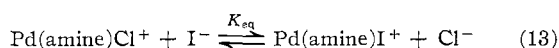


analogous  $\text{Pt}(\text{Et}_4\text{dien})\text{H}_2\text{O}^{2+}$ , the more inert  $\text{Pt}(\text{Et}_4\text{dien})\text{NH}_3^{2+}$  ion was used in a spectral study at a concentration of *ca.*  $10^{-3}$  *M*. Unfortunately, 0.5 *M* NaI and 0.01 *M*  $\text{Na}_2\text{S}_2\text{O}_8$  reacted slowly even with this complex; however, no significant *instantaneous* spectral shifts were seen at wavelengths where the reagents were transparent ( $\lambda > 280$   $\text{m}\mu$ ). At  $\lambda > 235$   $\text{m}\mu$ , 0.5 *M* NaBr does not shift the spectrum, nor does 0.5 *M*  $\text{Na}_2\text{SO}_4$  at  $\lambda > 210$   $\text{m}\mu$ . Measurements below these wavelengths are difficult to make because of the significant anion absorbance. With 0.5 *M* NaCl, small increases in absorbance (*ca.* 5%) are seen in the range 215–230  $\text{m}\mu$ , indicating perhaps a small percentage of ion-pair formation.

It is also seen that for the halide ion rate constants in Table V,  $\text{Cl} > \text{Br} > \text{I}$ . This is the opposite of what is expected for the attack on a soft Lewis acid like Pd(II), yet it is the order expected for ion-pair formation constants. Steric reasons might also be important, however, as the bulky  $\text{Et}_4\text{dien}$  may hinder the attack of the larger bromide and iodide ions relative to chloride ion. Hewkin and Poë have found<sup>23</sup> that for reac-



tion 13, the equilibrium constant  $K_{\text{eq}} = 90$  when amine = dien, but  $K_{\text{eq}} = 10$  when amine =  $\text{Et}_4\text{dien}$ . This destabilization of the iodo complex relative to the chloro complex in going from dien to  $\text{Et}_4\text{dien}$  was attributed to steric hindrance. Steric arguments have also been used to explain the fact that the five-coordinate complex  $\text{Ni}(\text{Et}_4\text{dien})\text{I}_2$  does not exist in organic solvents containing excess  $\text{I}^-$ ; the complex  $\text{Ni}(\text{Et}_4\text{dien})\text{Cl}_2$ , however, forms readily under the same conditions.<sup>15</sup>

It is true, of course, that the kinetics of these anation reactions given in Table V are described by rate law 9 without invoking ion pairing; yet the ion-pair concept seems necessary to explain the otherwise strange order of the rate constants.

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## Complexes of Zinc(II) with Tris(2-aminoethyl)amine

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Complexes of the potentially tetradentate ligand tris(2-aminoethyl)amine (tren), of the types  $\text{trenZn}(\text{ClO}_4)_2$ ,  $\text{trenZnX}_2$ , and  $\text{tren}(\text{ZnX}_2)_2$  (where  $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ), have been characterized. On the basis of infrared data, conductivity and molecular weight measurements, and metathetical reactions with  $\text{B}(\text{C}_6\text{H}_5)_4^-$ , it is proposed that all of these complexes are derivatives of five-coordinate  $[\text{Zn}(\text{tren})\text{A}]^+$  cations where A may be either a halide or a monodentate perchlorato group. The additional  $\text{ZnX}_2$  unit in the  $\text{tren}(\text{ZnX}_2)_2$  complexes appears to be associated with the anionic portion of these complexes, presumably as either solvated or halo-bridged  $(\text{ZnX}_3^-)_2$  species.

### Introduction

The compound tris(2-aminoethyl)amine (tren) and its close relative tris(2-dimethylaminoethyl)amine ( $\text{Me}_6\text{-tren}$ ) have received considerable attention in recent years as ligands which produce five-coordinate, high-spin complexes with the divalent, 3d transition metal ions.  $\text{Me}_6\text{tren}$  complexes of this type have been reported for all of the transition metal ions from Cr(II) to Zn(II).<sup>2</sup> However, in the case of tren the structure of the complex is apparently more sensitive to the size and electronic configuration of the metal ion as well as the availability of other donor groups, and both five- and six-coordinate complexes have been identified.

The nickel(II)–tren derivatives are apparently *cis* octahedral both in solution and in the solid state, as indicated by spectral evidence<sup>3</sup> and X-ray studies,<sup>4</sup> whereas both five-<sup>5</sup> and six-coordinate<sup>6</sup> copper(II) complexes of this ligand have been characterized. A five-coordinate, trigonal-bipyramidal structure has recently been assigned to the  $\text{Co}(\text{SCN})_2$  and  $\text{CoI}_2$  derivatives on the basis of spectral evidence and conductivity measurements.<sup>7</sup> In addition, indirect evidence for six-coordinate Mn(II) and Fe(II) and five-coordinate zinc(II) complexes of tren has been obtained from an analysis of the entropy change upon complex

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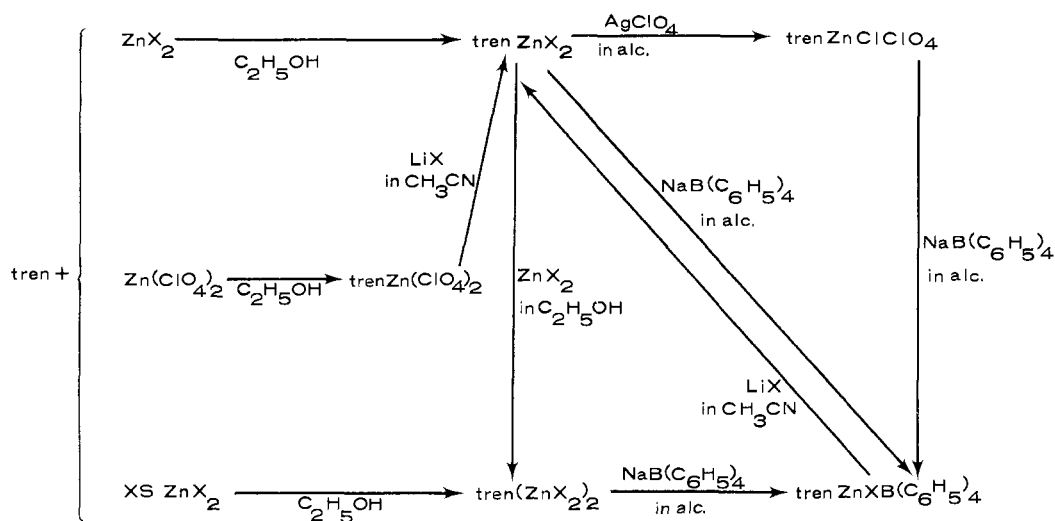


Figure 1.—Preparation and chemistry of the zinc(II)-tren complexes ( $X = \text{Cl}, \text{Br}, \text{I}$ ).

formation in aqueous solution.<sup>8</sup> Contrary to earlier expectations,<sup>9</sup> no four-coordinate derivatives of this ligand have yet been characterized.

