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# Coordination Chemistry of Scandium. X [1]. Macrocyclic Polyether Complexes of Scandium(III)

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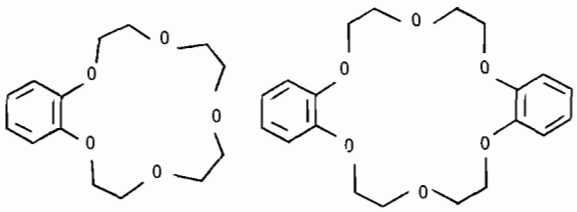
*The complexes $Sc(NCS)_3$(benzo-15-crown-5)·1.5-THF·$2H_2O$: $(ScCl_3)_3$(benzo-15-crown-5)$_2$·$H_2O$: $Sc(NCS)_3$(dibenzo-18-crown-6)$_2$·3THF: $ScCl_3$(dibenzo-18-crown-6)·1.5THF: $ScCl_3$(dibenzo-18-crown-6)·1.5$CH_3CN$ have been synthesized by reaction of $Sc(NCS)_3$ or $ScCl_3$ with the appropriate polyether. The complexes have been characterized by elemental analyses, conductance measurements, and infrared, ultraviolet and $^1H$ NMR spectroscopy; they exhibit weak bonding between the scandium(III) ion and the polyether. Structures are proposed and discussed with reference to the ionic size–cavity size relationship; some "unusual" coordination environments for the Sc(III) ion are suggested.*

## Introduction

Macrocyclic polyethers have been used primarily for selective complexation of alkali metal and alkaline earth metal cations [3–6], with only scant attention having been given to complexes of the transition metal ions [6–10], and lanthanides [11–14]. Although the similarity between the chemistry of the scandium(III) ion and the lanthanides has been noted [15, 16] and it has been demonstrated that Sc(III) forms strong complexes with oxygen donor ligands [17, 18], no Sc(III) complexes with macrocyclic polyethers have been isolated; however, complexes with neutral tetraaza macrocyclic ligands have been prepared [1]. A recent $^{45}Sc$ nmr investigation [19] of the ability of the scandium(III) ion to complex with macrocyclic polyethers in aqueous solution showed that whereas dicyclohexyl-18-crown-6 and benzo-15-crown-5 were unable to displace water molecules from the coordination sphere of Sc(III), evidence for complexation was obtained by using the cryptands C211 and C221 under similar conditions. Thus, in order to prepare complexes of macrocyclic polyethers and scandium(III), weakly coordinating solvents, such as tetrahydrofuran or acetonitrile and anhydrous conditions should be employed for the complexation reactions.

Several authors [3–6] have concluded that the relative sizes of the macrocycle cavity and the metal ion are important factors in controlling the stoichiometry of any resulting complex. Since the ionic diameter of the $3d^0$ scandium(III) ion, (~1.4 Å) is less than the cavity size of either benzo-15-crown-5, A, (~1.9 Å) or dibenzo-18-crown-6, B, (~2.9Å), it was anticipated that on complexation, these ligands would impose unusual coordination geometries on the scandium(III) ion. In the complex $[Sc(Me_4Bz_2[14]\text{-tetraene}N_4)NCS](NCS)_2$, it is concluded that the scandium(III) ion is five-coordinated, with a distorted square-pyramidal environment rather than six-coordinated, with an octahedral environment which is usually adopted by Sc(III) [17]. The five-coordinate geometry is adopted by the scandium(III) ion due to restrictions imposed by the macrocyclic ligand. The present investigation was initiated to further study the effects of ligand – imposed geometry on the scandium(III) ion and to examine the effect of the ionic size – cavity size relationship on the stoichiometry and structure of complexes of scandium(III) with benzo-15-crown-5, A, and dibenzo-18-crown-6, B.




