synthesize an arsacarborane[17]) offers some promise, however.

Acknowledgment. The authors thank Dr. L. J. Todd and Mr. G. Delbert Friesen for the boron NMR spectra and the Research Corp. and the University of Mississippi Committee on Faculty Research for support.

Registry No. I, 69531-86-8; II, 69531-87-9; III, 69668-66-2; IV, 69576-60-9; V, 69576-61-0; $(CH_3)_4NB_{10}H_{12}As$, 51292-89-8; $B_{10}H_{14}$, 17702-41-9; $(C_2H_5)_3NH^+B_{11}H_{14}^-$, 12106-44-4; $SbCl_3$, 10025-91-9; $CoCl_2$, 7646-79-9.

References and Notes

(1) Presented in part at the 173rd National Meeting of the American Chemical Society, New Orleans, LA, March 1977.
(2) Part 3: J. L. Little and S. S. Pao, *Inorg. Chem.*, **17**, 584 (1978).
(3) Address correspondence to this author at Callery Chemical Co., Callery, PA 16024.
(4) D. A. T. Young, R. J. Wiersema, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **93**, 5687 (1971).
(5) J. L. Spencer, M. Green, and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 1178 (1972).
(6) G. S. Wikholm and L. J. Todd, *J. Organomet. Chem.*, **71**, 219 (1974).
(7) R. W. Rudolf, R. L. Voorhees, and R. E. Cochoy, *J. Am. Chem. Soc.*, **92**, 3351 (1970).
(8) V. Chowdhry, W. R. Pretzer, D. N. Rai, and R. W. Rudolf, *J. Am. Chem. Soc.*, **95**, 4560 (1973).
(9) L. J. Todd, A. R. Burke, A. R. Garber, H. T. Silverstein, and B. N. Storhoff, *Inorg. Chem.*, **9**, 2175 (1970).
(10) N. N. Greenwood and J. A. McGinnety, *J. Chem. Soc., Chem. Commun.*, 331 (1965).
(11) N. N. Greenwood, N. F. Travers, and D. W. Waite, *J. Chem. Soc., Chem. Commun.*, 1027 (1971).
(12) R. E. Loffredo and A. D. Norman, *J. Am. Chem. Soc.*, **93**, 5587 (1971).
(13) J. L. Little, S. S. Pao, and K. K. Sugathan, *Inorg. Chem.*, **13**, 1752 (1974).
(14) J. L. Little, G. D. Friesen, and L. J. Todd, *Inorg. Chem.*, **16**, 869 (1977).
(15) V. D. Aftandilian, H. C. Miller, G. W. Parshall, and E. L. Muetterties, *Inorg. Chem.*, **1**, 734 (1962).
(16) J. L. Little, unreported results, 1975.
(17) G. D. Friesen and L. J. Todd, *J. Chem. Soc., Chem. Commun.*, 349 (1978).

Contribution from the Departments of Chemistry, The University of North Carolina, Chapel Hill, North Carolina 27514,
and The University of California at Los Angeles, Los Angeles, California 90024

Magnetic Studies of Chromium(II) and Chromium(III) Metallocarboranes

VAN H. CRAWFORD, WILLIAM E. HATFIELD,* CHRIS G. SALENTINE, KENNETH P. CALLAHAN,
and M. FREDERICK HAWTHORNE*

Received April 6, 1978

Temperature-dependent magnetic susceptibility data for $[(C_2H_5)_4N]_2[Cr^{II}(C_2B_{10}H_{12})_2]$ have been collected in the range 1.4–80 K. The magnetic data may be fit to the Curie–Weiss law $\chi = C/(T - \Theta)$ with $g = 2.00$ and $\Theta = -1.7$ K. Magnetic data for $Cs[Cr^{III}(C_2B_9H_{11})_2]$ yield $g = 1.98$ and $\Theta = -1.5$ K, in excellent agreement with results from EPR studies. The deviations from the Curie law, as indicated by the Θ values, are thought to arise from single-ion effects.

