in chloride media

In addition to spectra in melts, the spectrum of $NiCl_4^{2-}$ has been studied in recent years by a number of workers in crystals and nonaqueous solvents[42]. As a result of this and other work, tetrahedral $NiCl_4^{2-}$ appears to be a well established entity by now. A particularly striking example of the existence of the $NiCl_4^{2-}$ complex was discovered recently by (the late) Iberson, Gut and Gruen when the congruently melting compound Cs_3NiCl_5 was found in the $CsCl-NiCl_2$ phase diagram[43], and shown to be isomorphous with Cs_3CoCl_5.

The absorption spectrum of Ni^{2+} in Cs_2ZnCl_4 has also been studied recently by Weakliem and McClure[3]. These investigators suggest that the $\sim$1,000 cm^{-1} splitting of the visible band is due to the fact that the true symmetry of $ZnCl_4^{2-}$ in the Cs_2ZnCl_4 lattice is Cs. Since the splitting of this band in the melt (even at the highest temperatures) is larger than in the crystal, one may infer that the distortion from tetrahedral symmetry is larger in the melt than in the crystal. At low melt temperatures, the distortion is presumably quite severe as discussed above.

The spectrum of Cu^{2+} (d^9, ^2D) in chloride melts

The spectrum of Cu^{2+} in LiCl–KCl eutectic (*Figure 11*) is characterized by a single band centred at 9,500 cm^{-1}. This band has been assigned to the

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$T \rightarrow E$ transition of the $CuCl_4^{2-}$ complex[15]. The band maximum found in the crystal spectrum of pure Cs_2CuCl_4[44] and in $Cs_2Zn_{1-x}(Cu_x)Cl_4$ (present work) occurs at 7,000 cm^{-1}. In $CsCd_{1-x}(Cu_x)Cl_3$ the band maximum occurs at 12,400 cm^{-1}. In the melt spectrum, therefore, the maximum occurs about halfway between the maxima for an octahedral and a tetrahedral site. Crystal structure studies of Cs_2CuCl_4 have shown[44, 45] that the Cl—Cu—Cl angles are 120 $\pm$ 3° and 104 $\pm$ 3°. The chlorine atoms of the $CuCl_4^{2-}$ complex may, therefore, be thought of as being situated at the corners of a regular tetrahedron which has been slightly flattened.
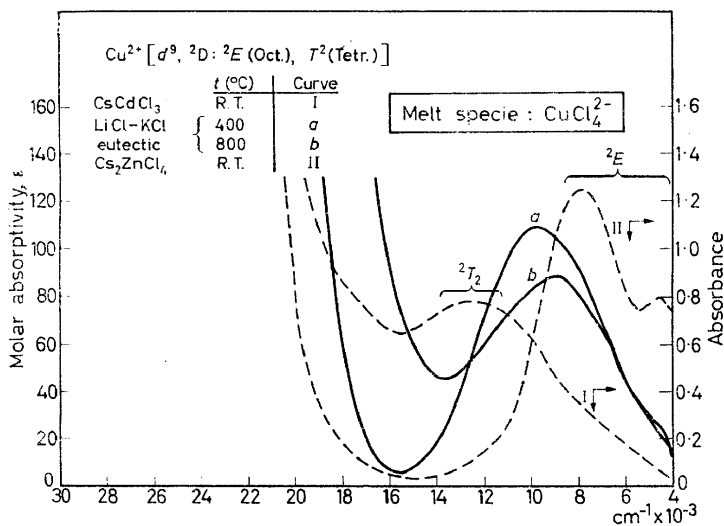

Figure 11. Absorption spectra of Cu^{2+} in chloride media

It would appear that in the melt, the " flattening " or tetragonal distortion of the $CuCl_4^{2-}$ complex is more severe than in the crystal but becomes less so with increasing temperature since the maximum is seen to shift to lower energies as the temperature is raised. These studies confirm a similar conjecture put forward by Harrington and Sundheim[2] on the basis of studies of ultra-violet absorption bands of Cu^{2+} in LiCl–KCl eutectic. Finally, it may be remarked that the $CuCl_4^{2-}$ complex provides an excellent example for theoretical calculations along the lines of those carried out by Felsenfeld[46]. Taking into account ligand field stabilization energies and electrostatic and van der Waals repulsion of the polarized chloride ions, he was able to predict equilibrium angles of 122·4° and 103·4° on a purely theoretical basis. With still further refinements which would include spin-orbit coupling and covalency effects one may ultimately be able to provide a theoretical basis for the changes in the band maximum and band intensity found on varying solvent temperature and composition.

