VISIBLE SPECTRA OF TRANSITION METAL IONS IN MOLTEN SALTS—1

THE SB (III) CHLORIDE AND SB(III) CHLORIDE–POTASSIUM CHLORIDE SYSTEMS

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Abstract—The electronic absorption spectra of solutions of some of the most common 3d metal chlorides have been studied in molten solvents SbCl₃ and SbCl₃-KCl (8 mole%KCl) and their solid reflectance spectra also recorded. These spectra are discussed in terms of the likely geometries of the species present in solution and are compared with results obtained by other workers in molten salt systems. The predominant environment observed is that of an octahedral field of ions and only in the case of the Mn(II) and Co(II) ions are tetrahedral geometries observed. The Co(II) system exhibits a tetrahedral–octahedral equilibrium which is dependent on the amount of chloride ion added to the melt. A value for a term, called by Gruen and MCBeth^[1] the "electrostatic factor", E^{2+} has been estimated for molten SbCl₃ and this is compared with the value of E^{2+} obtained by them for di positive metal ions in LiCl–KCl solutions.

INTRODUCTION

Visible absorption spectra of molten salt solutions have been extensively studied and this field is now too diverse to be summarised in detail here. Good reviews of this work up to 1964 are available by both Smith[2] and Gruen [3], whilst some of the more recent work has been reviewed by Johnson and Dickinson[4]. Other recent work of general interest on the use of spectroscopy to observe coordination equilibria includes that of Griffiths [5-8], Smith [9-12] and their co-workers. A review by Kerridge[13] also includes references to work on coordination equilibria some of which have been studied using visible spectroscopy. Coordination equilibria of 3d ions in fused chloride melts have been studied extensively for only a few systems; including the LiCl-KCl eutectic mixture where the geometry is variable, studied by Gruen and McBeth[1], and the molten AlCl₃ system studied by Øye and Gruen[14] where the only geometry observed in the case of the dispositive 3d ions was octahedral (except possibly for (ii), see discussion section). The predominance of octahedral geometries in the latter solvent was explained by postulating octahedral "holes" formed between two of the complex species present in liquid AlCl₃. Clearly a liquid chloride solvent which is highly covalent in the pure form and in which chloride ions are readily soluble, forming ionic species in solution, would be a useful medium in which to attempt to observe octahedral-tetrahedral equilibria of 3d metal chloro complexes.

Solvent properties of antimony trichloride

Most of the known physical properties of $SbCl_3$ have been collated by Texier[15]. $SbCl_3$ melts at 73.2°C to form a colourless liquid with a viscosity of 3.3 cp and boils at 222.6°C. At 99°C molten SbCl₃ has a specific conductivity of $0.85 \times 10^{-6} \,\Omega^{-1} \,\mathrm{cm}^{-1}$ and a density of 2.64 g cm⁻³. The conductivity of the melt can be accounted for by a self-ionisation:

$$2 \operatorname{SbCl}_3 \rightleftharpoons \operatorname{SbCl}_2^+ + \operatorname{SbCl}_4^-$$
.

The mobility of the chloride ion in molten SbCl₃ is \sim 0.9. This relatively high value indicates that exchange of chloride is rapid. Pure SbCl₃ has an ionic product of 1.6×10^{-8} . K⁺, Rb⁺, Cs⁺, NH₄⁺, Tl¹, Hg²⁺ chlorides, HgBr₂, HgI₂, KF and KBr are all readily soluble in molten SbCl₃. The chlorides of Li⁺, Na⁺, Sn²⁺, Bi³⁺ and Fe³⁺ are sparingly soluble. The majority of oxides and oxoacids so far investigated are either insoluble or decomposed on solution, the only exceptions being tetramethyl ammonium sulphate and perchlorate. Many addition compounds have been reported as being formed in SbCl₃ solutions, the best characterised of which are: MSbCl₄, M_2 SbCl₅, MSb₂Cl₇, M_2 SbCl₉ (where M = Li, Na, K, NH₄, Rb or Cs) M(SbCl₄)₂ and M(SbCl₅) (where M = Be, Mg, Ca, Sr or Ba). Other inorganic compounds have also been reported but are largely of ill-defined stoichiometry. The work summarised in this paragraph has been reviewed in detail in Waddington[16]