Introduction

The mode of bonding and the degree of electron delocalization in metal sandwich complexes have been the subjects of a number of investigations.[1,2] Sandwich complexes include the metallocenes and metallocarboranes, with the latter series offering more opportunity for subtle structural and chemical variety. Much of the work on paramagnetic metallocarboranes has involved analysis of the NMR shifts that have been observed. Recently Warren[3-5] has derived expressions for the magnetic properties of sandwich complexes and has noted some discrepancies between the reported results and the predictions from his models. The d^4 case is of particular interest since the ground state depends on the ligand field strength, and the differences in ground-state properties may be seen in the magnetic studies. With use of the notation for $C_{\infty v}$ symmetry, a $^3\Delta$ ground state is expected for the ligand field strengths usually observed in sandwich complexes with d^4 electronic configurations, and substantial orbital contributions to the magnetic moment are expected. The data for chromocene[6] yield a magnetic moment of $3.2 \pm 0.16\ \mu_B$ between 90 and 295 K, a value which is significantly greater than the spin-only value of $2.83\ \mu_B$ and which is consistent with a $^3\Delta$ ground state. For the isoelectronic bis(mesitylene)vanadium(I) cation,[7] the observed moment of $2.80 \pm 0.17\ \mu_B$ (88–193 K) suggests a $^3\Sigma^-$ ground state. The air-stable complex $[(C_2H_5)_4N]_2[Cr^{II}(C_2B_{10}H_{12})_2]$ has recently been prepared. It was of interest to determine the magnetic properties of this compound and to compare the results with the data for the two other sandwich compounds with d^4 electronic configurations. The results of magnetic susceptibility investigations between 1.8 and 90 K of the chromium(II) complex and of $Cs[Cr^{III}(1,2\text{-}C_2B_9H_{11})_2]$ are reported here.

Experimental Section

The Cr complexes were prepared according to the literature methods.[8] Anal. Calcd for $CrB_{20}C_{20}H_{64}N_2$: C, 39.97; H, 10.73; N, 4.66; B, 35.98; Cr, 8.65. Found: C, 39.89; H, 10.65; N, 4.50; B, 36.03; Cr, 8.57.

The magnetic susceptibilities were measured as described elsewhere.[9]

Results

The magnetic data for the unusual air-stable chromium(II) compound $[(C_2H_5)_4N]_2[Cr(C_2B_{10}H_{12})_2]$ are shown in Figure 1 as inverse susceptibility vs. temperature. The best least-squares fit to the Curie–Weiss law, $\chi = C/(T - \Theta)$, yielded $g = 2.00 \pm 0.01$ and $\Theta = -1.7 \pm 0.1$ K, where the g value was calculated from the expression

$$g = \left[\frac{3kC}{N\beta^2 S(S+1)}\right]^{1/2}$$

In this expression, C is the Curie constant, S is the spin and is equal to 1, and the other symbols have their usual meanings. The g value obtained from the Curie–Weiss fit is very nearly equal to the free electron g value; this indicates that the orbital angular momentum is almost completely quenched. The small Θ value may be assumed to arise primarily from single-ion effects since there is little chance for magnetic exchange through carborane ligands. NMR evidence has shown that the metal electron density is not delocalized throughout the ligand cage.[1]

---

* To whom correspondence should be addressed: W.E.H., The University of California; M.F.H., The University of California at Los Angeles.

0020-1669/79/1318-1600$01.00/0 © 1979 American Chemical Society

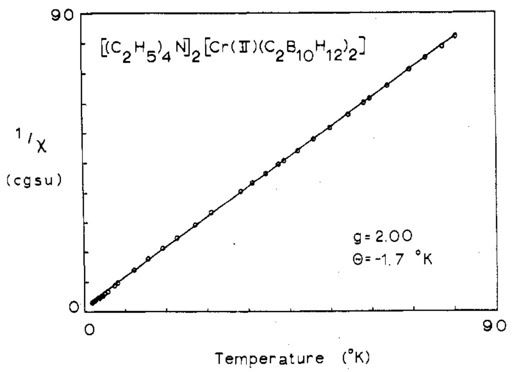


Figure 1. Inverse magnetic susceptibility data (O) for $[(C_2H_5)_4N]_2[Cr(C_2B_{10}H_{12})_2]$. Curie–Weiss line was calculated with $g = 2.00$ and $\Theta = -1.7$ K.

