

bond distance. The smaller electron density of  $C_2$  with respect to  $C_1$  is also an indication of charge donation to the metallic centers via two localized  $Fe_1-C_2$  and  $Fe_2-C_3$  bonds.

Although the body of these results seems to support the A type valence-bond description over the B one, the larger  $C_2-C_3$  overlap population with respect to  $C_1-C_2$  seems to us evidence for the inadequacy of the description of the bonding in terms of the formula A only. It is our opinion that a correct de-

scription of the present compounds requires both the A and the B type valence-bond formulas, each of them being too oversimplified, as already suggested by other authors.<sup>6</sup> On the other hand, also the  $^{13}C$  NMR data, which usually furnish very accurate evidence, do not allow us in this case to discriminate with enough confidence between the two formulas.

Registry No. I, 12211-98-2; II, 12212-46-3; Fe, 7439-89-6.

Contribution from the Chemistry Department,  
University of Rhode Island, Kingston, Rhode Island 02881

## Use of Ligands as Optical Structural Probes. 4. A Solution Kerr Effect Study of Organotin(IV) Tropolonates, Oxinates, and Dibenzoylmethanates

S. K. BRAHMA and W. H. NELSON\*

Received March 25, 1982

Molar Kerr constants have been determined for several complexes of the type  $R_2SnCh_2$  ( $R$  = methyl, ethyl, or butyl and  $Ch^-$  = oxinate, tropolonate, or dibenzoylmethanate) at 25 °C in cyclohexane with use of a 632.8-nm laser source. As expected *cis*-bis(8-quinolinolato)dimethyltin(IV) is strongly negatively birefringent. The other complexes, while polar, are all positively birefringent. Large positive Kerr constants accompanied by nonzero permanent dipole moments in several instances point toward the predominance of distorted trans-type molecules, which in several instances can best be characterized by skew-trapezoidal-bipyramidal structures. Results show that the Kerr effect should be an effective means of determining the structures of complexes of the type  $R_2SnCh_2$  in solution if the ligands  $Ch^-$  are planar and highly optically anisotropic.

### Introduction

Compounds of the type  $R_2SnCh_2$  have remained objects of considerable interest from the time they were first synthesized.<sup>1-7</sup> This has been true not only because there are a great variety of organic substituents,  $R$ , and chelates,  $Ch^-$ , that form stable complexes but also because these seemingly simple six-coordinate molecules have some unusual properties. In this paper some of the physical properties will be investigated which are impossible to ascribe to either simple *cis* or *trans* isomers.

In several instances there is strong evidence for a regular *cis*-type geometry in solution. NMR spectra<sup>8</sup> and dipole moments clearly indicate that several complexes of the type  $X_2SnCh_2$  are *cis* ( $X = Cl^-, Br^-, I^-$ ;  $Ch^- = \beta$ -keto enolate). A Kerr effect study<sup>9</sup> of bis(tropolonato)dimethyltin(IV) has provided additional conclusive evidence for a *cis*-type structure in solution.

Yet, carefully done Raman studies have strongly demonstrated that many dimethyltin derivatives in solution apparently are *trans* in solution.<sup>1,2,10,11</sup> There is no doubt that bis(2,4-pentanedionato)dimethyltin(IV) is *trans* in the solid state.<sup>12</sup>

A later infrared study<sup>13</sup> of deuteriomethyl derivatives detected the presence of *cis*-*trans* mixtures in carbon disulfide solution. Although some information concerning the mechanism of ligand exchange has been obtained, in the main  $^1H$  NMR studies<sup>14-16</sup> have shown primarily that ligand exchange is very rapid.

Perhaps what has been most difficult to reconcile with the results of the Raman studies has been the very large orientation polarization exhibited by these complexes.<sup>5,14</sup> At first, all of this polarization was attributed to atom polarization,<sup>5</sup> but later studies showed that substantial amounts of orientation polarization<sup>14,17</sup> were exhibited by most of these complexes. Typically permanent dipole moments are fairly large: 2-5 D.

