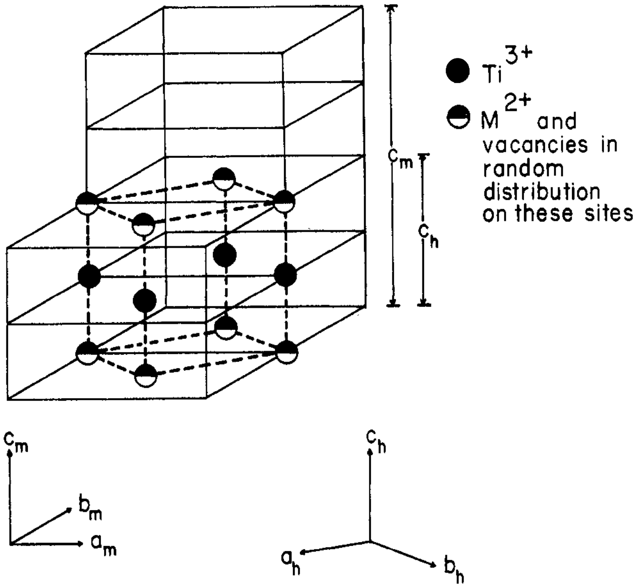

Figure 3.—Relationship between the ordered and disordered defect NiAs structures.

lationship between the dimensions of the monoclinic cell and the hexagonal cell associated with it is apparent from Figure 3, namely, $a_m \simeq a_h\sqrt{3}$, $b_m \simeq a_h$, $c_m \simeq 2c_h$, $\beta \simeq 90°$. The hexagonal cell associated with monoclinic $NiTi_2Se_4$, Table I, would have $a = 3.568$ A and $c_h = 5.90$ A. Accurate lattice parameters found for $Ni_{0.8}Ti_{2.13}Se_4$ and given above are evidence of the change in lattice parameters associated with changes in stoichiometry.

High stability of the ordered monoclinic structure for the compounds MTi_2X_4 (M = Fe, Co, Ni; X = S, Se) is shown by the absence of a temperature-dependent order–disorder transition in these compounds. Since marked disordering occurs only when the stoichiometry departs from MTi_2X_4, this ordered structure appears to have a limited homogeneity range for these sulfides and selenides. Stoichiometric ternary transition metal chalcogenides MTi_2X_4 with the trigonal structure could not be prepared under the conditions described in this paper. However, their existence cannot be totally excluded.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
MICHIGAN STATE UNIVERSITY, EAST LANSING, MICHIGAN 48823

Titanium(III) Chloro Complexes Containing Methanol, Methoxide Ion, or Acetonitrile

BY W. GIGGENBACH AND C. H. BRUBAKER, JR.

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A series of compounds has been prepared from $TiCl_3$ solutions in methanol and acetonitrile. The solutions were acidic with HCl, neutral, or basic with methoxide ion. All but one of the compounds isolated from acidic or neutral media appear to be octahedral and have near the spin-only magnetic moments. Basic compounds and species in basic solutions appear to have mostly tetrahedral Ti(III) and some contain polymeric, diamagnetic species. Electronic and infrared spectra and magnetic susceptibilities have been measured. Some properties and reactions of the compounds are described. Among the acidic compounds is a yellow, crystalline product, $(C_5H_6N)_4HTiCl_8$, isolated from acetonitrile, which had been saturated with pyridinium chloride and HCl. The compound does not appear to be a double salt and is *not* a mixture of C_5H_6NCl and $(C_5H_6N)_3TiCl_6$.

Introduction

Recent interest in this laboratory has centered on the preparation of d^1 transition element alkoxides and complexes containing alkoxide groups as ligands.[1–3] It was decided that titanium(III) alkoxides, alkoxide-containing complexes, and alcoholates might also be of interest because one could anticipate tetrahedral, octahedral, and tetragonal complexes, depending on the ligands which were used.

Schläfer and Götz have prepared a number of alcoholates of titanium trichloride and tribromide and have measured the magnetic moments of the compounds.[4] Hartmann, Schläfer, and Hansen[5] have examined solutions of Ti(III) in alcohols and measured spectra of various species formed in the solutions. Adams, *et al.*,[6] have prepared the titanium(III) methoxide.