A B

## Experimental

2, 3-Benzo-1,4,7,10,13-pentaoxacyclopentadeca-2-ene (benzo-15-crown-5), A, was prepared as previous-

ly described by Pedersen [11] and was recrystallized from n-heptane prior to use. 2,3,11,12-Dibenzo-1,4,7,10,13,16-hexaoxacyclooctadeca-2,11-diene (dibenzo-18-crown-6), B, was purchased from Aldrich Chemical Company, Inc. and was used without further purification. The scandium(III) salts, "$Sc(NCS)_3/Et_2O$" and anhydrous $ScCl_3$, were prepared from scandium oxide, $Sc_2O_3$ (99.9%, Research Organic/Inorganic Chemical Corporation), as previously described by Crawford and Melson [20] and Stotz and Melson [21], respectively. Tetrahydrofuran (THF) and acetonitrile were dried over calcium hydride and distilled prior to use; diethyl ether was dried over metallic sodium and n-hexane was dried over molecular sieves ("Linde", type 5A). All other chemicals used were of reagent grade.

*Preparation of Complexes*

All reactions were carried out under anhydrous conditions in an oxygen-free $N_2$ atmosphere provided by a Vacuum Atmospheres "Dri-Lab, Dri-Train" system.

*$Sc(NCS)_3$(benzo-15-crown-5)·1.5THF·$2H_2O$*

To a solution of 0.268 g (1 mmol) of benzo-15-crown-5 in 50 ml of THF was added 10 ml of 0.1 *M* "$Sc(NCS)_3/Et_2O$". To the resultant clear solution was slowly added ~100 ml of n-hexane. The white precipitate which formed upon allowing the reaction mixture to stir for ~24 hours was isolated by suction-filtration and was dried under vacuum over $P_4O_{10}$ for 24 hours at room temperature. Yield: 0.42 g (67%). Melting point: 146–149 °C, *Anal.* for $Sc(NCS)_3 \cdot C_{14}H_{20}O_5 \cdot 1.5C_4H_8O \cdot 2H_2O$. Calcd: C, 43,73; H, 5.74; N, 6.65; S, 15.23; Sc, 7.1. Found: C, 42.99; H, 5.56; N, 7.13; S, 14.80; Sc, 7.4%.

*$(ScCl_3)_3$(benzo-15-crown-5)$_2$·$H_2O$*

To a solution of 0.268 g (1 mmol) of benzo-15-crown-5 in 50 ml of $CH_3CN$ was added a solution of 0.152 g (1 mmol) of $ScCl_3$ in 150 ml of $CH_3CN$. The solution volume was reduced to ~100 ml (under reduced pressure) and to the resultant clear solution was slowly added ~200 ml of $Et_2O$. The white precipitate which formed was isolated by suction-filtration and was dried under vacuum over $P_4O_{10}$ for 24 hours at room temperature. Yield: 0.26 g (77%). Melting point: 205–208 °C. *Anal.* for $3ScCl_3 \cdot 2C_{14}H_{20}O_5 \cdot H_2O$. Calcd: C, 33.34; H, 4.20; Cl, 31.64; Sc, 13.4. Found: C, 33.44; H, 4.13; Cl, 32.67; Sc. 13.4%.

*$Sc(NCS)_3$(dibenzo-18-crown-6)$_2$·3THF*

To a solution of 0.360 g (1 mmol) of dibenzo-18-crown-6 in 100 ml of THF was added 10 ml of 0.1 *M* "$Sc(NCS)_3/Et_2O$". To the resultant clear solution was slowly added ~200 ml of n-hexane. The white precipitate which formed was isolated by suction-filtration and was dried under vacuum over $P_4O_{10}$ for 24 hours at room temperature. Yield: 0.40 g (69%). Melting point: 205–208 °C. *Anal.* for $Sc(NCS)_3 \cdot 2C_{20}H_{24}O_6 \cdot 3C_4H_8O$. Calcd: C, 57.13, H. 6.28; N, 3.63; S, 8.32; Sc, 3.9. Found: C, 56.27; H, 5.92; N, 3.33; S, 8.12; Sc, 4.1%.