In a recent review Kepert<sup>18</sup> has suggested that many octahedral complexes are of neither a regular *cis* nor a regular *trans* geometry but that a related geometry, a skew-trapezoidal bipyramid, should be considered. There is evidence for such structures in the solid state,<sup>19-21</sup> but until now there was no practical means of confirming the presence of such structures in solutions of labile complexes.

In this paper, it will be demonstrated that, by using the Kerr effect, one can distinguish *cis*, *trans*, and skew-trapezoidal-bipyramidal structures. Several tin complexes will be assigned a skew-trapezoidal-bipyramidal structure while others will be

- (1) M. M. McGrady and R. S. Tobias, *Inorg. Chem.*, **3**, 1160 (1964).
- (2) M. M. McGrady and R. S. Tobias, *J. Am. Chem. Soc.*, **87**, 1909 (1965).
- (3) R. Barbieri, G. Faroglia, M. Gustiniani, and L. Roncucci, *J. Inorg. Nucl. Chem.*, **26**, 203 (1964).
- (4) L. Roncucci, G. Faroglia, and R. Barbieri, *J. Organomet. Chem.*, **1**, 427 (1964).
- (5) W. H. Nelson and D. F. Martin, *J. Inorg. Nucl. Chem.*, **27**, 89 (1965).
- (6) T. Tanaka, M. Komura, Y. Kawasaki, and R. I. Okawara, *J. Organomet. Chem.*, **1**, 484 (1964).
- (7) R. Veeda, Y. Kawasaki, T. Tanaka, and R. I. Okawara, *J. Organomet. Chem.*, **5**, 1964 (1966).
- (8) W. H. Nelson, *Inorg. Chem.*, **6**, 1509 (1967).
- (9) W. H. Nelson and M. J. Aroney, *Inorg. Chem.*, **12**, 132 (1973).
- (10) V. B. Ramos and R. S. Tobias, *Spectrochim. Acta, Part A*, **29A**, 953 (1973).
- (11) V. B. Ramos and R. S. Tobias, *Spectrochim. Acta, Part A*, **30A**, 181 (1974).

- (12) G. A. Miller and E. O. Schlemper, *Inorg. Chem.*, **12**, 677 (1973).
- (13) R. LeBlanc and W. H. Nelson, *J. Organomet. Chem.*, **113**, 257 (1976).
- (14) C. Z. Moore and W. H. Nelson, *Inorg. Chem.*, **8**, 138 (1969).
- (15) R. W. Jones, Jr., and R. C. Fay, *Inorg. Chem.*, **12**, 2599 (1973).
- (16) N. Serpone and K. A. Hersh, *Inorg. Chem.*, **13**, 2901 (1974).
- (17) J. W. Hayes, W. H. Nelson, and D. V. Radford, *Aust. J. Chem.*, **26**, 871 (1973).
- (18) D. L. Kepert, *Prog. Inorg. Chem.*, **23**, 1 (1977).
- (19) P. G. Harrison, T. J. King, and J. A. Richards, *J. Chem. Soc., Dalton Trans.*, 826 (1975).
- (20) J. Hilton, E. K. Nunn, and S. C. Wallwork, *J. Chem. Soc., Dalton Trans.*, 173 (1973).
- (21) T. Kimura, N. Yasuoka, N. Kasai, and M. Kakudo, *Bull. Chem. Soc. Jpn.*, **45**, 1649 (1972).

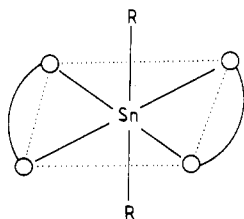


Figure 1. Regular trans isomer.

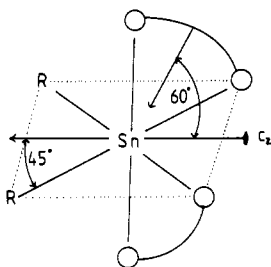


Figure 2. Regular cis isomer.