In this study we have endeavored to prepare a variety of complex compounds of Ti(III) from acidic (with

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[1] R. A. D. Wentworth and C. H. Brubaker, Jr., *Inorg. Chem.*, **3**, 47 (1964).

[2] P. G. Rasmussen, H. A. Kuska, and C. H. Brubaker, Jr., *ibid.*, **4**, 1351 (1965).

[3] D. A. McClung, L. R. Dalton, and C. H. Brubaker, Jr., *ibid.*, **5**, 1985 (1966).

[4] H. L. Schläfer and R. Götz, *Z. Anorg. Allgem. Chem.*, **328**, 1 (1964); *Z. Physik. Chem.* (Leipzig), **41**, 97 (1964).

[5] H. Hartmann, H. L. Schläfer, and K. H. Hansen, *Z. Anorg. Allgem. Chem.*, **289**, 40 (1957); **284**, 153 (1956).

[6] R. W. Adams, E. Bishop, R. L. Martin, and G. Winter, *Australian J. Chem.*, **19**, 207 (1966).

HCl), basic, and neutral solutions in anhydrous methanol or acetonitrile.

Experimental Section

Materials.—Fisher Certified ACS methanol was dried by distillation in the presence of magnesium and stored under dry nitrogen. Reagent grade acetonitrile was distilled from P_2O_5 and was stored under dry nitrogen. Pyridine and ether were reagent grade. Ether was stored over sodium and both were kept under nitrogen and used without further purification. Anhydrous gaseous HCl was used directly from the cylinder and anhydrous $TiCl_3$ was obtained from K & K Laboratories.

$TiCl_3(CH_3OH)_4$.—$TiCl_3$ (7.7 g, 0.05 mole) was added to 25 ml of anhydrous ether and the suspension was saturated with anhydrous HCl. Then 25 ml of methanol was added. After the vigorous reaction subsided, the mixture was again saturated with HCl which was allowed to continue bubbling through the solution while 100 ml of ether was slowly added. Blue crystals, 12.8 g, were formed and were filtered and dried *in vacuo*.

Anal. Calcd for $TiCl_3C_4H_{16}O_4$: Ti, 16.97; Cl, 37.69; CH_3OH, 45.55; C, 17.00; H, 5.67. Found: Ti, 16.96; Cl, 36.96; CH_3OH, 45.54; C, 16.76; H, 5.53.

$TiCl_3(CH_3OH)_5$.—$TiCl_3$ (7.7 g) was added to 25 ml of anhydrous ether, and 20 ml of anhydrous methanol was added with stirring. A blue solution formed, 150 ml of ether was added, and pale blue crystals separated and were washed with ether and dried *in vacuo*. A 14.6-g sample of dry product was obtained.

Anal. Calcd for $TiCl_3C_5H_{20}O_5$: Ti, 15.24; Cl, 33.85; CH_3OH, 50.94; C, 19.09; H, 6.36. Found: Ti, 15.18; Cl, 33.64; CH_3OH, 51.24; C, 18.70; H, 6.60.

$(C_5H_6N)_2TiCl_5(CH_3OH)_2$.—$TiCl_3$ (7.7 g) was added to a solution of 16 g of pyridine in 50 ml of methanol saturated with HCl. The solution was stirred for 2 hr and 100 ml of ether was added slowly and a green compound precipitated after the solution was saturated again with HCl. The compound was impure and was recrystallized from methanol and reprecipitated with the aid of ether.

Anal. Calcd for $TiCl_5C_{12}H_{20}O_2N_2$: Ti, 10.66; Cl, 39.47; C, 32.06; H, 4.45; N, 6.23. Found: Ti, (by Ce (IV)) 10.52, (gravimetric) 10.60; Cl, 39.48; C, 31.18; H, 4.16; N, 6.20.

$(C_5H_6N)_2TiCl_5CH_3CN$.—$TiCl_3$ (7.7 g) was dissolved in 7 g of pyridine in 100 ml of acetonitrile, which was saturated with HCl. The solution was stirred and refluxed for 1 hr and yellow-green crystals separated and were filtered, washed with acetonitrile and ether, and dried *in vacuo*.

