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Coordination Chemistry of Scandium. IX. Scandium (III) Complexes with the Neutral Macrocyclic Ligands Me_4Bz_2[14] tetraeneN_4 and Me_4[14] tetraeneN_4

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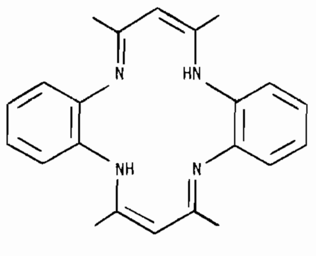
Metal ion complexes of polyaza macrocyclic ligands have been the subject of extensive investigations over the past decade [2–5]; however, there are very few reports of scandium(III) complexes containing these ligands in spite of the demonstrated ability of the scandium(III) ion to form strong complexes with nitrogen donor ligands [6, 7]. Complexes of Sc(III) with the octaethylporphyrin dianion [8, 9] and the phthalocyanine dianion [10, 11] have been synthesized and studied although there have been no published reports concerning scandium(III) complexes with the newer "synthetic" polyaza macrocyclic ligands.

As part of our overall program concerning the coordination chemistry of scandium, we report here the synthesis and characterization of some scandium (III) complexes containing the *neutral* macrocyclic ligands Me_4Bz_2[14] tetraeneN_4, I and Me_4[14] tetraeneN_4, II.



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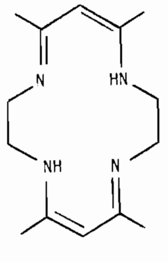

II

Experimental

Me_4Bz_2[14] tetraeneN_4 was prepared by the method of Goedken *et al.* [12] and Me_4[14] tetraeneN_4 was prepared as previously described by Holm and coworkers [13, 14]. The scandium(III) thiocyanate solution, "$Sc(NCS)_3/Et_2O$", was prepared from scandium oxide, Sc_2O_3 (99.9%, Research Organic/Inorganic Chemical Corporation) as previously described [15]. Tetrahydrofuran (THF) and n-hexane were dried over calcium hydride and molecular sieves respectively and distilled under an N_2 atmosphere prior to use. 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(Me_4Bz_2[14] tetraeneN_4)($NCS)_3$

To a solution of 0.344 g (1 mmol) of Me_4Bz_2[14]-tetraeneN_4 in 60 ml of a 1:1 THF/n-hexane solvent mixture was added 10 ml of 0.1 *M* "$Sc(NCS)_3/Et_2O$". The violet precipitate which formed upon allowing the reaction mixture to stir for ~ 4 hours was isolated by suction-filtration and was dried under vacuum over P_4O_{10} for 48 hours at 110 °C. Yield: 0.47 g (83%). *Anal.* for $Sc(NCS)_3 \cdot C_{22}H_{24}N_4$. Calcd: C, 53.27; H, 4.29; N, 17.39; Sc, 8.0. Found: C, 52.77; H, 4.41; N, 17.11; Sc, 8.0%.

Sc(Me_4[14] tetraeneN_4($NCS)_3 \cdot 0.5$THF

To a solution of 0.248 g (1 mmol) of Me_4[14]-tetraeneN_4 in 60 ml of a 1:1 THF/n-hexane solvent mixture was added 10 ml of 0.1 *M* "$Sc(NCS)_3/Et_2O$". The tan precipitate which formed upon allowing the reaction mixture to stir for ~ 4 hours was isolated by suction-filtration and was dried under vacuum over P_4O_{10} for 48 hours at 110 °C. Yield: 0.41 g (82%). *Anal.* for $Sc(NCS)_3 \cdot C_{14}H_{24}N_4 \cdot 0.5C_4H_8O$. Calcd: C, 45.31; H, 5.60; N, 19.47; Sc, 8.9. Found: C, 45.42; H, 6.03; N, 19.88; Sc, 9.0%.

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 5.0×10^{-5} *M* CH_3CN solutions by use of a Unicam SP800B spectrophotometer. Conductances were determined by using a YSI Model 31 Conductivity Bridge with a #3403 microdipping type cell which was calibrated with Et_4NCl at concentrations of 1.0×10^{-3} *M* and 5.0×10^{-5} *M* in CH_3CN, at 25 °C [16].

Elemental analyses for scandium were determined by ignition to Sc_2O_3 at 900 °C. The carbon, hydrogen and nitrogen analyses were performed by Chemalytics Inc., Tempe, AZ, and Galbraith Laboratories, Inc., Knoxville, TN.

Results and Discussion

The compounds Sc(Me_4Bz_2[14] tetraeneN_4)-($NCS)_3$ and Sc(Me_4[14] tetraeneN_4)($NCS)_3 \cdot 0.5$THF were isolated as products of the reactions of an

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

Compound	ν(N–H)	ν(C≡N)	ν(C=N)	δ(NCS)
Me_4Bz_2[14]tetraeneN_4	b	–	1610s 1594sh	–
Sc(Me_4Bz_2[14]tetraeneN_4)$(NCS)_3$	3265m 3210m	2080sh 2030s	1628m 1597m	492m
Me_4[14]tetraeneN_4	b	–	1618s	–
Sc(Me_4[14]tetraeneN_4)$(NCS)_3$.0.5THF	3195s 3050s	2045sh 2020s	1580s	502m

[a] All values in cm^{-1}. [b] Not observed.

