by irreversible reductions exhibiting $E_{p,c}$ values close to −0.3 and −0.8 V. On the other hand, the decomposition, which follows electrolytic oxidation of $[Mo(CNR)_5(dppm)](PF_6)_2$ (R = CH_3 or C_6H_{11}), $[Mo(CNR)_5(dppe)](PF_6)_2$ (R = CH_3, C_6H_{11}, or CMe_3), and $[W(CNCMe_3)_5(dppe)](PF_6)_2$, produces no significant quantities of $[M(CNR)_6]^{3+}$ as demonstrated by the cyclic voltammograms of the solutions and ESR spectral measurements.[30] The only reproducible product waves in these cyclic voltammograms are ones at $E_{p,c} \sim -0.25$ and −0.75 V of unknown origin. It seems likely that loss of the bidentate chelating dppm and dppe ligands does not occur following oxidation. On the other hand, with $[Mo(CNCH_3)_5(P\text{-}n\text{-}Pr_3)_2]^{3+}$ and $[Mo(CNC_6H_{11})_5(PEt_3)_2]^{3+}$, loss of CNR and/or loss of monodentate phosphine are viable decomposition pathways; the free isocyanide which is released could then explain why $[Mo(CNR)_6]^{3+}$ is formed, as we have detected in the cyclic voltammograms of these latter systems.

Acknowledgment. Support from the National Science Foundation through Grant No. CHE79-09233 is gratefully acknowledged. The Varian E-109 ESR spectrometer was purchased with a grant from the National Science Foundation (BMS 75-19127). We thank Dr. Thomas E. Wood for supplying several of the samples of the molybdenum complexes whose electrochemical properties we investigated.

Registry No. $[W(CNCMe_3)_7](PF_6)_2$, 66687-57-8; $[W(CNC_6H_{11})_7](PF_6)_2$, 76705-37-8; $[W(CNCMe_3)_6I]I$, 66652-48-0; $[W(CNCMe_3)_5(dppe)](PF_6)_2$, 76721-72-7; $[W(CNCMe_3)_6(P\text{-}n\text{-}Pr_3)](PF_6)_2$, 76721-74-9; $[W(CNCMe_3)_6(P\text{-}n\text{-}Bu_3)](PF_6)_2$, 76721-76-1; $[Mo(CNCH_3)_7](PF_6)_2$, 66632-84-6; $[Mo(CNC_6H_{11})_7](PF_6)_2$, 72155-82-9; $[Mo(CNCMe_3)_7](PF_6)_2$, 41982-05-2; $W_2(mhp)_4$, 67634-84-8; $W(CO)_4I_2$, 40813-52-3.

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[30] While the ESR spectrum of a dichloromethane glass (−160 °C) that contains the products from the oxidation of $[Mo(CNCH_3)_5(dppm)]^{2+}$ shows a weak signal, it differs from that which we attribute to $[Mo(CNCH_3)_6]^{3+}$ (Figure 2a).

Contribution from the Institutt for Uorganisk Kjemi, Norges Tekniske Høgskole, Universitetet i Trondheim, N-7034 Trondheim-NTH, Norway, and the F. J. Seiler Research Laboratory, U.S. Air Force Academy, Colorado 80840

Spectroscopic Study of the Coordination of Titanium Chlorides in Fused Chloroaluminates and Alkali Chloride Mixtures

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The spectra and the coordination chemistry of titanium chlorides in some fused salt solvents are reported. Spectra of Ti(III) and Ti(II) have been obtained in $AlCl_3$–KCl melts ($1.00 \geq X_{AlCl_3} \geq 0.49$) at temperatures 471–894 K and in the LiCl–KCl eutectic melt at temperatures 658–1185 K. Ti(III) is found to be octahedrally coordinated in pure $AlCl_3(l)$ and in $AlCl_3$–KCl melts with $X_{AlCl_3} \geq 0.67$ while octahedral–tetrahedral coordination equilibria are established at lower $AlCl_3$ contents. Ti(II) has octahedral coordination at compositions $1.00 \geq X_{AlCl_3} \geq 0.51$, but a disproportionation equilibrium is observed for $X_{AlCl_3} \leq 0.60$, culminating at $X_{AlCl_3} = 0.49$ where Ti(II) is unstable and the spectrum of Ti(III) in an octahedral–tetrahedral coordination equilibrium is found. In the LiCl–KCl eutectic Ti(III) is also present in an octahedral–tetrahedral coordination equilibrium. Ti(II) has octahedral coordination in this solvent, but a disproportionation equilibrium is established.

Introduction

High-temperature equilibria between titanium and aluminum chlorides may play an important part in ore processing by chlorination such as production of TiO_2 from ilmenite and production of $AlCl_3$ from clay. However, the literature on these equilibria are scarce, mainly due to the considerable experimental difficulties encountered from the oxygen and water sensitivity of the systems.

A previous publication[1] discussed the complexation and redox equilibrium of titanium chlorides in gaseous $AlCl_3$, while the present paper will deal with the coordinations of the different oxidation states of titanium in molten chloroaluminates and alkali chloride mixtures based on spectroscopic evidence.

The spectrophotometer is a sensitive instrument for characterization of the different oxidation states of titanium with various ligand coordinations, as the electronic transitions that arise usually lie within the wavelength span of a UV–vis–near IR spectrophotometer. The intensity of the electronic transitions in dilute solutions normally follows Beer's law (eq 1)

$$\epsilon_i = A_i/cl \qquad (1)$$

and the law of additivity (eq 2) which states that at a fixed

$$A = \sum_i A_i \qquad (2)$$

wavelength, *i*, the molar absorptivity, ϵ (L/(mol·cm)), is a constant independent of the concentration, *c* (mol/L), and optical path length, *l* (cm), and that in a solution of more than one light-absorbing species each contributes additively to the total absorbance at wavelength *i*. The absorption *A* is defined as log (I_0/I), where I_0 and I are the radiation intensities which enter and are transmitted through the sample, respectively.

Experimental Section

Instrumentation. Spectra were recorded with a Cary Model 17H spectrophotometer (Cary Instruments, Monrovia, CA). An interfacing device built at this university[2] transferred the spectrometer signals to a magnetic tape recorder (Model 1600, Kennedy Co., Altadena, CA) for temporary storage prior to computer processing of the spectra.

The furnace was specially built to fit into the Cary 17H sample compartment. The heating element was made of a cross-shaped pythagoras tubing with the light beam passing through the arms of the cross. It consisted of three separate heating zones, each controlled by a Eurotherm PID regulator (Eurotherm Ltd., Sussex, England). The upper and lower zone were regulated differentially from the one in the middle, as this arrangement made it easier to establish the required temperature gradient along the cell.