Anal. Calcd for $TiCl_5C_{12}H_{15}N_3$: Ti, 11.24; Cl, 41.60; C, 33.79; H, 3.52; N, 8.85. Found: Ti, (by Ce(IV)) 10.62, (gravimetric) 11.12; Cl, 41.07; C, 33.48; H, 3.22; N, 8.38.

$(C_5H_5N)_3TiCl_6$.—$TiCl_3$ (7.7 g) was dissolved in a solution of 12 g of pyridine in 150 ml of acetonitrile which was saturated with HCl. Orange platelets precipitated after the solution was refluxed and stirred for 3 hr and cooled. The crystals were filtered, washed with acetonitrile and ether, and dried. This compound has been prepared by Russ and Fowles from chloroform or chloroform–acetonitrile solutions.[7]

Anal. Calcd for $TiCl_6C_{15}H_{18}N_3$: Ti, 9.57; Cl, 42.49; C, 35.96; H, 3.59; N, 8 39. Found: Ti, 9.24; Cl, 40.39; C, 36.05; H, 3.79; N, 8.35.

$(C_5H_6N)_4HTiCl_8$.—$TiCl_3$ (7.7 g) was added to a boiling solution of 25 g of pyridine in 100 ml of acetonitrile, saturated with HCl. A slow stream of HCl was bubbled through the solution as the $TiCl_3$ dissolved and a yellow compound precipitated. After 3 hr of further stirring, 30 g of yellow needles was separated by filtration, washed with acetonitrile and ether, and dried. The presence of an acidic proton was verified by titration of the compound in methanol with KOH in methanol, and 1.02 equiv of KOH (compared to a $(C_5H_6N)_3TiCl_6$ "blank") was required per formula weight of the compound.

Anal. Calcd for $TiCl_8C_{20}H_{25}N_4$: Ti, 7.34; Cl, 43.46; $C_5H_6N^+$, 48.94. Found: Ti, (by Ce(IV)) 7.14, (gravimetric) 7.34; Cl, 43.39; $C_5H_6N^+$, 48.91.

Commercial C and H analyses were not satisfactory. The analyst found the compound "difficult to handle."

Reactions of Solutions of $TiCl_3$ and Alkali Methoxides in Methanol.—If a solution of $TiCl_3$ in methanol is examined spectrophotometrically, the spectrum corresponds to that obtained from the supernatant liquid in the preparation of $TiCl_3(CH_3OH)_5$ or that obtained by dissolving the compound in methanol. There is a maximum at 16.8×10^3 cm^{-1} (ϵ 4.8) and a shoulder at 15.1×10^3 cm^{-1}. The solution is blue. If $LiOCH_3$ or $NaOCH_3$ in methanol is added gradually, the color changes to green and then to yellow. When the ratio of CH_3O^- to Ti is 1.5, then there are maxima at 9.9 (ϵ 9.8) and 24.8×10^3 cm^{-1} (ϵ 95) and a compound approximating the composition $TiCl_{1.5}(OCH_3)_{1.5}(CH_3OH)_2$ can be isolated. The yellow compound is crystalline, containing 1.5 chlorides per titanium; the titanium is present as Ti(III), but analyses for C, H, and CH_3OH were not sufficiently good to warrant reporting a compound of definite composition. As more $NaOCH_3$ is added, the solution becomes brown owing to a shoulder appearing at about 17×10^3 cm^{-1}. The 9.9 and 24.8×10^3 cm^{-1} maxima are essentially unchanged. At $CH_3O^-/Ti = 2.5$ a brown solution forms, from which a yellow-brown solid can be precipitated, which is diamagnetic and very sensitive to air. Analyses show $Ti/Cl = 2/1$ but values did not conform well to any obvious formulation.