ethereal "Sc$(NCS)_3$" solution with the respective neutral macrocyclic ligands in a 1:1 THF/n-hexane mixture. Evidence for complex formation is obtained by analysis of the infrared spectra of the compounds (Table I). The free base macrocycles do not exhibit any bands which may be assigned to ν(N–H) between 3500 and 3000 cm^{-1}, although both complexes have two medium–strong bands in this region. Presumably in the uncomplexed macrocycles, hydrogen bonding causes broadening and a shift to lower frequency of ν(N–H) (recently [17], it has been shown that strong hydrogen bonding occurs in Me_4Bz_2[14]tetraeneN_4). Upon complex formation, the hydrogen bonding is disrupted by coordination of the Sc(III) ion and ν(N–H) bands are observed in the complexes. Bands assigned to ν(C=N) of the macrocycles are shifted to lower energy by 10–40 cm^{-1} and decreased in intensity on complexation. In the region 400–250 cm^{-1}, Me_4Bz_2[14]tetraeneN_4 has no absorption band whereas Me_4[14]tetraeneN_4 displays a weak band at 385 cm^{-1}. For each of the complexes a single broad absorption band is observed at 330 cm^{-1} and is assigned as a composite of ν(Sc–NCS) and $\nu(Sc–N_{ligand})$ [18]. The positions of ν(C≡N), δ(NCS) and ν(Sc–NCS) indicate that both complexes contain anionic and nitrogen coordinated thiocyanate ions [19]; the anticipated positions of ν(C–S) are obscured by ligand absorptions. Finally, the presence of THF in the complex with Me_4[14]tetraeneN_4 is confirmed by assignment [20] of ν(C–O) of THF at 1032 and 1013 cm^{-1}. The apparent lack of ν(Sc–O) bands [18, 21] suggests that the THF is present as lattice solvent and is not coordinated to the Sc(III) ion. The uv–visible spectrum of Sc(Me_4-Bz_2[14]tetraeneN_4)$(NCS)_3$, obtained for a 5.0×10^{-5} *M* solution in CH_3CN, consists of four bands at 231 nm (ϵ, 3.1×10^4), 260 nm (ϵ, 2.2×10^4), 267 nm (ϵ, 2.4×10^4) and 273 nm (ϵ, 2.1×10^4). The free base macrocycle exhibits three bands at 254 nm (ϵ, 1.9×10^4), 267 nm (ϵ, 1.6×10^4) and 340 nm (ϵ, 4.3×10^4). The differences in the spectra can be attributed to changes in energy levels of the ligand orbitals in coordination. The spectrum of Sc(Me_4-[14]tetraeneN_4)$(NCS)_3$·0.5THF could not be obtained due to its very low solubility in suitable solvents. The molar conductance of a 5.0×10^{-5} *M* solution of Sc(Me_4Bz_2[14]tetraeneN_4)$(NCS)_3$ in CH_3CN at 25 °C was found to be 317 ohm^{-1} cm^2 mol^{-1}. This value is close to that expected for a 2:1 electrolyte in CH_3CN [22]; thus the compound is formulated as [Sc(Me_4Bz_2[14]tetraeneN_4)NCS]-$(NCS)_2$. This formulation is consistent with the infrared spectral data.

The structures of Me_4Bz_2[14]tetraeneN_4 and some metal complexes containing the dianionic form of the ligand have been reported [17, 23]. In all the structures, the ligand adopts a non-planar, double saddle shape; in the metal complexes, the coordinated metal ions are displaced out of the N_4 donor atom plane on the same side as the *o*-phenylene groups, the extent of this displacement being dependent on the metal ion. Thus, the axial sites are not equivalent and in the five-coordinate complexes, the fifth ligand is located above the metal ion in the same direction as the out of plane displacement. We propose that [Sc(Me_4Bz_2[14]tetraeneN_4)NCS]$(NCS)_2$ contains five-coordinate Sc(III), with a structure similar to the five-coordinated complexes described above. This Sc(III) compound is the first example of a complex in which Me_4Bz_2[14]tetraeneN_4 is coordinated as a neutral, tetradentate ligand rather than as a dianionic tetradentate [23–25] or a neutral bidentate ligand [26]. It is probable that the Sc(III) ion is displaced out of the N_4 donor atom plane in the direction of the coordinated isothiocyanate ion by as much as 1.26 Å unless some adjustment of the ligand conformation reduces the extent of the displacement. This maximum value is calculated by assuming a Sc–N distance of 2.28 Å [27] and a nitrogen to center of ring distance of 1.902 Å for the neutral ligand [17]. The Sc(III) ion adopts this unusual five-coordinate geometry due to restrictions imposed on the metal ion by the ligand. Six-coordination, which is preferred for the Sc(III) ion is not achieved in this complex due to blocking of one of the axial sites by the ligand in its non-planar conformation.

For Sc(Me_4[14]tetraeneN_4)$(NCS)_3$·0.5THF, very low solubility in the more common organic solvents prevented an investigation of its molar conductivity. In this complex, the ligand, without the restrictions of the *o*-phenylene groups, is expected to be more flexible than $Me_4Bz_2[14]$tetraeneN_4 and thus able to adjust its conformation to incorporate a relatively large metal ion and remain nearly planar. Both axial sites would then be available for isothiocyanate bonding to give a six-coordinated Sc(III) ion in $[Sc(Me_4[14]$tetraene$N_4)(NCS)_2]NCS$; this formulation is consistent with the infrared spectral data. The Sc(III) species is the first example of a complex containing $Me_4[14]$tetraeneN_4 coordinated as a neutral ligand; all previously reported complexes contain the macrocycle in mono- or dianionic forms [13].

Confirmation of the coordination geometry about the Sc(III) ion for both complexes containing the neutral macrocyclic ligands awaits X-ray structural investigations.

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