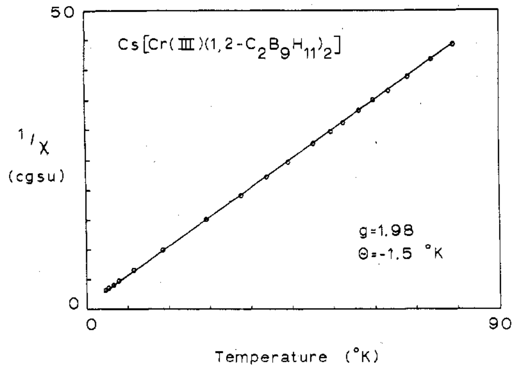


Figure 2. Inverse magnetic susceptibility data (O) for $Cs[Cr(1,2\text{-}C_2B_9H_{11})_2]$. Curie–Weiss line was calculated with $g = 1.98$ and $\Theta = -1.5$ K.

The magnetic susceptibility data for $Cs[Cr^{III}(1,2\text{-}C_2B_9H_{11})_2]$ are shown in Figure 2 as inverse susceptibility vs. temperature. The best least-squares fit to the Curie–Weiss law is also shown. The best-fit parameters are $g = 1.98 \pm 0.01$ and $\Theta = -1.5 \pm 0.1$ K. The g value is typical of chromium(III) complexes, and the small negative Θ value arises primarily from single-ion effects. EPR data for the similar complex $[(CH_3)_4N][Cr^{III}(C_2B_9H_9\{CH_3\}_2)_2]$ have been interpreted in terms of an anisotropic g tensor ($g_{\parallel} = 1.97$ and $g_{\perp} = 2.02$) and $|D| = 1.5$ cm^{-1}, where D is the zero-field splitting parameter in the usual axial spin Hamiltonian.[1] The present data are in excellent agreement with the EPR data.

Discussion

The electronic properties of sandwich compounds, e.g., metallocenes and bis(arene)metal derivatives, have been the subject of many investigations since these properties vary widely from compound to compound. Data exist for two triplet-state compounds with d^4 electronic configurations, those being chromocene[6] and the bis(mesitylene)vanadium(I) cation.[7] The limited magnetic data that are available indicate that the ground states are distinctly different. The recent preparation of the chromium(II) metallocarborane $[(C_2H_5)_4N]_2[Cr(C_2B_{10}H_{12})_2]$ provides a third example of a d^4 sandwich compound. As Warren has pointed out, there is a dearth of experimental observations on d^4 systems,[4] but the theoretical apparatus for the explanation of d^4 properties has been available for several years.[10]

Scott and Matsen[10] have shown that, in general, metal sandwich compounds may be treated as having axial symmetry $C_{\infty v}$ as long as only d^n configurations are involved, if a fivefold or higher rotation axis is present. Warren has presented a ligand field model in the strong-field limit[4] and has evaluated the problem in terms of the Racah parameters B and C and the crystal field quantities Ds and Dt. In sandwich compounds which have $C_{\infty v}$ symmetry, the fivefold degenerate set of d orbitals is usually split in the following manner:[5]

