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

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Summary. The condensation of 2,6-diacetylpyridine and *m*-phenylenediamine in the presence of scandium(III) perchlorate as a template agent affords a new 20-membered macrocyclic complex of formula $ScL(ClO_4)_3 \cdot 4H_2O$, where L is $Me_4bzo_2pyo_2$[20]octaene-N_6.

Keywords. Macrocyclic complexes; Scandium; Template synthesis.

Scandium(III) als Matrix für die Synthese eines makrocyclischen Hexaazaliganden

Zusammenfassung. Die Kondensation von 2,6-Diacetylpyridin und *m*-Phenylendiamin in Gegenwart von Scandium(III)perchlorat als Matrix liefert einen neuen makrocyclischen Komplex der Zusammensetzung $ScL(ClO_4)_3 \cdot 4H_2O$ ($L = Me_4bzo_2pyo_2$[20]octaen-N_6).

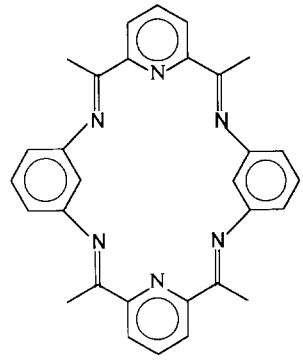
Introduction

Metal complexes of macrocyclic ligands have been the subject of extensive investigations over the past decades; the fundamental and interdisciplinary character of the metal chemistry of macrocycles has been recognized [1]. However, there are very few reports of scandium(III) complexes containing these ligands [2–4]. Recent findings demonstrating the possibility of using Sc^{3+} as a suitable probe for metal ion binding sites in macromolecules of biological interest [5] prompted us to study of the coordination of this ion by macrocycles. In order to extend the chemistry of Sc^{3+} in its reactions with nitrogen-donor ligands, we have previously reported the first examples of the template action of this ion in the synthesis of polyaza 14-membered macrocyclic compounds [6, 7]. In this paper, the synthesis and characterization of a 20-membered hexaaza macrocyclic complex of scandium(III) perchlorate is described.

Results and Discussion

The template reaction of 2,6-diacetylpyridine with *m*-phenylenediamine in the presence of scandium(III) perchlorate produces the 20-membered N_6 macrocyclic complex as a result of a [2+2] *Schiff* base cyclocondensation. The formulation of

this complex as $ScL(ClO_4)_3 \cdot 4H_2O$, where L is $Me_4bzo_2pyo_2$[20]octaene-N_6, follows from spectral data (IR, UV/Vis, ^1H NMR, and MS) and elemental analysis (see Experimental). The complex is a yellow air stable solid soluble in *DMSO* and slightly soluble in CH_3CN.



The infrared spectrum of the complex (in CsI pellets, 4000–200 cm^{-1}) exhibits a significant band at 1630 cm^{-1}, attributable to a C=N stretching mode and indicating the *Schiff* base condensation. The bonding of the pyridine nitrogen atom is indicated by the presence of the high energy pyridine bands at 1600 and 1460 cm^{-1} and the low energy pyridine ring in-plane and out-of-plane vibrations at 670 and 440 cm^{-1}. Absence of bands characteristic of carbonyl and amine groups confirms the formation of the macrocyclic compound. The spectrum shows a medium band at 350 cm^{-1} which is tentatively assigned to the metal-nitrogen stretching vibration [8]. The OH absorption appears as a broad diffuse band centered at 3400 cm^{-1}. In addition, weak bands are detectable at 870 and 535 cm^{-1} as expected for rocking and wagging modes of water molecules interacting with the metal ion [9]. The presence of uncoordinated perchlorates in the complex is inferred from the broad and intense band at about 1100 and a sharp band at 625 cm^{-1}, and also from the absence of splitting of the degenerate stretching and bending modes of ClO_4^-, which is indicative of coordination species [10].

The electronic spectrum of the acetonitrile solution of the complex contains intense and medium bands with maxima at 224 nm and 282 nm attributable to the $\pi \rightarrow \pi^*$ transitions of the coordinated macrocycle [11].

The ^1H NMR spectrum of the complex obtained in *DMSO*-d_6 solution shows methyl protons at 2.6, benzene protons at 6.7, and pyridine protons at 7.8–8.2 ppm. Integrated intensities of the above signals are in the ratio 6:4:3, respectively. This is consistent with the proposed formulation of the complex.

Further evidence for the formation of the macrocyclic compound results from the mass spectrum of the complex. The highest and most abundant fragment observed at $m/z = 470$ corresponds to the molecular weight of the macrocycle. Other principal fragmentation ions occur at $m/z = 455$, 352, 311, 235, and 194.