Aside from the thermochemical study<sup>8</sup> and the earlier measurement of stability constants in aqueous solution,<sup>10</sup> the zinc(II) complexes of tren have been little studied, and to the author's knowledge no mention of the isolation of such complexes in the solid state has previously appeared in the literature.<sup>10a</sup>

In this paper the preparation and composition of solid complexes of tren with various zinc salts is reported as well as the results of conductivity and molecular weight measurements designed to establish the identity of the species present in the solutions of these complexes in nonaqueous media.

### Results

The complexes were prepared by mixing, at room temperature, ethanol solutions of tren and the appropriate zinc salt. As is indicated in Figure 1, compounds containing 1 or 2 mol of  $\text{ZnX}_2$  ( $X = \text{Cl}, \text{Br}, \text{I}$ ) per mol of tren can be obtained by controlling the proportion of  $\text{ZnX}_2$  to tren in the reaction mixture.

The  $\text{tren}(\text{ZnX}_2)_2$  compounds can be recrystallized without change from acetonitrile or from ethanol containing added  $\text{ZnX}_2$ ; however, upon recrystallization from pure ethanol,  $\text{ZnX}_2$  is lost to give compounds of lower metal to ligand ratio. In the case of the iodide derivative, the  $\text{trenZnI}_2$  complex is isolated, whereas, with  $X = \text{Br}$  or  $\text{Cl}$ , compounds of the stoichiometry  $(\text{tren})_2(\text{ZnX}_2)_3$  result. The latter compounds were not further investigated owing to their limited solubility.

A compound containing only one  $\text{ClO}_4^-$  ion,  $\text{trenZnClClO}_4$ , was prepared from the  $\text{trenZnCl}_2$  complex by reaction with an equimolar amount of  $\text{AgClO}_4$  in methanol solution. Addition of an alcohol solution

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of this complex or any of the other halide-containing derivatives to an excess of  $\text{NaB}(\text{C}_6\text{H}_5)_4$  in alcohol resulted in the virtually quantitative precipitation of complexes of the type  $\text{trenZnXB}(\text{C}_6\text{H}_5)_4$  ( $X = \text{Cl}, \text{Br}, \text{I}$ ).

With the exception of the  $\text{tren}(\text{ZnI}_2)_2$  and  $\text{trenZnCl}_2$  derivatives, the zinc(II)-tren complexes were isolated without solvent of crystallization. Both  $\text{tren}(\text{ZnI}_2)_2$  and  $\text{trenZnCl}_2$  were generally obtained with ethanol of solvation; however, unlike  $\text{tren}(\text{ZnI}_2)_2$  which invariably contained 1 mol of ethanol even after heating to  $110^\circ$ , *in vacuo*, the amount of ethanol in  $\text{trenZnCl}_2$  was variable and a solvent-free compound could be easily obtained by drying at room temperature, *in vacuo*.

The infrared spectra of the complexes were obtained in the solid state as Nujol mulls (Table I). The most pronounced differences in these spectra occur among the bands assigned to the  $\text{NH}_2$  stretching and bending vibrations in the regions 3500–3000 and 1650–1550  $\text{cm}^{-1}$ . Changes in both the number of bands in these regions and their frequencies are observed upon proceeding from one compound type to another, permitting the identification of a compound as to type on the basis of its infrared spectrum alone. Among the features which were common to all of these spectra is the presence of a strong band near 890  $\text{cm}^{-1}$ , assigned to the  $\text{CH}_2$  rocking vibration.

In the case of the  $\text{trenZn}(\text{ClO}_4)_2$  complex, strong bands appear in the Nujol mull spectrum in the 1200–1000- and 700–600- $\text{cm}^{-1}$  regions which appear to be due to stretching and bending vibrations of both uncoordinated and coordinated  $\text{ClO}_4^-$  groups. The assignment of these bands was aided by the preparation of the  $\text{trenZnClClO}_4$  complex in which only one kind of  $\text{ClO}_4^-$  is presumably present. Figure 2 compares the infrared spectra in the regions of interest for the  $\text{trenZnCl}_2$ ,  $\text{trenZnClClO}_4$ , and  $\text{trenZn}(\text{ClO}_4)_2$  complexes. The strong, broad bands near 1100 and 620  $\text{cm}^{-1}$  in the spectrum of the  $\text{trenZnClClO}_4$  complex are characteristic of the uncoordinated  $\text{ClO}_4^-$  ion and may be assigned to the asymmetrical stretching and bending

TABLE I  
 INFRARED DATA FOR THE ZINC(II)-tren COMPLEXES<sup>a,b</sup> (CM<sup>-1</sup>)