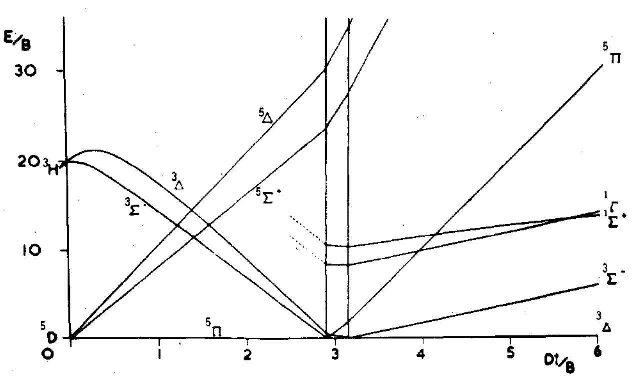


Figure 3. Tanabe–Sugano type diagram for the d^4 configuration in $C_{\infty v}$; $Dt/Ds = 0.55$ and $C/B = 4.0$.[4]

π	d_{xz}, d_{yz}	$E_\pi = Ds + 4Dt$
σ	d_{z^2}	$E_\sigma = 2Ds - 6Dt$
δ	$d_{xy}, d_{x^2-y^2}$	$E_\delta = 2Ds - Dt$

Analyses of spectral properties of a large number of metallocene systems show that the Dt/Ds ratios are in the range 0.5–0.6. Furthermore, a C/B ratio of 4.0 and a range of 4.5–6.5 for Dt/B have been found. With this information, Warren has constructed a Tanabe–Sugano diagram;[4] a portion of this diagram is shown in Figure 3, where it may be seen that the ground state is $^5\Pi$ for Dt/B less than 3, $^3\Sigma^-$ for a limited range of Dt/B close to 3, and $^3\Delta$ for larger values of Dt/B. The $^5\Pi$ state arises from the electronic configuration $\delta^2\sigma^1\pi^1$, while the $^3\Sigma^-$ arises from the configuration $\delta^2\sigma^2$, and the $^3\Delta$ state stems from $\delta^3\sigma$.

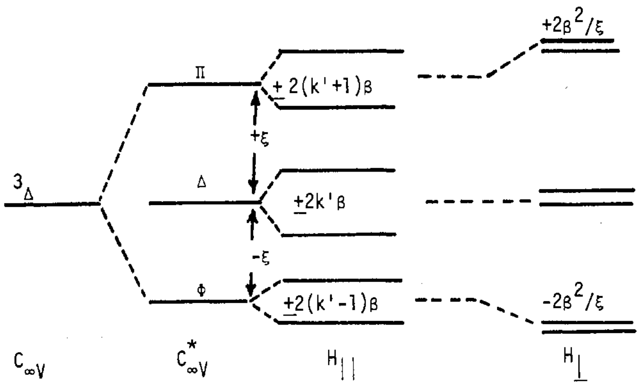
A similar calculation has been carried out for the d^3 case, and the $^4\Sigma^-$ state from configuration $\sigma\delta^2$ is the ground state for reasonable values of Dt/B.[3] Magnetic properties of the $^4\Sigma^-$ state should conform to spin-only behavior over the entire temperature range, and the magnetic susceptibility data obtained here confirm the theoretical expectation.

The magnetic properties of the $^3\Sigma^-$ state of the d^4 configuration should also conform to spin-only behavior, but from Figure 3 it may be seen that there is a low-lying quintet state, the $^5\Pi$, as well as a $^3\Delta$ state nearby. The temperature variation of the magnetic properties of a system characterized by $C/B = 4.0$ and Dt/B of approximately 3 may be expected to reflect the presence of these levels since they would, by necessity, be included in the Van Vleck magnetic susceptibility expression:[11]

$$\chi = \frac{N\sum_i [(E_i^{\mathrm{I}})^2/kT - 2E_i^{\mathrm{II}}] \exp(-E_i^0/kT)}{\sum_i \exp(-E_i^0/kT)}$$