Many organic compounds are soluble in SbCl₃[15] and recently interest has been centred around its use as a solvent for reactions of aryl species where radicals are involved. In particular anthracene has been used by Smith *et al.*[17, 18] to produce species such as anthra [2, 1- α] aceanthrylene.

SbCl₃ has also received attention as an inert medium for inorganic reactions. Guenther [19] has used molten SbCl₃ as a solvent for the reaction of TiCl₄ with KCl or TiCl to produce the compound M₂TiCl₆. O'Donnell *et al.*[20] have used molten SbCl₃ as a solvent for the disproportionation reaction UF₆ + SbCl₃ \rightarrow UF₄ + Cl₂ + SbF₃ and a similar reaction of VF₅ with SbCl₃[21] where the nature of the products is unclear.

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EXPERIMENTAL

Materials All materials were stored in a dry glove-box under an atmosphere of dry, deoxygenated dinitrogen.

The antimony trichloride used was either Hopkin and Williams reagent grade purified by vacuum sublimation, or B.D.H. "AnalaR" grade, used without purification. The potassium chloride was B.D.H. "AnalaR" grade. CrCl₃, MnCl₂, CoCl₂ and NiCl₂ were prepared by refluxing their hydrates with SOCl₂ for between one and five hours, depending on the chloride. The excess SOCl₂ was then distilled off and the anhydrous product heated at 110°C at a pressure of 10^{-3} torr for 6 hr. FeCl₃ was B.D.H. reagent grade, (anhydrous) used without further purification. VCl₃ was reagent grade dried under a stream of dry dinitrogen. The TiCl₃ was Alfa Products reagent grade.

Experimental procedure. Standard dry-box and vacuum techniques were used throughout. The cell assemblies were made of either soda or silica glass, depending on the wavelength range under investigation. A graded seal was fused to the top of the cell, joining the cell to a pyrex glass tube. A grade 2 or 3 glass sinter was fused to the cell assembly via a constriction, and standard "B14" socket was fused on top of the sinter. A quickfit tap could be inserted into the socket to enable the transfer of the cell assembly from the dry-box to the vacuum line whilst keeping the contents under an atmosphere of dry dinitrogen.

The cells were filled using the following procedure: The dry powdered sample was placed above the sinter in the dry-box and the vacuum tap fitted into the socket. The whole assembly was then transferred to a vacuum line where it was evacuated to a pressure of less than 10^{-3} torr. The sample was then melted and run into the cell by using either a hair-drier or a small concentric furnace kept at a temperature of 110°C. The cell and graded seal were then sealed off at the constriction with a gas-oxygen flame.

The solution spectra were recorded on a Perkin-Elmer 402 UV/visible spectrophotometer fitted with a heated cell compartment. This was heated by pumping hot water around the cell compartment from a thermostatically controlled water bath. To record a spectrum, the cell compartment was heated to the required temperature and the cell assembly then placed in position. The solid solution was then melted and run into the cell part of the assembly with a hair-drier. Ten minutes were allowed for the temperature to equilibrate before the spectrum was recorded. The reference used was an empty cell of the same material as the sample cell. This was used for convenience as pure SbCl₃ is transparent in the region of the spectrum under study.

The reflectance spectra of the solidified solutions were recorded on a Beckman DK2A spectrophotometer with a reflectance attachment fitted. This instrument measures the reflected spectrum from a sample against a magnesium oxide reference. The solution spectra are reported between 850 and 350 nm wavelength. The low wavelength limit is due to the presence of a large "charge transfer" band due to $SbCl_3$ just below this region. The reflectance spectra are reported between 1800 and 350 nm, since the spectra are in all cases identical (in band position and relative intensity). Both solution and reflectance spectra have been plotted as one trace on an energy scale. Thus the solution spectra do not extend below 11,800 cm⁻¹ in energy.