*$ScCl_3$(dibenzo-18-crown-6)1.5THF*

To a solution of 0.360 g (1 mmol) of dibenzo-18-crown-6 in 100 ml of THF was added a solution of 0.152 g (1 mmol) of $ScCl_3$ in 150 ml of THF. The solution volume was reduced to ~100 ml (under reduced pressure) and to the resultant clear solution was slowly added ~200 ml of n-hexane. The white precipitate which formed was isolated by suction-filtration and was dried under vacuum over $P_4O_{10}$ for 24 hours at room temperature. Yield: 0.42 g (68%). Melting point: 141–145 °C. *Anal.* for $ScCl_3 \cdot C_{20}H_{24}O_6 \cdot 1.5C_4H_8O$. Calcd: C, 50.38; H, 5.85; Cl, 17.16; Sc, 7.3. Found: C, 50.48; H, 6.04; Cl, 17.66; Sc, 7.7%.

*$ScCl_3$(dibenzo-18-crown-6)·1.5$CH_3CN$*

To a solution of 0.360 g (1 mmol) of dibenzo-18-crown-6 in 50 ml of $CH_3CN$ was added a solution of 0.152 g (1 mmol) of $ScCl_3$ in 150 ml of $CH_3CN$. The solution volume was reduced to ~100 ml (under reduced pressure) and to the resultant clear solution was slowly added ~200 ml of $Et_2O$. The white precipitate which formed was isolated by suction-filtration and was dried under vacuum over $P_4O_{10}$ for 24 hours at room temperature. Yield: 0.21 g (37%). Melting point: 193–197 °C. *Anal.* for $ScCl_3 \cdot C_{20}H_{24}O_6 \cdot 1.5CH_3CN$. Calcd: C, 48.19; H, 5.01; N, 3.66; Cl, 18.55; Sc, 7.8. Found: C, 48.38; H, 5.07; N, 3.49; Cl, 16.57; Sc, 7.5%.

*Physical Measurements*

Infrared spectra in the region 4000–250 $cm^{-1}$ were obtained by use of a Perkin–Elmer Model 457 grating spectrophotometer by using Nujol mulls between CsI plates. Visible and ultraviolet spectra in the region 450–220 nm were obtained for $2.0 \times 10^{-4}$ *M* or $1.0 \times 10^{-4}$ *M*/$CH_3CN$ solutions by use of a Unicam SP800 B spectrophotometer. Conductances were determined by use of a YSI Model 31 Conductivity Bridge with a #3403 microdipping type cell which was calibrated with tetraethylammonium chloride at concentrations of $1.0 \times 10^{-3}$ *M* and $5.0 \times 10^{-5}$ *M* in $CH_3CN$, at 25 °C [22]. Conductances were determined for a range of concentrations, at 25 °C, with $CH_3CN$ as the solvent. $^1H$ NMR spectra were recorded by use of a Varian A56/60 NMR spectrometer by using acetone-$d_6$ and deuterochloroform solutions with tetramethylsilane (TMS) as an internal standard. Mass spectra were determined by use of an Hitachi–Perkin–Elmer RMU-60 mass spectrometer. Melting points were obtained by use of a Thomas Hoover capillary melting point

TABLE I. Characteristic Vibrations of Ligands and Complexes[a].

| Compound | $\nu$(C–O)[b] | | $\nu$(C≡N) | $\delta$(NCS) | $\nu$(Sc–Anion) |
|---|---|---|---|---|---|
| | (Ar–O–R) | (R–O–R) | | | |
| A | 1252s, 1228s | 1118s | – | – | – |
| $Sc(NCS)_3(A)\cdot 1.5THF\cdot 2H_2O$ | 1251s, 1210s | 1120s, 1099s | 2008s[c] | 495m | 343s |
| $(ScCl_3)_3(A)_2\cdot H_2O$ | 1257s, 1239s, 1180s | 1114s | – | – | 351s, 330m |
| B | 1257s, 1230s | 1128s | – | – | – |
| $Sc(NCS)_3(B)_2\cdot 3THF$ | 1251s, 1232s, 1217s | 1121s | 2022s[d] | 490w | 320s |
| $ScCl_3(B)\cdot 1.5THF$ | 1257s, 1230s | 1129s | – | – | 356s, 333s, 330m |
| $ScCl_3(B)\cdot 1.5CH_3CN$ | 1251s, 1239m, 1223s | 1124s | – | – | 330s |