In this expression, for a principal direction x, y, or z, E_i^0 is the zero-field energy, $E_i^{\mathrm{I}} = \langle\Psi_i|k'L_p + 2S_p|\Psi_i\rangle\beta$, $E_i^{\mathrm{II}} = \sum_j(\langle\Psi_i|k'L_p + 2S_p|\Psi_j\rangle\beta)^2/(E_i^0 - E_j^0)$, and $p = x, y, z$. The factor k' in the Zeeman operator is the orbital reduction parameter; it allows for the delocalization of metal electron density onto the ligand atoms.[5]

For those cases in which Dt/B is greater than ~3.2 and for which the ground state is $^3\Delta$, the magnetic properties are expected to exhibit an interesting and characteristic temperature dependence. Under the influence of spin-orbit coupling and the Zeeman effect, the $^3\Delta$ state splits as follows:[4]



The magnetic properties are not complicated by the relatively low-lying $^3\Sigma^-$ state since the spin-orbit matrix elements connecting the $^3\Delta$ and $^3\Sigma^-$ states are zero, and there is no second-order Zeeman contribution. When the $^3\Delta$–$^3\Sigma^-$ energy separation is comparable to kT, there will be reduction of the moment toward the spin-only value. Anticipating the results, we ignore this complexity. The magnetic moments take the forms

$$\mu_\parallel = 2\sqrt{3}\{(k'^2 + 1) - [2k'(e^x - e^{-x}) + 1](1 + e^x + e^{-x})^{-1}\}^{1/2}$$

$$\mu_\perp = 2\sqrt{3}\{(e^x - e^{-x})x^{-1}(1 + e^x + e^{-x})^{-1}\}^{1/2}$$

where $x = -\xi/kT$.

It is clear that the metallocarboranes under study here do not have $C_{\infty v}$ symmetry and that the theoretical expressions must be modified to reflect the lower symmetry. The lowest practical case is one having a C_{2v} distortion, and fortunately Warren[5] has worked out the necessary expressions. The energy level diagram with the necessary information for the Van Vleck expression is shown in Figure 4. The magnetic susceptibility expression is given in the Appendix. This treatment neglects spin–orbit coupling with excited states, and König et al.[12] have noted that the approximation is of limited applicability. However, the magnetic properties are predominantly determined by the ground state, and a comparison of the experimental data for $[(C_2H_5)_4N]_2[Cr^{II}(C_2B_{10}H_{12})_2]$ with the magnetic moments predicted from Warren's equations for a $^3\Delta$ state is instructive. Toward this end we show, in Figure 5, the temperature dependence of the average moment for several values of the distortion parameter. The calculations were made with $k' = 0.7$. The important point to be noted here is that the magnetic moment is temperature independent and is 3.0 μ_B for large values of the distortion parameter.

With this background, it is now possible to examine the magnetic behavior of the complex $[(C_2H_5)_4N]_2[Cr(C_2B_{10}H_{12})_2]$. Although the structure of the compound is not known, based on known structures for metallocarborane compounds,[8,13,14] it is reasonable to assume a sandwich-type arrangement. The magnetic susceptibilities were fit with the premise that the ground state was $^3\Delta$, and the parameters $k' = 0.23$, $\Delta = 29$ cm^{-1}, and $\xi = 230$ cm^{-1} resulted. It is well-known that the orbitals containing the unpaired electrons in many metallocarboranes and metallocenes are largely d orbitals and that the degree of delocalization is not large. König et al.[12] also observed extremely small values of k' and the spin-orbit coupling constant, as well as the Racah parameter B, in their work on chromocene and cobaltocene, and they explained their observations in terms of the theoretical results of Ammeter and Swalen.[15] These latter authors have shown that a precise description of the ground state of chromocene or cobaltocene should include the effects of a dynamic Jahn–Teller effect on the double degenerate ground states and that the orbital reduction factor that is calculated is, in effect, a product of the true orbital-reduction factor and a vibrational overlap term. The Jahn–Teller effect is not operative in nickelocene, and an analysis of the magnetic data for nickelocene yields a value for k of 1.0.[16] The Jahn–Teller effect would not be operative in the chromium(II) carborane if the ground state were orbitally nondegenerate, and a k value near 1.0 would be expected. A comparison of the experimetal data of the chromium(II) carborane with the data for chromocene reveals a slight difference in the temperature dependence of the magnetic moments in the low-temperature range; the moment for chromocene has decreased to 1.6 μ_B at 1.8 K while the magnetic moment of the chromium(II) carborane has decreased a somewhat lesser amount, being 2.3 μ_B at 1.4 K. With these thoughts in mind the data were analyzed in a calculation in which the k' parameter was