Spectrometric Cells. In order to withstand the high internal pressures, the cells were made from square-base (10 × 10 mm internal

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[1] M. Sørlie and H. A. Øye, *Inorg. Chem.*, **17**, 2473 (1978).

[2] O. Borgen, T. Bruvoll, and H. Petersen, Technical Report 70, Division of Physical Chemistry, University of Trondheim, Trondheim-NTH, Norway, 1976.

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dimensions) heavy-wall quartz tubing (Thermal Syndicate Ltd., Wallsend, England). These heavy-wall cells withstood vapor pressures up to 30 atm before rupturing. The outer surfaces were ground and polished in order to enhance the optical properties, but little could be done to improve the interior surfaces which were not optically flat. The small difference between the refractive index of quartz glass and melt, however, reduced the light scattering to a low level.

The accuracy of the optical path length is equal or better than 10 ± 0.5 mm, thus making the error in the calculated molar absorptivities less than 5%.

Chemicals. All chemicals were either made or further purified from commercial products in our laboratory. The manufacture or purification procedures for titanium chlorides and aluminum chloride have been described in the previous publication.[1]

Lithium chloride (p.a., E. Merck) was predried in a stream of dry HCl(g), followed by melting under continuous bubbling of HCl through the melt. After some time the melt became completely clear and colorless. HCl was removed by stripping with pure Ar, and the melt was vacuum filtered in situ into an ampule and sealed. Further purification took place by controlled recrystallization from the fused salt in nitrogen atmosphere after previous heating under vacuum. Large, clear and colorless crystals grew from the walls and bottom of the crucible and could be easily separated from a small amount of eutectic phase crystallizing in the center. Only clear and colorless LiCl crystals were used.

Potassium chloride (p.a., E. Merck) was purified by a method identical with the last stage of the previously described procedure.

Experimental Procedures. All handling of salts and filling of spectrometric cells took place in a nitrogen-atmosphere glovebox with levels of H_2O or $O_2 \leq 1$ ppm. Sealing was performed on a vacuum line at pressures $\leq 10^{-5}$ torr. Routines for sample handling and data aquisition and processing have been described elsewhere.[1,3] Liquid density data for the KCl–$AlCl_3$ binary system necessary for the molar absorptivity calculations has been taken from the work of Morrey and Carter.[4]

Titanium(II) was added to the solvents as an unstoichiometric Ti(II)–Al–Cl compound except in the LiCl–KCl eutectic mixture where it was added as $TiCl_2$, prepared from the Ti(II)–Al–Cl compound as described by Sørlie and Øye.[1] Due to the unstoichiometry of the Ti(II) compound chemical analysis had to be performed in order to determine the amount of $TiCl_2$ added. The analysis was performed by Mikroanalytisches Laboratorium, Bonn, BRD.

Results and Discussion

$TiCl_4$ in $AlCl_3$(s) and $AlCl_3$(l). Neither Ti^{4+} nor Al^{3+} possesses any valence electrons; thus transitions in the visible part of the spectrum are not expected, only high-energy UV transitions. Although pure $AlCl_3$ and $TiCl_4$ are both clear, colorless crystals or liquids, a mixture of $TiCl_4$ in $AlCl_3$(s) at 20 °C has a brilliant yellow color. The spectrum of $TiCl_4$ in the solid $AlCl_3$ matrix at this temperature, however, displays no absorption peaks, only a very steep edge rising at about 18 000 cm^{-1}.

The liquid mixture of $TiCl_4$ and $AlCl_3$ at 200 °C also display a yellow color, although it is much weaker than the solid mixture. The absorption edge is shifted to higher energies with only a tail extending into the visible region. No interactions were reported in gaseous mixtures of $TiCl_4$ and $AlCl_3$[1] where the UV absorption edge was indistinguishable from what was found in pure $TiCl_4$(g).

The yellow $AlCl_3$–$TiCl_4$ crystals were clear and transparent as $TiCl_4$ apparently formed solid solutions with the $AlCl_3$ matrix. The sharp yellow color is believed to arise from the change in the ligand field and coordination of Ti(IV) in the $AlCl_3$ lattice relative to molecular $TiCl_4$. The lowest energy UV absorption band in $TiCl_4$ is close to the visible part of the spectrum,[1] and small ligand field perturbations may shift this band toward lower energies, thus extending the tail into the visible region. In the liquid state the coordination is less rigid, and we observe only a small red shift of the absorption cutoff. In the gaseous phase only free Al_2Cl_6(g) and $TiCl_4$(g) molecules are present.

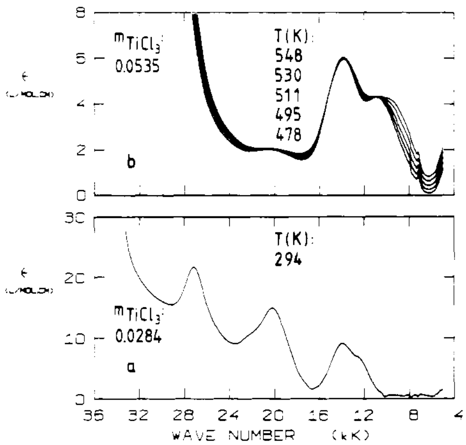

Figure 1. Spectra of $TiCl_3$ in pure $AlCl_3$. Temperatures (in K) and molal concentration of $TiCl_3$ (moles of $TiCl_3$ in 1000 g of solvent) are given: (a) $TiCl_3$ in $AlCl_3$(s); (b) $TiCl_3$ in $AlCl_3$(l).

$TiCl_3$ in $AlCl_3$(s) and $AlCl_3$(l). α-$TiCl_3$ (violet) forms solid solutions with $AlCl_3$,[5] giving a brownish salt. The spectrum shows three distinctive peaks or groups of peaks (Figure 1a). Considering the crystalline similarities between α-$TiCl_3$ and $AlCl_3$ (metal atoms in octahedral positions sandwiched between double layers of hexagonally packed chlorine atoms),[6,7] it is expected that a mere displacement of Al^{3+} by Ti^{3+} takes part in the host lattice upon mixing. Each Ti^{3+} is surrounded by a cage of six Cl^- ions which form a slightly distorted octahedron.

The spectrum shown in Figure 1a consists of one peak at 14 000 cm^{-1} with a low-energy shoulder, one peak at 20 200 cm^{-1} with a high-energy shoulder, and one peak at 27 200 cm^{-1}, thus giving a minimum of five transitions. There is no way all these can be explained by electron transitions within the d orbitals in Ti^{3+}. Trivalent titanium has the simple electronic structure d^1 and will in a purely octahedral field have a triple degenerate ground term and a double degenerate excited term giving a $^2T_{2g} \rightarrow {}^2E_g$ transition. Even in a very low symmetry, the lifting of all term degeneracies will lead only to a maximum of four excited states above the ground term. The high transition energy of some of the observed peaks does also indicate that more complex electronic excitations than purely within the d orbitals take place.