[a]All values in $cm^{-1}$. [b]Assignments for uncomplexed ligands from references 11 and 23. [c]Due to $NCS^-$. [d]Due to $CH_3CN$.

apparatus and are uncorrected. Elemental analyses for scandium were determined by ignition to the oxide $Sc_2O_3$ at 900 °C. The carbon, hydrogen, nitrogen, sulfur, and chlorine analyses were performed by Chemalytics, Inc. (Tempe, Arizona) and Galbraith Laboratories, Inc. (Knoxville, Tennessee).

## Results and Discussion

Reactions of scandium(III) thiocyanate and chloride with the macrocyclic polyethers-benzo-15-crown-5, A, and dibenzo-18-crown-6, B, result in the formation of complexes of varying salt: polyether ratios and varying degrees of solvation. With the former ligand, A, the complexes $Sc(NCS)_3(A)\cdot 1.5THF\cdot 2H_2O$ and $(ScCl_3)_3(A)_2\cdot H_2O$ were obtained whereas with the latter, B, the species $Sc(NCS)_3(B)_2\cdot 3THF$, $ScCl_3(B)\cdot 1.5THF$ and $ScCl_3(B)\cdot 1.5CH_3CN$ were isolated. The extent of solvation of these complexes is independent of the length of time that the products are vacuum dried, and vacuum drying at elevated temperature (>70 °C) results in the formation of amorphous, glassy products of uncertain composition. The tendency toward solvation in the Sc(III)–benzo-15-crown-5 complexes is apparently so great that the water molecules of hydration must arise from the solvents, even though precautions were taken to exclude water from solvents and the atmosphere. Many polyether complexes that have been isolated are solvated and King and Heckley [14] found that the tendency for solvation in lanthanide(III)–polyether complexes increases with decreasing size of the Ln(III) ion. Evidence for complexation between the scandium(III) ion and the polyethers is obtained from an analysis of the infrared spectra of the complexes (Table I). Upon complex formation, the $\nu$(C–O) bands are shifted to lower energy by ~1–20 $cm^{-1}$; in addition these bands are noticeably less intense in the spectra of the complexes. The relatively small shifts and intensity changes suggest weak scandium–oxygen interactions, the bonding being primarily ion–dipole in nature. This type of interaction has also been proposed as the primary bonding mode in polyether complexes of the alkali and alkaline earth metal ions [4]. Subtle shifts and intensity changes of polyether bands in the 1000–900 $cm^{-1}$ region, which can be attributed to either the wag or twist mode of vibration of the methylene groups [11, 24], and in the region 800–735 $cm^{-1}$, which may be attributed to the carbon–hydrogen out-of-plane bending mode of vibration for the aromatic group(s) [11, 25] provide further evidence for Sc(III)–polyether interaction. Infrared spectra in the region of metal–anion and metal–ligand vibrations have been recorded; bands assigned to $\nu$(Sc–NCS) [20, 26] and $\nu$(Sc–Cl) [20, 26, 21] have been observed (Table I). There is no evidence for bands in the region 500–350 $cm^{-1}$, where $\nu$(Sc–O) bands are generally observed for complexes in which there is significant covalent character in the Sc(III)–oxygen bond [26, 28]. This apparent lack of $\nu$(Sc–O) bands lends support to the earlier suggestion that weak ion–dipole interactions are present in the scandium(III)–polyether complexes. The characteristic vibrations of the thiocyanate group [29, 30], together with the presence of $\nu$(Sc–NCS) bands indicate that both ionic and coordinated isothiocyanate groups are present in the complexes. For the chloride-containing complexes, both coordinated and ionic chloride ions are assumed to be present from the infrared spectra (Table I) and conductivity data (see later). The infrared spectra also confirm the presence of solvent molecules in the complexes. The apparent lack of $\nu$(Sc–O) bands in the THF and water-containing species suggests that the solvent is present within the crystal lattice, rather than coordinated strongly to the scandium(III) ion.