$Ti(OCH_3)_3$ can be prepared by the method of Adams, *et al.*,[6] or by adding 7.7 g of $TiCl_3$ (0.05 mole) in methanol to a solution of 1.39 g (0.20 formula weight) of lithium in methanol. A deep yellow-brown solution is formed, and, if it is diluted with 200 ml of methanol, a yellow-green product forms. The composition is approximately that of $Ti(OCH_3)_3$. It is suggested that the $Ti(OCH_3)_4^-$ ion is first formed and on dilution with methanol the trimethoxide is produced.

A solution with four $LiOCH_3$ per Ti has a weak maximum at 9.90×10^3 cm^{-1} and end absorption beginning near 20×10^3 cm^{-1}. These solutions are stable under nitrogen.

Curiously enough, if sodium methoxide is used instead of lithium, a large excess of the methoxide is required to dissolve the $Ti(OCH_3)_3$ which forms. A bright yellow solution with a maximum at 8.95×10^3 cm^{-1} is formed. These solutions decompose rapidly to give H_2 and a white solid. They can be kept for hours at 0°. In addition, while dilution of the lithium ion solutions gives the yellow-green trimethoxide, dilution of the sodium methoxide solution results in a deep red solution with a maximum at 19.8×10^3 cm^{-1}, perhaps indicating octahedral geometry. Further dilution produces an air-sensitive violet precipitate, which has a ratio of $Ti/CH_3O^- = 1/4.5$, but a satisfactory formulation was not found.

Almost identical colors and spectra are obtained if ethanol and ethoxides are used instead of methanol and methoxides.

The visible–ultraviolet spectra suggest all of the basic solutions, except the deep red mentioned above, contain tetrahedral Ti(III) species. Absorption maxima appear at frequencies which are about $^4/_9$ those of the octahedral species and have higher molar absorptivities than the solutions of octahedral species.

Thermal Decomposition of Some Ti(III) Compounds.—If $TiCl_3(CH_3OH)_5$ is heated *in vacuo* at about 100° for several hours, a pink powder results which has the composition $TiCl_{2.28}(OCH_3)_{0.74}(CH_3OH)_2$ and if $TiCl_3(CH_3OH)_4$ is so heated a red-brown solid of the composition $TiClCl_{2.39}(OCH_3)_{0.62}(CH_3OH)_2$ is found. In both cases the sum of the ligands is about five and suggests that polymeric, six-coordinate species may be present. Both solids contain trivalent titanium and are diamagnetic. Both solids dissolve in methanol to give yellow solutions, which spectrophotometry shows to contain "$TiCl_{1.5}(OCH_3)_{1.5}(CH_3OH)_2$" and $TiCl_3(CH_3OH)_5$ in the proportions indicated by the empirical formulas of the solids.

If the two original compounds are heated to 200° other solids are formed with the approximate composition $TiCl_{1.5}(OCH_3)_{1.5}$. The solutions have the same spectrum as the $TiCl_{1.5}(OCH_3)_{1.5}$-

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(7) B. T. Russ and G. W. A. Fowles, *Chem. Commun.*, 19 (1966).

$(CH_3OH)_2$. Heating to 250° gives black, diamagnetic pyrophoric powders, whose infrared spectra, however, show the same features as the other pyrolysis products. Heating *in vacuo* appears to bring about the elimination of HCl and the formation of CH_3O^- ions.

Some Reactions of the Titanium(III) Compounds.—All of the above compounds are sensitive to moisture and air. All dissolve in dilute H_2SO_4 and form the $Ti(H_2O)_6^{3+}$ ion.

Pyridinium hexachlorotitanate(III) in acetonitrile "disproportionates" to produce $(C_5H_6N)_2TiCl_5(CH_3CN)$ and $(C_5H_6N)_4HTiCl_8$ when HCl is bubbled through the solution. If the resulting yellow-green suspension of the two compounds is refluxed to drive off the HCl, the original hexachlorotitanate is regenerated.

Experimental Techniques.—Because these compounds are all air and moisture sensitive, all reactions were carried out in inert atmospheres (dry N_2) or under vacuum. Filtration and washings were all performed by application of nitrogen under pressure or by suction. All drying was *in vacuo* and compounds were stored under nitrogen or *in vacuo*.