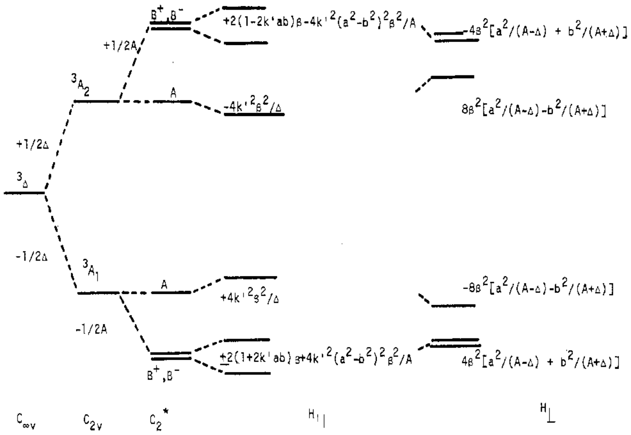


Figure 4. Energy level diagram for d^4 $C_{\infty v}$ systems with C_{2v} distortion.[5] $C_{\infty v}$ and C_∞* nomenclature is from ref 3. a and b are defined in the Appendix; $A = (4\xi^2 + \Delta^2)^{1/2}$.

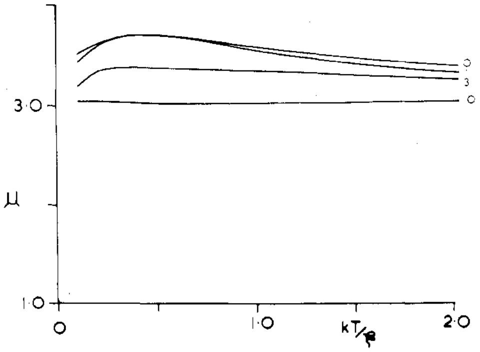


Figure 5. Variation of magnetic moment with C_{2v} distortion for d^4 systems.[5] δ values are as shown; $k' = 0.7$.

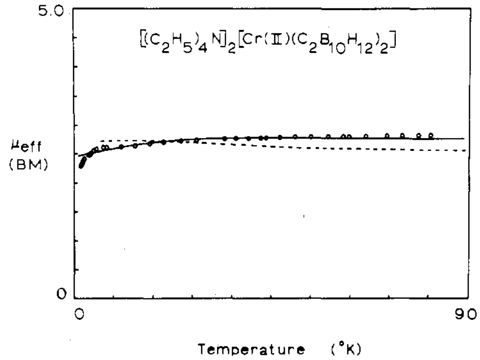


Figure 6. Magnetic moment data (○) for $[(C_2H_5)_4N]_2[Cr(C_2B_{10}H_{12})_2]$. Solid line was calculated with $k' = 0.23$, $\Delta = 29$ cm^{-1}, and $\xi = 230$ cm^{-1}. Dashed line was calculated with $k' = 0.7$, $\Delta = 555$ cm^{-1}, and $\xi = 230$ cm^{-1}.

constrained to be 0.7, a value which would admit some covalency in the chromium–carborane bonds. The resulting best fit, which yielded a value for the distortion parameter Δ of 555 cm^{-1}, is shown in Figure 6, where it may be seen that the fit is not good, even qualitatively. These data suggest that the chromium(II) carborane complex and chromocene have comparable electronic ground states, but it is clear that a structural study of the former is needed before a definitive answer can be had for this problem.