In obtaining the Cu^{2+} spectra, we found that at temperatures above ~600° in LiCl–KCl eutectic the decomposition reaction

$$CuCl_2 \rightarrow CuCl + \tfrac{1}{2}Cl_2 \qquad (7)$$

D
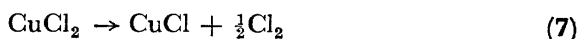
had to be taken into account. Since equilibrium was found to be established slowly under the conditions of our experiments, rate studies were undertaken in order to be able to correct the observed absorption curves and thus to obtain the true molar absorptivities of Cu^{2+}. Fortunately, Cu^+ the product of reaction (7), does not absorb in the spectral region of interest, so that to correct for its formation one need merely subtract the appropriate quantity from the Cu^{2+} concentration term.

DISCUSSION OF RESULTS

Summary remarks

The spectral data and their interpretation in terms of coordination numbers and configurations of the $3d$ metal ions in chloride melts are summarized in *Table 3*. There are a number of features which are emphasized by presenting the data in this way.

First, an octahedral tetrahedral transformation can be observed and studied as a function of temperature and solvent cation composition in the case of some ions. For other ions, (*e.g.*, Cr^{3+}), only the octahedral form is

Table 3. Coordination numbers and configurations of $3d$ metal ions in chloride melts

Electronic configuration	Ion	Solvent	Temperature (°C)	Energy at maximum (cm⁻¹ × 10⁻³)	Transition	Dq (cm⁻¹)	Configuration	Ref.
d^1	$TiCl^-$	$CsGaCl_4$	700	6·0 8·8	$E \to T$	~700	Dist. tetrahedral	15
	$TiCl_6^{3-}$	LiCl-KCl	400	10·0 13·0	$T_2 \to E$	~1,150	Dist. octahedral	15
d^2	VCl_4^-	$CsAlCl_4$	800	8·0 9·5 10·5 15·0	$A_2 \to T_2(^3F)$ $A_9 \to {}^3F + {}^3P$	~500	Dist. tetrahedral	
	VCl_6^{3-}	LiCl-KCl	400	11·0 18·0	$T_1 \to T_2(^3F)$ $T_1 \to T_1(^3P)$	1,200	Octahedral	
d^3	VCl_4^{2-}	Cs_2ZnCl_4	900	6·0-11·0 14·5	$^4F \to {}^4F$ $^4F \to {}^4P + {}^4F$	~400	Dist. tetrahedral	
	VCl_6^{4-}	LiCl-KCl	400	7·2 12·0 19·0	$A_2 \to T_2(^4F)$ $A_2 \to T_1(^4F)$ $A_2 \to T_1(^4P)$	700	Octahedral	
	$CrCl_6^{3-}$	LiCl-KCl	400–1,000	12·5 18·5	$A_2 \to T_2(^4F)$ $A_2 \to T_1(^4F)$	1,250	Octahedral	
d^4	$CrCl_4^-$	LiCl-KCl	400–1,000	9·8	$T_2 \to E$	980	Dist. tetrahedral	15
d^5	$MnCl_4^{2-}$	LiCl-KCl	400–1,000	23·4 28·2	$^6S \to {}^4G$ $^6S \to {}^4D + {}^4P$	~500 (from half-width)	Tetrahedral	
d^6	$FeCl_4^{2-}$	LiCl-KCl	400	5·1	$E \to T_2$	510	Tetrahedral	15
	$FeCl^-$	LiCl-KCl	1,000	6·0	$E \to T_2$	600	Dist. tetrahedral	
d^7	$CoCl_4^{2-}$	LiCl-KCl	400–1,000	5·6 14·3 15·1 16·4	$A_2 \to T_1(^4F)$ $A_2 \to T_1(^4P)$	~350	Tetrahedral	
d^8	$NiCl_4^{2-}$	LiCl-KCl	700–1,000	8·0 14·2 15·3	$T_1 \to A_2(^3F)$ $T_1 \to T_2(^3P)$ $T_1 \to T_1(^3P)$	~400	Dist. tetrahedral	
d^9	$CuCl_4^{2-}$	LiCl-KCl	400–1,000	9·5	$T_2 \to E$	950	Dist. tetrahedral	15