Analyses.—Titanium was determined by two methods. Titanium(III) was determined by titration with cerium(IV) in 5% aqueous H_2SO_4. The titration was carried out under nitrogen and ferroin was used as an indicator. Ti was also determined gravimetrically as TiO_2 after it had been precipitated with cupferron in the presence of nitric acid, filtered, and ignited.

Chloride was determined by potentiometric titration with silver nitrate after the Ti(III) had been oxidized to Ti(IV) catalytically ($CuSO_4$) in 1% H_2SO_4 with oxygen in the air.

Methanol was determined in water by oxidation with excess dichromate; then the excess dichromate was treated with KI and the iodine liberated was determined with thiosulfate.

C, H, and N were determined by Spang Microanalytical Laboratories, Ann Arbor, Mich., which reported the compounds very difficult to analyze and handle.

Pyridinium ion was determined spectrophotometrically as in previous studies,[1] but with present experimental arrangements, ϵ was 5320 at 38.2×10^3 cm^{-1}.

Magnetic Moments.—Magnetic susceptibilities were determined by the Gouy method at 77, 198, and 297°K. (The temperatures are actual, measured temperatures with a thermocouple adjacent to the sample tube.) Copper sulfate and $Hg[Co(SCN)_4]$ served for calibration. All samples were measured at several field strengths to check for ferromagnetism. Corrections for diamagnetism of the ligands were made.[8]

Optical Spectra.—Visible and ultraviolet spectra were determined in methanol and acetonitrile solutions by means of a Cary Model 14 spectrophotometer. The visible–ultraviolet spectra were determined in the supernatant liquids from the preparations and/or by dissolving the compound directly in the solvent methanol or acetonitrile. Infrared spectra were determined in mineral oil mulls and KBr salt disks, and a Unicam Model SP-200 spectrophotometer was used. Far-infrared spectra were determined with mineral oil mulls and a Perkin-Elmer Model 301 spectrometer.

Results and Discussion

For each of the compounds described in the Experimental Section, visible–ultraviolet and infrared spectra were obtained. Table I gives the important spectroscopic features for the compounds. In Table II are given the magnetic moments and some related quantities for each of the paramagnetic substances. The spectra of solutions in the various stages of the "spectrophotometric titration" of $TiCl_3$ with methoxide in methanol are shown in Figure 1.

TABLE I

OPTICAL SPECTROSCOPIC FEATURES OF THE CHLOROMETHOXO, CHLOROMETHANOL, AND CHLOROACETONITRILE COMPOUNDS OF TITANIUM(III)

Compound	Electronic absorptions, maxima $\times 10^{-3}$, cm^{-1}	Infrared absorptions, maxima, cm^{-1}
$TiCl_3(CH_3OH)_4$ in CH_3OH satd with HCl	15.3, 14.4 sh	3150, 1110, 990
$TiCl_3(CH_3OH)_5$ in CH_3OH soln or supernatant liq	16.8 (ϵ 4.8), 15.1 sh	3150, 1120, 1020, 990, 455, 385, 290
$(C_5H_6N)_2TiCl_5(CH_3OH)_2$ in supernatant liq or CH_3OH satd with HCl	14.8, 14.0 sh	3080, 3150 sh, 3240 sh, 1125, 1018, and all C_5H_6NCl bands
$(C_5H_6N)_2TiCl_5CH_3CN$ in CH_3CN soln	15.2, 13.6 sh	3100, 3210, 2295, 1050, 940, and all C_5H_6NCl bands
$(C_5H_6N)_3TiCl_6$ in CH_3CN	13.7, 11.8 sh	All C_5H_6NCl bands except 1005
$(C_5H_6N)_4HTiCl_8$ in CH_3CN	13.4, 10.9 sh	3110, 3120, all C_5H_6NCl bands, 1055, 790 b

