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Metal-Template Synthesis and Characterization of a Nitrogen-Oxygen Donor *Schiff* Base Macrocyclic System

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Summary. Reaction of 2,6-diacetylpyridine with 1,12-diamine-4,9-dioxadodecane in the presence of magnesium(II), zinc(II), and cadmium(II) perchlorates as template agents gives the complexes of 19-membered macrocyclic ligand **1** with a set of two N and three O donor atoms. The complexes were characterized by spectroscopic methods (IR, ^{1}H NMR, FAB-MS) and thermogravimetric and elemental analyses.

Keywords. Macrocyclic complexes; Magnesium(II); Zinc(II); Cadmium(II); Template synthesis.

Metallunterstützte Synthese und Charakterisierung eines makrocyclischen Stickstoff-Sauerstoff-Donor-Liganden

Zusammenfassung. Reaktion von 2,6-Diacetylpyridin mit 1,12-Diamin-4,9-dioxadodecan in Gegenwart von Magnesium(II)-, Zink(II)- und Cadmium(II)perchlorat ergibt die entsprechenden Komplexe des 19-gliedrigen Makrocyclus **1**, der über 5 Donoratome verfügt (3×N, 2×O). Die Komplexe wurden mit spektroskopischen Methoden (IR, ^{1}H-NMR, FAB-MS) sowie mittels thermogravimetrischer Analyse und Elementaranalyse charakterisiert.

Introduction

We have recently reported the effectiveness of rare earth metal ions in the synthesis of pentadenate azaoxa *Schiff* base macrocyclic complexes [1]. The 19-membered macrocyclic product of the template process (**1**), contrary to the 15-membered coronand with a similar set of donor atoms [2], appears to be large enough to encapsulate all the lanthanide and yttrium ions irrespective of the ionic radius size of the central atoms. In view of these results and the possibility of using these complexes as informative spectroscopic probes for binding sites of biometals which do not show a comparable multitude of spectroscopic and magnetic properties and in biomedical applications [3–7], it seems to be of interest to relate

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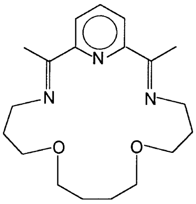
the template action of rare earth metal ions and the biologically important magnesium(II), zinc(II), and cadmium(II) ions in the synthesis of this macrocyclic system. The preparation and characterization of new 19-membered macrocyclic *Schiff* base complexes formed in the metal-promoted condensation reactions between one molecule of 2,6-diacetylpyridine and one molecule of 1,12-diamine-4,9-dioxadodecane is the subject of this paper.

Results and Discussion

The template reaction of 2,6-diacetylpyridine with 1,12-diamine-4,9-dioxadodecane in the presence of magnesium(II), zinc(II), and cadmium(II) perchlorates produces the respective complexes of the 19-membered macrocycle **1** with an N_3O_2 set of donor atoms as a result of a *Schiff* base cyclocondensation. The formation of these complexes as $\mathrm{Mg}L(\mathrm{ClO_4})_2(\mathrm{H_2O})_2 \cdot 4\mathrm{H_2O}$, $\mathrm{Zn}L(\mathrm{ClO_4})_2(\mathrm{H_2O})$, and $\mathrm{Cd}L(\mathrm{ClO_4})_2(\mathrm{H_2O})$ ($L = \mathbf{1} = \mathrm{Me_2}\mathit{pyo}[19]\mathrm{trieneN_3O_2}$) follows from spectroscopic data (IR, ^{1}H NMR, FAB-MS) as well as from thermogravimetric and elemental analysis (see Experimental). The complexes are orange air stable solids moderately soluble in *DMSO*.