The molar extinction coefficients reported are not accurate. To calculate the concentration of the transition metal chloride, it was necessary to calculate the volume of SbCl₃ from the weight used and its density. However no account was taken of the volume change on dissolution of the chloride and, more importantly, when the solutions were filtered during the cell filling procedure some of the solution was left on the sinter. It is likely that due to the low solubility of the transition metal chlorides in SbCl₃ these were preferentially absorbed on the sinter.

RESULTS AND DISCUSSION

(1) Solubilities

The transition metal chlorides were all dissolved in a solution of 8 mole% KCl in SbCl₃ and in pure SbCl₃. All were readily soluble in the former, but only sparingly soluble in the latter. To get a solution concentrated enough for spectroscopic analysis it was necessary to leave a suspension of the transition metal chloride, in equilibrium with the melt, at 110°C overnight. These suspensions were then filtered before being examined spectroscopically. The SbCl₃-KCl solutions required only melting together of the components to achieve dissolution.

(2) Spectra

The results of the spectroscopic investigation are reported and compared with those of Gruen and McBeth[1], and Øye and Gruen (14).

Ti(III) Chloride. The solution spectra of TiCl₃ dissolved in SbCl₃ and SbCl₃-KCl (8 mole% KCl) are shown in Fig. 1. The solid reflectance spectrum is not significantly different. The pure SbCl₃ shows a broad absorption centred at 23,800 cm⁻¹ with a shoulder at 20,000 cm⁻¹, on addition of 8 mole% KCl the band shifts to 21,500 cm⁻¹. A marked contrast can be seen when these spectra are compared with that of Ti(III) dissolved in LiCl-KCl, where Gruen and McBeth[1] observed an equilibrium



between TiCl6³⁻ (an octahedral species with a band due to the ²Eg to ²T_{2g} transition at 13,000 cm⁻¹, and the predominant species at 400°C) and TiCl₄ (a tetrahedral complex with a band at 8000 cm⁻¹ favoured at 1000°C) in solution. The species present in SbCl₃ solution is clearly neither of these. The only donor species present in solution are Cl⁻, SbCl₃ and SbCl₄⁻, and as these are all very poor donors it seems unlikely that the band observed above 20,000 cm⁻¹ is due to a d-d transition. Thus the only reasonable explanation seems to be that the band is in fact due to a charge transfer process. However, if the species in solution is due to Ti(III) a d-dband at low energy would be expected. No such band is seen. It is known from the work of Guenther [19] that the Ti(IV) species $TiCl_6^{2-}$ is stable in SbCl₃-KCl solutions. A spectrum of TiCl₄ dissolved in SbCl₃ was observed to be identical with the spectrum of TiCl₃ in the same solvent. These results can be explained by assuming that Ti(III) is oxidised to Ti(IV) in the solvent and that the band seen in the spectrum is due to a charge transfer process in a Ti(IV) species. The low value for the extinction coefficient of the band implies that such a charge transfer process would be "spin forbidden"

V(III) chloride. The spectrum of VCl₃ dissolved in pure SbCl₃ shows two features in both the solution and solid reflectance spectra (see Fig. 2). One band occurs at $16,700 \text{ cm}^{-1}$ and the other at $12,340 \text{ cm}^{-1}$ with a shoulder at 9090 cm⁻¹. In 8 mole% KCl solution the bands are shifted towards the blue. The lower energy band is at 14,500 cm⁻¹ and the higher at 22,200 cm⁻¹. Gruen and McBeth[1,22] compared the spectrum of V(III) in LiCl-KCl solution with that of V(III) doped into crystals of known geometry (octahedral or tetrahedral). They concluded that there was an equilibrium in solution (analagous to the Ti(III) system) between the octahedral VCl_6^{3-} and the tetrahedral VCl_4^{-} . A comparison of the band positions in the crystal data of Gruen and McBeth with those in pure SbCl₃ shows that the pure SbCl₃ spectrum is consistent with a slightly distorted octahedral arrangement of chloride ions (the shoulder at 9090 cm⁻¹ could be due to a splitting due to slight lowering of symmetry). The 8 mole% KCl solution spectrum is not consistent with a tetrahedral arrangement of chloride ions, but other than this little more can be deduced about the geometry of the species in solution.