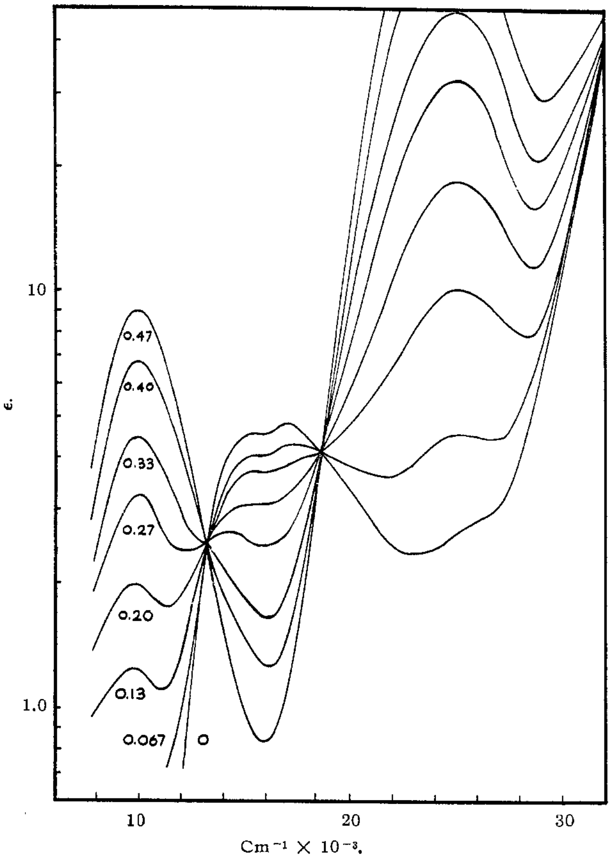

Figure 1.—The spectra of solutions of 0.05 *M* $TiCl_3$ in methanol with various amounts of $NaOCH_3$ added. The numbers under the curves are the ratios of moles of added $NaOCH_3$ to moles of chloride originally present. The ordinate is on a two-cycle log scale.

The acidic compounds, *i.e.*, those which have chloride and alcohol as ligands but not alkoxide, have electronic spectra which suggest octahedral or tetragonal geometry and have magnetic moments near the expected spin-only value.

Since the acidic compounds are probably tetragonal, it

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(8) G. Foex, "Constantes Selectionnees: Diamagnetisme et Paramagnetisme. Relaxation Paramagnetique," Masson & Cie., Paris, 1957.

TABLE II

MAGNETIC PROPERTIES OF SOME CHLOROMETHOXO, CHLOROMETHANOL, AND CHLOROACETONITRILE COMPOUNDS OF TITANIUM(III)

Compound	χ_M', cgs units $\times 10^6$	μ, BM	Temp, °K	θ, °K	k	ν	Δ, cm^{-1}
$TiCl_3(CH_3OH)_4$	1346	1.79	297	−14	0.8	>10	>1500
		1.76	195				
		1.69	78				
$TiCl_3(CH_3OH)_5$	1332	1.79	297	−12	0.8	>10	>1500
		1.74	195				
		1.68	78				
$(C_5H_6N)_2TiCl_5(CH_3OH)_2$	1289	1.76	297	−15	0.8	9	1250
		1.74	195				
		1.65	77				
$(C_5H_6N)_2TiCl_5CH_3CN$	1294	1.76	297	−32	0.8	3.8	530
		1.68	195				
		1.54	77				
$(C_5H_6N)_4HTiCl_8$	1415	1.84	297	−72	0.9–10	2.8	390
		1.73	195	(if octahedral)			
		1.48	77				
$(C_5H_6N)_3TiCl_6$	1304	1.76	297	−62	0.8–0.9	2	280
		1.67	195				
		1.43	77				

seemed worthwhile to employ the calculations outlined by Figgis[9] based on the measured magnetic susceptibilities. It is thus possible to calculate the constant k (a measure of the delocalization of the 3d^1 electron on the ligands), Δ (the separation between the orbital levels of $^2T_{2g}$ created by tetragonal distortion of the ligand field), and ν (which is Δ/λ, where λ is the spin-orbit coupling constant). These quantities are listed in Table II. Delocalization as indicated by k is highest for $(C_5H_6N)_4HTiCl_8$ and the splitting, Δ, is fairly low. (If the $TiCl_8^-$ ion is not octahedral, the treatment does not apply to it.) In the other compounds k falls and Δ increases as the compounds go from most to least acidic, *i.e.*, from most to least ligand chloride. Large negative values of the Weiss constant, θ, are observed for some of the compounds.