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The infrared spectra of the complexes (in CsI pellets, 4000–200 cm^{-1}) are all very similar and confirm the formation of the macrocyclic compounds by the absence of bands characteristic of carbonyl and amine groups of the starting materials. An important feature is the occurrence of a strong band at 1646–1625 cm^{-1} attributable to C=N stretching modes, indicating the *Schiff* base condensation. The spectra exhibit medium to strong bands at 1590–1585 cm^{-1} as expected for the high energy ring vibrations of the coordinated pyridine. The bonding of the pyridine nitrogen atom is also shown by the presence of bands at 1030–1020 cm^{-1}, 670–651 cm^{-1}, and 460–450 cm^{-1} attributable to the ring breathing frequency and the low energy pyridine ring in-plane and out-of-plane vibrations, respectively. The complexes show a broad diffuse band centered at *ca.* 3450–3420 cm^{-1} due to the stretching and bending modes of water. In addition, weak bands are detectable at 855–813 cm^{-1} which may be assigned to rocking or wagging modes of water molecules coordinated to the metal ion [8]. The strong band centered at 1096–1091 cm^{-1} along with the sharp band at 625–622 cm^{-1} indicates the presence of noncoordinated perchlorate anions. The involvement of the perchlorates in the coordination sphere of the metal ion normally manifests itself by a splitting of the antisymmetric Cl–O stretching mode due to the reduced symmetry of the coordinated species [9]. In the cadmium complex, three maxima are actually observed: at 1091, 1110, and 1145 cm^{-1}. However, the C–O–C stretching vibrations of the polyether chain in the ligand also fall in this region. Our earlier findings [1, 2, 10, 11] and literature values for similar polyoxaaza macrocyclic complexes [12, 13] allow us to assign the bands at 1110 and 1145 cm^{-1} to the coordinated ether oxygen atoms. The presence of noncoordinated perchlorates was confirmed by FAB mass spectroscopic results. The FAB mass spectrum of the cadmium perchlorate complex gives a parent peak at $m/z = 460.6$ corresponding to $(CdLH_2O)^{2+}$. This species loses its water molecule, resulting in the formation of the fragment $(CdL)^{2+}$ at $m/z = 442.6$. The spectrum also exhibits a peak due to the free ligand at $m/z = 333.3$, providing strong evidence for the formation of the macrocyclic complex with **1** as a [1+1] product of the template condensation of one molecule of diketone with one molecule of diamine. The presence of water in the inner sphere of the complexes is supported by the results of thermogravimetric analysis. The magnesium complex indicates the loss of four lattice water molecules at 65°C and two water molecules coordinated to the metal ion at 145°C, confirming the presence of water bound in two different ways. The complexes of zinc and cadmium lose one mol of water per mol of metal ion in the temperature range of 135–145°C.

The ^1H NMR spectrum of the cadmium complex in *DMSO*-d_6 exhibits three multiplets in a ratio of 1:1:2: the protons α to nitrogen give raise to a triplet (4H) at $\delta = 2.81$, the protons β to nitrogen to a quintet (4H) at $\delta = 1.75$, and the protons adjacent to oxygen to a triplet (8H) at $\delta = 3.44$ ppm. The remaining protons of the $OCH_2CH_2CH_2CH_2O$ chain (4H) occur at 1.56 ppm. The pyridine protons are observed at $\delta = 8.7$–8.3 (3H) and the methyl protons of the two CH_3CN groups (6H) at $\delta = 2.53$ ppm. The integrated relative intensities of the above signals are in good agreement with the ratio required from the proposed formulation of the complex.

The ^1H NMR spectra of the magnesium and zinc complexes appeared to be very complicated and difficult to resolve due to the presence of various products. It is likely that metal-solvent interaction occurs in these two complexes. *DMSO* with its strong donor properties is known to compete for the coordination sphere of the metal ions. This might result in removal of the metal ion from the macrocycle, followed by ligand breakdown. The FAB mass spectra were also not very informative, and no clear peaks corresponding to the molecular ion can be observed. These results suggest that the magnesium and zinc complexes are less stable in comparision with the complex of cadmium as well as with lanthanide complexes of this macrocycle reported earlier [1]. The differences in the stability of these complexes may be explained on the basis of the idea of size-match selectivity in the design and synthesis of *Schiff* base macrocyclic systems. The cadmium and lanthanide ions have similar ionic radii and appear to be large enough to coordinate with the 19-membered macrocycle in a planar conformation. This assumption is supported by our earlier results concerning the lanthanide ion complexes of **1** which incorporate two counterions in the coordination sphere [1] and by references to the crystal structure of similar macrocyclic complexes [14, 15]. These findings reveal that in these complexes the macrocycle is considerably flattened when the lanthanide ion is held in the same plane by one group of counterions on each side. However, the cadmium ion, contrary to the lanthanides and similar to the magnesium and zinc ions, displays a tendency to attain the lower coordination number. On the basis of spectroscopic and analytical data it seems resonable to propose the coordination number six for the cadmium ion. The metal ion is presumably surrounded by the N_3O_2 set of donor atoms of the 19-membered macrocycle, and the oxygen of the water molecule completes the coordination sphere. A similar mode of coordination was found in the 17-membered pentadentate N_5 macrocyclic cadmium complex whose geometry is best described as pentagonal pyramidal with the metal ion bound to five nitrogen atoms of the macrocycle and to a bromine anion in an axial position [16]. The magnesium and zinc ions are evidently smaller, and formation of the macrocyclic complexes in metal-promoted synthesis requires the adoption of an appreciably folded conformation of the macrocycle in order to maintain the pentadentate coordinating behaviour of the ligand. This may cause steric crowding on one side of the macrocycle. Consistent with this view is our failure to prepare complexes of **1** in the presence of salts of these metals containing bulky and strongly coordinated nitrate counterions. However, the sterically crowded axial side can be still occupied by the unidentate water molecule with its small steric demands as it has been shown in the case of the seven-coordinated magnesium complex of **1**. In the zinc complex, the metal ion is presumably six-coordinated being bound to the five nitrogen donor atoms of the folded macrocycle and to one water molecule and leaving the other axial position unoccupied. The readjustment of the macrocycle conformation from the preferred one could explain the observed lower stability of the two latter macrocyclic complexes with smaller metal ions in contrast to the behaviour of the corresponding cadmium and lanthanide complexes.