Assignment <sup>c</sup>	trenZn-(ClO <sub>4</sub> ) <sub>2</sub> <sup>d</sup>	trenZnClClO <sub>4</sub> <sup>d</sup>	trenZnCl <sub>2</sub>	trenZn-Br <sub>2</sub>	trenZnI <sub>2</sub>	tren-(ZnCl <sub>2</sub> ) <sub>2</sub>	tren-(ZnBr <sub>2</sub> ) <sub>2</sub>	tren-(ZnI <sub>2</sub> ) <sub>2</sub>	trenZn-C <sub>2</sub> H <sub>5</sub> OH	trenZn-C <sub>2</sub> H <sub>5</sub> OH	trenZn-BrB(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub>	trenZn-I(B(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> ) <sub>4</sub>
OH str, C <sub>2</sub> H <sub>5</sub> OH									3401 w, b			
NH <sub>2</sub> str	3356 s	3344 s	3236 s	3226 s, b	3236 s	3257 s, b	3300 s	3300 s	3279 ms	3289 ms	3289 ms	3300 ms
	3300 s	3311 s	3164 s	3145 s	3144 m	3145 m	3257 s	3236 s	3226 ms	3257 ms	3247 ms	3247 ms
NH <sub>2</sub> bend		3268 s										
		1607 ms							1629 w	1613 w		
CH <sub>2</sub> rock	1584 s	1590 s	1595 ms, b	1597 ms	1580 m	1590 m	1575 ms	1595 s, b	1582 s	1580 s	1585 s	
						1577 m						
	875 ms	885 ms	880 ms	882 ms	879 ms	880 ms	879 ms	882 ms	884 ms	882 ms	885 ms	
								873 ms				

<sup>a</sup> Only the major absorption bands in the regions 3500–3000, 1650–1550, and 900–850 cm<sup>-1</sup> are included. <sup>b</sup> vs, very strong; s, strong; ms, medium strong; m, medium; w, weak; b, broad. <sup>c</sup> M. E. Baldwin, *J. Chem. Soc.*, 4369 (1960); L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1958. <sup>d</sup> In these complexes additional bands assigned to ClO<sub>4</sub> vibrations appear as follows: trenZn(ClO<sub>4</sub>)<sub>2</sub>: 1147 s, ~1094 vs, b, 1001 ms (?), 930 m, 654 s, b, 621 vs, b; trenZnClClO<sub>4</sub>: ~1081 vs, b, 932 w, 622 s, b. References: S. F. Pavkovic and D. W. Meek, *Inorg. Chem.*, 4, 1093 (1965); B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.*, 3091 (1961).

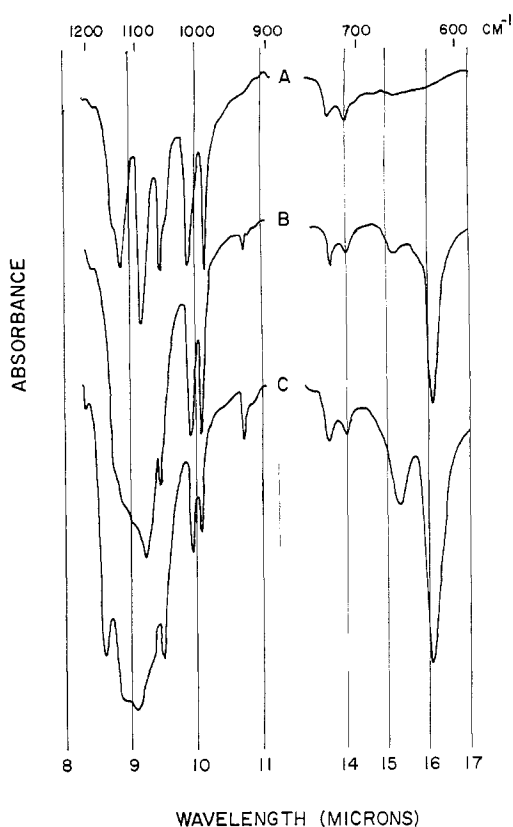


Figure 2.—The 1200–900- and 750–600-cm<sup>-1</sup> regions of the infrared spectra of (A) trenZnCl<sub>2</sub>, (B) trenZnClClO<sub>4</sub>, and (C) trenZn(ClO<sub>4</sub>)<sub>2</sub>, in Nujol.

vibrations, respectively, of the approximately tetrahedral ClO<sub>4</sub><sup>-</sup> group.<sup>10</sup> The very weak band at 932 cm<sup>-1</sup> in this spectrum probably arises from the symmetrical stretching frequency of the ClO<sub>4</sub><sup>-</sup> ion, which, although theoretically forbidden in the infrared, is often observed in ionic perchlorates, possibly owing to slight distortions from T<sub>d</sub> symmetry arising from crystal lattice effects.<sup>11</sup> This band gains appreciably in relative intensity upon proceeding to the trenZn(ClO<sub>4</sub>)<sub>2</sub> complex, and strong bands appear at 1147 and 654 cm<sup>-1</sup> in addition to those previously assigned to the ionic ClO<sub>4</sub><sup>-</sup> group. Moreover the ligand band at 998 cm<sup>-1</sup> appears to have increased in intensity relative

to the other ligand bands possibly indicating another ClO<sub>4</sub><sup>-</sup> absorption at this position. Assuming that the additional band expected in the 700–600-cm<sup>-1</sup> region is hidden under the broad ionic ClO<sub>4</sub><sup>-</sup> absorption near 620 cm<sup>-1</sup>, the number and frequencies of these new bands are consistent with the presence of a monodentate perchlorato group of C<sub>3v</sub> symmetry in the trenZn(ClO<sub>4</sub>)<sub>2</sub> complex.<sup>11,12</sup>

Most of the zinc(II)-tren complexes were found to be moderately soluble (*ca.* 10<sup>-3</sup>–10<sup>-2</sup>M) in acetonitrile, nitromethane, methanol, and other solvents of high donor ability but insoluble in chloroform and other halogenated hydrocarbons. Electrical conductivity measurements performed on these solutions indicated appreciable ionic dissociation. Except for the trenZn(ClO<sub>4</sub>)<sub>2</sub> complex, the molar conductivity (Λ<sub>M</sub>) values obtained assuming a molecular weight equal to the formula weight of the monomer are all close to that expected for 1:1 electrolytes under similar conditions of solvent and concentration (Table II). In the case of trenZn(ClO<sub>4</sub>)<sub>2</sub> the value obtained was much closer to that usually observed for 2:1 electrolytes. As has been previously noted,<sup>13</sup> however, measurements of molar conductivity at one concentration do not unambiguously determine the ion type in solution owing to the wide range of Λ<sub>M</sub> values possible within each ion type and the uncertainty regarding the degree of polymerization of the compound. One way of removing this ambiguity is to measure the conductivity as a function of concentration. According to the Onsager limiting law [Λ<sub>0</sub> = Λ<sub>∞</sub> - (aΛ<sub>∞</sub> + b)√c<sub>e</sub> = Λ<sub>∞</sub> - A√c<sub>e</sub>], the equivalent conductivity (Λ<sub>e</sub>) varies linearly with the square root of equivalent concentration (c<sub>e</sub>) in dilute solutions of strong electrolytes, and the slope (A) of this line is determined largely by the ion type and the solvent.<sup>14</sup> The value of A may be calculated using an experimentally determined Λ<sub>∞</sub> (the equivalent conductivity at infinite dilution) and constants a and b appropriate to the conditions of the measurement and the assumption regarding the ion type of the complex.