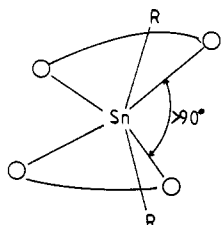


Figure 3. Skew-trapezoidal-bipyramidal isomer.

shown to be more nearly akin to regular cis- or trans-octahedral geometries. The Kerr effect is unusually useful in studies of this type because, if one examines the trans (Figure 1), cis (Figure 2), or the skew-trapezoidal-bipyramidal (Figure 3) structures, it can be noted easily that there will be very large differences in the magnitude or sign of the Kerr constants for the three structural types.

The simple trans structure (Figure 1), which can possess no permanent dipole moment, will exhibit a small positive Kerr effect proportional to the square of the molecular optical anisotropy,  $\gamma^2$ . It has been shown that trans structures having coplanar highly anisotropic ligands will have  $\gamma^2$  values 4 times<sup>22</sup> that of the free ligand. For molecules of  $C_2$  or higher symmetry,  $\gamma = b_1 - b_3$ , where the polarizability components  $b_1$ ,  $b_2$ , and  $b_3$  along the principal axes are related  $b_1 \neq b_2 = b_3$ .

The cis isomer (Figure 2) in contrast possesses a dipole moment collinear with the  $C_2$  axis. Of critical importance is the existence of a plane of maximum polarizability perpendicular<sup>22</sup> to the principal axis. Since the permanent dipole moment will be much larger than the induced moment, the Kerr effect will be negative in sign with a magnitude depending upon the size of the permanent dipole moment and the optical anisotropy,  $\gamma$ .

The skew-trapezoidal-bipyramidal structure (Figure 3) also is polar, but its moment lies in the plane of maximum polarizability. Hence, one predicts a much larger positive Kerr constant for this structure than for the trans isomer even though both structures will show similar optical anisotropy values. It follows that the Kerr effect is a good means of distinguishing between the three structures. Furthermore, the apparent dilemma of having polar complexes with what appears to be trans-oriented chelate and alkyl groups may now be resolved since the structure in Figure 3 is both polar and highly anisotropic.

Table I. Polarization and Kerr Effect Data<sup>a</sup>

	$\alpha\epsilon_1$	$\beta$	$\gamma$	$\delta$	$\mu^b$	$10^{12} \times$ $(mK_2)^b$
tropolone	8.39	0.725	0.14	912	3.38	1464
$(C_6H_5)_2Sn(dbzm)_2$	1.32	0.604	0.58	74.63	2.07	666
$(C_6H_5)_2Sn(dbzm)_2$	1.14	1.11	0.682	1066	1.84	8817
$(CH_3)_2Sn(dbzm)_2$	2.23	1.33	0.593	1017	3.18	8028
$(CH_3)_2Sn(OX)_2$	1.14	1.57	0.143	-248.5	5.30	-1468.32
$(C_6H_5)_2Sn(Trop)_2$	4.5	1.16	0.12	377.82	4.59	2091.13

<sup>a</sup> The solvent used for all experiments was cyclohexane.

<sup>b</sup> Kerr constants are expressed in esu mol<sup>-1</sup>;  $1 \text{ m}^5 \text{ V}^{-2} \text{ mol}^{-1} = 0.8988 \times 10^{15} \text{ esu mol}^{-1}$ .

## Experimental Section

**Kerr Constants.** Techniques for the measurement of the Kerr effect in nonconducting liquids have been described in detail.<sup>23,24</sup> Aroney has reviewed<sup>25</sup> progress in the application of the technique. Our apparatus used for measuring the Kerr effect is a modification of the one used by the Sydney group.<sup>9,23</sup> A 2-mW He-Ne laser was used as a light source, and intensity minima were measured with the aid of a photomultiplier.

**Reagents.** Cyclohexane used as solvent was of reagent grade and was used without modification after storage over  $CaCl_2$  or molecular sieves to remove traces of water. All complexes studied had been prepared and described earlier.<sup>1,14,26</sup>

**Physical Constants.** The constants for cyclohexane used in all calculations were determined previously<sup>27</sup> and reported as a function of wavelength.

