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YTTRIUM(III) COMPLEXES OF PENTADENTATE SCHIFF BASE MACROCYCLIC LIGANDS WITH N_3O_2 AND N_5 SET OF DONOR ATOMS†

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Abstract—The template reactions of 2,6-diacetylpyridine with 3,6-dioxaoctane-1,8-diamine or 3,7-diazanonane-1,9-diamine in the presence of yttrium(III) chloride and perchlorate produce the 15-membered N_3O_2 and 16-membered N_5 macrocyclic complexes as a result of [1+1] Schiff base cyclocondensation. They are formulated as $[YL^1(H_2O)_2]Cl_3 \cdot H_2O$ and $[YL^2(H_2O)_2](ClO_4)_3 \cdot 2H_2O$, where L^1 is Me_2pyo[15]trieneN_3O_2 and L^2 is Me_2pyo[16]trieneN_5 on the basis of IR, UV–vis, ^1H NMR and MS data, and elemental and thermogravimetric analyses

Interest in exploring the encapsulation of the lanthanide elements by polyoxa and polyaza macrocycles has continually increased since they can be used for metal ion separation, stabilization of the unusual oxidation states, for studying the high coordination numbers and geometries and for probing metal ion binding sites of macromolecules of biological interest.[1–3] The new areas of application for these macrocyclic systems, in particular those containing nitrogen donor atoms, involve their use as magnetic resonance imaging contrast-enhancing agents,[4–8] synthetic nucleases for efficient catalytic cleavage of RNA[9] and the clinical use of radioactive metal macrocyclic complexes bound to proteins.[10] The conjugation of metals to monoclonal antibodies results in agents for immunotherapy and other medical applications. Chelators that can hold the metal ion with high stability under physiological conditions are essential to avoid damage to non-target cells. The introduction of macrocyclic ligands, which form neutral or cationic complexes with the metal of interest and are inert with respect to release of the metal ion and therefore more resistant to acid catalysed dissociation, has led to some very encouraging results with ^{90}Y.[11–13] Recent ^{89}Y NMR studies have demonstrated the possibility of employing the calcium(II)-like behaviour of yttrium(III) ion for probing metal ion binding sites in proteins.[14] These new findings give impetus to the study of the macrocyclic complexes of yttrium.

In seeking the new strong chelating agents for yttrium and as a continuation of our investigations concerning the effectiveness of metal ions of varying radius and electron configuration in the synthesis of macrocyclic compounds we have previously reported the template action of yttrium ion in the synthesis of polyaza macrocyclic compounds.[15–17] In this paper the template synthesis and characterization of the N_3O_2 and N_5-donor macrocyclic complexes of yttrium(III) ion derived from 2,6-diacetylpyridine and 3,6-dioxaoctane-1,8-diamine or 3,7-diazanonane-1,9-diamine is described.

EXPERIMENTAL

The hydrated yttrium(III) salts were prepared by dissolving the 99.99% oxide (Fluka) in a slight excess of appropriate acid. The solutions were evaporated and precipitates recrystallized from methanol. 2,6-Diacetylpyridine and 3,7-diazanonane-1,9-diamine were purchased from Aldrich Chemical

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Company and 3,6-dioxaoctane-1,8-diamine from Fluka and were used without further purification.

Preparation of the L^1 *complex of yttrium chloride*

To a mixture of $YCL_3 \cdot 6H_2O$ (0.1 mmol) in methanol (10 cm^3) and 2,6-diacetylpyridine (0.1 mmol) in methanol (10 cm^3), 3,6-dioxaoctane-1,8-diamine (0.1 mmol) in methanol (10 cm^3) was added dropwise with stirring. The reaction was carried out for 3 h. The solution volume was then reduced to 10 cm^3 by roto-evaporation, and an orange precipitate formed on addition of a small amount of diethyl ether. This was filtered off, washed with ether, and dried *in vacuo*; yield, 73.8%. Found: C, 34.5; H, 5.6; N, 8.4. Calc. for $[YL^1(H_2O)_2]Cl_3 \cdot H_2O$: C, 34.3; H, 5.2: N, 8.0%. IR (CsI pellets, cm^{-1}): 3420m, br, ν(OH); 1630s, ν(C═N); 1110m, ν(C—O—C); 1590m, 1460s, 1010w, 670w, 430w (py); 860w, δ(OH). ^{1}H NMR (DMSO-d_6, ppm): 3.63 (t, J = 5.4 Hz, 4H, ═NCH_2CH$_2$O), 2.95 (t, J = 5.4 Hz, 4H, ═NCH$_2$CH_2O), 3.59 (s, 4H, —OCH_2CH_2O—), 2.51 (6H, CH_3), 7.8–8.2 (m, 3H, py). MS: m/z 275 (L^+), 250, 220, 206, 187, 148, 118, 104, 89, 77.

