into six trigonal components. It appears, then, that the absorption manifold observed between 28 000 and 33 000 cm^{-1} results from transitions to spin–orbit components of ${}^4T_1(P)$ and those of a doublet level which interact strongly with these.

Summary and Conclusions

When viewed in total, this work has measured oscillator strengths of spin-forbidden ${}^6A_1 \rightarrow {}^4\Gamma$ transitions in TMMB which are enhanced 2–3 orders of magnitude over those of isolated Mn^{2+} complexes. The apparent observation of transitions to states of substantial doublet character indicates the operative mechanism of enhancement is not limited to $\Delta S = 1$ transitions and, since this is not observed in TMMC, implicates the bridging bromide ligands as important contributors. The observed anomalies in oscillator strengths as functions of temperature and the increased splitting of measured components all near 150 K indicate a phase transition in TMMB which is not analogous to the phase transition in TMMC[7,8] and suggest a need for low-temperature structural information to more fully understand the phenomenon.

Acknowledgment. The authors wish to thank Dr. B. B. Garrett for many useful discussions of this work. This research was supported by National Science Foundation Grant No. GP-41056 and by the Office of Naval Research.

Registry No. TMMB, 51139-56-1.

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Reactions of MCl_6^{2-} (M = Ti, Mo, W) with $CrCl_2$ and Cl^- in CH_2Cl_2

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Received February 17, 1976 AIC601232

The reactions of $[(n\text{-}C_4H_9)_4N]_2MCl_6$ (M = Ti, Mo, W) with equimolar quantities of $CrCl_2$ and $[(n\text{-}C_4H_9)_4N]Cl$ in CH_2Cl_2 have been examined. When M = Mo, the smooth reaction in the absence of air produces the anion $CrMoCl_9^{3-}$ which does not dissociate into $Cr_2Cl_9^{3-}$ and $Mo_2Cl_9^{3-}$. The reaction of this substance with either dry air or O_2 produces $CrMoOCl_9^{3-}$. No reaction occurs when M = W. When M = Ti, an equilibrium mixture of $Ti_2Cl_9^{3-}$, $Cr_2Cl_9^{3-}$, and $TiCrCl_9^{3-}$ is obtained. Additional studies have indicated that $Cr_3Cl_{10}^{4-}$ is formed when $CrCl_2$ dissolves in CH_2Cl_2 which contains an equimolar quantity of $[(n\text{-}C_4H_9)_4N]Cl$. The formation of $CrCl_4^{2-}$ appears to occur upon the addition of more alkylammonium chloride.

Introduction

Although there are increasing numbers of metal cluster compounds, their syntheses have been discovered generally by chance. One of the long-range goals of this laboratory has been the development of rational syntheses for the confacial, bioctahedral anions $M_2Cl_9^{3-}$. Our first effort, which was directed toward the synthesis of $W_2Cl_9^{3-}$, ended in failure.[1] However, more recent investigations[2,3] led to the designed synthesis of $Mo_2Cl_9^{3-}$, as well as a new anion, $Mo_3Cl_{12}^{3-}$. Another long-range goal was to develop extensions of these methods such that anions containing two different metal atoms, $MM'Cl_9^{3-}$, could be synthesized. Any synthetic system which seemed to rely principally upon entropy to achieve the desired goal was not considered. Thus, there was no attempt to achieve success by the route

$$M_2Cl_9^{3-} + M'_2Cl_9^{3-} \rightleftharpoons 2MM'Cl_9^{3-}$$

However, the synthesis of $CrMoCl_9^{3-}$, according to reaction 1 in CH_2Cl_2, as well as the logic behind that synthesis, has

$$MoCl_6^{2-} + CrCl_2 + Cl^- \rightarrow CrMoCl_9^{3-} \qquad (1)$$

been presented in a previous communication.[4] Crucial, irrefutable evidence showed that the product was not an equimolar mixture of $Cr_2Cl_9^{3-}$ and $Mo_2Cl_9^{3-}$.

Further details about reaction 1 and the characterization of $CrMoCl_9^{3-}$ and its oxidation product need to be discussed. The successful isolation and characterization of this anion prompted attempts to prepare $CrWCl_9^{3-}$ and $TiCrCl_9^{3-}$ through corresponding reactions using WCl_6^{2-} and $TiCl_6^{2-}$, respectively. Details about these reactions and their products will be discussed. Finally, the nature of $CrCl_2$ and Cl^- in CH_2Cl_2 will be explored.

Experimental Section

Reagents and Procedures. Samples of $[(n\text{-}C_4H_9)_4N]Cl$ were dried at 45 °C over P_2O_5 under a dynamic vacuum for 15–24 h. Argon was purified by passing it successively through heated copper turnings and P_2O_5. The solvents were dried and distilled before placing in storage flasks on the vacuum line. Solutions of $[(n\text{-}C_4H_9)_4N]Mo(CO)_4Cl_3$ were prepared by a procedure similar to that of Bowden and Colton[5] which involves the chlorination of known quantities of $Mo(CO)_6$ at −80 °C in a container sealed by a stopcock. Gases were then removed under vacuum before the addition of stoichiometric quantity of $[(n\text{-}C_4H_9)_4N]Cl$ in CH_2Cl_2 at −80 °C. The synthesis of $[(n\text{-}C_4H_9)_4N]_2TiCl_6$ was accomplished by the reaction of stoichiometric quantities of distilled $TiCl_4$ and the alkylammonium halide in CH_2Cl_2, followed by precipitation with ether. The preparation of $[n\text{-}C_4H_9)_4N]_2MoCl_6$ was accomplished by a new method from $Mo(CO)_6$, $[(n\text{-}C_4H_9)_4N]Cl$ (1:2 mole ratio), and excess Cl_2 in CH_2Cl_2 at room temperature. Anal. Calcd: Cl, 26.8. Found: Cl, 26.7. Similar procedures with $W(CO)_6$ afforded $[(n\text{-}C_4H_9)_4N]WCl_6$. Reduction to $[(n\text{-}C_4H_9)_4N]_2WCl_6$ was accomplished with Sn powder suspended in CH_2Cl_2 in the presence of a stoichiometric quantity of $[(n\text{-}C_4H_9)_4N]Cl$. The electronic and infrared spectra were identical with those which were published earlier.[1] Samples of the $[(n\text{-}C_4H_9)_4N]^+$ salts of $Cr_2Cl_9^{3-}$ and $Mo_2Cl_9^{3-}$ were obtained from published procedures,[3,6] but the yield of the latter was increased to 95%. Two methods were used for the preparation of $[(n\text{-}C_4H_9)_4N]_3Ti_2Cl_9$: the combination of stoichiometric quantities of $TiCl_3$ and $[(n\text{-}C_4H_9)_4N]Cl$ in CH_2Cl_2 or the reduction of $TiCl_4$ with Sn powder in CH_2Cl_2 in the presence of stoichiometric quantities of the alkylammonium chloride. In each case, the addition of ether afforded an orange solid. Anal. Calcd: Cl, 28.0; Ti, 8.41. Found: Cl, 27.5; Ti, 8.55.