**Measurements.** Incremental changes in the dielectric constants, densities, refractive indices, and Kerr constants ( $\Delta\epsilon$ ,  $\Delta d$ ,  $\Delta n$ , and  $\Delta\beta$ , respectively) were measured for solutions having solute weight fractions,  $w_2$ . The coefficients  $\alpha\epsilon_1$ ,  $\beta$ ,  $\gamma$ , and  $\delta$  were derived by using the relationships  $\alpha\epsilon_1 = \sum \Delta\epsilon / \sum w_2$ ,  $\beta = \sum \Delta d / (d_1 \sum w_2)$ ,  $\gamma = \sum \Delta n / (n_1 \sum w_2)$ , and  $\delta = \sum \Delta\beta / (\beta_1 \sum w_2)$ . The subscripts 1 and 2 refer to solvent and solute components, respectively. From these data are calculated the solute dipole moments<sup>28</sup> and molar Kerr constants<sup>23</sup> shown in Table I. The term  $\infty(mK_2)$ , which refers to the solute molar Kerr constant at infinite dilution, is obtained as

$$\infty(mK_2) = {}_sK_1(1 - \beta + \gamma + \delta - H\gamma - J\alpha\epsilon_1)M_2$$

where  ${}_sK_1$  (the specific Kerr constant of the solvent),  $H$ , and  $J$  are solvent constants<sup>27</sup> and  $M_2$  is the solute molecular weight.

## Discussion

**Dipole Moments.** In a previous paper<sup>29</sup> it has been determined that the ring (group) dipole moments of acetylacetonates and dibenzoylmethanate groups attached to Sn(IV) are surprisingly small and pointed toward the metal ion. Ignoring the effects of atom polarization, one obtains values between 1.0 and 1.6 D depending upon the values of the Sn-Cl bond dipole moment<sup>30,31</sup> used in the calculations. Dielectric loss measurements of tin complexes showed<sup>17</sup> later that, indeed, the complexes possess substantial amounts of atom polarization and that in an account for such polarization the ring moments should be reduced by an additional 0.6 D. Thus, it appears that the ring dipole moments associated with these complexes are less than 1 D and perhaps very close to zero. Such an observation certainly is consistent with the high solubilities in nonpolar solvents observed for many highly symmetrical metal- $\beta$ -keto enolate complexes.

(22) N. Asting and W. H. Nelson, *J. Phys. Chem.*, **81**, 629 (1977).

- (23) C. G. LeFevre and R. J. W. LeFevre, "Physical Methods of Organic Chemistry", Vol. 1, A. Weissberger, Ed., 3rd ed., Interscience, New York, 1960, Chapter XXXVI.
- (24) C. G. LeFevre and R. J. W. LeFevre, "Techniques of Chemistry", Vol. 1/III C, A. Weissberger, Ed., Wiley, New York, 1972, p 399.
- (25) M. J. Aroney, *Angew. Chem., Int. Ed. Engl.*, **16**, 663 (1977).
- (26) N. Asting and W. H. Nelson, *Inorg. Chem.*, **16**, 148 (1977).
- (27) R. J. W. LeFevre and R. K. Pierens, *Aust. J. Chem.*, **25**, 413 (1972).
- (28) R. J. W. LeFevre, "Dipole Moments", Methuen, London, 1953.
- (29) C. Z. Moore and W. H. Nelson, *Inorg. Chem.*, **8**, 143 (1969).
- (30) J. W. Smith, "Electric Dipole Moments", Butterworths, London, 1955.
- (31) J. Lorberth and H. Nöth, *Chem. Ber.*, **98**, 969 (1965).
- (32) E. O. Schlemper, *Inorg. Chem.*, **6**, 2012 (1967).