The formulation of $TiCl_3(CH_3OH)_5$ should probably be $[TiCl(CH_3OH)_5]Cl_2$ because replacement of two chlorides with iodide ion, by addition of NaI and precipitation of NaCl, does not change the spectrum of a solution of the compound, but addition of a third iodide produces a violet solution with absorption maxima at 15.1 and 19.8 $\times 10^3$ cm^{-1}. (Similar considerations lead to a formulation of $[TiCl_2(CH_3OH)_4]Cl$ for $TiCl_3(CH_3OH)_4$.) NaBr is not effective in replacing all of the chlorides. Sodium hydroxide in methanol produces a new species with one OH$^-$ per Ti, which may be $TiOH(CH_3OH)_5Cl_2$.

Addition of alkoxide ions to the Ti(III) produces $TiCl_{1.5}(OCH_3)_{1.5}(CH_3OH)_2$, which could be $Ti_4Cl_6(OCH_3)_6(CH_3OH)_8$, and for which a reasonable, methoxide-bridged formula can be written. The infrared spectrum indicates bridging methoxides[1,10] and the compound is diamagnetic. The spectroscopic data, Figure 1, and the formation of an impure precipitate when 2.5 g-ions of CH_3O^- per Ti have been added suggest that another polymeric species, possibly also a tetramer, exists. The impure solid shows the bridging methoxide absorptions in the infrared and absorption at 1085 cm^{-1}, which may indicate terminal methoxide. This substance is also diamagnetic. Winter has reported the existence of trimeric titanium ions, such as $[Ti(OCH_3)_3(CH_3OH)_6]^{6+}$. The Ti would, in both the suspected trimers and our proposed tetramers, be tetrahedral.[11] The $TiCl_{0.5}(OCH_3)_{2.5}(CH_3OH)_{2.5}$ could be formulated as $Ti_4Cl_2(OCH_3)_{10}(CH_3OH)_{10}$ and could be represented as a methoxo-bridged tetramer or tetrameric cation.

Perhaps the most interesting compound which has been prepared and definitely identified with respect to stoichiometry is the $(C_5H_6N)_4HTiCl_8$. The material is in the form of bright yellow crystals. The spectrum either of the supernatant liquid from the preparation or of the compound in acetonitrile saturated with pyridinium chloride and HCl has a similar shape to that of hexachlorotitanate(III), but the maximum occurs at 13.4 $\times 10^3$ cm^{-1} with a shoulder at 10.9, whereas the features in the $TiCl_6^{3-}$ appear at 13.7 and 11.8 $\times 10^3$ cm^{-1}. The infrared spectrum of the octachloro compound shows all of the expected bands of the pyridinium ion plus absorptions at 3110, 3120, 1055, and 790 cm^{-1}. The hexachlorotitanate exhibits the bands at essentially the same positions.

The extra proton is acidic as shown by titration (see above). The magnetic moment at room temperature is slightly greater than the spin-only value and slightly greater than that of the $TiCl_6^{3-}$ salt. The octachloro compound in acetonitrile is converted to the hexachlorotitanate by refluxing to drive off the excess HCl, and the "disproportionation" of $TiCl_6^{3-}$ to give $TiCl_8^{5-}$ and $(TiCl_5CH_3CN)^{2-}$ is accomplished by saturation of a solution with HCl.

The composition of the compound seems certain, but

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[9] B. N. Figgis, *Trans. Faraday Soc.*, **157**, 198 (1961).

[10] C. G. Barraclough, D. C. Bradley, J. Lewis, and I. M. Thomas, *J. Chem. Soc.*, 2601 (1961).

[11] G. Winter, *Inorg. Nucl. Chem. Letters*, **2**, 161 (1966).

one hesitates to postulate a structure from the evidence available. It may be simply a double salt, but the spectra suggest that this is not the case. It is hoped that suitable crystals can be obtained for X-ray crystallographic determination of the structure. The products from different preparations are closely reproducible.