The double band at 12 000–14 000 cm^{-1} (Figure 1a) is readily identified as the $^2T_{2g} \rightarrow {}^2E_g$ transition in octahedrally coordinated Ti^{3+}, with the observed splitting due to the low-symmetry component introduced in the nearby octahedral Cl^- surroundings. Crystal spectra of α-$TiCl_3$ do also yield this double band at comparable wavelengths.[8-10]

The bands at 20 200 cm^{-1} and the one at 27 200 cm^{-1} must be attributed to charge-transfer transitions (ligand → 3d) or to excitations between the 3d level and 4s level (or 4p level) within Ti^{3+}. The peak around 20 000 cm^{-1} has also been observed in crystal spectra of α-$TiCl_3$[8-10] and was interpreted as a charge-transfer transition between the ligand and the central atoms.[8,9] Baldini et al.[10] also observed the band at wavenumbers around 27 000 cm^{-1} and interpreted the tran-

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[3] A. Anundskås and H. A. Øye, *J. Inorg. Nucl. Chem.*, **37**, 1609 (1975).

[4] J. R. Morrey and D. G. Carter, *J. Chem. Eng. Data*, **13**, 94 (1968).

[5] E. G. M. Tornqvist, J. T. Richardson, Z. W. Wilchinsky, and R. W. Looney, *J. Catal.*, **8**, 189 (1967).

[6] G. Natta, P. Corradini, and G. Allegra, *J. Polymer Sci.*, **51**, 399 (1961).

[7] J. A. A. Ketelaar, C. H. MacGillavry, and P. A. Renes, *Recl. Trav. Chim. Pays-Bas*, **66**, 501 (1947).

[8] R. J. H. Clark, *J. Chem. Soc.*, 417 (1964).

[9] C. Dijkgraaf and J. P. G. Rousseau, *Spectrochim. Acta, Part A*, **23A**, 1267 (1967).

[10] G. Baldini, I. Pollini, and G. Spinolo, *Phys. Status Solidi*, **27**, 95 (1968).

sitions as 3d → 4s and 3d → 4p excitations in Ti^{3+}.

Since Laporte-allowed, charge-transfer transitions usually have molar absorption values within the magnitude 10^3–10^4 L/mol·cm) we find the model proposed by Baldini et al.[10] most probable; a forbidden excitation of Ti^{3+} from 3d → 4s (20 200 cm^{-1}) followed by an allowed 3d → 4p excitation.

β-$TiCl_3$ (brown) has a linear chain structure[6] compared to the layer lattice of α-$TiCl_3$, but Ti^{3+} is still surrounded by six Cl^- ions, the brown color arising from a different distortion of the chlorine octahedron. The brown color of $TiCl_3$–$AlCl_3$ solid solutions is similar, most likely due to a slight distortion of the octahedral Cl^- cage around Ti^{3+} in the $AlCl_3$ layer lattice relative to the structure of violet α-$TiCl_3$.

Large hexagonal Ti^{3+}-doped $AlCl_3$ crystals could be grown from the melt by slow cooling. The spectrum was obtained from a single crystal grown on the wall inside a spectrometric cell. The crystals grow with one crystallization plane parallel to the wall, and although this crystal surface is not optically flat, the transparency is quite good. Ti^{3+} did not segregate upon crystallization, thus making a calculation of the molar absorption possible, as given on the ordinate in Figure 1a. The molar absorptivity of the $^2T_{2g} \rightarrow {}^2E_g$ band at 14 000 cm^{-1} is of a magnitude which is expected for a d → d transition in octahedral symmetry. The steadily rising background absorption above 16 000 cm^{-1} is the result of light scattering from the imperfect crystal surface.

Solutions of α-$TiCl_3$ in $AlCl_3$(l) have a faint blue hue, due to the absorption band at 13 800 cm^{-1} which extends into the visible part of the spectrum (Figure 1b). It is a double band with the second peak at 10 700 cm^{-1} and a flat, broad peak at 20 500 cm^{-1}. The irregularities on the low-energy slope at 7000–8000 cm^{-1} are due to absorptions in the vitreous silica cell.

The spectrum was recorded at five different temperatures ranging from 207 to 274 °C. The band at 14 000 cm^{-1} is clearly due to the d → d transition $^2T_{2g} \rightarrow {}^2E_g$ in an octahedral symmetry, similar to the corresponding band in the solid state. The only significant difference is the broadening and red shift of the low-energy shoulder which becomes more pronounced with increasing temperature. The increased splitting is due to a temperature-induced lowering of the octahedral symmetry, and the low-energy broadening may be attributed to vibrational effects.

Gruen and McBeth[11] measured the spectra of $TiCl_3$ in LiCl–KCl eutectic between 400 and 1000 °C and attributed the low-temperature spectrum to the $^2T_{2g} \rightarrow {}^2E_g$ transition in an octahedral field. These particular spectra will be discussed in a later section, but is of interest here to point out the similarity between their spectrum in a highly ionic liquid and ours in the covalent $AlCl_3$ melt. Both yield the same double peak with comparable molar absorption values, only shifted 1000 cm^{-1} toward lower energy in the LiCl–KCl eutectic system.

Also the position of the band at 20 500 cm^{-1} is nearly similar in both the liquid and the solid, although it is much less intense in the fused mixture. The most plausible interpretation is also the same; a 3d → 4s excitation in Ti^{3+} which is becoming strongly suppressed in the liquid state compared to the solid.

The addition of $TiCl_4$ to a dilute solution of $TiCl_3$ in $AlCl_3$(l) at 200 °C does not have any influence on the spectrum other than superimposing the steep absorption edge at 18 000–20 000 cm^{-1}, thus totally obscuring any bands at higher energies.