Table II. Bond and Group Polarizabilities from Calculation<sup>a</sup> and Light Scattering

bond or group	$10^{24} \times$ $(b_1 - b_3)$ , $\text{cm}^3$		$10^{24} \times$ $(b_1 - b_3)$ , $\text{cm}^3$
	bond or group	bond or group	
tropolone	3.9	Sn(Trop)	$7.4 \times 10^{-24}$
dibenzoylmethane	10.9	Sn(dbzm)	$14.4 \times 10^{-24}$
Sn-O <sup>a</sup>	3.5		

<sup>a</sup> Values of  $b_1 - b_3$  have been obtained for the Sn-O bond by calculation (E. R. Lippincott and J. M. Stutman, *J. Phys. Chem.*, 68, 2926 (1964)). The anisotropy of the Sn-chelate moiety has been obtained by adding Sn-O bond components to chelate components obtained from light scattering with the assumption that Sn-O bonds are located 90° to one another.

Unfortunately, because of the small size of the ring moments and the presence of substantial amounts of atom polarization, the use of dipole moments as a means of determining structure of  $\beta$ -keto enolate complexes has been difficult. It is clear that a regular centrosymmetric octahedral structure such as *trans*-R<sub>2</sub>SnCh<sub>2</sub> (Figure 1) should have zero orientation polarization. In comparison, there should be small permanent dipole moments associated with either a cis-octahedral structure (Figure 2) or a skew-trapezoidal-bipyramidal structure (Figure 3).

Coincidentally, both the direction and the magnitude of the molecular dipole moments should be very similar for both cis-octahedral and skew-trapezoidal-bipyramidal structures. In both instances, the moment lies along the C<sub>2</sub> principal axis, and Sn-R group dipole moments and ring moments combine additively. It is not entirely clear what the exact magnitude of the ring contribution should be for the skew structure. It is likely that any deviation from values predicted for ring moments previously<sup>29</sup> will be small and due to likely Sn-O bond lengthening on the side of the molecule containing the Sn-R groups.

Dipole moment data are consistent with structures displaced only to a modest degree from the regular trans geometry because dipole moment values<sup>9</sup> observed for acetylacetonates and dibenzoylmethanate are somewhat less than those predicted for the regular cis geometry. Still it is very difficult to demonstrate on the basis of dipole moments alone whether the molecules are more nearly cis or trans.

**Kerr Effect Data.** The Kerr constants are related to the principal optical polarizability components,  $b_1$ ,  $b_2$ , and  $b_3$ , by<sup>23</sup>

$$\begin{aligned} mK = & (2\pi N/405kT)[[D^2P/E^2P(b_1 - b_2)^2 + (b_2 - b_3)^2 + \\ & (b_3 - b_1)^2] + (1/kT)[(\mu_1^2 - \mu_2^2)(b_1 - b_2) + \\ & (\mu_2^2 - \mu_3^2)(b_2 - b_3) + (\mu_3^2 - \mu_1^2)(b_3 - b_1)]] \end{aligned}$$

where  $\mu_1$ ,  $\mu_2$ , and  $\mu_3$  are the resolved components of the permanent electric dipole moment along the corresponding axes.  $D^2P/E^2P$  is the ratio of distortion polarization to electronic polarization.  $N$  is Avogadro's number,  $k$  is the Boltzmann constant, and  $T$  is the absolute temperature. In the experiment to be discussed, the approximation is made that  $b_1 \neq b_2 = b_3$ . Thus, the equation simplifies to

$$mK = (2\pi N/405kT)[2(D^2P/E^2P)(b_1 - b_3)^2 + (1/kT)\mu_{\text{obsd}}^2(b_1 - b_3)]$$

Using the known dipole moments of the compounds studied and the  $b_1 - b_3$  values for the chelates determined recently from depolarized Rayleigh scattering<sup>33</sup> (Table II), it is possible to calculate Kerr constants for the various candidate structures in Figures 1-3. A number of these are listed in Table III along with the experimentally determined values. Although the true

