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New supramolecular dinuclear Schiff base complexes of yttrium and lanthanides

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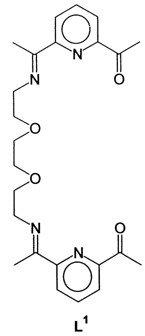
Abstract

The metal-promoted reactions between 2,6-diacetylpyridine and 3,6-dioxaoctane-1,8-diamine, 4,9-dioxadodecane-1,12-diamine or 4,7,10-trioxatridecane-1,13-diamine in the presence of yttrium(III) and lanthanide(III) ions acting as template agents afford new supramolecular dinuclear complexes of podate type with terminal acetylpyridyl groups and N_4O_4 and N_4O_5 set of donor atoms as a result of [2+1] Schiff base condensation. The complexes were characterized by spectral data (IR, ^{1}H NMR, FAB-MS) and elemental analysis. © 2001 Elsevier Science B.V. All rights reserved.

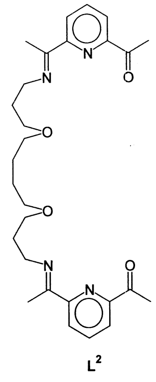
Keywords: Dinuclear complexes; Schiff base podates; Yttrium complexes; Lanthanide complexes; Template synthesis

1. Introduction

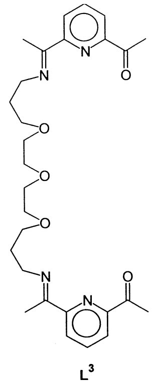
Schiff base dinuclear complexes of rare earth elements have been the subject of growing interest. These complexes are used to study the metal–metal interaction and magnetic exchange for understanding technological application of rare earths and as spectroscopic probes for active sites in metalloproteins, they are also important for biomedical diagnostics and fluorescence imaging, potential radioimmunopharmaceticals for monoclonal antibody technology [1]. The new applications involve the use of heterodinuclear complexes with predeterminated properties as novel supramolecular tunable photonic light-converting devices [2–4] and as catalysts for hydrolyzing phosphate diesters [5,6]. The Schiff base complexes of lanthanides obtained by us [7–9] have found to be very effective catalyst with high site selectivity for hydrolysis of tRNA [10,11]. Recently it was found that binuclear lanthanide(III) complexes can accelerate the cleavage of double-stranded DNA more efficiently that with metal ion alone. The relative activity order appears to depend on distance between two metal centers [12,13]. It seems to be in accord with general observation related to bioinorganic processes that the catalytic activity of dinuclear metal complexes is clearly higher [14]. This result has prompted us to synthesis of new dinuclear complexes with different ligand size. We have recently reported the template action of the rare earth metal ions in the synthesis of the new Schiff base podands terminated with two carbonyl groups or one amino and one carbonyl group which are able to encapsulate two metal centers [15–17]. The present paper is concerned with the preparation and characterization of dinuclear yttrium(III) and lanthanide(III) complexes of open-chain (podand) Schiff base ligands terminated by two carbonyl groups formed in the metal-promoted condensation reaction between 2,6-diacetylpyridine and 3,6-dioxaoctane-1,8-diamine (**L^1** complexes), 4,9-dioxadodecane-1,12-diamine (**L^2** complexes) or 4,7,10-trioxatridecane-1,13-diamine (**L^3**complexes).



L^1



L^2



L^3

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2. Experimental details

2.1. Preparation of the lanthanide salts

The hydrated lanthanide(III) salts were prepared by dissolving the 99.99% oxides (Fluka) in a slight excess of appropriate acid. The solutions were evaporated and precipitates recrystallized from methanol. 2,6-Diacetylpyridine, 3,6-dioxaoctane-1,8-diamine, 4,9-dioxadodecane-1,12-diamine and 4,7,10-trioxatridecane-1,13-diamine (Aldrich Chemical Company) were used without further purification.

2.2. Preparation of the complexes

2.2.1. $\mathbf{L^1}$ complexes

All complexes were performed under similar conditions. To a mixture of appropriate metal salt (0.1 mmol) in methanol (10 cm^3) and 2,6-diacetylpyridine (0.2 mmol) in methanol (10 cm^3), 3,6-dioxaooctane-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. Yields: 62–69%.