The $^1H$ NMR spectra of the macrocyclic polyethers and their scandium(III) complexes were recorded and the data are presented in Table II. The data provide further evidence for weak interactions between the polyether and the scandium(III) ion and for the presence of solvent in the complexes.

TABLE II. $^1$H NMR Spectral Data for Ligands and Complexes[a].

| Compound | Polyether | | Lattice Solvent | | |
|---|---|---|---|---|---|
| | $C_6H_4$ | $CH_2$ | THF | $CH_3CN$ | $H_2O$ |
| A | 3.18 | 6.12[b] 6.38[c] | – | – | |
| $Sn(NCS)_3(A)\cdot 1.5THF\cdot 2H_2O$ | 3.12 | 6.00[b] 6.31[c] | 6.35[d] 8.21[e] | – | 5.17 |
| $(ScCl_3)(A)_2\cdot H_2O$ | 3.08 | 6.02[b] 6.32[c] | – | – | [f] |
| B | 3.17 | 6.00 | – | – | – |
| $Sc(NCS)_3(B)_2\cdot 3THF$ | 3.10 | 5.90 | 6.38[d] 8.22[e] | – | – |
| $ScCl_3(B)\cdot 1.5THF$ | 3.12 | 5.95 | 6.33[d] 8.13[e] | – | – |
| $ScCl_3(B)\cdot 1.5CH_3CN$ | 3.07 | 5.90 | 2298w[d] 2268s | 7.97 | – |

[a]Chemical shifts in $\tau$ values; all acetone-$d_6$ solutions. [b]Assigned to the four protons of the two methylene groups bonded to oxygen atoms also bonded to the benzene ring [11, 14]. [c]Assigned to the twelve protons of the six methylene groups bonded to oxygen atoms only bonded to methylene groups [11, 14]. [d]Assigned to the four protons of the two methylene groups bonded to the ether oxygen atom [31]. [e]Assigned to the four protons of the two methylene groups bonded only to methylene groups [31]. [f]Not observed.

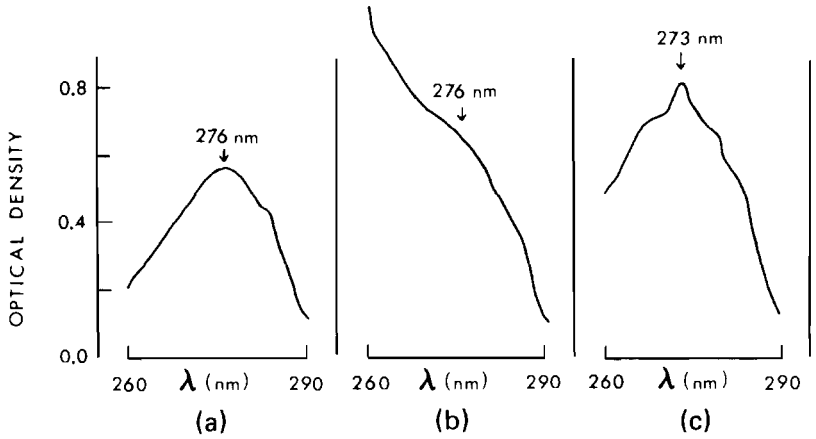



Figure 1. Ultraviolet spectra of Benzo-15-crown-5 and its Sc(III) complexes. (a) Benzo-15-crown-5. (b) $Sc(NCS)_3$(benzo-15-crown-5)$\cdot 1.5THF\cdot 2H_2O$. (c) $(ScCl_3)_3$(benzo-15-crown-5)$_2\cdot H_2O$.