observed under our experimental conditions. For still other ions (e.g., Co^{2+}, Mn^{2+} etc.), only the four-coordinate form is found. One may speculate that

(i) The di- and tri-positive 3d metal ions in chloride melts can exist as four- or six-coordinate chloride complexes with a mobile equilibrium between the two forms. However, the equilibrium constant for each ion is determined by a number of factors and turns out to be of the right order of magnitude in the case of only a few ions for both forms to be experimentally observed.

Second, it will be noted that the tripositive ions Ti^{3+}, V^{3+} and Cr^{3+} occur in the form of octahedral MCl_6^{3-} complexes. Of the dipositive ions, only V^{2+} forms a six-coordinate complex, all others occurring only as four-coordinate complexes. One deduces that

(ii) Tripositive ions form six-coordinate chlorocomplexes more readily than dipositive ions pointing to the operation of a strong electrostatic factor in determining coordination numbers in melts.

Third, the spectra of some of the chlorocomplexes can be understood in terms of regular tetrahedral or octahedral structures whereas others require for their interpretation the introduction of tetragonal distortions of varying degree. Implicit both in Statement (i) and in this last sentence is the operation of a factor in addition to the electrostatic factor cited in Statement (ii). One may speculate that

(iii) Crystal field stabilization energies play an important rôle in determining coordination numbers and configurations of 3d metal ions in chloride melts.

Correlation of results with electrostatic energies and with crystal field stabilization energies

In this section, extensive use will be made of Table 4 in which the results are correlated with electrostatic and crystal field stabilization energies. In Table 4, all of the ions studied in the present investigation are listed in column 1. The situation with respect to the complexes found in chloride melts is summarized in column 7. With Cr^{3+}, only octahedral $CrCl_6^{3-}$ complexes were found. In the case of Ti^{3+}, V^{3+} and V^{2+}, octahedral-tetrahedral equilibria were found together with strong tetragonal distortions of the four-coordinate complexes. The ions Ni^{2+}, Cu^{2+} and Cr^{2+} were observed only in the four-coordinate state but the spectra could be interpreted only on the basis of strong tetragonal distortions. In contradistinction, the spectrum of Fe^{2+} can be interpreted in terms of small distortions from tetrahedral symmetry and the spectra of Co^{2+} and Mn^{2+} can be understood in terms of regular tetrahedral structures with very small or zero distortions.

A correlation of these results with crystal field stabilization energies is given in columns 2, 3 and particularly 4. In column 2, the crystal field splitting parameter Dq for the octahedral MCl_6 complex is given. The values were obtained from spectral data gathered in the course of the present investigations either on melts or on crystals with octahedral site symmetry about the 3d metal ion. Column 3 gives the octahedral site stabilization energies (O.S.S.E.) in units of Dq which were obtained as described in Table 2. Multiplication of columns 2 by 3 and conversion of cm^{-1} to kcal gives the O.S.S.E. in units of kcal/mole. The tendency towards octahedral

complex formation (or strong distortion from tetrahedral symmetry which is another way of gaining crystal field stabilization energy) would be expected to be a function simply of the magnitude of the octahedral site stabilization energy if this were the only important factor. However, it has already been pointed out that an electrostatic factor must also be considered. Thus, the correlation in terms of O.S.S.E. alone breaks down in the case of Ti^{3+} and V^{3+}, and it becomes highly desirable to estimate the magnitude of the electrostatic factor in the hope of achieving a correlation by consideration of both factors.