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(13) R. D. Feltham and R. G. Hayter, *ibid.*, 4587 (1964).

(14) R. M. Fuoss and F. Accascina, "Electrolytic Conductance," Interscience Publishers, Inc., New York, N. Y., 1959, p 7.

(11) B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.*, 3091 (1961).

TABLE II  
CONDUCTIVITY DATA

Complex	Solvent	Molar conductivity <sup>a</sup>	—Slope of $\Lambda_e$ vs. $\sqrt{c_e}$ plot <sup>b</sup> —			
			1:1 electrolyte		2:1 electrolyte	
			Calcd <sup>c</sup>	Found	Calcd <sup>c</sup>	Found
trenZn(ClO <sub>4</sub> ) <sub>2</sub>	CH <sub>3</sub> CN	321	355	1429	820	505
trenZnCl <sub>2</sub>	CH <sub>3</sub> OH	99	250	313	600	111
trenZnBr <sub>2</sub> <sup>d</sup>	CH <sub>3</sub> CN	117	...	...	...	...
trenZnI <sub>2</sub> <sup>d</sup>	CH <sub>3</sub> CN	138	...	...	...	...
tren(ZnCl <sub>2</sub> ) <sub>2</sub> <sup>d</sup>	CH <sub>3</sub> OH	111	...	...	...	...
tren(ZnCl <sub>2</sub> ) <sub>2</sub> <sup>d</sup>	CH <sub>3</sub> CN	112	...	...	...	...
tren(ZnBr <sub>2</sub> ) <sub>2</sub> <sup>d</sup>	CH <sub>3</sub> CN	125	...	...	...	...
tren(ZnI <sub>2</sub> ) <sub>2</sub>	CH <sub>3</sub> CN	126	335	432	800	153
trenZnClB(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub>	CH <sub>3</sub> CN	117	325	290	790	103
trenZnBrB(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub>	CH <sub>3</sub> CN	119	325	351	795	124
trenZnIB(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub>	CH <sub>3</sub> CN	126	325	332	795	117
trenZnClClO <sub>4</sub>	CH <sub>3</sub> CN	154	360	512	815	181

<sup>a</sup> Cm<sup>2</sup> ohm<sup>-1</sup> mole<sup>-1</sup> at 10<sup>-3</sup> M concentration, assuming molecular weight of complex equals the formula weight. Values previously reported for 1:1 and 2:1 electrolytes in these solvents are: 140 and 310 in CH<sub>3</sub>CN, 100 and 180 in CH<sub>3</sub>OH, respectively: R. A. Krause and D. H. Busch, *J. Am. Chem. Soc.*, **82**, 4830 (1960); R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," 2nd ed, Academic Press Inc., New York, N. Y., 1959, p 162; also ref 7 and 9. <sup>b</sup> Above ca. 4 × 10<sup>-3</sup> M concentration;  $\Lambda$  values calculated from data assuming molecular weight of complex equals the formula weight. <sup>c</sup> Calculated from the equivalent conductivity at infinite dilution ( $\Lambda_0$ ), the individual ionic conductivities ( $\lambda_0^\pm$ ), and constants appropriate to the solvent in question: R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," 2nd ed, Academic Press Inc., New York, N. Y., 1959, p 143; P. Walden and E. J. Birr, *Z. Physik. Chem.*, **144**, 269 (1929); J. F. Coetzee and G. P. Cunningham, *J. Am. Chem. Soc.*, **87**, 2529 (1965). <sup>d</sup> Only soluble to the extent of ~10<sup>-3</sup> M.

Comparison with the observed slope can then be made to determine the nature of the electrolyte.

Typical  $\Lambda_e$  vs.  $\sqrt{c_e}$  plots for the zinc(II)-tren complexes are shown in Figures 3 and 4. As is evident in these examples, some of the  $\Lambda_e$  vs.  $\sqrt{c_e}$  curves deviate markedly from linearity, especially at low concentrations, and approach  $\Lambda_0$  values characteristic of 2:1 electrolytes. The extent of this deviation is dependent upon both the anions associated with the zinc(II)-tren complexes and the solvent employed in the measurements. Thus, in acetonitrile solution, upon proceeding from Cl to Br to I in the trenZnXB(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub> series, the deviation of the  $\Lambda_e$  vs.  $\sqrt{c_e}$  curves from linearity becomes increasingly apparent (Figure 3). For the analogous trenZnCl<sub>2</sub> complex in methanol solution this curvature is obvious at concentrations as high as ca. 10<sup>-3</sup> M (Figure 4). However, even in this case, a region between  $c = 4 \times 10^{-3}$  M and at least 10<sup>-2</sup> M over which the curve remains approximately linear is observed. Moreover, the slope of the  $\Lambda_e$  vs.  $\sqrt{c_e}$  curve in this region agrees quite closely with that calculated for a monomeric, 1:1 electrolyte using the Onsager limiting law. In fact, except for the trenZn(ClO<sub>4</sub>)<sub>2</sub> derivative, all of the zinc(II)-tren complexes which were more soluble than ca. 4 × 10<sup>-3</sup> M in either acetonitrile or methanol exhibited a similar region of linearity, and the slopes in this region were in each case consistent with those calculated assuming a monomeric, 1:1 electrolyte formulation (Table II). Also, comparison with earlier work in these solvents<sup>13,15</sup> shows that the measured slopes are within the range of values previously observed for this electrolyte type.