Table III. Comparison of Calculated and Measured Kerr Constants

molecule	structure	$10^{12} \times$	$10^{12} \times$
		[ $mK(\text{calcd})$ ]	[ $mK(\text{obsd})$ ]
(C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> Sn(dbzm) <sub>2</sub>	trans	+414	+666
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> Sn(dbzm) <sub>2</sub>	skew	+2222	+8817
(CH <sub>3</sub> ) <sub>2</sub> Sn(dbzm) <sub>2</sub>	skew	+2222	+8028
(CH <sub>3</sub> ) <sub>2</sub> Sn(OX) <sub>2</sub>	cis		-1468
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> Sn(Trop) <sub>2</sub>	skew	+1852	+2091
(CH <sub>3</sub> ) <sub>2</sub> Sn(dbzm) <sub>2</sub>	cis	-803	
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> Sn(Trop) <sub>2</sub>	trans	+110	
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> Sn(Trop) <sub>2</sub>	cis	-811	

values must be somewhat higher, a value of  $(D^2P/E^2P) = 1.1$  was used throughout. There may be a twofold uncertainty in this quantity, but it does not affect the conclusion to be drawn, since the differences between predicted Kerr constants for the structures given in Figures 1-3 are absolutely enormous.

Most significant is the fact that the skew structure is easily distinguished from the regular cis-octahedral counterpart by the sign of its Kerr constant. Solutions of the skew-trapezoidal-bipyramidal molecules are predicted to be very positively birefringent while the solutions of the cis-octahedral molecules should be very negatively birefringent. Thus, it is highly significant that the solutions of (CH<sub>3</sub>)<sub>2</sub>Sn(OX)<sub>2</sub> experimentally have been shown to be strongly negatively birefringent. (CH<sub>3</sub>)<sub>2</sub>Sn(OX)<sub>2</sub> is well-known to be cis.<sup>32</sup> Similarly, it is significant that (C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>Sn(dbzm)<sub>2</sub>, which has been shown<sup>33</sup> to have nearly coplanar dibenzoylmethanate rings, shows a positive Kerr effect of modest magnitude as expected from a trans structure.

It is suggested that at long last spectroscopic and dipole moment data can be reconciled. Early Raman studies<sup>1</sup> pointed toward regular trans-octahedral structures primarily because only one single strong band below 520 cm<sup>-1</sup> assigned to the symmetric stretch was active. The absence of the antisymmetric stretching vibration around 530 cm<sup>-1</sup> in the Raman spectrum strongly indicated<sup>1</sup> a nearly linear (CH<sub>3</sub>)<sub>2</sub>Sn moiety. Yet the infrared activity of the symmetric stretch seemed puzzling<sup>13</sup> in that light. On the other hand, a skew-trapezoidal-bipyramidal structure would show an infrared-active (CH<sub>3</sub>)<sub>2</sub>Sn symmetric stretching vibration and a permanent dipole moment in the plane of the chelate rings.

It is not surprising that the Kerr constant of (CH<sub>3</sub>)<sub>2</sub>Sn-(dbzm)<sub>2</sub> is much larger than that of the butyl derivative. It is likely that the bulk of the butyl groups will bias that structure toward the regular trans geometry while the methyl derivative will be more distorted toward the skew geometry. Noteworthy as well is the lower dipole moment of the butyl derivative, which is also consistent with a more nearly regular trans geometry. The large Kerr constant of the ethyl derivative points toward a skew structure also even though its dipole moment is nearly the same as the butyl derivative. No attempt has been made to assign specific bond angles. Uncertainties in  $D^2P/E^2P$  ratios and Sn-O bond polarizability components are far too great to allow such an exercise. There are many sources of uncertainty in a study of this type. The precision of the experimental data is probably the least of these. It is estimated that Kerr constants are subject to an uncertainty of  $\pm 5\%$ . Group anisotropies (Table II) are much less certainly known. Recent light-scattering experiments have produced values of  $b_1 - b_3$  which should be transferable to Kerr effect studies. However, Sn-O bond data remain a significant uncertainty and could vary appreciably as the Sn-O bond length changes.

Fortunately, the magnitude and sign of the Kerr constants are far less dependent upon the magnitudes of the Sn-O bond polarizability components than they are on the relative position of the dipole moment and the principal polarizability axis. The anisotropies of the Sn-O bonds and the chelate rings are mutually reinforcing, and an uncertainty in the Sn-O bond

(33) W. H. Nelson, W. F. Howard, Jr., and R. Pecora, *Inorg. Chem.*, 21, 1483 (1982).

anisotropy will produce a potentially large uncertainty in the magnitude of the Kerr constant but not its sign. Thus, a difference by a factor of 3 or 4 in the magnitude of experimental and calculated values of the Kerr constant is not surprising or even distressing. It is interesting to note that large positive Kerr constants of the ethyl and methyl derivatives

(Table III) require the skew-trapezoidal-bipyramidal geometry and rule out the cis configuration entirely for those structures.