Cr(III) chloride. In pure SbCl₃ the spectrum of Cr(III) shows bands (see Fig. 3) at $15,630 \text{ cm}^{-1}$ and $22,000 \text{ cm}^{-1}$ which shift to 13,500 and $19,400 \text{ cm}^{-1}$ on addition of 8 mole% KCl. The latter spectrum is almost identical with that of V(III) in LiCl-KCl observed by Gruen and McBeth[1]. It seems reasonable to assign the 8 mole% KCl spectrum to the same species as in LiCl-KCl, i.e. CrCl₆³⁻, an octahedral complex. In the case of pure SbCl₃, the separation of the bands makes anything other than octahedral geometry unlikely. The low extinction coefficients imply a centre of symmetry, making a tetrahedral geometry unlikely, lower symmetry than octahedral should cause splitting of the bands.

Mn(II) chloride. Figure 4 shows the spectrum of Mn(II) dissolved in SbCl₃. There is one band, at 22,000 cm⁻¹, which shifts by only 500 cm⁻¹ on addition of KCl. The spectrum of Mn(II) in LiCl-KCl shows bands at 23,000 and 28,000 cm⁻¹ but in SbCl₃ the solvent charge transfer band itself obscures the spectrum above 26,000 cm⁻¹. The spectrum of rigorously tetrahedral MnCl₄²⁻ in a host crystal lattice studied by Gruen and McBeth[1], shows a band at 22,000 cm⁻¹, thus the SbCl₃ and SbCl₃-KCl spectra are consistent with the species MnCl₄²⁻, a tetrahedral complex.

Fe(III) chloride. There are no distinct bands in the spectra of Fe(III) in SbCl₃ and SbCl₃-KCl (Fig. 5), the tail of an intense "charge-transfer" band obscures any d-d transitions, which would be expected to be weak in any case as Fe(III) is a d⁵ system. The "ripples" which can be seen on both spectra are not mentioned by Harrington and Sundheim[23] who observed the spectrum of Fe(III) dissolved in LiCl-KCl, but commented on by Silcox and Haendler[24] who also studied a similar system. Little of value can be gleaned from these spectra without recourse to complex techniques.

Co(II) chloride. The spectra of Co(II) dissolved in SbCl₃ and SbCl₃-KCl are shown in Fig. 6. The 8 mole% KCl spectrum shows a complicated system of bands with maxima at 16,390, 15,100 and 14,280 cm⁻¹. In pure SbCl₃ the spectrum has only one broad band, centred at 21,500 cm⁻¹. A 1 mole% KCl solution shows both features





with corresponding reductions in intensity. The 8 mole% KCl spectrum is almost identical in shape and position with that of $CoCl_{4}^{2-}$ reported by Gruen and McBeth[1] in LiCl-KCl solution. The band at 21,500 cm⁻¹ is consistent, both in energy and extinction coefficient with a change from tetrahedral to octahedral geometry. The obvious interpretation of these results is that an equilibrium of the form:

$$"CoCl_6^{4-}" + 2SbCl_3 \rightleftharpoons CoCl_4^{2-} + 2SbCl_4"$$

is present in solution. The reason for the tetrahedral species being favoured at higher chloride concentrations can be explained in terms of an "electrostatic factor" similar to that used by Gruen and McBeth[1] to explain the LiCl-KCl results (see later). Øye and Gruen[14] have reported a spectrum of Co(II) in molten AlCl₃ solution. They explain their results as being indicative of only an octahedral species present in solution. A close examination of the spectra they present, however, reveals two bands at positions almost identical to those observed in SbCl₃ and 8 mole% SbCl₃-KCl superimposed on the same spectrum (i.e. almost exactly identical with a 1 mole% KCl-SbCl₃ solution). This would imply that if the above equilibrium which is proposed for SbCl₃ solutions is applicable to AlCl₃ solutions, then in fact Øye and Gruen have observed an equilibrium mixture of both tetrahedral and octahedral species. This could be explained by noting that the Co(II) dissolved in AlCl₃ solution was present as the Cs₂CoCl₄ salt, thus for each mole of Co(II), they introduced 2 moles of chloride ions and it is reasonable to suppose that this was responsible for the presence of both octahedral and tetrahedral species. This would also explain why only Co(II), of all the 3d dipositive ions studied in AlCl₃ solution, showed a tetrahedral species as all the other ions were either added as MCl_x neutral species, or were prepared in situ.

Ni(II) chloride. The spectrum of Ni(II) in SbCl₃ is shown in Fig. 7. It consists of a band at 22,000 cm⁻¹ which shifts only very slightly on addition of 8 mole% KCl. From a comparison of these results with those of Gruen and McBeth[1] and Griffiths *et al.*[6] who describe a band



Fig. 7.

seen in other chloride containing melts around $22,000 \text{ cm}^{-1}$ as being due to the octahedral species NiCl₆⁴⁻, we can conclude that an octahedral geometry is likely. Øye and Gruen[14] report a spectrum of Ni(II) dissolved in molten AlCl₃ which has a maximum at $21,000 \text{ cm}^{-1}$ which they assign to an octahedral species – this adds more evidence to support the conclusion that the octahedral geometry is present in SbCl₃ solution.

CONCLUSION,

The results discussed above are shown compared to those of Gruen and McBeth in Table 1. There are three important features:

(1) The predominant geometry in pure $SbCl_3$ is octahedral or distorted octahedral, this is to be expected when the results are considered in the light of those in AlCl₃ solution, investigated by Øye and Gruen[14], where the predominant species are also of octahedral geometry.

(2) Only Mn(II) shows tetrahedral geometry in pure $SbCl_3$.

(3) The Co(II) system exhibits an octahedral geometry in pure $SbCl_3$ with an increasing concentration of a tetrahedral species as the amount of added chloride is increased.

Gruen and McBeth interpreted the LiCl-KCl systems in terms of the general equilibrium:

$$MCl_6^{(6-n)-} \rightleftharpoons MCl_4^{(4-n)-} + 2Cl^-$$

where n = oxidation state of metal and

$$\Delta G = -RT \ln \frac{[\mathrm{MCL}^{(4-n)}][C]]^2}{[\mathrm{MCL}^{(6-n)}]}.$$

They proposed that ΔG can also be expressed:

$$\Delta G = E^{n+} + \text{O.S.S.E.}$$

where O.S.S.E. = the crystal field stabilisation energy for the octahedral chloro complex $MCl_6^{(6-n)-}$, and E^{n+} is an "electrostatic factor" dependant only on the oxidation state of the metal. Values for E^{2+} and E^{3+} were experimentally determined from the V^{2+} and V^{3+} spectra and thus the position of the equilibrium in the other systems was predicted.

In the case of the $SbCl_3$ system, an unsophisticated view is to assume that the equilibrium involved is the same in all the systems studied and is of the form:

$$MCl_6^{(6-n)-} + 2SbCl_3 \rightleftharpoons MCl_4^{(4-n)-} + 2SbCl_4^{-}$$

and

$$\Delta G = -RT \ln \frac{[MCl_4^{(4-n)}][SbCl_4^{-}]^2}{[MCl_6^{(6-n)}][SbCl_3]^2}$$
(1)

and to make the same assumption as Gruen and McBeth, i.e. that:

$$\Delta G = E^{n+} + \text{O.S.S.E.}$$

Note that the value of E^{n+} in SbCl₃ will be different from that in LiCl-KCl, and should be less negative because of the lower ionic product of pure SbCl₃ ([SbCl₂⁺][SbCl₄⁻] = 1.6×10^{-8} [14]).