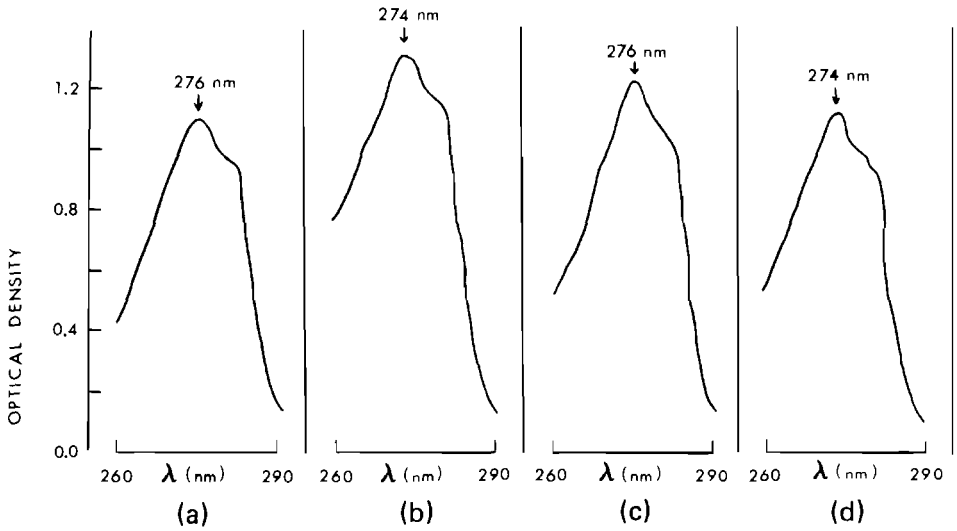



Figure 2. Ultraviolet spectra of Dibenzo-18-crown-6 and its Sc(III) complexes. (a) Dibenzo-18-crown-6. (b) $Sc(NCS)_3$(dibenzo-18-crown-6)$_2\cdot 3THF$. (c) $ScCl_3$(dibenzo-18-crown-6)$\cdot 1.5THF$. (d) $ScCl_3$(dibenzo-18-crown-6)$\cdot 1.5CH_3CN$.

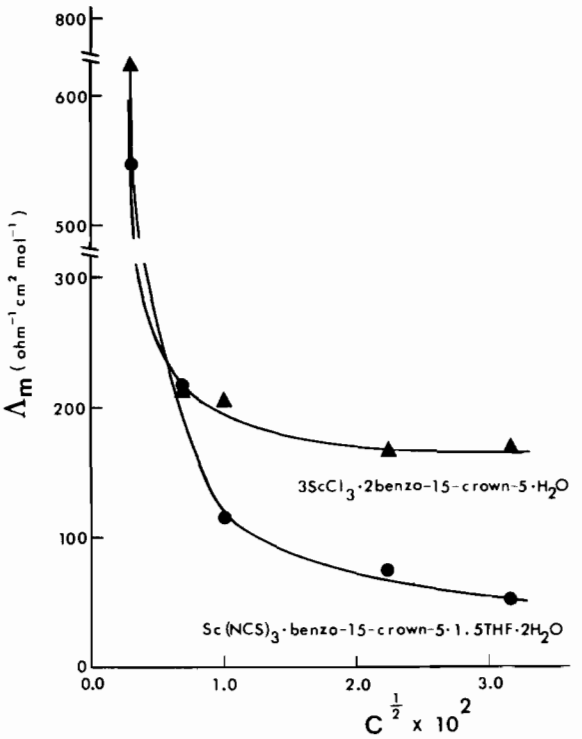



Figure 3. Molar conductance curves for Sc(III)–benzo-15-crown-5 complexes.