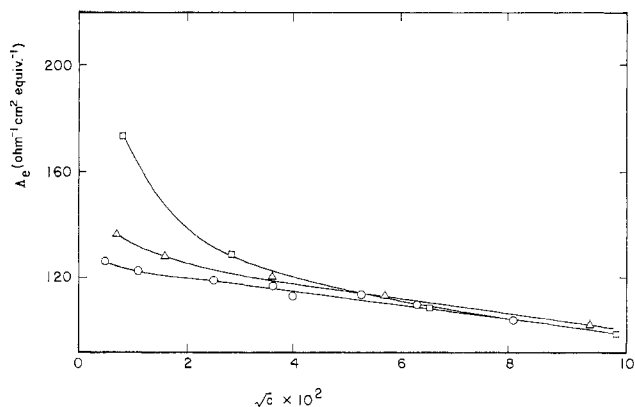


Figure 3.—The equivalent conductivities of the trenZnXB(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub> complexes in acetonitrile solution: O, X = Cl; Δ, X = Br; □, X = I.

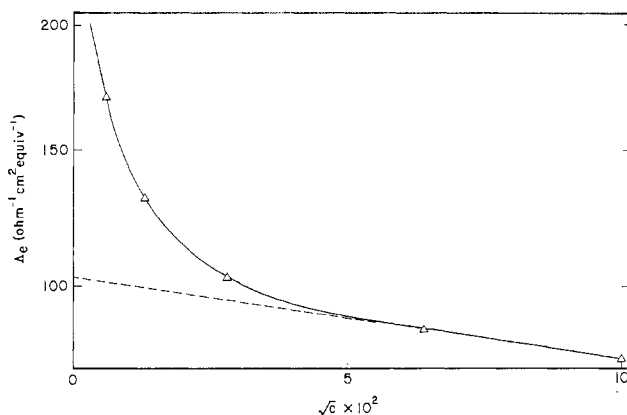


Figure 4.—The equivalent conductivity of the trenZnCl<sub>2</sub> complex in methanol solution.

The average slope for the trenZn(ClO<sub>4</sub>)<sub>2</sub>  $\Lambda_e$  vs.  $\sqrt{c_e}$  curve in this region is closest to the value calculated for a monomeric, 2:1 electrolyte; however, both the general appearance of the curve in this case and the measured slope evidence some association of ClO<sub>4</sub><sup>-</sup> in this concentration range.

These conclusions are entirely substantiated by the results of molecular weight measurements performed on these complexes in acetonitrile (Table III). Thus the observed molecular weights for all the complexes except for trenZn(ClO<sub>4</sub>)<sub>2</sub> are reasonably close to the values expected for monomeric, 1:1 electrolytes, whereas the trenZn(ClO<sub>4</sub>)<sub>2</sub> complex again shows behavior intermediate between that expected for a 1:1 and a 2:1 electrolyte.

Further information regarding the nature of the zinc(II)-tren complexes in solution was obtained by means of conductivity titrations. The titration curve obtained for the addition of a methanol solution of AgClO<sub>4</sub> to the trenZnCl<sub>2</sub> complex is illustrated in Figure 5. The break in this curve near the 1:1 equivalence point indicates that the two chloride ions are not chemically equivalent in solution and thus argues against a [Zn(tren)]Cl<sub>2</sub> formulation for the

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TABLE III  
 MOLECULAR WEIGHT DATA

Complex	Formula wt	Mol wt		Found <sup>b</sup>
		Calcd <sup>a</sup>		
		2:1 electrolyte	1:1 electrolyte	
trenZn(ClO <sub>4</sub> ) <sub>2</sub>	411	137	205	177
trenZnBr <sub>2</sub>	371	124	186	190
trenZnI <sub>2</sub>	465	155	233	247
tren(ZnCl <sub>2</sub> ) <sub>2</sub>	419	140	209	189
tren(ZnBr <sub>2</sub> ) <sub>2</sub>	597	199	299	312
tren(ZnI <sub>2</sub> ) <sub>2</sub>	785	262	393	376
trenZnClB(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub>	566	189	283	289
trenZnBrB(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub>	611	204	305	297
trenZnIB(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub>	658	219	329	315
trenZnClClO <sub>4</sub>	347	116	174	180

<sup>a</sup> Assuming molecular weight equals the formula weight of monomer/*i*, where *i* = moles of solute particles per mole of solute.

<sup>b</sup> In acetonitrile solution (10<sup>-3</sup>–10<sup>-2</sup> M) by vapor pressure lowering.

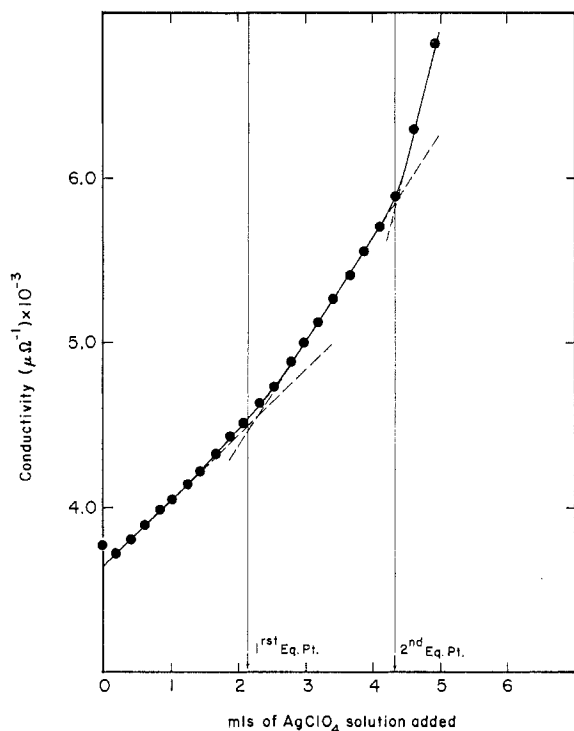


Figure 5.—Titration of 15.0 ml of  $4.34 \times 10^{-3}$  M trenZnCl<sub>2</sub> with  $3.01 \times 10^{-2}$  M AgClO<sub>4</sub> in methanol solution. Conductivity readings corrected for dilution.

complex. Indeed, as is shown by the sharp break in the  $n\text{-}(\text{C}_3\text{H}_7)_4\text{NI} + \text{trenZn}(\text{ClO}_4)_2$  titration curve (Figure 6) at the 1:1 equivalence point and the constant slope thereafter, the Zn(tren)<sup>2+</sup> unit associates quite strongly with one, and apparently only one, halide ion.