The preparation of $CrCl_2$ involved a modified version of the procedure described by Hein and Herzog.[7] Approximately 50 ml of ether was condensed in a flask containing about 1 g of $Cr(C_2H_3O_2)_2$. Several milliliters of HCl, purified by trap-to-trap distillation, were then condensed in the resulting slurry at the temperature of liquid nitrogen. After warming to room temperature, the mixture was stirred for several hours which resulted in the gradual formation of a pink solution and fibrous, off-white $CrCl_2$. After filtration, the entire procedure was repeated until the product was completely white. This solid was then washed several times with ether, dried under vacuum, and powdered with a stirring magnet.

The spectrophotometric titrations were accomplished using a 25-ml volumetric flask with a side arm leading to the spectrophotometric cell. The top of the flask was attached to a piece of glassware containing an outlet which led to both a vacuum line and the argon supply and an additional outlet through which solid $[(n\text{-}C_4H_9)_4N]Cl$ could be introduced. This outlet also provided the means for the introduction of the filtered solution containing the soluble product from the reaction of equimolar quantities of $CrCl_2$ and $[(n\text{-}C_4H_9)_4N]Cl$ as well as the means to accomplish transfer of the solution to a larger flask for dilution during the course of the titration.

Molybdenum analyses when chromium was absent were performed gravimetrically by precipitation as the oxime after decomposition of the sample by base and peroxide. The oxime was ignited and weighed as MoO_3. When chromium was present, molybdenum was determined by the method of Rao.[8] Chromium was determined spectrophotometrically[9] as chromate at 372 nm using an extinction coefficient of 4.83×10^3 M^{-1} cm^{-1}. Samples were decomposed by base and peroxide, diluted to an appropriate volume, and adjusted to pH 8.0 by addition of KOH. Titanium was determined spectrophotometrically[10] at 360 nm in the presence of L-ascorbic acid using an extinction coefficient of 65.9 M^{-1} cm^{-1}. Chloride analyses were obtained by potentiometric titration with $AgNO_3$ at pH 1.

The magnetic moments of samples in solution were determined by the NMR method of Evans[11] at either 60 or 100 MHz.

Reaction of $CrCl_2$ + Cl^- with $MoCl_6^{2-}$. The addition of 0.1774 g (1.442 mmol) of $CrCl_2$ to a yellow solution of 0.4020 g (1.446 mmol) of $[(n\text{-}C_4H_9)_4N]Cl$ and 1.146 g (1.444 mmol) of $[(n\text{-}C_4H_9)_4N]_2MoCl_6$ in approximately 40 ml of CH_2Cl_2 caused an immediate color change to deep red-brown. The mixture was stirred overnight although the $CrCl_2$ seemed to disappear after about 40 min. The slow distillation of ether into the filtered solution produced 1.15 g of $[(n\text{-}C_4H_9)_4N]_3CrMoCl_9$ as long, acicular, red-brown crystals. These were washed by distillation of the mother liquor and dried under vacuum. Anal. Calcd: Cr, 4.36; Mo, 8.05; Cl, 26.7; C, 48.3; H, 9.05; N, 3.52. Found: Cr, 4.38; Mo, 8.00; Cl, 26.8; C, 48.4; H, 9.36; N, 3.80. Yields were typically about 70%. When a sample was dissolved in a solution containing dichromate in the absence of air, titration of the excess Cr(VI) with Fe(II) revealed 3.04 reducing equiv/mol of Mo.

When a sample of the compound (0.0367 mmol) in CH_2Cl_2 was exposed to 0.0188 mmol of dry O_2, all of the O_2 was consumed and a violet solution was formed. When a larger sample in CH_2Cl_2 was exposed to dry air for several hours, the slow distillation of ether into the solution produced needlelike violet crystals of $[(n\text{-}C_4H_9)_4N]_3CrMoOCl_9$. Anal. Calcd: Cr, 4.30; Cl, 26.4; N, 3.47. Found: Cr, 4.10; Cl, 26.4; N, 3.67. The infrared spectrum contains a band at 950 cm^{-1} due to Mo═O.

Competition between $CrCl_2$ + Cl^- and $Mo(CO)_4Cl_3^-$ for $MoCl_6^{2-}$. A 25-ml CH_2Cl_2 solution at −80 °C containing 0.135 g (1.09 mmol) of $CrCl_2$, 0.313 g (1.14 mmol) of $[(n\text{-}C_4H_9)_4N]Cl$, and 1.09 mmol of $[(n\text{-}C_4H_9)_4N]Mo(CO)_4Cl_3$ (prepared from 0.288 g (109 mmol) of $Mo(CO)_6$) was added to a 15-ml CH_2Cl_2 solution of 0.857 g (1.08 mmol) of $[(n\text{-}C_4H_9)_4N]_2MoCl_6$. The resulting solution was allowed to warm to room temperature. After 3 h, ether was added to precipitate all of the product which contained 2.78% Cr and 10.3% Mo. The electronic spectra of a known portion of the sample and the product obtained from its oxidation by dry air established that the mole fractions of $CrMoCl_9^{3-}$, $Mo_2Cl_9^{3-}$, and $Cr_2Cl_9^{3-}$ were 0.65, 0.34, and 0.01.