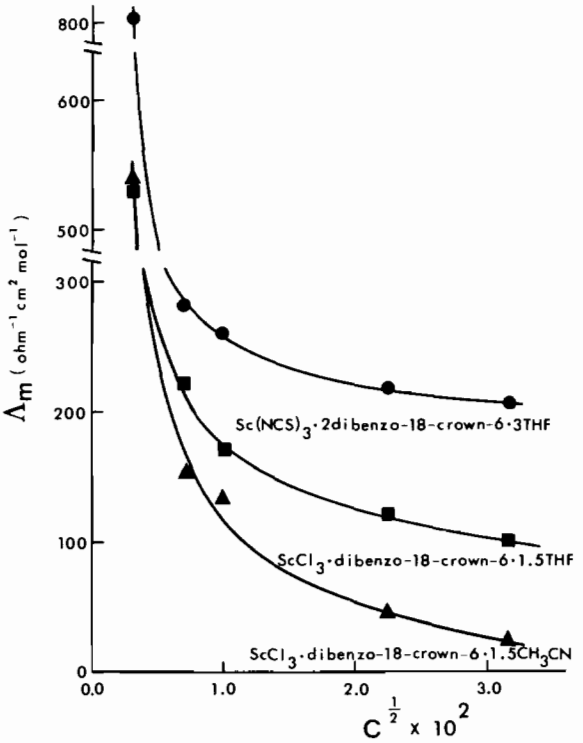



Figure 4. Molar conductance curves for Sc(III)–dibenzo-18-crown-6 complexes.

Mass spectra of the scandium–polyether complexes were measured. In each case, the highest m/e fragment peak observed corresponded to the molecular weight of the particular polyether ligand present. This is consistent with the proposed weak bonding in the complexes and with the thermogravimetric analysis of Ln(dibenzo-18-crown-6)(NCS)$_3$ complexes where the first decomposition process corresponds to loss of dibenzo-18-crown-6 [13].

Both of the macrocyclic polyethers used in this study are derivatives of catechol and, as such, have a characteristic maximum in their ultraviolet spectra; this maximum is centered around 276 nm. Changes in shape, though slight, and slight shifts in positions of this absorption peak upon addition of a salt to a polyether solution have been cited as evidence of complex formation [11, 12]. The UV spectra of all the complexes in acetonitrile provide evidence for Sc(III)–polyether interaction in this solvent. The spectra in the region 290–260 nm are shown in Figures 1 and 2, with the wavelength at the maximum clearly labelled.

The conductivities of the complexes have been studied over a range of concentrations in acetonitrile. The results are shown graphically in Figures 3 and 4 for the benzo-15-crown-5 and dibenzo-18-crown-6 complexes, respectively. It is apparent that the electrolytic behavior of these complexes in acetonitrile is complex. At low concentrations, the nonlinearity of the conductance curves may be attributed to solvolytic displacement of coordinated anions by $CH_3CN$ [32] whereas at higher concentrations, the conductivity behavior suggests the presence of complexes containing coordinated anions. The limiting molar conductances of the species, *i.e.* values of $\Lambda_m$ where "levelling out" of the $\Lambda_m/C^{1/2}$ curves occurs, suggest that at the higher concentrations, the complexes containing one molecule of polyether per scandium(III) ion, *viz.*: $Sc(NCS)_3(A)\cdot 1.5THF\cdot 2H_2O$; $ScCl_3(B)\cdot 1.5THF$ and $ScCl_3(B)\cdot 1.5CH_3CN$ may be formulated as 1:1 electrolytes whereas the limiting conductivity values for $(ScCl_3)_3(A)_2\cdot H_2O$ and $Sc(NCS)_3(B)_2\cdot 3THF$ fall within the range observed for 2:1 electrolytes [32]. Since most of the observed limiting values are at the low end of the range of $\Lambda_m$ values usually found for 1:1 or 2:1 electrolytes, some ion-pairing must be present at the higher concentrations. Similar conclusions have been reached for complexes of Sc(III) with bipyridyl and *o*-phenanthroline [20]. Thus, both the behavior of the polyether complexes in acetonitrile solution and the data obtained from the infrared spectra of the solid compounds indicate the presence of both coordinated and uncoordinated anions.