The absorption of $TiCl_3$ in $AlCl_3$(l) follows Beer's law, and the peak values at 13 800 and 10 700 cm^{-1} (converted to molar absorptivities) are virtually temperature independent. Corrections has been made for density variations with temperature and for the amount of $AlCl_3$ in the vapor phase.[12]

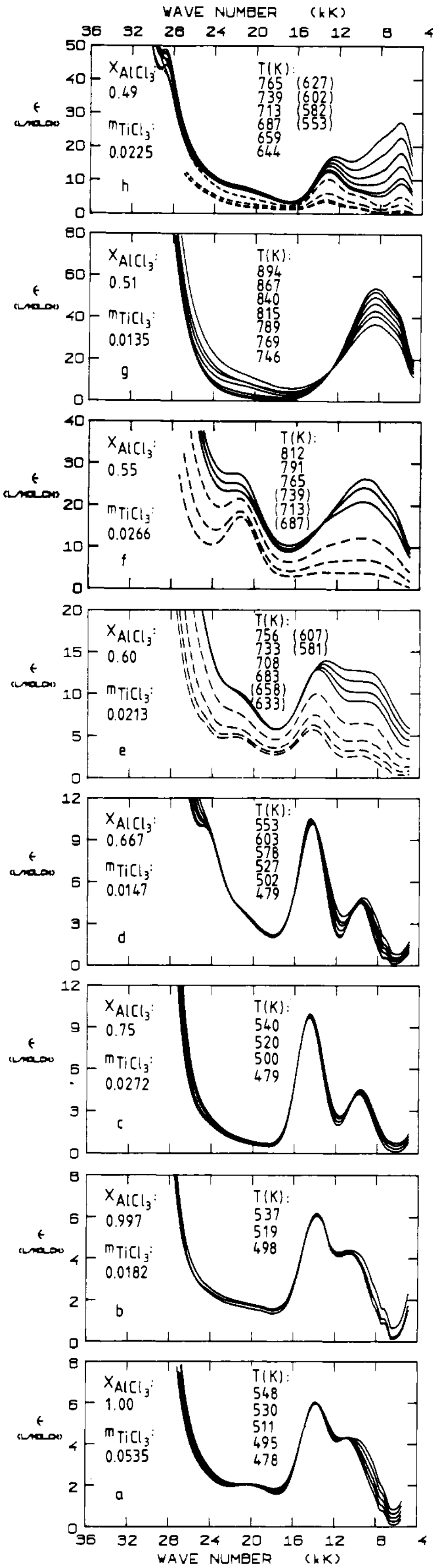

Figure 2. Spectra of $TiCl_3$ in molten KCl–$AlCl_3$ mixtures. For each set of curves the temperatures (in K), molal solute concentration (i.e., moles of $TiCl_3$ in 1000 g of solvent), and solvent composition (as mole fraction of $AlCl_3$) are given. Where it may clarify the spectral changes vs. temperature, spectra of saturated $TiCl_3$ solutions (stipulated curves which do not agree with the molar absorptivity scale) are drawn. Corresponding temperatures are given in parentheses.

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(11) D. M. Gruen and R. L. McBeth, *Pure Appl. Chem.*, **6**, 23 (1963).
(12) L. A. King and D. W. Seegmiller, *J. Chem. Eng. Data*, **16**, 23 (1971).

$TiCl_3$ in KCl–$AlCl_3$ Liquid Mixtures. Fused mixtures of $AlCl_3$ with alkali chlorides display a Lewis acid–base behavior ranging from the strong acid $AlCl_3$ to strong basic melts when the molar fraction of alkali chloride exceeds 0.50.[13]

Figure 2 shows the spectra at a number of compositions in the KCl–$AlCl_3$ system, ranging from pure $AlCl_3$ solvent in Figure 2a to $X_{AlCl_3} = 0.49$ in Figure 2h. The spectra of $TiCl_3$ for each composition are given at various temperatures.

It appears from the figures that the coordination of Ti^{3+} in these melts changes a number of times as the composition and thus the acidity is changed. The acid–base equilibria of this[13] and similar systems can be rationalized by the equilibria in eq 3 and 4. At high $AlCl_3$ content it is also probable that

$$2AlCl_4^- = Al_2Cl_7^- + Cl^- \tag{3}$$

$$Al_2Cl_7^- = Al_2Cl_6 + Cl^- \tag{4}$$

the trimer ion exists (eq 5).

$$3Al_2Cl_7^- = 2Al_3Cl_{10}^- + Cl^- \tag{5}$$

The spectra recorded at the composition $X_{AlCl_3} = 0.997$ are given in Figure 2b for the three temperatures ranging from 225 to 264 °C. Phase diagrams of the KCl–$AlCl_3$ system show that there exist a liquid immiscibility gap in the region $0.818 \le X_{AlCl_3} \le 0.996$.[14] These compositions need not be very accurate as we found that the KCl added did not totally dissolve in the fused $AlCl_3$ but did form an immiscible liquid droplet at the bottom of the cell. The distribution coefficient for $TiCl_3$ between the two liquid phases is not known, but any error due to a concentration enrichment in the KCl-rich phase is negligible as both the spectrum and the molar absorptivities are nearly similar to what was found for $TiCl_3$ in pure $AlCl_3$(l) (Figure 2a).

On the opposite side of the immiscibility gap (at $X_{AlCl_3} = 0.75$, Figure 2c) the spectrum still reveals nearly similar double bands, but the splitting has increased to more than 5000 cm^{-1}, and the molar absorptivity has increased from ca. 6 L $(mol{\cdot}cm)^{-1}$ to ca. 10 L $(mol{\cdot}cm)^{-1}$ for the peak at highest energy. This spectrum remains nearly unchanged up to a solvent composition of $X_{AlCl_3} = 0.667$ (Figure 2c).

The coordination of Ti^{3+} is still interpreted as being nearly octahedral, but it is not unexpected that the change in solvent species, from purely covalent Al_2Cl_6 molecules in pure $AlCl_3$(l) to a dominantly ionic melt at 75 and 66.7 mol % $AlCl_3$, will introduce elements of lower symmetry on the ligand field surrounding the central ion.

The increased splitting of the ^2E_g energy level may therefore be interpreted as a tetragonal distortion of the octahedron, resulting in a larger separation of the $^2B_{1g}$ and $^2A_{1g}$ terms. The ground term in O_h symmetry, $^2T_{2g}$, will split into $^2B_{2g}$ and a double degenerate ^2E_g term, thus giving the observed transitions $^2E_g \rightarrow {}^2A_{1g}$ at ~9700 cm^{-1} and $^2E_g \rightarrow {}^2B_{1g}$ at ~14 500 cm^{-1}. Neither the splitting nor the molar absorptivity values are very temperature dependent, as can be seen from Figure 2c,d. For $X_{AlCl_3} = 0.667$ a weak transition which is not of the d → d type is observed (Figure 2d).

More radical changes in the spectrum start at compositions with $AlCl_3$ content smaller than that corresponding to KAl_2Cl_7 ($X_{AlCl_3} < 0.667$) and proceed on to $X_{AlCl_3} = 0.51$ (Figure 2e–g).