Reaction of $CrCl_2$ + Cl^- with $TiCl_6^{2-}$. When 0.181 g (1.47 mmol) of $CrCl_2$ was added to a yellow solution of 0.463 g (1.57 mmol) of $[(n\text{-}C_4H_9)_4N]Cl$ and 1.203 g (1.47 mol) of $[(n\text{-}C_4H_9)_4N]_2TiCl_6$ in 40 ml of CH_2Cl_2, the color of the solution changed immediately to brown. The reaction was allowed to continue overnight which resulted in a purple-brown solution. After filtration, the addition of ether caused the precipitation of a solid of the same color which was washed with the distillate from the mother liquor and dried under vacuum. Analyses indicated that the Cr, Ti, and Cl compositions were 4.54%, 4.20%, and 27.8%, respectively, in accord with Cr:Ti:Cl = 1:1:9. The product was extremely sensitive to both moisture and oxygen.

Results and Discussion

Synthesis and Characterization of $CrMoCl_9^{3-}$. The previous report[4] delineated the synthesis and partial characterization of $CrMoCl_9^{3-}$ according to reaction 1. Of particular interest was the observation that the reactivity of this anion with dry air was exceptionally greater than that of an equimolar mixture of $Mo_2Cl_9^{3-}$ and $Cr_2Cl_9^{3-}$. This observation provided the basis for estimating that the stereospecificity of this reaction was about 96%. The relative concentrations of $CrMoCl_9^{3-}$, $Cr_2Cl_9^{3-}$, and $Mo_2Cl_9^{3-}$ were approximately 48:1:1. When equimolar quantities of $CrCl_2$ + Cl^- and $Mo(CO)_4Cl_3^-$ were allowed to compete for an identical molar quantity of $MoCl_6^{2-}$ over a period of 3 h, the formation of $CrMoCl_9^{3-}$, $Mo_2Cl_9^{3-}$, and $Cr_2Cl_9^{3-}$ occurred in the approximate ratio of 65:34:1. These results probably reflect kinetic phenomena principally rather than thermodynamic stability since we have observed that reaction 1 proceeds more rapidly than the corresponding reaction[2,3] of $Mo(CO)_4Cl_3^-$ and $MoCl_6^{2-}$ at comparable concentrations.

The magnetic moments per formula unit of solid $[(n\text{-}C_4H_9)_4N]_3CrMoCl_9$ are 4.38 μ_B at 295 K and 3.10 μ_B at 77 K. The values obtained from a CH_2Cl_2 solution of this compound are 4.53 μ_B at 300 K and 3.87 μ_B at 206 K. The latter is the lowest practical temperature for obtaining a reasonable NMR spectrum from CH_2Cl_2. Antiferromagnetic coupling is evident in either phase. The magnetic moments per formula unit obtained for solutions of $Cr_2Cl_9^{3-}$ and $Mo_2Cl_9^{3-}$ at 300 K are 5.48 and 2.42 μ_B, respectively.

The product which results from the oxidation of $CrMoCl_9^{3-}$ with either dry air or O_2 has also been examined. Gas consumption as well as analyses of the product agree with $CrMoOCl_9^{3-}$. The infrared spectrum contains a band at 950 cm^{-1} which is attributed to a terminal Mo═O stretching vibration. If a Cr═O moiety were present, the band would probably occur in the same region of the spectrum. However, this notion is rejected because the oxidation of Mo(III) by O_2 to Mo(V) is a known reaction[12] but the oxidation of Cr(III) by O_2 does not occur. The structure of $CrMoOCl_9^{3-}$ is presumed to consist of two octahedra sharing a common edge, i.e., with two bridging chlorine atoms. The position of the Mo═O group with respect to the bridging system is unknown.

Attempted Preparation of $CrWCl_9^{3-}$. When $CrCl_2$ was added to equimolar quantities of $[(n\text{-}C_4H_9)_4N]Cl$ and $[(n\text{-}C_4H_9)_4N]_2WCl_6$, no reaction occurred except the dissolution of $CrCl_2$. The fact that WCl_6^{2-} is unreactive toward $CrCl_2$ while $MoCl_6^{2-}$ reacts readily with the same reagent is explicable in terms of the relative ease of reduction of these complexes. We have also found that $MoCl_6^{2-}$ is readily reduced to $Mo_2Cl_9^{3-}$ by Sn in CH_2Cl_2 but again WCl_6^{2-} is not reduced.

Reaction of $CrCl_2$ and Cl^- with $TiCl_6^{2-}$. The electronic spectrum of the reaction products obtained from the reactions of equimolar quantities of $CrCl_2$, $[(n\text{-}C_4H_9)_4]Cl$, and $[(n\text{-}C_4H_9)_4N]_2TiCl_6$ is completely identical with that obtained from an equimolar mixture of the corresponding alkylammonium salts of $Cr_2Cl_9^{3-}$ and $Ti_2Cl_9^{3-}$. However, neither coincides with the superposition of the separate spectra of these anions, as shown in Figure 1. Further understanding was sought from the spectrophotometric titration of $Ti_2Cl_9^{3-}$ with $Cr_2Cl_9^{3-}$. Although the final ratio of the molar concentrations of $Cr_2Cl_9^{3-}$ to $Ti_2Cl_9^{3-}$ was 2.80, a constant spectrum was not obtained. Two twofold dilutions resulted in no change in the

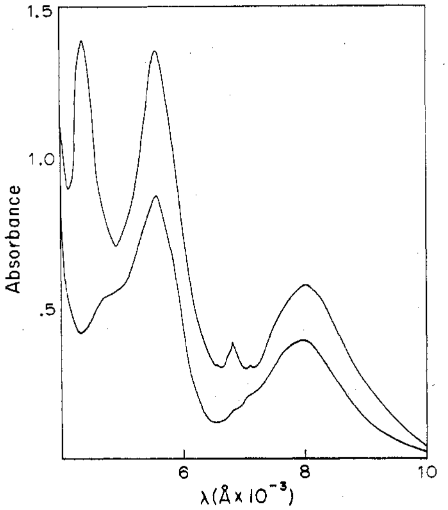

Figure 1. Comparison of the actual visible spectrum of an equimolar mixture of $Cr_2Cl_9^{3-}$ and $Ti_2Cl_9^{3-}$ (top) with the spectrum which would be expected if no reaction occurred (bottom). Spectra were recorded in CH_2Cl_2.