Because of the terms in [SbCl₄⁻] and [SbCl₃] in eqn (1) which are unknown, it is impossible to calculate directly, a value for E^{2+} or E^{3+} . In the case of Co(II) and Mn(II) however, we know that in pure SbCl₃ the former is octahedral and the latter is tegrahedral thus the value of E^{2+} must lie between the values of -O.S.S.E. for Co(II) and Mn(II) i.e. E^{2+} in SbCl₃ lies approximately between 0 and -4 kJ mol⁻¹. The value of E^{2+} in LiCl-KCl calculated by Gruen and McBeth[1] is -120 kJ mol⁻¹. This indicates that SbCl₃ is much less ionised in the melt than LiCl-KCl, which is consistent for the comparatively low value for the ionic product quoted above. As KCl is added to the Co(II) solution an increasing concentration of the tetrahedral species is observed, i.e. the value of E^{2+} must become more negative on addition of chloride ions, i.e. the melt must be more ionised. This is consistent with the view that as chloride is added to the melt it becomes more like a true ionic chloride. It should be noted that the value of E^{2+} is only approximate and that in order to calculate an exact value concentrations of SbCl₃ and SbCl₄⁻ would have to be measured.

The discrepancy between the band positions of the

Ion	Geometry in SbCl ₃	Geometry in LiCl-KCl	0.S.E.E.*
Cr(III)	"Octahedral"	Octahedral	146.2
Ni(II)	Octahedral	Tetrahedral	54.4
Ti(III)	(Oxidised to Ti(IV))	Octahedral ≓ Tetrahedral	17.2
V(III)	Octahedral	Octahedral ≠ Tetrahedral	8 .6
Co(II)	Octahedral≓Tetrahedral	Tetrahedral	4.3
Mn(II)	Tetrahedral	Tetrahedral	0.0
Fe(III)	?	?	0.0

Table 1. A summary of the geometries observed in pure SbCl₃ solution and in LiCI-KCl solution (after Gruen and McBeth)

(*O.S.S.E. = Crystal field stabilisation energy of octahedral chloro complex in units of kJ mol⁻¹).

rigorously octahedral ions $MCl_6^{(6-n)-}$ and some of the bands observed in SbCl₃ spectra which are attributed above to octahedral geometries, can be explained by postulating a coordination model where the metal ion is surrounded by 6 chloride ions, the chloride ions being bonded to Sb(III) ions:



Also other complex ions (e.g. $SbCl_4^-$ etc) could be involved. This arrangement would provide an "octahedral" site for the metal ion and would explain the slight differences in band positions from those in the strictly octahedral species $MCl_6^{(6-n)-}$. Increasing tendency to form tetrahedral species on addition of chloride, can be accounted for in this model by postulating the species:



Which provides approximately tetrahedral coordination. This model is directly analagous to that proposed by Øye and Gruen[14] to explain the octahedral geometry observed in solutions of dispositive 3d ions in pure AlCl₃. Another alternative explanation might involve the SbCl₃ being either bidentate or even mono-dentate, although the latter is somewhat unlikely due to steric consideration. It must be stressed, however that these results are consistent with the assumptions of Gruen and McBeth[1] and Øye and Gruen[14] in all systems studied except for Cr(II) in AlCl₃ which can be explained by the addition of extra chloride ions not present in the other AlCl₃ systems, and Ti(III) in LiCl-KCl which can be explained on the basis that Ti(III) is oxidised to Ti(IV) by the solvent.

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