Acknowledgment. This research was supported in part by the National Science Foundation through Grant No. CHE77-09913.

Appendix

The magnetic susceptibility expression for the $^3\Delta$ state of the d^4 electronic configuration under the influence of a C_{2v} distortion is as follows:

$$\chi_{\parallel} = 3T\{(1 + 2k'ab)^2e^{-\alpha/2} + (1 - 2k'ab)^2e^{\alpha/2} + k'^2[2(a^2 - b^2)^2(e^{\alpha/2} - e^{-\alpha/2})\alpha^{-1} + (e^{\delta x/2} - e^{-\delta x/2})(\delta x)^{-1}]\}/ \{2(e^{\alpha/2} + e^{-\alpha/2}) + e^{\delta x/2} + e^{-x/2}\}$$

$$\chi_{\perp} = 6T\{a^2(e^{\alpha/2} - e^{-\alpha/2} - e^{\delta x/2} + e^{-\delta x/2}) \times (\alpha - \delta x)^{-1} + b^2(e^{\alpha/2} - e^{-\alpha/2} + e^{\delta x/2} - e^{-\delta x/2})(\alpha - \delta x)^{-1}\}/ \{2(e^{\alpha/2} + e^{-\alpha/2}) + e^{\delta x/2} + e^{-\delta x/2}\}$$

$$\chi = \tfrac{1}{3}(\chi_{\parallel} + 2\chi_{\perp})$$

where $x = -\xi/kT$, $\delta = \Delta/\xi$, $a = {}^1/_2[\delta + (4 + \delta^2)^{1/2}]\{{}^1/_4[\delta + (4 + \delta^2)^{1/2}]^2 + 1\}^{-1/2}$, $b = \{{}^1/_4[\delta + (4 + \delta^2)^{1/2}]^2 + 1\}^{-1/2}$, and $\alpha = x(4 + \delta^2)^{1/2}$.

Registry No. $[(C_2H_5)_4N]_2[Cr(C_2B_{10}H_{12})_2]$, 60270-25-9; $Cs[Cr(1,2\text{-}C_2B_9H_{11})_2]$, 12373-83-0.

References and Notes

(1) R. J. Wiersema and M. F. Hawthorne, *J. Am. Chem. Soc.*, **96**, 761 (1974).
(2) M. F. Rettig in "Chemical Applications of NMR in Paramagnetic Molecules", G. N. LaMar, W. D. Horrocks, Jr., and R. H. Holm, Eds., Academic Press, New York, 1973.
(3) K. D. Warren, *J. Chem. Phys.*, **77**, 1681 (1973).
(4) K. D. Warren, *Inorg. Chem.*, **13**, 1243 (1974).
(5) K. D. Warren, *Inorg. Chem.*, **13**, 1317 (1974).
(6) F. Engelmann, *Z. Naturforsch., B*, **8**, 775 (1953).
(7) E. O. Fischer, G. Joos, and W. Meer, *Z. Naturforsch., B*, **13**, 456 (1958).
(8) H. W. Ruhle and M. F. Hawthorne, *Inorg. Chem.*, **7**, 2279 (1968); C. G. Salentine and M. F. Hawthorne, *ibid.*, **15**, 2872 (1976).
(9) D. B. Losee and W. E. Hatfield, *Phys. Rev. B*, **10**, 212 (1974).
(10) D. R. Scott and F. A. Matsen, *J. Phys. Chem.*, **72**, 16 (1968).
(11) J. H. Van Vleck, "The Theory of Electric and Magnetic Susceptibilities", Oxford University Press, London, 1932, Chapter 9.
(12) E. König, R. Schnakig, S. Kremer, B. Kanellakopulos, and R. Klenze, *Chem. Phys.*, **27**, 331 (1978).
(13) D. St. Clair, A. Zalkin, and D. H. Templeton, *Inorg. Chem.*, **10**, 2587 (1971).
(14) F. Y. Lo, C. E. Strouse, K. P. Callahan, C. B. Knobler, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **97**, 428 (1975).
(15) J. H. Ammeter and J. D. Swalen, *J. Chem. Phys.*, **57**, 678 (1972).
(16) V. Cerny, *Collect. Czech. Chem. Commun.*, **40**, 1829 (1975).