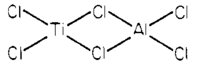
The spectral changes in this concentration range can be described broadly as follows. The "octahedral" spectrum diminishes in intensity while a broad band with much higher molar absorptivity develops at ~8500 cm^{-1}. While some of the increase in intensity with temperature can be attributed to an equilibrium shift, it is seen from Figure 2g that the molar absorptivity increases with temperature contrary to what was observed for the octahedral spectra.

The fully developed new peak for $X_{AlCl_3} = 0.51$ with a maximum at 8400 cm^{-1} and $\epsilon = 54$ L/(mol·cm) at 621 °C and with a shoulder at ~6000 cm^{-1} may be compared with the spectra of Ti_2Cl_6(g) and $TiAlCl_6$(g) which have the following spectral characteristics.[1] Ti_2Cl_6(g): peak at 10 500 cm^{-1}; $\epsilon = 74$ ($\epsilon = 37$ per g-atom of Ti); 550 °C < t < 700 °C. $TiAlCl_6$(g): peak at 10 900 cm^{-1}; shoulder at 9000 cm^{-1}; $\epsilon = 20$; $t = 600$ °C.

For stoichiometric reasons Ti^{3+} is expected to be four-coordinated in both Ti_2Cl_6 and $TiAlCl_6$. Although the spectra also are rather similar, there are notable differences both in molar absorptivity and the development of shoulders demonstrating the spectral sensitivity to small distortions.

In view of the spectral sensitivity to small coordination distortions, the low-energy shift of Ti^{3+} dissolved in 51 mol % $AlCl_3$ relative to the octahedral spectrum, the high molar absorptivity, and the similarity of this spectrum to that of Ti_2Cl_6(g), it is considered highly likely that the Ti^{3+} spectra for 51 mol % $AlCl_3$ (Figure 2g) represents a tetrahedral-like coordination. The double band is then due to the $^2E \rightarrow {}^2T_2$ transition in Ti^{3+}, with a splitting of the excited level caused by a Jahn-Teller effect or some minor distortions of the tetrahedral symmetry.

The light-absorbing species cannot be $TiCl_4^-$ ions as this would not explain the decrease in solubility of $TiCl_3$ with decreasing $AlCl_3$ content and hence increasing Cl^- activity. A species like $[Cl_3TiAlCl_4]^-$ is ruled out for the same reason. Neither does a molecule like



appear likely as the spectrum then should be more similar to that of $TiAlCl_6$(g).[1]

The most probable explanation of the spectral changes between $0.67 < X_{AlCl_3} < 0.51$ is an exchange of $Al_2Cl_7^-$ ligands with $AlCl_4^-$ parallel to what was earlier suggested for $CoCl_2$ in the same system[15] (eq 6). The tetrahedral Cl^- cage created

$$Ti(oct)(Al_2Cl_7)_m^{3-m} + nAlCl_4^- = Ti(tetr)(AlCl_4)_n^{3-m} + mAl_2Cl_7^- \tag{6}$$

by $AlCl_4^-$ relative to the octahedral coordination by $Al_2Cl_7^-$ may be understood from the Ti^{3+}–Al^{3+} repulsion which will be greater for the $AlCl_4^-$ ions than for the longer $Al_2Cl_7^-$ ion. $AlCl_4^-$ ligands may hence give a reduced coordination number due to this repulsion. Such a ligand-exchange reaction makes it also plausible that the spectral changes cannot be considered a simple two-species equilibrium as is demonstrated by the spectra for $X_{AlCl_3} = 0.55$ (Figure 2f) which is not a simple superposition of the two end spectra for $X_{AlCl_3} = 0.667$ and 0.51. This spectrum contains a pronounced peak at 21 500 cm^{-1} not seen in the end spectra. The origin of this peak is not clear, but it is not due to a d → d transition in Ti^{3+} and probably arises from an excitation within the d and s levels of Ti^{3+}.

A dramatic change in coordination is observed when the solvent melt becomes basic at compositions $X_{AlCl_3} < 0.50$. The spectrum given in Figure 2h has been obtained in a 49 mol % $AlCl_3$–51 mol % KCl melt at temperatures ranging from 280 to 492 °C. Only the fully drawn curves in Figure 2h have any relevance to the molar absorptivity scale, as $TiCl_3$ was not fully dissolved at the lowest temperatures.

The low-temperature spectrum has been fully reversed to an octahedral coordination with a major peak at ~13 000 cm^{-1}

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(13) E. Rytter, H. A. Øye, S. J. Cyvin, B. N. Cyvin, and P. Klaeboe, *J. Inorg. Nucl. Chem.*, **35**, 1185 (1973).

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

(15) H. A. Øye and D. M. Gruen, *Inorg. Chem.*, **4**, 1173 (1965).

and a shoulder at ~10 000 cm^{-1}, nearly similar to what we found for $TiCl_3$ in a pure $AlCl_3(l)$ solvent (Figure 2a).

As the temperature is increased, a band at ~6000 cm^{-1} increases in intensity. This band has a complex structure, with at least one, possibly two, shoulders on the high-energy slope. The apparent intensity increase of the ~13 000 cm^{-1} transition is probably due to the superimposing of the high-energy slope of the new band, which appears to cover the wavenumbers from <4000 to 14 000 cm^{-1}.

The similarity of the spectral changes with temperature, with the spectral change observed when the composition is varied between $0.51 < X_{AlCl_3} < 0.67$, suggests again an octahedral–tetrahedral equilibrium. While, however, the previous changes were attributed to an exchange of $Al_2Cl_7^-$ with $AlCl_4^-$ ligand, the present solvent contains free Cl^- ions, and the equilibrium should be formulated as

$$TiCl_6^{3-}(oct) \underset{\text{low temp}}{\overset{\text{high temp}}{\rightleftarrows}} TiCl_4^-(tetr) + 2Cl^- \qquad (7)$$

This equilibrium is previously proposed by Gruen and McBeth[11] for $TiCl_3$ in LiCl–KCl(l) eutectic and in $GaAlCl_4(l)$. The spectra at the highest temperatures in Figure 2h are remarkably similar to what Gruen and McBeth obtained in $CsGaCl_4(l)$ at 600 °C. It is also interesting to note that, when they heated their solvent to 900 °C, they obtained a spectrum attributed to tetrahedral symmetry which is very similar to our spectra for $X_{AlCl_3} = 0.51$ (Figure 2g).