2.2.2. $\mathbf{L^2}$ complex

To a mixture of hydrated yttrium perchlorate (0.2 mmol) in methanol (10 cm^3) and 2,6-diacetylpyridine (0.2 mmol) in methanol (10 cm^3), 4,9-dioxadodecane-1,12-diamine (0.1 mmol) in methanol (10 cm^3) was added dropwise with stirring. The reaction was carried out for 3 h at ambient temperature. 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: 68%.

2.2.3. $\mathbf{L^3}$ complexes

All complexes were performed under similar conditions. To a mixture of appropriate metal salt (0.2 mmol) in methanol (20 cm^3) and 2,6-diacetylpyridine (0.2 mmol) in methanol (20 cm^3), 4,7,10-trioxatridecane-1,13-diamine (0.2 mmol) in methanol (20 cm^3) was added dropwise with stirring. The reactions were carried out for 5 and 12 h. The solution volume was then reduced to 10 cm^3 by roto-evaporation and an yellow precipitate formed on addition of a small amount of diethyl ether. This was filtered off, washed with ether, and dried in vacuo. Yields: 61–65%.

2.3. Measurements

IR spectra were recorded using CsI pellets in the range 4000–200 cm^{-1} on a Perkin–Elmer 580 spectrophotometer. ^{1}H NMR spectra were run in DMSO-d_6 on a Varian Gemini 300 spectrometer using TMS as an internal reference. Positive ion FAB-mass spectra were obtained on a AMD-604 mass spectrometer with the nitrobenzyl alcohol/acetic acid or glycerol/acetic acid as matrix. 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.

3. Results and discussion

The dinuclear complexes of rare earth elements – products of a Schiff base condensation of two molecules of 2,6-diacetylpyridine with one molecule of 3,6-dioxaoctane-1,8-diamine ($\mathbf{L^1}$ complexes), one molecule of 4,9-dioxadodecane-1,12-diamine ($\mathbf{L^2}$ complex) or one molecule of 4,7,10-trioxatridecane-1,13-diamine ($\mathbf{L^3}$ complexes) were prepared by the reaction of appropriate metal salts acting as template agents with diketone and amine.

The formulation of these complexes as $Eu_2\mathbf{L^1}Cl_6\cdot7H_2O$, $Tb_2\mathbf{L^1}Cl_6\cdot8H_2O$, $Ho_2\mathbf{L^1}Cl_6\cdot12H_2O$, $Lu_2\mathbf{L^1}Cl_6\cdot4H_2O$, $Y_2\mathbf{L^2}(ClO_4)_3\cdot6H_2O$, $Y_2\mathbf{L^3}Cl_6\cdot5H_2O$, $Pr_2\mathbf{L^3}Cl_6\cdot4H_2O$, $Nd_2\mathbf{L^3}Cl_6\cdot4H_2O$, $Sm_2\mathbf{L^3}Cl_6\cdot4H_2O$, $Gd_2\mathbf{L^3}Cl_6\cdot6H_2O$, $Dy_2\mathbf{L^3}Cl_6\cdot4H_2O$, $Ho_2\mathbf{L^3}Cl_6\cdot6H_2O$, $Er_2\mathbf{L^3}Cl_6\cdot8H_2O$ and $Yb_2\mathbf{L^3}Cl_6\cdot6H_2O$ follows from spectroscopic data (IR, FAB-MS, ^{1}H NMR) and elemental analysis. Elemental analysis figures are consistent with the above formulas. The complexes are air stable solids, soluble in DMSO.