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CONTRIBUTION FROM THE RADIOCHEMISTRY DEPARTMENT, SOREQ NUCLEAR RESEARCH CENTRE,
ISRAEL ATOMIC ENERGY COMMISSION, YAVNE, ISRAEL

Solvent Extraction from Molten Salts. V.[1] Zinc(II) Chloride, Bromide, and Iodide

BY M. ZANGEN

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The distribution ratio *D* of zinc chloride, bromide, and iodide between a eutectic mixture of molten $LiNO_3$ and KNO_3 and a eutectic mixture of polyphenyls was determined radiometrically. Addition of small amounts of the corresponding potassium halide causes a slight increase in *D*. Further addition of potassium halide has no effect in the case of iodide, while *D* is slightly decreased for the bromide and strongly for the chloride. This can be explained by formation of the inextractable anionic complexes $ZnCl_3^-$, $ZnCl_4^{2-}$, and $ZnBr_3^-$, for which the formation constants were calculated. Values were also calculated for the stability constants of the complexes ZnX^+ and ZnX_2. ΔH values for the various reactions in the range 150–200° are given.

Introduction

Zinc chloride in the molten state, whether pure or mixed with molten alkali chloride, has been extensively investigated. Pure molten zinc chloride is said to consist of polymer molecules, $(ZnCl_2)_n$, in equilibrium with the ions Zn^{2+}, $ZnCl^+$, and Cl^-.[2] As to the mixtures with alkali halides, some authors[3-5] find evidence for the complex $ZnCl_4^{2-}$ only, while others claim the existence of $ZnCl_3^-$ alone[6] or in addition to $ZnCl_4^{2-}$;[7,8] in one instance,[9] evidence was found for a species Cs_3ZnCl_5, which might imply the existence of $ZnCl_5^{3-}$. The existence of some complex species of zinc and cadmium chloride in molten sodium nitrate was shown by Van Artsdalen,[10] who used cryoscopic measurements to determine stability constants; the method of calculation was later criticized,[11] but alternative calculations were made only in the case of cadmium chloride.

Very little work seems to have been done on zinc bromide and iodide in the molten state, but some evidence was found for the existence of both $ZnBr_3^-$ and $ZnBr_4^{2-}$ in fused $AsBr_3$.[12] It may be of interest to note that present knowledge of zinc halide complexes in aqueous solution presents the same picture: a large number of mostly conflicting data in the case of chloride, few data on bromide, and almost none on iodide.[13,14]

Previous work on solvent extraction of mercuric halides from molten nitrate[15] showed the possibility of using this tool to investigate the complex species in molten salts; this should be especially true in the case of zinc halides, which are expected to be structurally similar to mercuric halides.

Experimental Section

As in the work with Hg(II) halides,[15] the molten-salt phase was the $LiNO_3$–KNO_3 eutectic mixture, mole ratio 3:4 (mp 120°). In some experiments, Zn halide and/or nitrate in various concentrations was also added. The nitrate mixture was fused and homogenized at 350°, after which dry nitrogen was bubbled through for 6 hr at 250° to remove any water. The organic phase consisted of a eutectic mixture of biphenyl, *o*-terphenyl, and *m*-terphenyl in the mole ratio 37:48:15 (mp 25°).

A Zn^{65} tracer (γ, 245 days) solution of high activity was obtained from Oak Ridge National Laboratory. This solution (5 μl) was added to larger amounts of analytically pure $ZnCl_2$, $ZnBr_2$, and ZnI_2 solutions, which were then evaporated to dryness. The dry zinc halides were made up to 10^{-3} *m* solutions in the polyphenyl mixture and further diluted in some experiments.

Measured quantities of these polyphenyl solutions were added to Pyrex test tubes containing the nitrate eutectic mixture, in which varying amounts of the corresponding potassium halide had been dissolved. The weight to weight ratio of salt to polyphenyl was near 3.5 in all experiments.

The tube was sealed and tumbled for 15 min in an oil bath at constant temperature, regulated to ±1°, after which the phases were allowed to separate in the bath. The tube was then rapidly cooled to 30° and opened; the polyphenyl phase (liquid) was

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(1) Previous paper in series: M. Zangen, *J. Phys. Chem.*, **69**, 1835 (1965).

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