We therefore conclude that the peak at ~6000 cm^{-1} and the corresponding high-energy shoulder is due to a $^2E \rightarrow {}^2T_2$ transition in tetrahedrally coordinated Ti^{3+}. The splitting is due to elements of lower symmetry which tend to be lifted by increasing temperature.[11]

$TiCl_2$ in $AlCl_3(l)$. The characteristic spectrum of Ti^{2+} in liquid $AlCl_3$[16,17] is also found in matrixes such as $AlCl_3(s)$[17] and NaCl(s)[18] as well as in gaseous $AlCl_3$.[1] It is characterized by two absorption bands (Figure 3a), one at 14 600 cm^{-1} and the other at 7550 cm^{-1} (201 °C). These spectra have been assigned to octahedrally coordinated Ti^{2+} with the bands attributed to the transition $^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)$ at 14 600 cm^{-1} and $^3T_{1g}(F) \rightarrow {}^3T_{2g}(F)$ at 7550 cm^{-1}. As titanium(II) has a d^2 electronic structure, a third spin-allowed transition, $^3T_{1g}(F) \rightarrow {}^2A_{2g}(F)$, will also be expected. The unability to detect this band has been explained by its probable closeness to the more intense $^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)$ transition[16] and by the transition being largely a two-electron transition ($t_2^2 \rightarrow e^2$) and, hence, very weak.[17]

The molar absorptivities of the two bands are nearly temperature independent, and the wavenumber shift is only 150 cm^{-1} toward lower energy in a temperature span of 63 °C (Figure 3a). The molar absorptivity of Ti^{2+} in $AlCl_3(l)$ follows Beer's law within the investigated concentration range (0.0051–0.3583 M). The molar absorptivity of 18.5 L/(mol·cm) found for the transition at 14 600 cm^{-1} (200 °C) is somewhat lower than the value of 29.4 L/(mol·cm) previously reported by Øye and Gruen[16] but close to the value of Brynestad et al.[17] of 21.0 L/(mol·cm) after their reported value of 52 L/(mol·cm) had to be corrected for a calculational error.[1,19]

$TiCl_2$ is stable in pure $AlCl_3(l)$, and no significant disproportionation was observed within the studied temperature range and over a 24-h period at 200 °C.

$TiCl_2$ in KCl–$AlCl_3$ Liquid Mixtures. The changes in acidity in the KCl–$AlCl_3$ solvent have remarkably little influence on

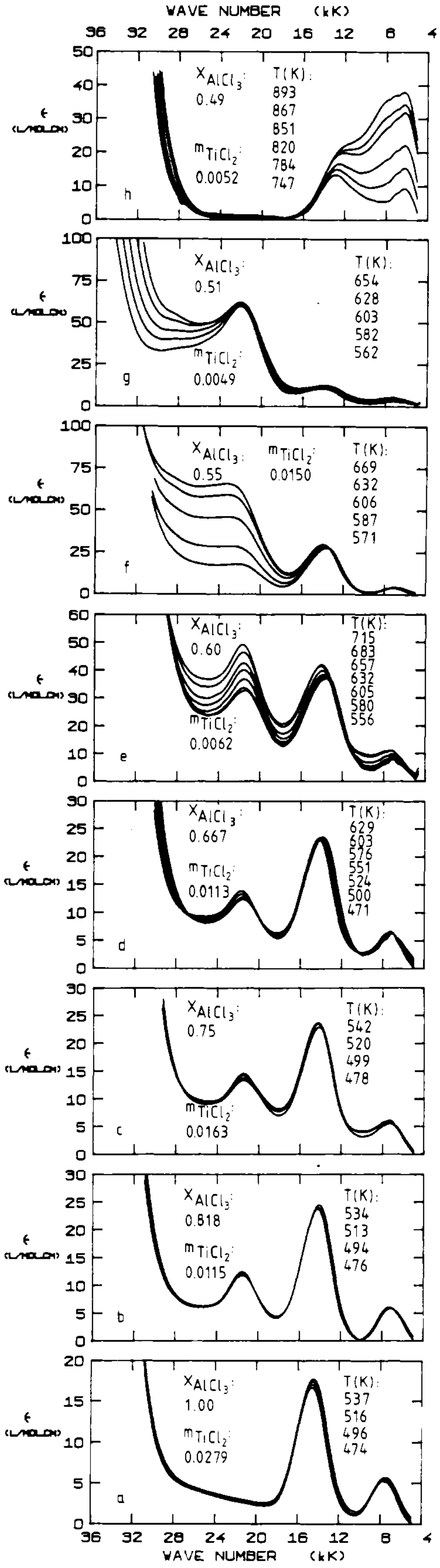

Figure 3. Spectra of $TiCl_2$ in molten KCl–$AlCl_3$ solvents. For each set of spectra the temperatures (in K), molal solute concentration (i.e., moles of $TiCl_2$ in 1000 g of solvent), and solvent composition (as mole fraction of $AlCl_3$) are given.

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(16) H. A. Øye and D. M. Gruen, *Inorg. Chem.*, 3, 836 (1964).
(17) J. Brynestad, S. von Winbush, H. L. Yakel, and G. P. Smith, *Inorg. Nucl. Chem. Lett.*, 6, 889 (1970).
(18) W. E. Smith, *J. Chem. Soc., Chem. Commun.*, 1121 (1972).
(19) J. Brynestad, private communication.

the recorded titanium(II) spectra compared to the changes observed for titanium in the trivalent state in the same solvent. The spectra at composition $X_{AlCl_3} = 0.818$ (Figure 3b) yields three distinct Gaussian-shaped absorption bands at 7250, 14 250, and 21 550 cm^{-1}, respectively (203 °C). This is exactly the type of spectrum we would expect for Ti^{2+} in an octahedral field, having three spin-allowed transitions. Two of these, at 7250 and 14 250 cm^{-1}, appear similar to what was found in pure $AlCl_3$(l) solvent (Figure 3a), yielding the same shape and relative intensity and nearly the same molar absorptivity, and the shift in transition energies is only about 300 cm^{-1} toward red. This small shift is only attributed to the solvent effect.

We therefore conclude that Ti^{2+} remains in an octahedral coordination when the solvent acidity is changed by adding the Lewis base KCl to the system. The ligand field strength changes, however, as the solvent species changes from the pure covalent Al_2Cl_6 molecules in $AlCl_3$(l) to a dominantly ionic melt containing $Al_2Cl_7^-$, $AlCl_4^-$, and K^+ ions as KCl is added. The lowering of the field strength moves the transitions closer towards the weak-field approximation; hence the predicted $t_2^2 \rightarrow e^2$ transition which was expected to be largely a weak two-electron transition[17] no longer is important, and we find the expected ${}^3T_{1g}(F) \rightarrow {}^3A_{2g}(F)$ band at 21 550 cm^{-1}. The two other bands are assigned to the ${}^3T_{1g}(F) \rightarrow {}^3T_{2g}(F)$ and the ${}^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)$ transitions at 7250 and 14 250 cm^{-1}, respectively.