Table 4. Correlation of results with electrostatic and crystal field stabilization energies

1	2	3	4	5	6	7
Ion	*Dq* oct. (cm^{-1})	*O.S.S.E.* (*Dq* units)	*O.S.S.E.* (kcal/ mole)	ΔG O—T *Trans-form*	T/O *ratio in* LiCl–KCl *at* 1,000°K	*Coordination numbers and configurations of chlorocomplexes in melts*
Cr^{3+}	1,250	9·3	34	24	5×10^{-3}	Only octahedral $CrCl_6^-$
Ti^{3+}	1,150	1·3	4	−6	3×10^{-2}	Octahedral–tetrahedral equilibria $MCl_6^{4-} = MCl_4^{2-} + 2Cl^-$
V^{3+}	1,200	0·7	2	−8*	0·2	$MCl_6^{3-} = MCl_4^- + 2Cl^-$
V^{2+}	700	9·3	19	−11*	0·3	Strong tetragonal distortions
Ni^{2+}	600	9·3	16	−14	1·4	Coordination number four
Cu^{2+}	1,250	4·2	15	−15	2·2	Strong distortions from
Cr^{2+}	1,000	4·2	12	−18	10	tetrahedral symmetry
Fe^{2+}	670	1·3	3	−27	10^3	Only tetrahedral complexes
Co^{2+}	500	0·7	1	−29	3×10^3	Small or zero distortions
Mn^{2+}	—	0	0	−30	4×10^3	

* Experimentally determined values.

We begin by noting that the free energies of the octahedral–tetrahedral equilibria

$$MCl_6^{3-} = MCl_4^- + 2Cl^- \tag{8}$$

$$MCl_6^{4-} = MCl_4^{2} + 2Cl^- \tag{9}$$
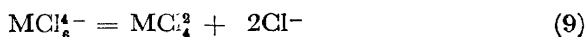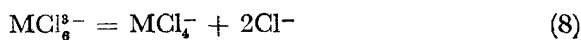
are given by equations (10) and (11):

$$\Delta G(M^{3+}) = -RT \ln \frac{[MCl_4^-][Cl^-]^2}{[MCl_6^{3-}]} \tag{10}$$

$$\Delta G(M^{2+}) = -RT \ln \frac{[MCl_4^{2-}][Cl^-]^2}{[MCl_6^{4-}]} \tag{11}$$

It has been assumed so far that these equilibria are determined only by electrostatic and crystal field stabilization energies. This is of course a great oversimplification of the actual situation as has been pointed out for example by Katzin[47]. Our argument can be rephrased by saying that the equilibria (8) and (9) are determined by octahedral site stabilization energies (O.S.S.E.) and in addition by another energy term, E. We believe that the difference in electrostatic energies between hexa- and tetra-coordinated chlorocomplexes makes the most important contribution to E. Other contributions to the energy term E, such as covalent bonding effects, Jahn-Teller forces, spin–orbit coupling interactions, entropy differences, *etc.*, are probably relatively small.

We now postulate that the free energy, $\Delta G(M^{n+})$ of a generalized octahedral–tetrahedral equilibrium

$$MCl_6^{n-6} = MCl_4^{n-4} + 2Cl^- \qquad (12)$$
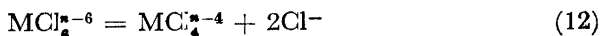
is given by

$$\Delta G(M^{n+}) = \text{O.S.S.E. } (M^{n+}) + E^{n+} \qquad (13)$$

The O.S.S.E. term varies, of course, from ion to ion depending on the electronic configuration and Dq of the particular ion. However, the E-term in this approximation depends only on the degree of ionization of the complex. Thus, one need know only two E-terms: one for dipositive, the other for tripositive metal ions.