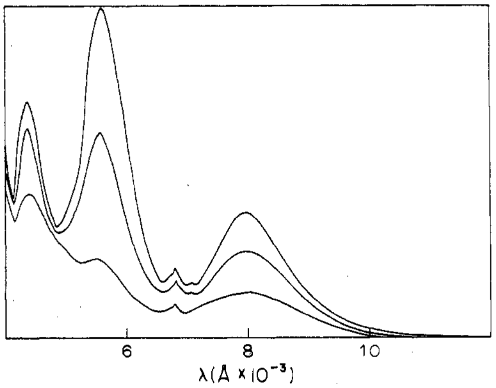

Figure 2. Some representative spectra which were obtained during the spectrophotometric titration of $Ti_2Cl_9^{3-}$ with $Cr_2Cl_9^{3-}$ in CH_2Cl_2. Proceeding from the lowest spectrum to the top, the ratios of the formal molar concentrations of $Cr_2Cl_9^{3-}$ and $Ti_2Cl_9^{3-}$ are 0.30, 0.97, and 1.71.

apparent extinction coefficient at any wavelength. Representative spectra are shown in Figure 2.

Since the equilibrium position is independent of volume, there would appear to be only four equilibria which might be considered, as shown in eq 2–5. Reaction 4 can be ignored

$$Ti_2Cl_9^{3-} + Cr_2Cl_9^{3-} \rightleftharpoons 2TiCrCl_9^{3-} \quad (2)$$

$$Ti_2Cl_9^{3-} + Cr_2Cl_9^{3-} \rightleftharpoons Cr_2Ti_2Cl_{17}^{5-} + Cl^- \quad (3)$$

$$Ti_2Cl_9^{3-} + Cr_2Cl_9^{3-} \rightleftharpoons Ti_2CrCl_{12}^{3-} + CrCl_6^{3-} \quad (4)$$

$$Ti_2Cl_9^{3-} + Cr_2Cl_9^{3-} \rightleftharpoons TiCr_2Cl_{12}^{3-} + TiCl_6^{3-} \quad (5)$$

safely because $CrCl_6^{3-}$ is incapable of existence in CH_2Cl_2. Syntheses which were designed to yield that ion have led inevitably to the formation of $Cr_2Cl_9^{3-}$. Similarly, we have been unable to prepare $MoCl_6^{3-}$ due to the stability of $Mo_2Cl_9^{3-}$. We ascribe the greater stability of a dinuclear ion, $M_2Cl_9^{3-}$, with respect to a mononuclear ion of the same charge, MCl_6^{3-}, to the decreased charge density of the former which in turn decreases unfavorable interactions between the ion and organic solvent. This reasoning would also rule out the stable existence of $TiCl_6^{3-}$ in reaction 5. Reaction 3 leads to a tetranuclear ion with an inordinately large negative charge. However, there is another reason for discounting this reaction. It is possible that the chloride ion which is released could react further with either $Ti_2Cl_9^{3-}$ or $Cr_2Cl_9^{3-}$, leading to a complex overall reaction.

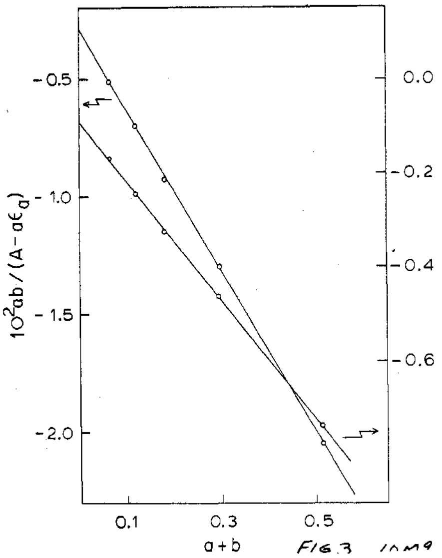

Figure 3. Plots of $ab(A - a\epsilon_a)^{-1}$ vs. $(a + b)$ for the reaction $Ti_2Cl_9^{3-} + Cl^- \rightleftharpoons Ti_2Cl_{10}^{4-}$. The left-hand scale is for the results at 800 nm while the right-hand scale is for those at 470 nm.

We have studied the result of adding $[(n\text{-}C_4H_9)_4N]Cl$ to solutions which contained either $Cr_2Cl_9^{3-}$ or $Ti_2Cl_9^{3-}$ by spectrophotometric titration at constant volume. No spectroscopic changes were observed with $Cr_2Cl_9^{3-}$ even when $[Cl^-]/[Cr_2Cl_9^{3-}] = 22$. The addition of Cl^- to solutions of $Ti_2Cl_9^{3-}$ resulted in major changes in the spectrum and a constant spectrum was not obtained even when $[Cl^-]/[Ti_2Cl_9^{3-}] = 40$. Both bands in the spectrum of $Ti_2Cl_9^{3-}$ decreased in intensity while the band at 470 nm shifted to a slightly shorter wavelength. Two reactions were considered as possibilities, i.e.

$$Ti_2Cl_9^{3-} + 3Cl^- \rightleftharpoons 2TiCl_6^{3-} \quad (6)$$

$$Ti_2Cl_9^{3-} + Cl^- \rightleftharpoons Ti_2Cl_{10}^{4-} \quad (7)$$

Reaction 6, which should be unlikely because of the suspected instability of $TiCl_6^{3-}$, was eliminated completely because treatment of the data led to meaningless results. Reaction 7 was then treated in the following manner.