Contribution from the Department of Chemistry,
Colorado State University, Fort Collins, Colorado 80523

Potentiometric Investigation of Dialuminum Heptachloride Formation in Aluminum Chloride–1-Butylpyridinium Chloride Mixtures

R. J. GALE and R. A. OSTERYOUNG*

Received October 18, 1978

The solvent acid–base properties of $AlCl_3$:1-butylpyridinium chloride melts from 2.2:1.0 to 0.6:1.0 molar ratios have been investigated by potentiometry. An equilibrium constant, K_3, for the dissociation reaction $2AlCl_4^- \rightleftarrows Al_2Cl_7^- + Cl^-$ was determined to be $<3.8 \times 10^{-13}$ at 30 °C. The 1-butylpyridinium cation is spontaneously reduced by elemental aluminum in the basic composition range.

Introduction

Considerable interest has been shown recently in molten-salt mixtures that are liquid at ambient temperatures, in view of the possibilities for their use as novel matrix solvents or electrolytes. The fused aluminum halide–alkylpyridinium halide systems are low melting, relatively easy to synthesize, and miscible with organic solvents such as benzene.[1-4] An investigation of the ionic species equilibria in $AlCl_3$–1-butylpyridinium chloride mixtures, by Raman spectroscopy,[5] has indicated that association reaction 1 is virtually complete and

$$2AlCl_4^- + Al_2Cl_6 \rightleftarrows 2Al_2Cl_7^- \qquad (1)$$

that no molecular aluminum chloride could be detected in the 2:1 molar ratio mixture at room temperature.

Equilibria 2–6 have been commonly used to relate the major solvent species in $AlCl_3$–MCl systems, M usually being an alkali metal cation.[6-11] If an aluminum reference electrode behaves as a reversible indicator electrode, model equilibria may be applied to potentiometric titration data by using the Nernst equation (7) which, incorporated with the association constants for reaction 2, gives eq 8 for a reference state (superscript °) and any other state i (superscript i). Hence, an electrochemical cell of the type

$$Al^{3+} + 4Cl^- \rightleftarrows AlCl_4^- \qquad (2)$$

$$2AlCl_4^- \rightleftarrows Al_2Cl_7^- + Cl^- \qquad (3)$$

$$Al_2Cl_6 + Cl^- \rightleftarrows Al_2Cl_7^- \qquad (4)$$

$$2AlCl_3 \rightleftarrows Al_2Cl_6 \qquad (5)$$

$$AlCl_4^- + Al_2Cl_6 \rightleftarrows Al_3Cl_{10}^- \qquad (6)$$

$$E = E^\circ + (RT/3F)\ln(a_{Al(III)}/a_{Al(0)}) \qquad (7)$$

$$\Delta E = (RT/3F)\ln(a^\circ_{AlCl_4^-}/a^i_{AlCl_4^-}) + (4RT/3F)\ln(a^i_{Cl^-}/a^\circ_{Cl^-}) \qquad (8)$$

Al|RCl, $AlCl_3$(ref)⁝fritted disk⁝$AlCl_3$(c), RCl|Al

where R represents an alkylpyridinium cation, may be used as a pCl$^-$ electrode. The purpose of the present investigation is twofold: (i) to quantitatively assess the association constants for the major ionic equilibria and (ii) to examine the effects that the nature of the cationic moiety of the halide salt has on the solvent equilibria.

Experimental Section

Melts were prepared by mixing accurately weighed quantities of purified aluminum chloride and 1-butylpyridinium chloride. The purification procedures for these compounds are described elsewhere.[5] In order to avoid discoloration and thermal decomposition, we added

0020-1669/79/1318-1603$01.00/0