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The Scandium(III) Ion as a Template for the Synthesis of Hexaaza Quadridentate Macrocyclic Ligand

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We have recently reported the template synthesis of magnesium(II) and zinc(II) complexes containing a 14-membered hexaaza quadridentate macrocyclic ligand [1]. The free ligand has also been prepared without the aid of metal, albeit with very low yield. The macrocyclic complexes of this type seem to be of interest because of the structural similarity to naturally occurring systems in which the equatorial macrocycle is also quadridentate.

We are currently extending our investigations to the template synthesis of complexes of other metal ions of varying radius and electron configuration. We now report what we believe to be the first example of the effectiveness of scandium(III) ion as a template for the synthesis of a macrocyclic compound.

Scandium(III) complex of 2,5,11,14-tetramethyl-3,4,12,13,19,20-hexaazatricyclo[13.3.1.1. [6, 10]-eicosa-1(19),2,4,6,8,10(20),11,13,15,17-decaene ligand has been prepared as its perchlorate salt by the template condensation of 2,6-diacetylpyridine with hydrazine in the presence of $Sc(ClO_4)_3 \cdot 6H_2O$. A mixture of $Sc(ClO_4)_3 \cdot 6H_2O$ (2 mmol) (prepared from Sc_2O_3 by the method of Petru and Kutek) in ethanol (25 ml) and 2,6-diacetylpyridine (1 mmol) in ethanol (15 ml) was heated under reflux with stirring. To this solution hydrazine hydrate (1 mmol) in ethanol (15 ml) was added dropwise. The reaction mixture was refluxed for 24 hours and the course of reaction was controlled by thin layer chromatography. Removal of the solvent left a brown oily solid which, on washing with ether, gave a yellow powder. This was dried under vacuum.

The formulation of this complex as $[Sc(C_{18}H_{18}N_6)(H_2O)_2] \cdot (ClO_4)_3 \cdot 4H_2O$ follows from spectral data (i.r., u.v.–vis, n.m.r.) and thermal analysis. Elemental analysis figures are consistent with the above formula. The complex is a yellow, air stable solid, soluble in polar solvents, *e.g.*, H_2O, CH_3OH, C_2H_5OH, CH_3CN.

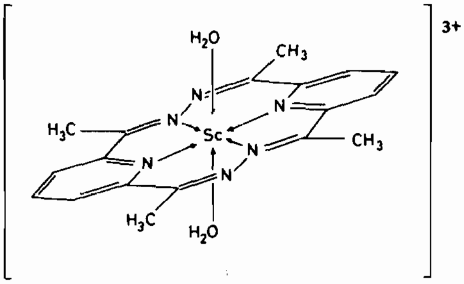
The infrared spectrum of that complex (in KBr pellets, 4000–400 cm^{-1} region) shows significant bands at 1610, 1570, and 1470 cm^{-1} which may be assigned to C=N stretching modes and two high energy pyridine vibrations [3, 4]. The low energy pyridine bands are observed at 635 and 425 cm^{-1} suggesting coordination of pyridine [5]. The spectrum exhibits a broad intense band centered at 1100 cm^{-1} with shoulder at 1025 cm^{-1} and a strong sharp band at 625 cm^{-1}, which are characteristic of perchlorate stretching and bending modes, respectively [6]. These absorption bands indicate that the perchlorate anion does not coordinate with the central metal in this complex. A broad diffuse band of strong intensity in the 3500–3100 cm^{-1} region may be assigned to O–H stretching vibration for lattice water [7]. A weak absorption found at 530 cm^{-1} may suggest the presence of coordinated water [8]. Absence of bands characteristic of carbonyl and amine groups confirms the formation of the macrocyclic compound.

Electronic spectra of the solid complex and its solution in water (taken in the range 50,000–14,000 cm^{-1}) show high energy bands at *ca.* 47,000, 39,000, and 34,000 cm^{-1} attributable to the coordinated macrocycle [9], and two weaker bands appearing as shoulders at *ca.* 31,000 and 26,000 cm^{-1}. The similarity of spectra obtained in the solid state and in solution suggests, in agreement with other data, that axial ligands are water molecules.

The nuclear magnetic resonance spectrum of the complex (in CD_3OD solution with TMS as internal standard) shows methyl protons of $CH_3\overset{|}{C}=N-$ groups at δ 2.25 and 2.35, pyridine protons at δ 8.20, and water protons at δ 5.10. Intergrated intensities of the above signals are in the ratio 1:1:1:2, respectively. This is consistent with the proposed formulation of the complex.

Thermogravimetric analysis indicates the loss of four molecules of water at 35–60 °C and two molecules of water at 120–160 °C.

All these data support a six-coordinate octahedral structure of the perchlorate complex of scandium(III) ion with the four nitrogen donors of hexaaza 14-membered macrocycle occupying the equatorial plane and two water molecules in axial positions. This structure is highly stabilized by the presence of 5–6–5–6 chelation mode [10].



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