The equilibrium expression for that reaction is given by

$$K = c[(a - c)(b - c)]^{-1}$$

where a is the initial concentration of $Ti_2Cl_9^{3-}$, b is the analytical concentration of added Cl^-, and c is the concentration of $Ti_2Cl_{10}^{4-}$. The results make it clear that K must be small and under those conditions it may be safely assumed that $c \gg c^2$. Expansion of the equilibrium expression leads then to a simple equation for c

$$c = Kab[K(a + b) + 1]^{-1}$$

When this value of c is inserted into the Beer–Lambert equation, the following relationship may be obtained for a 1-cm path length

$$ab(A - a\epsilon_a)^{-1} = (a + b)(\epsilon_c - \epsilon_a)^{-1} + [K(\epsilon_c - \epsilon_a)]^{-1}$$

The molar extinction coefficients of $Ti_2Cl_9^{3-}$ and $Ti_2Cl_{10}^{4-}$ are given by ϵ_a and ϵ_c, respectively, while A is the absorbancy. When $ab(A - a\epsilon_a)^{-1}$ is plotted against $(a + b)$, the result should be a straight line whose slope is the reciprocal of $(\epsilon_c - \epsilon_a)$ and whose intercept is the reciprocal of $K(\epsilon_c - \epsilon_a)$. The results from data taken at two wavelengths, 470 and 800 nm, are shown in Figure 3. We found from each case that $K = 12.4 \pm 0.4$ M^{-1}. Another possibility must also be considered before

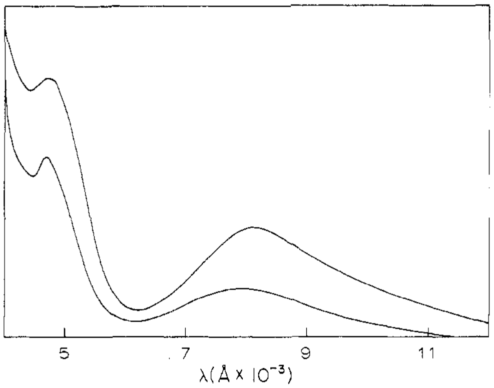

Figure 4. Visible spectrum of $[(n\text{-}C_4H_9)_4N]_3Ti_2Cl_9$ in the solid phase suspended in a mull (top) and in solution in CH_2Cl_2 (bottom).

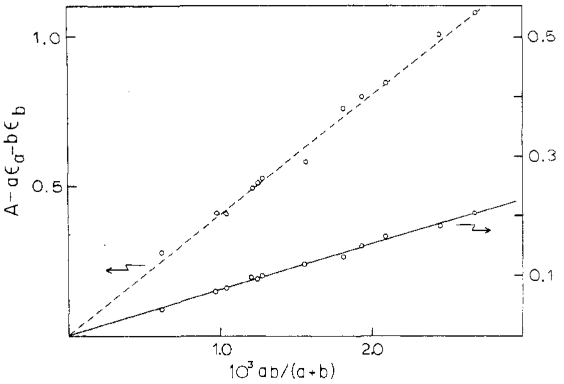

Figure 5. Plots of $(A - a\epsilon_a - b\epsilon_b)$ vs. $ab(a + b)^{-1}$ for the reaction $Ti_2Cl_9^{3-} + Cr_2Cl_9^{3-} \rightleftharpoons 2TiCrCl_9^{3-}$. The left-hand scale is for the results at 438 nm while the right-hand scale is for those at 679 nm.

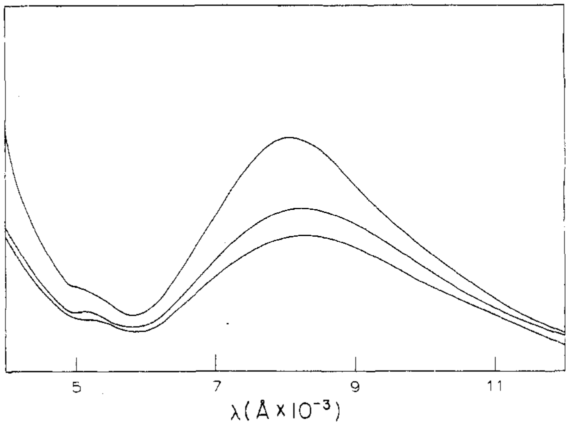

Figure 6. Some representative spectra which were obtained during the spectrophotometric titration of $Cr_3Cl_{10}^{4-}$ with Cl^- in CH_2Cl_2. Proceeding from the lowest spectrum to the top, the ratios of the formal concentrations of Cl^- and $Cr_3Cl_{10}^{4-}$ are 0, 0.38, and 7.02.

reaction 7 can be believed completely. It is possible that $Ti_2Cl_9^{3-}$, which exists in the solid phase, dissociates completely to $Ti_2Cl_8^{2-}$ in solution. Subsequent addition of Cl^- to re-form $Ti_2Cl_9^{3-}$ would follow the same mathematical approach provided the analytical concentration of Cl^- includes that which resulted from the initial dissociation. However, this possibility is rejected since the spectrum of $[(n\text{-}C_4H_9)_4N]_3Ti_2Cl_9$ in the solid phase matches that obtained from a solution of that compound (Figure 4).

It is now possible to see that, if reaction 3 is occurring, it must be coupled to reaction 7. However, a mathematical treatment of the data, using the known equilibrium constant from reaction 7, led to meaningless results. Thus, eq 2 should be appropriate for the titration of $Ti_2Cl_9^{3-}$ with $Cr_2Cl_9^{3-}$.

An equation which predicts the results of that titration can be derived assuming that the equilibrium constant for reaction 2 is small such that only first power functions of $[TiCrCl_9^{3-}]$ are important. Proceeding in a fashion which is analogous to that which was given above for the titration of $Ti_2Cl_9^{3-}$ with Cl^-, the following equations for a path length of 1 cm are obtained

$$[TiCrCl_9^{3-}] = 2ab(a + b)^{-1}$$

$$A - a\epsilon_a - b\epsilon_b = ab(a + b)^{-1}(2\epsilon_c - \epsilon_a - \epsilon_b)$$

The analytical concentrations of $Ti_2Cl_9^{3-}$ and $Cr_2Cl_9^{3-}$ are given by a and b while their molar extinction coefficients are represented by ϵ_a and ϵ_b. The molar extinction coefficient of $TiCrCl_9^{3-}$ is given by ϵ_c and the absorbancy is A. When the left-hand side of the second equation is plotted against $ab(a + b)^{-1}$, the result should be a straight line passing through the origin with a slope of $(2\epsilon_c - \epsilon_a - \epsilon_c)$. Since this equation does not contain K, it can only be used to verify the stoichiometry. A treatment of the data at two wavelengths, 438 and 679 nm, is shown in Figure 5. The equilibrium constant, which was calculated at each titration point and at each wavelength from the mass balance relationships, was shown to be 1.0 ± 0.1. If reaction 2 were totally random, an equilibrium constant of 4 would be expected.