Figure 3c,d shows that the octahedral coordination of Ti^{2+} is very stable as the solvent acidity is further decreased by KCl additions. No significant changes in the spectra are encountered until compositions with $X_{AlCl_3} \leq 0.60$ are reached (Figure 3e). The basic spectrum is still the same with three well-defined bands at the same transition energies as previously found in more acidic melts, but the intensity as a function of temperature is no longer constant. Further decreases in acidity enhances the high-energy, temperature-dependent shoulder (Figure 3f) until it becomes a distinct band at composition $X_{AlCl_3} = 0.51$ (Figure 3g). The two bands at lowest energy attributed to transitions in octahedrally coordinated Ti^{2+} can still readily be distinguished although they no longer dominate the spectrum due to the relatively intense transition at 22 050 cm^{-1}.

We do not believe that this band is due to electronic transitions within the d orbitals in Ti^{2+} but rather attributed to a mixed-valence charge transfer involving the two oxidation states Ti^{2+} and Ti^{3+}. Oxidation of $TiCl_2$ in the melt was observed at compositions $X_{AlCl_3} \leq 0.60$. Although the degree of oxidation is very low since no trace of the known Ti^{3+} spectrum can be seen on Figure 3e–g, $TiCl_3$ must nevertheless be present since a thin film of metal was deposited on the inner walls of the spectrometric cell. This film acted as a neutral density screen which increased the background level of the spectra. Correction for this has been made on the figures presented here.

Charge-transfer spectra in mixed-valence systems have been reported in chlorocuprates[20,21] and in hexachloroantimonates.[22] Mixtures which contain the same metal in two different oxidation states have often been found to exhibit absorption bands not found in any one of the pure oxidation states alone. We therefore correlate the occurrence of the high-energy band in spectra of Ti^{2+} in melts with $0.51 \leq X_{AlCl_3} \leq 0.60$ to a mixed-valence charge-transfer transition involving Ti^{2+} and Ti^{3+}.

The intensity of the band is about 2 orders of magnitude lower than what might be expected for allowed charge-transfer transitions between metal and ligands, but the low intensity is expected since the only increase in intensity will take place through electron delocalization from the metal to the ligand orbitals, the latter forming a pathway from a Ti^{2+} complex to neighboring Ti^{3+} complex, similar to what was proposed in Cu^+/Cu^{2+} mixed-valence charge transfers.[20] The low concentration of Ti^{3+} must also be taken into consideration in order to explain the low intensity.

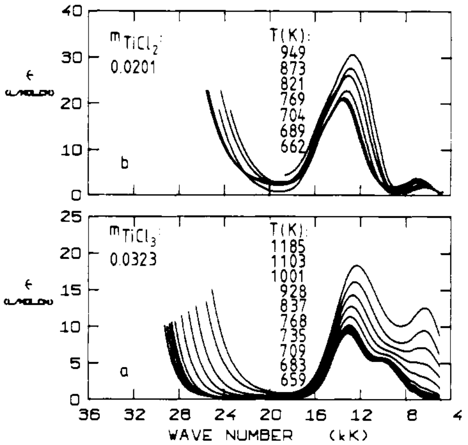

Figure 4. Spectra of titanium chlorides in the molten LiCl–KCl eutectic mixture. Temperatures (in K) and molal solute concentration (i.e., moles of $TiCl_x$ in 1000 g of solvent) are given for each set of spectra: (a) $TiCl_3$ in LiCl–KCl eutectic; (b) $TiCl_2$ in LiCl–KCl eutectic.

A basic chloroaluminate melt ($X_{AlCl_3} = 0.49$, Figure 3h) gives a spectrum totally different from any found in an acidic melt when $TiCl_2$ was added. In fact, we no longer find any Ti^{2+} in the melt as it quantitatively reacts to form $TiCl_3$ and a metal precipitate. Hence the spectrum is similar to that found for Ti^{3+} in the same solvent (Figure 2h) displaying the coordination equilibrium between octahedrally and tetrahedrally coordinated Ti^{3+} (eq 7).

$TiCl_3$ and $TiCl_2$ in LiCl–KCl(l) Eutectic. With the exception of a minor red shift, the spectrum of $TiCl_3$ dissolved in the LiCl–KCl(l) eutectic at 386 °C (Figure 4a) is like the spectrum obtained in pure $AlCl_3$(l) (Figure 1b), showing octahedrally coordinated $TiCl_6^{3-}$ species. Further increase in temperature leads to the appearance of a new band at about 6400 cm^{-1}. The new band is attributed to the tetrahedral $TiCl_4^-$ species, reflecting the octahedral–tetrahedral equilibrium favoring tetrahedrally coordinated Ti^{3+} at elevated temperatures. These spectra are identical with those presented by Gruen and McBeth,[11] and the similarity to the spectra of $TiCl_3$ in the basic KCl–$AlCl_3$ solvent (Figure 2h) is also evident.

$TiCl_2$ dissolved in the same solvent gives three bands (Figure 4b) which are in accordance with the number of spin-allowed transitions in the d^2 electronic configuration. These are found at 6950 and 13 550 cm^{-1} and a shoulder is found at about 15 000 cm^{-1} (389 °C). No new bands appear at elevated temperatures; the bands are only shifted somewhat toward lower energies.

On the basis of the energy level correlation diagrams for d^2 in cubic fields,[23] a tetrahedral coordination of Ti^{2+} must be disregarded. The observed transition can, however, be readily interpreted as due to an octahedral arrangement of the ligands. The ligand field is considerably weakened compared to what was found in $AlCl_3$(l) and $AlCl_3$–KCl(l) solvents, probably due to the polarizing effect of the Li^+ ion. The main result of this is that the ${}^3T_{1g}(F) \rightarrow {}^3A_{2g}(F)$ transition has decreased considerably in energy relative to the ${}^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)$ transition, making them fall very close to each other.

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(20) P. Day and D. W. Smith, *J. Chem. Soc. A*, 1045 (1967).
(21) D. Culpin, P. Day, P. R. Edwards, and R. J. P. Williams, *J. Chem. Soc. A*, 1838 (1968).
(22) L. Atkinson and P. Day, *J. Chem. Soc. A*, 2433 (1967).
(23) G. P. Smith in "Molten Salts Chemistry", M. Blander, Ed., Interscience, New York, 1964.

This is similar to the interpretation Øye and Gruen[16] made for Ti^{2+} in pure $AlCl_3(l)$.

We do indeed find these two transitions close as the former appears as a shoulder on the high-energy side of the more intense $^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)$ band (Figure 4b). In addition to the pronounced shift of the high-energy transition, a small general decrease in transition energies for the other bands is also found in accordance with the weakening of the field strength.