The E-terms could be obtained according to equation (13) if ΔG's for one di- and one tripositive ion were available. The O.S.S.E.'s are known for all ions. Fortunately, it is possible to obtain ΔG's directly from the spectral data in the case of Ti^{3+}, V^{3+} and V^{2+}. The equilibria which have been studied most thoroughly are those of V^{3+} and V^{2+} in LiCl–KCl eutectic[29]. Substituting the appropriate concentration terms into equations (10) and (11) for V^{3+} and V^{2+} gives for $\Delta G(V^{3+}) = -8$ kcal; $\Delta G(V^{2+}) = -11$ kcal. Substitution of the appropriate quantities into equation (13) gives for

I. Dipositive ions: $E^{2+} = -30$ kcal

II. Tripositive ions: $E^{3+} = -10$ kcal.

This result implies that the E- factor drives reactions (8) and (9) strongly to the right making it unlikely that octahedral complexes of *any* 3d ions would be observed in melts were it not for octahedral site stabilization energies.

The ΔG's calculated using the O.S.S.E. value given in column 4 (*Table 4*) and $E^{2+} = -30$ kcal, $E^{3+} = -10$ kcal, are given in column 5 (*Table 4*). Furthermore, the tetrahedral–octahedral ratios calculated for a temperature of 1,000°K are given in column 6. These ratios were obtained from equations (10) and (11) using the ΔG's of column 5 and a chloride ion concentration of 27 mol/l. in LiCl–KCl eutectic at 1,000°K.

A comparison of column 5 with column 7 shows complete qualitative agreement between the calculated ΔG's and observed trends. Thus, only Cr^{3+} has a positive ΔG in agreement with the experimental observation of Cr^{3+} as the only ion for which only octahedral complexes were observed. For the next three ions, Ti^{3+}, V^{3+} and V^{2+}, the ΔG's are negative but because of the large Cl^- concentration and the high temperatures, the T/O

ratios are such that both octahedral and tetrahedral forms are in fact observed.

With Ni^{2+}, Cu^{2+} and Cr^{2+}, the ΔG's vary from -14 to -18 kcal/m. The T/O ratios are greater than one so that only low concentrations of the octahedral form are expected. In these cases, however, the octahedral form is not observed in melts since apparently the ions prefer to assume distorted tetrahedral structures and to gain crystal field stabilization energy in this way rather than by increasing their coordination number.

Finally, the ions Fe^{2+}, Co^{2+} and Mn^{2+} with very large negative ΔG's and large T/O ratios are found only in the tetrahedral form which is quite stable against distortion except in the case of Fe^{2+} where small distortions are energetically favoured.

COMPARISON OF THERMODYNAMIC WITH SPECTROSCOPIC DATA

It is not our intention here to trace historically the development of the concept of complex ions in fused salts, fascinating as such an undertaking would be. Having resisted this temptation, it is, nonetheless, fitting to conclude this paper with a few remarks concerned with the information which has been obtained about complex ions in melts from purely thermodynamic data. We will restrict ourselves here very severely by considering only one kind of study—the thermodynamic analysis of binary phase diagrams.

In a paper of 1955, Flood and Urnes[48] calculated the freezing point depressions to be expected in alkali chloride–$MgCl_2$ melts assuming a variety of different structural models. Of direct interest to our work are their calculations of KCl activities on the KCl-rich side of the binary phase diagram. Using the Temkin[49] model based on a statistical distribution of K^+ and Mg^{2+}, Flood and Urnes showed that the calculated freezing point depressions are in serious disagreement with the experimental results. Flood and Urnes then made calculations on the assumption that $MgCl_4^{2-}$ complexes are formed according to the equation:

$$2K^+ + 2Cl^- + MgCl_2 = 2K^+ + MgCl_4^{2-} \qquad (14)$$
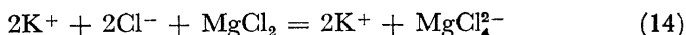
Freezing point depressions calculated on the basis of this model turned out to be in excellent agreement with the experimental data of Klemm et al.[50] in the range 0–30 mol per cent $MgCl_2$.

Since the work of Flood and Urnes, numerous attempts have been made to apply analogous calculations to an analysis of other binary phase diagrams. It seems clear that the conclusions drawn from these and other thermodynamic calculations are in substantial agreement with spectroscopic results.

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