### Discussion

On the basis of the results obtained, it appears that all of the zinc(II)–tren complexes prepared in this investigation can be accommodated by the molecular formula  $[\text{Zn}(\text{tren})\text{A}]^+\text{Y}^-$ , where A = X, ClO<sub>4</sub>; X = Cl, Br, I; Y = X, ClO<sub>4</sub>, ZnX<sub>3</sub>, B(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>.

This formula accounts for the monomeric, 1:1 electrolyte behavior of most of the zinc(II)–tren complexes in solution and also is consistent with the specific evi-

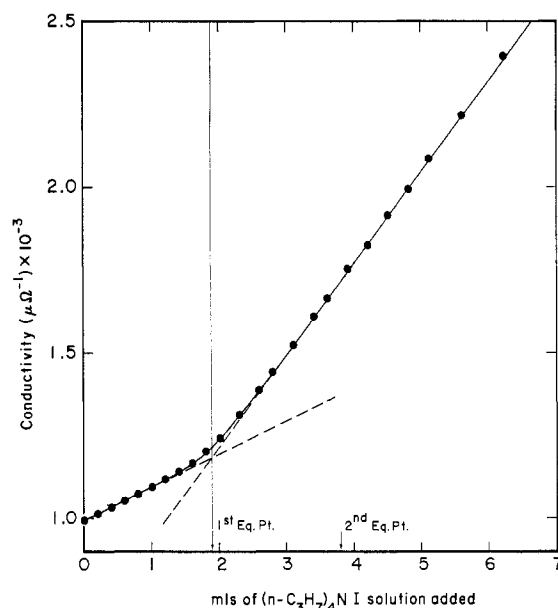


Figure 6.—Titration of 10.0 ml of  $4.36 \times 10^{-3}$  M trenZn(ClO<sub>4</sub>)<sub>2</sub> with  $2.30 \times 10^{-2}$  M  $n\text{-}(\text{C}_3\text{H}_7)_4\text{NI}$  in acetonitrile solution. Conductivity readings corrected for dilution.

dence for  $[\text{Zn}(\text{tren})\text{X}]^+$  cations provided by the conductivity titrations and the reactions with B(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub><sup>-</sup>. The ClO<sub>4</sub><sup>-</sup> ion is included as a possible A<sup>-</sup> group principally on the basis of the infrared evidence for a monodentate perchlorato group in the solid trenZn(ClO<sub>4</sub>)<sub>2</sub> complex. Upon solution of this complex in acetonitrile, this coordinated ClO<sub>4</sub><sup>-</sup> ion is apparently largely replaced by solvent although some association between Zn(tren)<sup>2+</sup> and ClO<sub>4</sub><sup>-</sup> in this medium is clearly evident at concentrations above  $5 \times 10^{-3}$  M.

In the case of the remaining zinc(II)–tren complexes, *i.e.*, those with A = X, the dissociation constants for the  $[\text{Zn}(\text{tren})\text{A}]^+$  species in both acetonitrile and methanol solution are apparently appreciably smaller resulting in the 1:1 electrolyte behavior observed at concentrations above *ca.* 10<sup>-3</sup> M. However, as is evidenced by the  $\Lambda_e$  vs.  $\sqrt{c}$  curves obtained for these complexes, at sufficiently low concentrations all of the zinc(II)–tren derivatives show some evidence of this further dissociation and in the limit of infinite dilution are all presumably at least 2:1 electrolytes.<sup>16</sup>

In the context of this proposed  $\text{Zn}(\text{tren})\text{X}^+ \rightleftharpoons \text{Zn}(\text{tren})^{2+} + \text{X}^-$  equilibrium, it is clear that the nature of X<sup>-</sup> and the solvent should both help to determine the extent to which the  $\Lambda_e$  vs.  $\sqrt{c}$  curves deviate from linearity at low concentrations. The influence of the X group is clearly evident from the  $\Lambda_e$  vs.  $\sqrt{c}$  curves obtained for the trenZnXB(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub> complexes in acetonitrile (Figure 3). These curves suggest that the dissociation constants for the  $[\text{Zn}(\text{tren})\text{X}]^+$  species in this medium increase in the order X = Cl < Br < I, a conclusion which is entirely consistent with the results of stability constant measurements on other zinc(II)–halide complexes. The<sup>17</sup> increase in the dissociation constant of

(16) In the case of the tren(ZnX<sub>2</sub>)<sub>2</sub> complexes, further dissociation of the presumed ZnX<sub>3</sub><sup>-</sup> anions also occurs leading to even higher  $\Lambda_e$  values.

(17) S. Ahrland, J. Chatt, and N. R. Davies, *Quart. Rev. (London)*, **12**, 271 (1958).

the  $[\text{Zn}(\text{tren})\text{Cl}]^+$  ion upon proceeding from acetonitrile to methanol, as evidenced by the conductivity curves obtained for the  $[\text{Zn}(\text{tren})\text{Cl}][\text{Y}]$  ( $\text{Y} = \text{Cl}, \text{B}(\text{C}_6\text{H}_5)_4$ ) complexes in these solvents (Figures 3 and 4), probably reflects the higher solvation energy of  $\text{Cl}^-$  in methanol.<sup>18</sup>