Experimental

IR spectra were recorded using CsI pellets in the range of 4000–200 cm^{-1} on a Perkin-Elmer 580 spectrophotometer. ^1H NMR spectra were run on a Varian Gemini 300 spectrometer using *TMS* as an internal reference. FAB mass spectra were obtained on an AMD-604 mass spectrometer with glycerol as matrix. Thermogravimetric measurements were performed using a Shimadzu TGA-50 derivatograph (up to 250°C, heating rate $10°C \cdot min^{-1}$, air). All data reported refer to isolated materials judged to be homogenous by thin layer chromatography performed on precoated silica gel plates (0.2 mm 60 F-254, E. Merck) and visualized by UV light.

All complexes of **1** were prepared under similar conditions. To a mixture of the appropriate metal salt (0.1 mmol) in methanol (10 cm^3) and 2,6-diacetylpyridine (0.1 mmol) in methanol (10 cm^3), 1,12-diamine-4,9-dioxadodecane (0.1 mmol) in methanol (10 cm^3) was added dropwise with stirring. The reaction was carried out for 4 h. The solution volume was then reduced to 10 cm^3 by evaporation, and an orange precipitate formed upon addition of a small amount of diethyl ether. This was filtered off, washed with ether, and dried *in vacuo*.

$C_{19}H_{31}N_3O_{11}Cl_2Cd$

Calcd.: C 34.50, H 4.73, N 6.36; found: C 35.06, H 4.76, N 6.71; IR: 3446 m (br, ν(OH)), 1646s (ν(C=N)), 1586 m, 1020 s, 668 w, 460 w (*py*), 837 w (δ(OH)), 1145s, 1110s (ν(COC)), 1091 vs (ν_3(ionic ClO_4)), 622 m (ν_4(ionic ClO_4)) cm^{-1}; ^1H NMR (*DMSO*-d_6): $\delta = 8.7–8.3$ (3H, *py*), 2.53 (6H, CH_3), 2.81 (4H, t, -CH_2CH_2-N), 1.75 (4H, q, -CH_2CH_2-N), 3.44 (8H, t, -CH_2-O-CH_2-), 1.56 (4H, O-$CH_2CH_2CH_2CH_2$-O) ppm; FAB-MS: $m/z = 460.06$ $(CdL(H_2O))^{2+}$, 442.6 $(CdL)^{2+}$, 333.3 (L^+).

$C_{19}H_{41}N_3O_{16}Cl_2Mg$

Calcd.: 34.43, H 6.24, N 6.34; found: C 33.32, H 6.05, N 6.43; IR: 3420 m (br, ν(OH)), 1625 s (ν(C=N)), 1585 m, 1030 s, 670 w, 450 w (*py*), 855 w (δ(OH)) 1096 vs (br, ν_3(ionic ClO_4)), 625 m (ν_4(ionic ClO_4) cm^{-1}.

$C_{19}H_{31}N_3O_{11}Cl_2Zn$

Calcd.: C 37.18, H 5.09, N 6.84; found: C 37.50, H 4.87, N 6.47; IR: 3450 m (br, ν(OH)), 1642 s (ν(C=N)), 1590 m, 1028 s, 651 w, 460 w (*py*), 813 w, (δ(OH)), 1094 vs (br, ν_3(ionic ClO_4)), 623 m (ν_4(ionic ClO_4) cm^{-1}.

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