Preparation of the L^2 *complex of yttrium perchlorate*

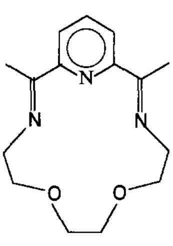
A mixture of $Y(ClO_4)_3 \cdot 6H_2O$(0.1 mmol) in methanol (10 cm^3) and 2,6-diacetylprine (0.1 mmol) in methanol (10 cm^3) was heated under reflux with stirring. To this solution 3,7-diazanonane-1,9-diamine (0.1 mmol) in methanol (10 cm^3) was added dropwise. The reaction mixture was refluxed for 12 h. The resulting orange precipitate was filtered off, washed with ether, and dried *in vacuo*; yield, 66.7%. Found : C, 26.2, H, 4.5; N, 9.5. Calc. for $[YL^2(H_2O)_2](ClO_4)_3 \cdot 2H_2O$: C, 25.7; H, 4.4; N, 9.4%. IR (CsI pellets, cm^{-1}): 3420m, br, ν(OH); 3200–3080m, ν(NH); 1630s, ν(C═N); 1590m, 1460s, 1010w, 670w, 430w (py); 1010vs, br, ν_3(ionic ClO_4); 620m, ν_4(ionic ClO_4); 860w, δ(OH). ^{1}H NMR (DMSO-d_6, ppm): 2.84 (t, J = 6.1 Hz, 4H, ═NCH_2CH$_2$NH—), 2.72 (t, J = 6.1 Hz, 4H, ═NCH$_2$CH_2NH—), 2.62 (t, J = 7.1 Hz, 4H, —NHCH_2CH$_2$), 2.17 (m, 2H, CH$_2$CH_2CH$_2$), 1.6 (2H, —NH), 2.55 (6H, CH_3), 7.8–8.4 (m, 3H, py).

Measurements

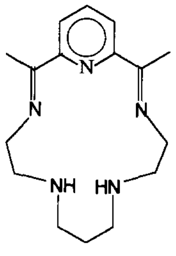
IR spectra were recorded using CsI pellets in the range 4000–200 cm^{-1} on a Perkin–Elmer 580 spectrophotometer. Electronic spectra were measured on a Shimadzu UV-160 spectrophotometer. ^{1}H NMR spectra were run in DMSO-d_6 on a Varian Gemini 300 spectrometer using TMS as an internal reference. Mass spectra were obtained on a Jeol-JMS D100 mass spectrometer. Thermogravimetric measurements were performed using Shimadzu TGA-50 derivatograph.

RESULTS AND DISCUSSION

The template reactions of 2,6-diacetylpridine with 3,6-dioxaoctane-1,8-diamine or 3,7-diazanonane-1,9-diamine in the presence of yttrium(III) chloride and perchlorate produce the 15-membered N_3O_2 and 16-membered N_5 macrocyclic complexes as a result of [1 + 1] Schiff base cyclocondensation. The formulations of these complexes as $[YL^1(H_2O)_2]Cl_3 \cdot H_2O$ and $[YL^2(H_2O)_2](ClO_4)_3 \cdot 2H_2O$, where L^1 is Me$_2$pyo[15]triene N_3O_2 and L^2 is Me$_2$pyo[16]triene N_5, follow from spectral data (IR, UV–vis, ^{1}H NMR, MS) and thermogravimetric analysis. Elemental analysis figures (see Experimental) are consistent with the above formulas. The complexes appear to be orange, air stable solids, moderately soluble in CH_3CN and DMSO.



L^1



L^2

Attempts to obtain these macrocyclic compounds in the presence of yttrium(III) nitrate were unsuccessful. The nitrate anions, contrary to chlorides and perchlorates, are very good complexing agents for rare earth elements. The involvement of nitrate groups in the coordination with yttrium ion may result in increasing of the ionic radius of Y^{III} to the value for which the metal ion does not perfectly fit to the cavity of the macrocycles. Therefore, the chloride and perchlorate salts were employed to reduce the effect of donor anions on the primary coordination sphere around the metal ion.

The infrared spectra of both complexes 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 1630 cm^{-1} attributable to C═N stretching modes indicating the Schiff base condensation. The spectra exhibit medium to strong bands at 1590 and 1460 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 the band at *ca* 1010 cm^{-1} attributable to the ring breathing frequency and the low energy pyridine ring in-plane and out-of-plane vibrations at 670 and 430 cm^{-1}. In the IR spectrum of L^1 complex the C—O—C stretching mode occurs at 1110 cm^{-1} indicating ether oxygen co-ordination.[18,19] The profile of the secondary amino group vibrations observed in the IR spectrum of complex L^2 in the 3200–3080 cm^{-1} region is characteristic of coordinated nitrogen atoms.[20] Information about the bonding mode of the counterions in these complexes may also be obtained from IR spectra. The spectra do not exhibit absorptions characteristic of coordinated anions.[21] The M—Cl frequency usually occurs around 240–220 cm^{-1}. The spectrum of the yttrium chloride L^1 complex does not show any additional absorption bands in this region indicating the absence of the coordinated chloride anions. The presence of uncoordinated perchlorates is inferred from the broad band centred at 1100 cm^{-1} and the sharp medium band at 620 cm^{-1} observed in the spectrum of the yttrium perchlorate L^2 complex. The complexes show the broad diffuse band centred at *ca* 3420 cm^{-1} due to the stretching and bending modes of water. In addition, weak bands are detectable around 860 cm^{-1} which may be assigned to rocking or wagging modes of water molecules coordinated to the metal ion.[22] The presence of water bound in two different ways is supported by the results of thermogravimetric analysis. Both of the complexes lose two water molecules below 100°C. Moreover, the L^1 complex indicates the loss of one water molecule at 140–170°C, whereas the L^2 complex loses two water molecules at 150–170°C.