The nature of the presumed " $\text{ZnX}_3^-$ " anions in the case of the  $\text{tren}(\text{ZnX}_2)_2$  complexes is subject to some speculation. In solution these ions are presumably solvated and in equilibrium with the lower and higher zinc(II)-halide complexes. Species of this type have been evidenced in both alcoholic and aqueous solutions but in these media are invariably admixed with large amounts of the other  $\text{ZnX}_n^{+2-n}$  complexes.<sup>19</sup> Indeed, in the case of the  $\text{tren}(\text{ZnX}_2)_2$  derivatives, extensive dissociation of the  $\text{ZnX}_3^-$  ions in hydroxylic solvents is evidenced by the loss of  $\text{ZnX}_2$  upon recrystallization from ethanol. However, in acetonitrile solution the close agreement observed between the molecular weight values obtained for the  $\text{tren}(\text{ZnX}_2)_2$  complexes and those calculated assuming only  $\text{ZnX}_3^-$  as the anion is not consistent with extensive  $\text{ZnX}_3^-$  dissociation (Table III). In view of the lower solvating ability of acetonitrile toward the halide ions evidenced by other studies,<sup>18</sup> it is possible that in this case the stepwise dissociation constants for the  $\text{ZnX}_3^-$  species are sufficiently small to permit their existence in solution without large amounts of the other  $\text{ZnX}_n^{+2-n}$  species. In the case of the solid  $\text{tren}(\text{ZnX}_2)_2$  complexes a " $\text{ZnX}_3^-$ " anion could conceivably be accommodated as either dimeric halo-bridged  $[\text{ZnX}_3]_2^{2-}$  units, involving tetrahedral Zn(II), or as polymeric, octahedrally coordinated Zn(II) species analogous to those in the known  $\text{Cs}[\text{MCl}_3]$  ( $\text{M} = \text{Cu}, \text{Ni}$ ) structures.<sup>20</sup> In view of the difficulty with which alcohol is lost from the  $\text{tren}(\text{ZnI}_2)_2 \cdot \text{C}_2\text{H}_5\text{OH}$  complex, an alternative,  $[\text{Zn}(\text{C}_2\text{H}_5\text{OH})\text{I}_3]^-$ , formulation for the anion, similar to the pseudo-tetrahedral  $[\text{Zn}(\text{H}_2\text{O})\text{Cl}_3]^-$  anion in  $\text{KZnCl}_3 \cdot \text{H}_2\text{O}$ ,<sup>21</sup> may be more likely in this case.

Although the infrared spectra of the complexes in the solid state show appreciable differences from one complex type to another, these differences do appear to be associated largely with the various  $-\text{NH}_2$  vibrational modes and, as previously evidenced in the case of cobalt(III)-ethylenediamine complexes,<sup>22</sup> may arise entirely from interactions with the anions in the crystal. On the other hand, the bands in the  $\text{CH}_2$  rocking region, *i.e.*,  $850\text{--}900\text{ cm}^{-1}$ , in the infrared spectra of these cobalt(III)-ethylenediamine complexes do appear to be sensitive to changes in coordination geometry and yet relatively insensitive to variations in the associated anion. In particular, a wide range of *cis*-octahedral complexes of the type  $[\text{Co}(\text{en})_2\text{AB}]\text{X}$  (where

A and B are ionic or molecular unidentate ligands and X is the associated anion) have been found to exhibit two strong absorption bands in this region whereas the *trans* complexes show only one such band.<sup>22</sup> Similarly, two  $\text{CH}_2$  rocking vibrations have recently been identified in the case of the corresponding *cis*-octahedral cobalt(III) complexes of *tren*.<sup>23</sup> Therefore, the observation that all of the zinc(II) complexes of *tren*, except for the  $\text{tren}(\text{ZnI}_2)_2 \cdot \text{C}_2\text{H}_5\text{OH}$  derivative, show only one strong band in the  $\text{CH}_2$  rocking region may be indicative of a basic structural similarity among these complexes and also possibly a higher symmetry for the coordinated *tren* ligand than in the *cis*-octahedral case. As for the  $\text{tren}(\text{ZnI}_2)_2 \cdot \text{C}_2\text{H}_5\text{OH}$  complex, the additional band observed in the  $\text{CH}_2$  rocking region probably arises from the  $\text{C}_2\text{H}_5\text{OH}$  portion of this compound, as pure ethanol exhibits a strong band in this region.

In view of the results obtained in this investigation, it appears likely that the zinc(II) complexes of *tren* are indeed five-coordinate as suggested earlier on the basis of thermochemical measurements.<sup>8,10a</sup> Recently further evidence in support of this conclusion has been obtained in the form of a three-dimensional X-ray analysis of the  $\text{trenZnClB}(\text{C}_6\text{H}_5)_4$  complex.<sup>24</sup> Preliminary data from this study indicate that the zinc(II) ion in this complex is bonded to the  $\text{Cl}^-$  ion as well as all of the *tren* nitrogen atoms and that the resulting  $[\text{Zn}(\text{tren})\text{Cl}]^+$  cation has a trigonal-bipyramidal configuration with  $\text{C}_3$  symmetry.

### Experimental Section

**Materials.**—All solvents and chemicals used were of reagent grade quality. The acetonitrile and methanol used in the conductivity and molecular weight measurements were dried over molecular sieves, refluxed over  $\text{CaH}_2$ , and then fractionally distilled. The zinc salts were all obtained commercially as the anhydrous materials except for  $\text{Zn}(\text{ClO}_4)_2$  which was obtained as the hexahydrate and dried using 2,2-dimethoxypropane. The  $\text{AgClO}_4$  used in the conductivity titration was the anhydrous salt obtained by drying the monohydrate at  $110^\circ$ , *in vacuo*, over  $\text{P}_2\text{O}_5$ . Tris(2-aminoethyl)amine (*tren*) was prepared according to the procedure of Ciampolini and Nardi.<sup>2b</sup>

**Preparation of Complexes.**  $\text{tren}(\text{ZnX}_2)_2$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ).—A solution of *tren* (2 mmol) in 35 ml of ethanol was added slowly with stirring to a filtered solution of the appropriate zinc halide (*ca.* 16 mmol) in 70 ml of ethanol. The complex precipitated during the course of the addition and was obtained as a white powder (77–92% yield) upon filtration. Purification could be effected by recrystallization from acetonitrile or from ethanol containing *ca.* 0.2 M  $\text{ZnX}_2$ .

Upon recrystallization of the  $\text{tren}(\text{ZnX}_2)_2$  ( $\text{X} = \text{Cl}, \text{Br}$ ) complexes from hot ethanol in the absence of added  $\text{ZnX}_2$ , compounds of the stoichiometry  $\text{tren}_2(\text{ZnX}_2)_3$  occurred, whereas  $\text{tren}(\text{ZnI}_2)_2 \cdot \text{C}_2\text{H}_5\text{OH}$  under these conditions gave the  $\text{trenZnI}_2$  complex.