The average molar magnetic susceptibility of a solution containing equimolar quantities of $Cr_2Cl_9^{3-}$, $Ti_2Cl_9^{3-}$, and $TiCrCl_9^{3-}$ (each at 0.015 M) was found to be 7.50×10^{-3} cgsu. The magnetic susceptibilities for $Ti_2Cl_9^{3-}$ and $Cr_2Cl_9^{3-}$ were shown to be 2.47×10^{-3} and 12.36×10^{-3} cgsu, respectively. The calculated susceptibility and magnetic moment of $TiCrCl_9^{3-}$ are then 7.67×10^{-3} cgsu and 4.29 μ_B per formula unit. The total absence of coupling within a d^1–d^3 system would lead to a susceptibility of 7.50×10^{-3} cgsu and a magnetic moment of 4.26 μ_B.

The Nature of Cr(II) in Solution. When equimolar quantities of $CrCl_2$ and $[(n\text{-}C_4H_9)_4N]Cl$ were placed in CH_2Cl_2, the reaction led after several hours to a green solution in which some gray solid was suspended. After filtration, analyses of the solution showed that the Cl:Cr ratio was 3.30 ± 0.15, with 75% of the chromium in solution. These figures suggest that the suspended solid was only $CrCl_2$ which had not reacted, but its gray color must mean then that some small amount of chromophoric impurity was also present. This solid was not investigated. The analytical composition of the solution suggests an anion, $Cr_3Cl_{10}^{4-}$, although an equilibrium mixture of various anions is also possible providing their overall composition agrees with the experimental results.

To gain further insight into the nature of the species in solution, a filtered solution of known composition was then titrated spectrophotometrically with solid $[(n\text{-}C_4H_9)_4N]Cl$. Representative spectra are shown in Figure 6. Before titration, the band maximum occurs at 830 nm. One twofold dilution was accomplished during the course of the titration, but no change in the apparent extinction coefficient occurred at any wavelength. Since the equilibrium which exists on addition of Cl^- is clearly independent of volume, the general equilibrium in eq 8 was considered.

$$Cr_3Cl_{10}^{4-} + 2Cl^- \rightleftharpoons 3CrCl_4^{2-} \qquad (8)$$

Assuming that the equilibrium constant for this reaction is rather small so that only first-power functions of $[CrCl_4^{2-}]$ are important, it is possible to derive eq 9 for solutions

$$b[A - a\epsilon_a]^{-1} = b[a(3\epsilon_c - \epsilon_a)]^{-1} + 4[3\epsilon_c - \epsilon_a]^{-1} \qquad (9)$$

contained in a 1-cm cell. In this equation, a is the initial

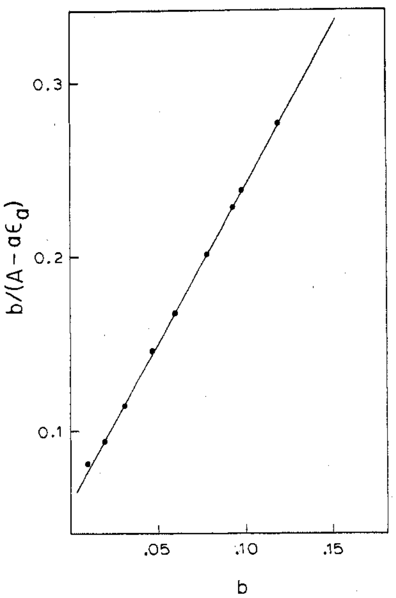

Figure 7. Plot of $b(A - a\epsilon_a)$ vs. b for the reaction $Cr_3Cl_{10}^{4-}$ + $2Cl^- \rightleftharpoons 3CrCl_4^{2-}$.

concentration of $Cr_3Cl_{10}^{4-}$ and b is the analytical concentration of added Cl^- while A is the absorbancy and ϵ_a and ϵ_c are the molar extinction coefficients of $Cr_3Cl_{10}^{4-}$ and $CrCl_4^{2-}$, respectively. If reaction 8 is occurring, a plot of $b[A - a\epsilon_a]^{-1}$ against b should be a straight line. As shown in Figure 7, a straight line was obtained from data taken at 800 nm.[13]

The concentration of $CrCl_4^{2-}$ was then determined at each point in the titration from the relationship

$$[CrCl_4^{2-}] = 3ab[4a + b]^{-1}$$

Mass balance relationships then allowed the calculation of the concentrations of $Cr_3Cl_{10}^{4-}$ and free Cl^-. The equilibrium constant for eq 8, evaluated at each point, was shown to be 0.5 ± 0.2.

The magnetic moment of $Cr_3Cl_{10}^{4-}$ in solution was 4.78 μ_B per Cr(II) atom while a value of 4.89 μ_B was obtained from a solution in which the ratio of $CrCl_4^{2-}$ and $Cr_3Cl_{10}^{4-}$ was calculated to be 1.5. It is clear from these results that $CrCl_4^{2-}$ has a high-spin configuration.

These results do not define the true molecularity of either $Cr_3Cl_{10}^{4-}$ or $CrCl_4^{2-}$. However, it is reasonable to assume that the former is really a trinuclear complex since higher multiples of the charge would probably lead to both instability and low solubility. The structure of the latter is of greater interest. Although the dinuclear, metal-to-metal bonded anion, $Mo_2Cl_8^{4-}$, is very well-known, an isostructural chromium complex is ruled out by the magnetic moment. Furthermore, it is reasonable to assume that $CrCl_4^{2-}$ is a mononuclear complex since complexes of this stoichiometry are known for all metals of the first transition series when the atomic numbers of those metals exceed that of chromium. Those complexes are all tetrahedral with the exception of $CuCl_4^{2-}$ which is distorted from tetrahedral geometry because of Jahn–Teller effects. Those effects would also distort the geometry of $CrCl_4^{2-}$. However, it should also be noted that Cr(II) in the LiCl–KCl eutectic was also presumed to be in a distorted tetrahedral environment.[14] The absorption spectrum in that case consists of a single band at 9800 cm^{-1} which does not match the absorption maximum at 12 050 cm^{-1} found in the present case. Recently, however some evidence has appeared which suggests that polymeric, six-coordinate complexes in the molten eutectic are responsible for the 9800-cm^{-1} band.[15] If that is the case and if $CrCl_4^{2-}$ is a distorted tetrahedron whose symmetry may be D_{2d}, which is the case for $CuCl_4^{2-}$, the band at 12 050 cm^{-1} would be due to the allowed $^2B_2 \rightarrow {}^2A_1$ transition. The other allowed transition, $^2B_2 \rightarrow {}^2E$, should then appear at much lower frequencies.[16] This transition has not yet been detected.