The electronic spectra of the complexes for solutions in acetonitrile contain intense and medium bands with maxima at 214–218, 223–229 and 269–271 nm attributable to the $\pi \rightarrow \pi^*$ transition of the coordinated macrocycle.[23]

The ^1H NMR spectra of DMSO-d_6 solutions of the L^1 and L^2 yttrium complexes strongly suggest the presence of the macrocyclic ligands. In the ^1H NMR spectrum of L^1 complex two well-resolved triplets of the methylene protons in the $=NCH_2CH_2O$ chain are observed in a 1 : 1 ratio : the protons adjacent to the nitrogen give raise to a triplet at $\delta 3.63$ (4H) and the remaining protons to another triplet at $\delta 2.95$ (4H) ($J = 5.4$ Hz). A sharp singlet at $\delta 3.59$ (4H) assigned to the methylene protons in the $—OCH_2CH_2O$ bridge is in accordance with the planarity of the macrocyclic system. The pyridine protons and methyl protons appear at $\delta 7.8$–8.2 (3H) and $\delta 2.51$ (6H), respectively. The ^1H NMR spectrum of L^2 complex exhibits three well-resolved triplets in a ratio of 1 : 1 : 1 : the proton signals of two methylene groups of the $=NCH_2CH_2N$ chain appear as two triplets at $\delta 2.84$ (4H) and $\delta 2.72$ (4H) ($J = 6.1$ Hz), and the α to nitrogen methylene protons of the propylene bridge give the third triplet at $\delta 2.62$ (4H) ($J = 7.1$ Hz). The remaining protons of the propylene bridge occur at $\delta 2.17$ (2H). The signal at $\delta 1.6$ (2H) is due to protons of the secondary amino groups. The pyridine protons are observed at $\delta 7.8$–8.4 (3H) and the methyl protons at $\delta 2.55$ (6H). The integrated relative intensities of the above signals are in good agreement with the required ratios consistent with the proposed formulations of the complexes.

Further evidence for the formation of the macrocycle comes from the mass spectrum of the L^1 complex of yttrium chloride. The fragment observed at *m*/*z* 275 corresponds to the molecular weight of the free macrocycle. Other principal fragmentation ions occur at *m*/*z* 250, 220, 206, 187, 148, 118, 104, 89, 77 ; no peaks of significant intensity were observed at higher *m*/*z* values. The spectrum of the perchlorate complex was not measured.

Efforts to prepare free macrocycles in the reactions of the 2,6-diacetylpyrine with 3,6-dioxaoctane-1,8-diamine or 3,7-diazanonane-1,9-diamine in the absence of metal salt were unsuccessful and resulted in the formation of insoluble yellow compounds of polymeric character terminated with carbonyl functions. The failure of these systems to undergo complete condensation and cyclization confirms the importance of the metal ion in directing the steric course of the condensation process, which ultimately ends with ring closure. However, in the planning of the template synthesis of macrocyclic compounds with particular geometry around the metal ion the complexing properties of counterions should be also taken into account.

On the basis of available data it can be concluded that the yttrium(III) chloride and perchlorate are effective templating agents for the synthesis of 15-membered N_3O_2 and 16-membered N_5 macrocyclic compounds. All five potential donor atoms of these ligands may be regarded as coordinated to the metal ion. Thus, the seven-coordination is tentatively assigned for L^1 and L^2 complexes of yttrium(III) with non-coordinating chloride and perchlorate counterions assuming the filling of the coordination sphere by an equatorial N_3O_2 or N_5 set of macrocyclic donor atoms and two water molecules in axial positions. The trimethine unit of the L^1 and L^2 macrocycles is rigid and it seems unlikely that the remaining donor atoms could be other than coplanar with these three nitrogens.[24] References to the known structures of similar macrocyclic complexes[23,25,26] allow us to predict the pentagonal bipyramidal geometry for both of the complexes.

Since there is no ligand field stabilization energy effect in the yttrium(III) ion (d^0 configuration) its coordination environment is determined mainly by the chelating power of the ligand (preferred conformation, nature and disposition of donor atoms). Thus the yttrium ion can readily be accommodated by the particular stereochemical constraints enforced by the template process. Seven-coordination complexes of yttrium are relatively uncommon.[27–29] The results discussed in this paper extend the number of such compounds and, to our best knowledge, provide the first examples of template action of yttrium(III) ion in the synthesis of pentadentate Schiff base macrocyclic ligands. They confirm the effectiveness of specially designed macrocycles with sufficient rigidity to present a donor set with a defined geometry in imposing an unusual coordination arrangement around the metal ion.

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