$TiCl_2$ disproportionated to a certain degree to $TiCl_3$ and Ti metal (eq 8) as evidenced by the formation of a metal film

$$3TiCl_2 = Ti(s) + 2TiCl_3 \qquad (8)$$

on the inner cell walls. The total amount of disproportionated $TiCl_2$ must be very small, however, as no spectroscopic evidence of $TiCl_3$ can be seen (Figure 4b). This confirms the observations of Kreye and Kellogg,[24] who found that divalent titanium is the predominant species in equilibrium with Ti metal in a NaCl–KCl melt.

Stability of Di- and Trivalent Titanium in Chloride Melts. The stability of titanium chlorides can be summarized as follows: (a) $TiCl_3$ is stable in alkali chloride (LiCl–KCl) as well as in chloroaluminate melts ($AlCl_3$–KCl). (b) $TiCl_2$ disproportionates slightly in alkali chloride melts; the equilibrium is shifted strongly toward the dichloride. (c) $TiCl_2$ is stable in strongly acidic chloroaluminate melts ($X_{AlCl_3} > 0.60$) but is slightly unstable in chloroaluminate melts of intermediate acidity ($0.50 < X_{AlCl_3} < 0.60$), and is completely unstable in basic chloroaluminate melts ($X_{AlCl_3} = 0.49$).

While the slight unstability of $TiCl_2$ in alkali chloride melts most probably is due to a simple disproportionation equilibrium (eq 8) the unstability of $TiCl_2$ in the basic chloroaluminate, which also has a high chloride activity, is due to oxidation by $AlCl_3$. The following experiment was carried out at 500 °C in a 49 mol % $AlCl_3$–51 mol % KCl melt to show that this indeed was the case. By adding Ti(s) to the solvent, the spectrum of Ti^{3+} was observed. The unstability of $TiCl_2$ is hence due to reaction 9 and not to the disproportionation

$$3TiCl_2 + AlCl_3 = 3TiCl_3 + Al \qquad (9)$$

equilibrium (8).

Since $AlCl_3$ appears on the left side of eq 9, it may appear surprising that decreased acidity (lower $AlCl_3$ activity) in acidic melts leads to a slight oxidation of $TiCl_2$ and that $TiCl_2$ is completely oxidized in basic chloroaluminate melts. It is, however, to be noted that the relative stability of $TiCl_2$ vs. $TiCl_3$ is nearly at a balance point, illustrated by the equilibrium constants[25] in eq 10 and 11.

$$TiCl_2(s) = {}^2/_3TiCl_3(s) + {}^1/_3Ti(s) \qquad (10)$$

$$TiCl_2(s) + {}^1/_3AlCl_3(l) = TiCl_3(s) + {}^1/_3Al(s) \qquad (11)$$

	log *K*		
	400 K	600 K	800 K
eq 10	−3.637	−2.132	−1.383
eq 11	−2.231	−1.481	−1.145

Hence some differences due to complex formation may reverse one of the above equilibria.

When an explanation is sought as to why $TiCl_2$ is oxidized in basic and moderately acidic melts, it is important to be aware of that these melts are quite different. In acidic melts the metal ion will coordinate to $AlCl_3$, $Al_2Cl_7^-$, or $AlCl_4^-$ while Cl^- probably is the sole ligand in basic melts.

The unstability of $TiCl_2$ with decreasing acidity in acidic melts will first be examined. From gas complexation work[1,3] it is demonstrated that divalent chlorides are more basic than trivalent chlorides in the sense that they are able to bind a higher number of acidic $AlCl_3$ molecules. In 1 atm $Al_2Cl_6(g)$ the dominant gas molecules are $V^{II}Al_3Cl_{11}$ vs. $V^{III}AlCl_6$ and $V^{III}Al_2Cl_9$ and $Ti^{II}Al_3Cl_{11}$ vs. $Ti^{III}AlCl_6$. If one assumes that titanium might form neutral complexes in acidic chloroaluminate melts,[26] the redox reaction is most straightforwardly described by either eq 12 or 13.

$$3TiAl_3Cl_{11}(l) = 3TiAlCl_6(l) + Al(s) + 5AlCl_3(l) \qquad (12)$$

$$3TiAl_2Cl_8(l) = 3TiAlCl_6(l) + Al(s) + 2AlCl_3(l) \qquad (13)$$

The equilibria are formulated with reference to which molecule are found in the $Al_2Cl_6(g)$ atmosphere, and they both will predict octahedral coordination of Ti(II) and tetrahedral coordination of Ti(III) in agreement with observation in the concentration range $0.50 < X_{AlCl_3} < 0.60$ when $TiCl_2$ is oxidized. Since $AlCl_3$ now appears on the right side of the equation, the decreased stability of divalent titanium with decreased $AlCl_3$ activity is explained as well.

In basic melts Ti(II) and Ti(III) are found to be octahedrally coordinated, and the equilibria to be considered are (LiCl–KCl)

$$TiCl_6^{4-} = {}^2/_3TiCl_6^{3-} + 2Cl^- + {}^1/_3Ti(s) \qquad (14)$$

and (49 mol % $AlCl_3$–51 mol % KCl)

$$TiCl_6^{4-} + {}^1/_3AlCl_4^- = TiCl_6^{3-} + {}^4/_3Cl^- + {}^1/_3Al(s) \qquad (15)$$

In spite of the low activity of $AlCl_3$ in basic chloroaluminates eq 15 is shifted to the right while eq 14 is not. By comparison of the two equilibria above, the oxidation of Ti^{2+} is understood by a combination of the oxidation power of $AlCl_4^-$ and the greater stability of $TiCl_6^{3-}$ as compared to $TiCl_6^{4-}$ as an extra $^1/_3$ mol of $TiCl_6^{3-}$ is formed by the last reaction. Contrary to what is expected in acidic melts, it is predicted that decreased activity of $AlCl_3$ will stabilize divalent titanium.

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Registry No. $TiCl_3$, 7705-07-9; $TiCl_2$, 10049-06-6; $AlCl_3$, 7446-70-0; KCl, 7447-40-7; LiCl, 7447-41-8; $TiCl_4$, 7550-45-0.

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[24] W. C. Kreye and H. H. Kellogg, *J. Electrochem. Soc.*, **104**, 504 (1957).

[25] D. R. Stull and H. Prophet, "JANAF Thermochemical Tables", *Natl. Stand. Ref. Data Ser.* (*U.S. Natl. Bur. Stand.*), **NSRDS-NBS 37** (1971).

[26] This assumption is somewhat speculative but not unlikely in view of the presence of neutral Al_2Cl_6 in these melts.[13]