Conclusion

Although $CrMoCl_9^{3-}$ is formed smoothly by the reaction of $MoCl_6^{2-}$ with $CrCl_2$ and Cl^-, $CrWCl_9^{3-}$ could not be prepared by the reaction of WCl_6^{2-} with the same reagents. Each reaction requires bridge formation as well as reduction of the M(IV) (M = Mo or W) center by $CrCl_2$. The crucial difference between the molybdenum and tungsten reactions appears to be that Mo(IV) is reduced much more readily than W(IV). This behavior is expected because of the position of these elements in the periodic table and is demonstrated by the differing behaviors of $MoCl_6^{2-}$ and WCl_6^{2-} with Sn in CH_2Cl_2. The smooth reduction of $MoCl_6^{2-}$ occurs yielding $Mo_2Cl_9^{3-}$ but no reaction occurs with WCl_6^{2-}.

It is possible that $CrMCl_9^{3-}$, consisting of Cr(II) and M(IV), could be formed without election transfer. However, the fact that synthesis of the anion has occurred only when the thermodynamic barrier to electron transfer is a minimum may indicate that bridge formation is coupled to electron transfer.

Not only is $CrMoCl_9^{3-}$ formed easily but it is also stable toward dissociation into $Cr_2Cl_9^{3-}$ and $Mo_2Cl_9^{3-}$. However, the reaction of $TiCl_6^{2-}$ with $CrCl_2$ and Cl^- leads to an equilibrium distribution of complexes that can also be obtained from equimolar quantities of $Cr_2Cl_9^{3-}$ and $Ti_2Cl_9^{3-}$. A treatment of the results suggests that the equilibrium distribution consists of $TiCrCl_9^{3-}$, $Cr_2Cl_9^{3-}$, and $Ti_2Cl_9^{3-}$ as in reaction 2. It would appear that the formal d^1 configuration of Ti(III) in $TiCrCl_9^{3-}$ leads to instability, unlike the case of $CrMoCl_9^{3-}$ in which both metals possess the d^3 configuration. This instability is seen again in the reaction of $Ti_2Cl_9^{3-}$ with Cl^- to give $Ti_2Cl_{10}^{4-}$. Comparable additions of Cl^- have not been found for either $Cr_2Cl_9^{3-}$ or $Mo_2Cl_9^{3-}$.

When $CrCl_2$ dissolves partially in CH_2Cl_2 containing an equimolar quantity of an alkylammonium chloride, analytical data suggest that the species in solution is $Cr_3Cl_{10}^{4-}$. The stability of this anion is not due to metal-to-metal interactions since the magnetic moment indicates that each metal atom has four unpaired electrons. Further additions of the alkylammonium chloride lead to the conversion of that anion to $CrCl_4^{2-}$.

Registry No. $[(n\text{-}C_4H_9)_4N]_3CrMoCl_9$, 53964-46-8; $[(n\text{-}C_4H_9)_4N]_3Mo_2Cl_9$, 51472-37-8; $[(n\text{-}C_4H_9)_4N]_3Cr_2Cl_9$, 38845-35-1; $[(n\text{-}C_4H_9)_4N]_3CrMoOCl_9$, 59830-96-5; $[(n\text{-}C_4H_9)_4N]_3Ti_2Cl_9$, 59830-97-6; $CrCl_2$, 10049-05-5; $[(n\text{-}C_4H_9)_4N]_2MoCl_6$, 19964-31-9; $[(n\text{-}C_4H_9)_4N]Mo(CO)_4Cl_3$, 59840-41-4; $[(n\text{-}C_4H_9)_4N]_2TiCl_6$, 59830-98-7; $TiCrCl_9^{3-}$, 59830-99-8; $CrCl_4^{2-}$, 21740-44-3; $Cr_3Cl_{10}^{4-}$, 59839-86-0; $[(n\text{-}C_4H_9)_4N]Cl$, 1112-67-0.

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(13) An alternative treatment of the data can be used to rule out $Cr_2Cl_7^{3-}$ as the initial complex. The following general equations can be written: $Cr_nCl_{3n+1}^{(n+1)-} + (n - 1)Cl^- \rightarrow nCrCl_4^{2-}$; $b[A - a\epsilon_a]^{-1} = b[a(n\epsilon_c - \epsilon_a)]^{-1} + (n - 1)^2[n\epsilon_c - \epsilon_a]^{-1}$. The last equation is equivalent to eq 9 with n

= 3. However, the value of *n* may be obtained from the general equation from the ratio of intercept and the slope, i.e., $(n - 1)^2[Cr_T]/n$ since $a = [Cr_T]/n$. The actual results show that $n = 3.1 \pm 0.2$ which points only to $Cr_3Cl_{10}^{4-}$.
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Coordination Compounds of Indium. 32. Preparation and Properties of Hexahalogenatodiindate(II) Anions

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Received February 18, 1976

AIC601277

The salts $(Bu_4N)_2[In_2X_6]$ (X = Cl, Br, I) have been prepared by the reaction of Bu_4NX and InX_2 in xylene. The vibrational spectra lead to the formulation of the anions as $[X_3In{-}InX_3]^{2-}$ species, so that these are the first unambiguous indium(II) complexes to be prepared. Force constant calculations support the vibrational assignments. A possible reaction scheme for the preparation is discussed. The reaction of $(Me_2bpy)InX_3$ (Me_2bpy^{2+} = *N,N*-dimethyl-4,4′-bipyridinium cation) with InX_3 yields a lattice of $Me_2bpy^{2+} + InX_2^- + InX_4^-$; the reasons for the difference between this reaction and that giving $(Bu_4N)_2[In_2X_6]$ are discussed.