**Registry No.** *trans*-(C<sub>4</sub>H<sub>9</sub>)Sn(dbzm)<sub>2</sub>, 22673-17-2; *skew*-(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Sn(dbzm)<sub>2</sub>, 60828-32-2; *skew*-(CH<sub>3</sub>)<sub>2</sub>Sn(dbzm)<sub>2</sub>, 53319-86-1; *cis*-(CH<sub>3</sub>)<sub>2</sub>Sn(OX)<sub>2</sub>, 20347-45-9; *trans*-(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Sn(Trop)<sub>2</sub>, 21729-19-1; *cis*-(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Sn(dbzm)<sub>2</sub>, 60828-31-1.

Contribution from the Department of Chemistry,  
The University of Mississippi, University, Mississippi 38677

## Electrochemical Studies of Chloro Complex Formation in Low-Temperature Chloroaluminate Melts. 1. Iron(II), Iron(III), and Nickel(II)

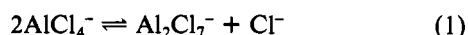
T. M. LAHER and G. L. HUSSEY\*

Received February 17, 1982

A potentiometric titration procedure was used to study the coordination of iron(II) and iron(III) in the aluminum chloride-*N-n*-butylpyridinium chloride (AlCl<sub>3</sub>-BPC) melt containing excess chloride ion (basic melt). Potentiometric measurements on the cells Al|AlCl<sub>3</sub>-BPC (66.7:33.3 mol %)|fritted disk|AlCl<sub>3</sub>-BPC, Fe(II)<sub>aq</sub>|Fe and Al|AlCl<sub>3</sub>-BPC (66.7:33.3 mol %)|fritted disk|AlCl<sub>3</sub>-BPC, Fe(II)<sub>aq</sub>, Fe(III)<sub>aq</sub>|Pt were made while the ratio of AlCl<sub>3</sub> to BPC was varied in the right-hand cell compartment. Analysis of the data obtained indicated that iron(II) and iron(III) are complexed as FeCl<sub>4</sub><sup>2-</sup> and FeCl<sub>4</sub><sup>-</sup>, respectively, in basic melt. Similar potentiometric titration data for the Fe(III)/Fe(II) couple in AlCl<sub>3</sub>-rich (acidic) melt were consistent with a two-chloride-ion dependence. Average stoichiometric formation constants for FeCl<sub>4</sub><sup>2-</sup> and FeCl<sub>4</sub><sup>-</sup> were found to be 5.0 × 10<sup>46</sup> and 7.9 × 10<sup>77</sup>, respectively. The formation constant for NiCl<sub>4</sub><sup>2-</sup>, redetermined in the present study, was 5.0 × 10<sup>49</sup>, referenced to the 66.7:33.3 mol % melt.

### Introduction

Mixtures of aluminum chloride and certain *N*-alkylpyridinium halides form molten salts that are liquid at or close to room temperature. One of these systems, aluminum chloride-*N-n*-butylpyridinium chloride (AlCl<sub>3</sub>-BPC), is liquid at 27 °C over a composition range that includes mixtures containing from 66.7 to 44.0 mol % AlCl<sub>3</sub>.<sup>1</sup> Potentiometric studies indicate that the distribution of chloroaluminate species in the AlCl<sub>3</sub>-BPC melt can be expressed by means of a single equilibrium reaction<sup>2</sup>



with a value of  $K = 1.2 \times 10^{-13}$  at 40 °C.<sup>3</sup> The variation in AlCl<sub>3</sub> content possible in this melt system permits substantial changes in melt chloride ion activity to be made at relatively low liquidus temperatures.