$\text{trenZnX}_2$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ).—A filtered solution of the zinc halide (2 mmol) in 35 ml of ethanol was added with stirring to a solution of an equimolar amount of *tren* in ethanol (70 ml). The clear solution obtained was evaporated at the boiling point to *ca.* 40 ml total volume and hexane was added to the point of saturation. The solid complexes were recovered by filtration upon cooling to  $0^\circ$ ; yield, 48–57%.

$\text{trenZn}(\text{ClO}_4)_2$ .—An excess of  $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (*ca.* 8 mmol) was

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(24) The author wishes to thank Drs. R. Dodge, R. Sime, A. Zalkin, and D. H. Templeton for making available the results of this X-ray investigation prior to publication.

TABLE IV  
ANALYTICAL DATA

Compound	% C		% H		% N		% halogen	
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
trenZnCl <sub>2</sub> ·0.5C <sub>2</sub> H <sub>5</sub> OH	27.53	27.97	6.91	6.98	18.33	18.69	23.21	23.72
tren(ZnCl <sub>2</sub> ) <sub>2</sub> <sup>a</sup>	17.22	17.13	4.32	4.48	13.37	13.15	33.86	33.92
trenZnBr <sub>2</sub>	19.41	19.57	4.87	5.01	15.08	15.27	43.03	42.88
tren(ZnBr <sub>2</sub> ) <sub>2</sub>	12.09	12.55	3.03	3.29	9.39	9.02	53.57	52.88
trenZnI <sub>2</sub>	15.49	15.79	3.89	4.38	12.03	12.16	54.53	54.48
tren(ZnI <sub>2</sub> ) <sub>2</sub> ·C <sub>2</sub> H <sub>5</sub> OH	11.55	11.63	2.90	2.81	6.74	6.40	61.11	60.36
trenZnClB(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub>	63.62	63.71	6.76	6.60	9.89	10.53	6.27	6.44
trenZnBrB(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub>	59.01	59.07	6.27	6.29	9.17	8.92	13.08	13.02
trenZnIB(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub>	54.78	54.46	5.82	5.64	8.51	8.38	19.29	19.53
trenZn(ClO <sub>4</sub> ) <sub>2</sub>	17.56	17.37	4.41	4.56	13.64	13.20	17.27	16.70
trenZnClClO <sub>4</sub>	20.81	21.03	5.22	5.75	16.16	15.90	20.46	18.95

<sup>a</sup> This compound was also analyzed for % Zn by precipitation with 8-hydroxyquinoline. Results for % Zn: calcd, 31.23; found, 30.2.

dehydrated by stirring with a solution of 20 ml of 2,2-dimethoxypropane plus 8 ml of methanol for *ca.* 12 hr. Anhydrous ether (*ca.* 100 ml) was added, whereupon a heavy liquid phase separated. Further treatment with ether left a crystalline solid which was washed well with ether and dried at room temperature *in vacuo*.

This solid was then redissolved in methanol (25 ml) and heated to reflux. A solution of tren (1.4 mmol) in 25 ml of methanol was added slowly with stirring, and the mixture was cooled to room temperature. The white crystals obtained were collected by filtration and recrystallized from ethanol; yield, 0.140 g (70.6%).

**trenZnXB(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub> (X = Cl, Br, I).**—These complexes were prepared from both the tren(ZnX<sub>2</sub>)<sub>2</sub> and trenZnX<sub>2</sub> salts by mixing a filtered solution of the appropriate zinc salt in ethanol with a solution of excess NaB(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub> in ethanol. The trenZnXB(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub> complexes crystallized out in platelets shortly after mixing and were collected by filtration, washed with alcohol, and dried *in vacuo*. Recrystallization could be effected from either acetonitrile or nitromethane; a typical preparation follows.

**trenZnClB(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub> from tren(ZnCl<sub>2</sub>)<sub>2</sub>.**—A hot solution of 0.0681 g (0.163 mmol) of tren(ZnCl<sub>2</sub>)<sub>2</sub> in ethanol was added quantitatively to a filtered solution of 0.33 g (1.0 mmol) of NaB(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub> in ethanol. After standing for 3 hr the resulting precipitate was transferred quantitatively to a tared sintered-glass funnel, washed with ethanol, and then dried, *in vacuo*, for 12 hr; yield, 0.0882 g (95.8%).

**trenZnClClO<sub>4</sub>.**—A solution prepared by dissolving 62.6 mg of trenZnCl<sub>2</sub> in 20 ml of absolute methanol was treated with 18.6 ml of a 0.0119 M solution of AgClO<sub>4</sub>·H<sub>2</sub>O in methanol. After heating

at the boiling point for a few minutes to coagulate the AgCl, the mixture was filtered and the filtrate was added to *ca.* 100 ml of ethyl ether. The white precipitate was then recrystallized from ethanol; yield, 65 mg (81%).

**Attempted Preparation of a tren Complex Using Zn(BF<sub>4</sub>)<sub>2</sub>.**—Several attempts were made to prepare a tren complex with zinc tetrafluoroborate (Alfa Inorganics, Inc.) using the method previously described for the tren(ZnX<sub>2</sub>)<sub>2</sub> complexes. Upon concentration of the resulting reaction mixture and cooling to 0°, a white solid was obtained. This product was subsequently identified as tren·3HBF<sub>4</sub> by elemental analyses, infrared spectral data, and exchange of Br<sup>-</sup> for BF<sub>4</sub><sup>-</sup> in acetonitrile.

**Measurements.**—All conductivity measurements were performed using an Industrial Instruments Model RC 16B2 conductivity bridge. The conductivity cell was calibrated with 0.0200 M KCl solution and all measurements were taken at 25.0 ± 0.1°. The infrared spectra were obtained using Perkin-Elmer Models 237 and 337 ir spectrophotometers. Nujol mulls of the trenZnCl<sub>2</sub>, trenZnClClO<sub>4</sub>, and trenZn(ClO<sub>4</sub>)<sub>2</sub> complexes were prepared in a drybox. Microanalyses and molecular weight measurements were performed by the Microanalytical Laboratory of the University of California at Berkeley. For the molecular weight measurements a Mechrolab vapor pressure osmometer was used and was calibrated with NaB(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>. The results of the analytical measurements are summarized in Table IV.

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