In addition to the macrocyclic complex, the scandium(III) perchlorate complex of 2,6-diacetylpyridine (*DAP*) was isolated from the reaction solution of 2,6-diacetylpyridine with *m*-phenylenediamine in the presence of the metal salt and identified by spectroscopic methods. Elemental analysis established the stoichiometry of the isolated complex as $Sc(DAP)_2(ClO_4)_3 \cdot 7H_2O$. The yellow compound is soluble in polar solvents. The evidence for coordination of the carbonyl oxygen atoms and pyridine nitrogen atoms to the scandium(III) ion stems from the IR and ^1H NMR spectra of the complex. The C=O absorption band observed in the IR spectrum of

2,6-diacetylpyridine at 1700 cm^{-1} is shifted by 40 cm^{-1} to lower wavenumbers in the complex as a result of the decrease in the C=O double bond length owing to coordination. The interaction of the pyridine nitrogen atoms with the scandium(III) ion is indicated by the increasing frequency of high and low energy pyridine ring vibrations found at 1570, 640, and 400 cm^{-1}, in the spectrum of the ligand by 30–35 cm^{-1} upon complex formation. The ^1H NMR spectrum obtained in CD_3CN solution confirms the bonding mode discussed above, showing a downfield shifts of the methyl and pyridine proton resonances from 2.75 and 8.18 ppm in the free ligand to 2.98 and 8.35 ppm, respectively, in the complex IR absorptions attributable to perchlorate groups occur as unsplit bands at *ca.* 1080 and 630 cm^{-1} as expected for the ionic state. The electronic spectrum of this complex in acetonitrile consists of three bands with maxima at 225, 269, and 304 nm. 2,6-Diacetylpyridine shows bands at 211, 236, and 274 nm. The shift of all three bands in the complex relative to the free ligand may be explained by the metal–ligand interaction. Treatment of the complex with *m*-phenylenediamine in methanol for 24 h in a 1:2 molar ratio leads to the isolation of a product which appears to be identical with the macrocyclic complex discussed above. Thus, the scandium complex of 2,6-diacetylpyridine might be regarded as a possible intermediate in the [2+2] cyclocondensation reaction leading to the formation of the macrocyclic complex. It seems reasonable to assume that the initial coordination of the metal ion to the pyridine nitrogen and two carbonyl oxygen atoms makes the carbon atoms of carbonyl moieties more susceptible to nucleophilic attack by the amine nitrogen atoms.

The scandium(III) ion has been therefore found to be an effective template in the synthesis of a 20-membered *Schiff* base macrocyclic compound. A survey of the literature on coordination chemistry of scandium reveals that in known X-ray crystal structures Sc^{3+} is predominantly six-coordinated [12–18], although eight-fold coordination is quite common occurrence [19–22]. Coordination numbers of seven [3, 4, 23] and nine [22, 24], though known, occur only rarely. References to these structures indicate that the six-coordinated complexes display an octahedral [12–14] or distorted octahedral [15, 16], trigonal antiprismatic [17], or intermediate between trigonal antiprismatic and prismatic geometry [18]. The sterochemistry of seven-coordinated scandium is approximately pentagonal-bipyramidal. The structure of the eight-coordinated scandium complexes is best described as an irregular bicapped trigonal prism distorted toward a dodecahedron [19] or as a distorted dodecahedron [20–22]. Since there is no ligand field stabilization effect in the scandium(III) ion (d° configuration), its coordination environment is influenced by the nature of the ligands. In the macrocyclic complex of *L* with an N_6 set of donor atoms, six-coordination can be achieved; however, the interaction of water molecules with the central metal ion which might lead to the higher coordination numbers cannot be ruled out.

Experimental

IR spectra were recorded in the range of 4000–200 cm^{-1} on a Perkin-Elmer 580 spectrophotometer (CsI pellets). Electronic spectra were measured on a Shimadzu UV-160 spectrophotometer. ^1H NMR spectra were run on a Varian Gemini 300 spectrometer using *TMS* as an internal reference. Mass spectra were obtained on a Jeol-JMS D100 mass spectrometer.

The complex of *L* was prepared as its perchlorate salt by adding *m*-phenylenediamine (0.2 mmol) in methanol (20 cm^3) to the mixture of $Sc(ClO_4)_3 \cdot 6H_2O$ (0.1 mmol, prepared from Sc_2O_3 [25]) in

methanol (15 cm^3) and 2,6-diacetylpyridine (0.2 mmol) in methanol (20 cm^3). The reaction was heated under reflux with stirring for 18 h. The resulting yellow precipitate was filtered off, washed with ether, and dried under vacuum. Anal.: calcd. for $C_{30}H_{34}N_6O_{16}Cl_3Sc$: C, 40.67; H, 3.86; N, 9.48; found: C, 41.34; H, 3.92; N, 9.46; IR (cm^{-1}): 3400m, br, ν(OH); 1630s, ν(C=N); 1600m, 1460s, 670w, 440w (py); 860w, 535w, δ(OH); 350w (Sc–N); 1100vs, br, ν_3(ionic ClO_4); 625m, ν_4(ionic ClO_4); ^{1}H NMR (*DMSO*-d_6 ppm): 2.6 (12H, CH_3), 6.7 (8H, bz), 7.8–8.2 (6H, py); MS: $m/z = 470$ (L^+), 455, 352, 311, 235, 194.

A small amount of microcrystalline product which turned out to be the scandium(III) perchlorate complex of 2,6-diacetylpyridine was obtained from the filtrate after removal of the solvent by rotary evaporation. Anal.: calcd. for $C_{18}H_{32}N_2O_{23}Cl_3Sc$: C, 27.16; H, 4.05; N, 3.52; found: C, 27.26; H, 3.93; N, 3.44; IR (cm^{-1}): 3460m, br, ν(OH); 1660s, ν(C=O); 1600m, 1460s, 675w, 430w (py); 1080vs, br, ν_3(ionic ClO_4); 630m, ν_4(ionic ClO_4); ^{1}H NMR (CD_3CN, ppm): 2.98 (6H, CH_3), 8.35 (3H, py).

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