## Conclusions

Macrocyclic polyethers form 1:1 metal:polyether complexes with many metal ions although species

with 1:2, 2:3 and 2:1 ratios have also been reported depending on the metal ion diameter and the cavity size of the polyether [3–14]. For most of the complexes, particularly those with ratios other than 1:1, a variety of structures have been proposed although very few of these have been confirmed.

In the scandium(III) complexes for which a 1:1 metal: polyether ratio is found, the physical data presented above indicate only weak bonding between Sc(III) and either benzo-15-crown-5, A or dibenzo-18-crown-6, B. In these complexes, where the diameter of the metal ion (~1.4 Å) is less than that of the cavity size (A, ~1.9 Å; B, ~2.9 Å) several possible structures should be considered. First, the Sc(III) ion is located at the center of the cavity, with little or no distortion of the planar macrocyclic ligand and roughly equal Sc–O distances of 2.4 Å and 2.8 Å for complexes with benzo-15-crown-5 and dibenzo-18-crown-6 respectively. These distances are significantly longer than the sum of the radii of the Sc(III) ion and oxygen atom (2.1 Å); thus any bonding in such a structure is expected to be weak. (Bright and Truter [33] found a similar mode of coordination in the (Rb, Na)NCS complex with dibenzo-18-crown-6). If we conclude that two anions are coordinated to the Sc(III) ion in addition to the polyether ligand, as evidenced by the infrared spectra and conductivity data, the coordination environment will be pentagonal bipyramidal in $Sc(NCS)_3(A)\cdot 1.5THF\cdot 2H_2O$ and hexagonal bipyramidal in $ScCl_3(B)\cdot 1.5$-THF and $ScCl_3(B)\cdot 1.5CH_3CN$. Second, the Sc(III) ion may deviate significantly from the center of the cavity, resulting in shorter Sc–O distances with some oxygens and longer distances with others. This type of coordination has been found in the $NaBr\cdot 2H_2O$ complex with dibenzo-18-crown-6 [34]. Coordination of two anions will result in distorted pentagonal bipyramidal and hexagonal bipyramidal coordination environments about the Sc(III) ion. Third, the polyethers may adopt a different (non-planar) conformation consistent with the formation of the more common six-coordination environment of the Sc(III) ion. However, since the scandium(III) ion, with its $3d^0$ configuration, has no stereochemical preference based upon CFSE considerations, it is anticipated that the coordination environment about Sc(III) will be governed by stereochemical preferences of the ligand and by intermolecular interactions. Thus, in these 1:1 Sc(III): polyether complexes, it is concluded that the polyether ligands impose unusual coordination environments on the Sc(III) ion, as described above, *i.e.* it is anticipated that the first or second type of structure will be adopted. Confirmation of this conclusion must await complete X-ray structural investigations.

For the complexes $(ScCl_3)_3(A)_2\cdot H_2O$ and $Sc(NCS)_3(B)_2\cdot 3THF$, few conclusions concerning the structures may be drawn at this time. "Sandwich" complexes containing two polyethers per metal ion or 3 polyethers per two metal ions have been proposed for complexes in which the metal ion diameter is greater than the cavity size of the polyether [5, 6]. However, Poonia *et al.* [35] have recently reported the synthesis of $Mg(benzo\text{-}15\text{-}crown\text{-}5)_2(picrate)_2\cdot 2H_2O$ and proposed but not confirmed, a sandwich structure; the diameter of the $Mg^{2+}$ ion (~1.3 Å) is considerably less than the cavity size of the polyether. Again X-ray structural investigations of the scandium(III) complexes are needed to establish the structures of these complexes with unusual stoichiometries. It is possible that interesting coordination environments may be imposed on the scandium(III) ion, however the possibility of simple, perhaps 1:1 species with uncomplexed polyethers in the lattice, as found in a rubidium complex with dibenzo-18-crown-6 [33] cannot be ruled out.

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