Introduction

The coordination chemistry of indium(III) is now reasonably well understood, and there have been some encouraging recent developments in our knowledge of indium(I) complexes,[1] but information on indium(II) remains sparse. The only well-established compounds whose stoichiometry implies indium in the +II state are the dihalides InX_2 (X = F, Cl, Br, I), whose structure in the solid and liquid states has been the subject of considerable discussion, reviewed elsewhere.[1-3] A brief summary of the situation is that these InX_2 compounds, and other indium subhalides, are mixed oxidation state compounds, for which ionic formulations (e.g., $In[InX_4]$, $In_3[InX_6]$) represent the structure within the very considerable limits of present information. More importantly, such compounds are apparently not genuine indium(II) species, and earlier suggestions of a dimeric indium–indium bonded structure for InX_2 can therefore be discounted. We may also note that the polarographic reduction of indium(III) chelate[5-7] complexes yields indium(II) species, but none of these reduction products has been isolated. Monomeric indium(II) species would, of course, contain an unpaired electron, and might be expected to be highly reactive.

We recently reported[8] a simple synthesis of indium dihalides involving the reduction of indium(III) halide by the metal in aromatic solvents, in which the InX_2 products are reasonably soluble. It has now been found that these compounds react in such solvents with tetrabutylammonium halides to yield $(Bu_4N)_2[In_2X_6]$ salts (X = Cl, Br, I). Spectroscopic measurements and force constant calculations establish that the anions are correctly formulated as $[X_3In{-}InX_3]^{2-}$, analogous to a group of gallium(II) compounds[9-11] whose structure has been confirmed by an x-ray study[12] of $(Et_4N)_2[Cl_3Ga{-}GaCl_3]$. The $[In_2X_6]^{2-}$ anion has been postulated in discussions of the structure of In_2X_3 (X = Cl, Br) which are held to be $(In^I)_2[In_2X_6]$ compounds[13,14] (cf. previous paragraph).

The present work also leads to an understanding of earlier studies of the reaction of $InCl_3^{2-}$, a potential electron pair donor,[15] with $InCl_3$; this reaction is believed to involve halide transfer and rearrangement following adduct formation, eventually yielding InX_2^- and InX_4^-.

Experimental Section

General Data. Experimental methods in general were similar to those reported in ref 8. Raman spectra were recorded over the range 100–500 cm^{-1} on a Spectrophysics Model 700 spectrometer in conjunction with a Model 164 argon ion laser and Model 265 exciter unit. Power output was typically 100–300 mW with the 20 492-cm^{-1} exciting frequency. The infrared spectra, kindly provided by Professor A. J. Carty (University of Waterloo), were obtained as Nujol mulls between polythene plates on a Perkin-Elmer 180 spectrophotometer.

Magnetic susceptibilities were determined on a conventional Gouy balance. Conductivity measurements were as in earlier work.[3]

Preparative Data. Indium diiodide (1.6 g, 2.17 mmol, calculated as In_2I_4) was suspended in xylene (75 ml), and tetrabutylammonium iodide (1.6 g, 4.34 mmol) was added. The suspension was warmed, with stirring, and finally heated to reflux; the formation of a yellow oil was apparent at this stage. After 10 min, the reaction mixture was allowed to cool to room temperature, whereupon the oil yielded a yellow solid. Solvent was removed by decantation, and the solid was washed with diethyl ether (100 ml) and then triturated with more ether. The final solid was again washed with diethyl ether and dried in vacuo; analysis showed this solid to be $(Bu_4N)_2[In_2I_6]$; yield 2.53 g (79%). The preparations of the $In_2Cl_6^{2-}$ and $In_2Br_6^{2-}$ salts were essentially identical. Anal. Calcd for $(Bu_4N)_2[In_2Cl_6]$: C, 41.4; H, 7.8; N, 3.0; Cl, 23.0. Found: C, 42.3; H, 7.9; N, 3.9; Cl, 22.0. Calcd for $(Bu_4N)_2[In_2Br_6]$: C, 32.2; H, 6.0; N, 2.4; Br, 40.2. Found: C, 32.2; H, 6.0; N, 2.5; Br, 40.2. Calcd for $(Bu_4N)_2[In_2I_6]$: C, 26.0; H, 4.9; N, 1.9; I, 51.6. Found: C, 25.9; H, 4.9; N, 1.7; I, 50.7. The chloride complex gave relatively poor analytical results, which is no doubt connected with the fact that the reaction of $InCl_2$ and Bu_4NCl was the least satisfactory of the preparations, since $InCl_2$ is the least soluble of the indium dihalides in xylene.[8] We were unable to find a satisfactory solvent for the recrystallization of $(Bu_4N)_2[In_2Cl_6]$.

Rapid decomposition in solvents such as acetonitrile prevented any conductometric studies of these compounds in solution.

Reaction between InX_3^{2-} and InX_3. Indium(III) halides dissolved in dry methanol were added to the corresponding $(Me_2bpy)In^IX_3$ salts (Me_2bpy^{2+} = *N,N*-dimethyl-4,4′-bipyridinium cation) prepared by the method described earlier,[3] and the mixture was refluxed for 10 h. The resultant solids (colorless for X = Cl or Br, orange for X = I) were collected, washed with methanol, and dried in vacuo. Each analyzed as the compound $(Me_2bpy)In_2X_6$. Anal. Calcd for $C_{12}H_{14}N_2In_2Cl_6$: C, 22.9; H, 2.2; N, 4.5; Cl, 33.9; In, 36.5. Found: C, 22.3; H, 2.1; N, 4.3; Cl, 33.4; In, 36.4. Calcd for $C_{12}H_{14}N_2In_2Br_6$: C, 16.5; H, 1.6; N, 3.2; Br, 54.8; In, 26.2. Found: C, 14.2; H, 1.7; N, 3.6; Br, 54.8; In, 26.1. Calcd for $C_{12}H_{14}N_2In_2I_6$: C, 12.2; H, 1.2; N, 2.4; I, 64.7; In, 19.6. Found: C, 12.6; H, 1.5; N, 2.2; I, 64.3; In, 19.4. These compounds are sufficiently soluble in acetonitrile for conductivity studies (see below).

Results and Discussion

The ready availability of gram quantities of the indium dihalides and their solubility in aromatic solvents[8] has prompted the investigation of their mode of reaction in such