Previous investigations involving nickel(II)<sup>4</sup> and cobalt(II)<sup>5</sup> indicated that the basic (BPC-rich) AlCl<sub>3</sub>-BPC melt is an interesting, anhydrous, ionic solvent in which to study the coordination of transition-metal ions by chloride ion. For example, Gale et al.<sup>4</sup> reported that nickel(II) exists in the form of a very stable, tetrahedral NiCl<sub>4</sub><sup>2-</sup> species in this melt composition region. Similarly, cobalt(II) was complexed as a tetrahedral CoCl<sub>4</sub><sup>2-</sup> species in basic AlCl<sub>3</sub>-BPC melt.<sup>5</sup> The stoichiometric formation constant, based on ion mole fractions, for CoCl<sub>4</sub><sup>2-</sup> in an AlCl<sub>3</sub>-BPC melt was considerably larger than values obtained in inorganic chloroaluminate melts.<sup>5</sup>

In the present study iron(II) and iron(III) chloro complex formation was examined in the basic AlCl<sub>3</sub>-BPC melt. This study was undertaken as part of a continuing investigation of the nature and energetics of the coordination of transition-metal ions by melt chloride ion in the low-melting chloro-

aluminate melt system, AlCl<sub>3</sub>-BPC. Additional data concerning formation of NiCl<sub>4</sub><sup>2-</sup> were also obtained in this study.

### Experimental Section

All experiments were conducted in a dry, oxygen-free nitrogen atmosphere inside a Kewaunee Scientific Equipment Corp. drybox equipped with a 3-cfm inert-gas purifier. The quality of the atmosphere inside the drybox was tested daily by observing the lifetime of a lighted 25-W light bulb with a hole pierced in its glass envelope. The drybox atmosphere was found acceptable when the bulb remained lighted for 2 h or more.

Potentiometric titration experiments were carried out in a Pyrex H-cell. One side arm of this cell served as the working compartment and had a total volume of about 10 mL. Melt solution in this compartment was stirred continuously by means of a miniature Teflon-covered stirbar and magnetic stirrer. The other side arm was used as the reference compartment. The working and reference compartments of the cell were separated from one another by a center compartment with 10-mm fine porosity fritted disks at each end. The porous areas of both fritted disks were decreased substantially by heating them strongly in the flame of a glass-blowing torch. This greatly reduced leakage between compartments but permitted electrical contact. The center compartment of the cell was filled with melt through a small side arm.

The temperature of the cell was maintained at 40 ± 0.2 °C in a furnace machined from a massive aluminum block. The furnace was heated by two 150-W Vulcan Electric cartridges. Regulated current to power the furnace was provided by an Ace Glass temperature controller equipped with a thermistor sensor. The temperature of the cell was monitored by means of a glass-sheathed chromel-alumel thermocouple connected to a Model 410A Doric Trendicator. Potentials were measured with a Keithley Model 178 digital multimeter. The cell and instrumentation used to coulometrically generate metal ions in the melt and to perform cyclic voltammetry were identical with those described previously.<sup>5</sup>

Anhydrous AlCl<sub>3</sub> (Fluka, A.G.) was sublimed under vacuum directly inside the drybox a minimum of three times. The preparation and purification of BPC are detailed in a previous publication.<sup>6</sup> For

(1) Robinson, J.; Osteryoung, R. A. *J. Am. Chem. Soc.* **1979**, *101*, 323.  
(2) Gale, R. J.; Osteryoung, R. A. *Inorg. Chem.* **1979**, *18*, 1603.  
(3) Schoebrechts, J. P.; Gilbert, B. P. *J. Electrochem. Soc.* **1981**, *128*, 2679.  
(4) Gale, R. J.; Gilbert, B.; Osteryoung, R. A. *Inorg. Chem.* **1979**, *18*, 2723.  
(5) Hussey, C. L.; Laher, T. M. *Inorg. Chem.* **1981**, *20*, 4201.

(6) Carpio, R. A.; King, L. A.; Lindstrom, R. E.; Nardi, J. C.; Hussey, C. L. *J. Electrochem. Soc.* **1979**, *126*, 1644.