The infrared spectra of these complexes taken in the region 4000–200 cm^{-1} provide some information regarding the bonding in the complexes. The important feature common to all complexes is the occurrence of strong absorption band at 1685–1664 cm^{-1} assigned to the C=O stretching vibration, indicating the formation of the open-chain products containing terminal acetylpyridyl groups. The comparision of the spectra of mononuclear and dinuclear complexes in this region can add useful information about the encapsulation of the one or two metal ions by the donor sites of the multidentate ligand. In the dinuclear complexes the νC=O lies at considerable lower frequency than in the corresponding mononuclear complexes, because the involvement of the second metal in the coordination moiety causes a decrease of the bond order in the C=O groups, owing to the stronger donation of electron density towards the two metal ions [15,16,18]. The magnitude of shift of this band from 1705 cm^{-1}in uncomplexed 2,6-diacetylpyridine to lower wavenumbers suggests coordination through the two oxygen atoms to the two metal ions. All the spectra confirm the Schiff base condensation by the presence of a strong band at 1625–1590 cm^{-1} characteristic of C=N stretching modes. The C–O–C stretching mode occurs at 1120–1085 cm^{-1} indicating ether oxygen coordination.The spectra show medium to strong bands at 1596–1565 cm^{-1} region 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 bands at 1190–919 cm^{-1} and 695–550 cm^{-1} attributable to the ring breathing frequency and the low energy pyridine ring vibrations, respectively. The complexes show the broad diffuse band centered at ca. 3469–3382 cm^{-1} due to the stretching and bending modes of lattice and coordinated water. In addition, very weak bands are detectable at 870–815 cm^{-1} region which may be assigned to rocking or wagging modes of water molecules interacting with the metal ion. The spectra of the chloride complexes show medium absorption bands at 292–220 cm^{-1} region attributable to the M–Cl frequency indicating the interaction of at least part of the chloride counterions with the metal. The IR spectrum of the yttrium perchlorate $\mathbf{L}^{2}$ complex exhibits the strong absorption band at 1200–950 cm^{-1} typical of the asymmetric Cl–O stretching mode and a weak band at 625 cm^{-1} associated with the asymmetric Cl–O bending mode. The considerable broadening of the higher energy band suggests that the perchlorate counterions are partially involved in the coordination sphere of the metal ion. However the C–O–C stretching mode for the polyether chain also falls in this region.

The ^{1}H NMR spectrum of DMSO-d_6 solution of the diamagnetic lutetium $\mathbf{L}^{1}$ complex exhibits the expected splitting patterns and chemical shifts for acetylpyridine ring protons at δ 7.8–8.1 (6 H). The methylene protons adjacent to the nitrogen in the $=NCH_2CH_2O-$ chain are observed δ 2.96 (4 H, t, $J=5.3$) and the remaining protons at δ 3.63 (4 H, t, $J=5.3$). The methylene protons in the $-OCH_2CH_2O-$ bridge appear at δ 3.59 (4 H). The methyl protons of the two CH_3CO and two CH_3CN groups occur at δ 2.73 (6 H) and δ 2.50 (6 H), respectively. The integrated relative intensities of the above signals are in good agreement with the required ratios consistent with the proposed formulation of the complex.

The ^{1}H NMR spectrum of DMSO-d_6 solution of the yttrium complex of $\mathbf{L}^{2}$ exhibits three multiplets in a ratio 1:1:2: the protons α to nitrogen give raise to a triplet at δ 2.75 (4 H, $J=7.1$), the protons β to nitrogen to quintet at δ 1.69 (4 H, $J=6.9$) and the protons adjacent to the oxygen to the triplet at δ 3.40 (8 H) ($J=6.1$). The remaining protons of the $-OCH_2C\mathit{H}_2C\mathit{H}_2CH_2O-$ chain occur at δ 1.52 (4 H). The pyridine protons are observed at δ 8.2–7.7 (6 H) and the methyl protons of the two CH_3CO and two CH_3CN groups at δ 2.73 (6 H) and δ 3.35 (6 H), respectively. The integrated relative intensities of the above signals are in good agreement with the required ratios consistent with the proposed formulation of the complex. The stability of these complexes in DMSO solution is demonstrated by the absence of any additional signals. Hence, it is evident that no metal–solvent interaction occurs. Contrary to these results, the ^{1}H NMR spectrum of the yttrium $\mathbf{L}^{3}$ complex 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 this complex. The DMSO with strong donor properties is known to compete for the coordination sphere of the metal ions. It could result in removal of the metal ion from the ligand followed by ligand breakdown [18]. These results may suggest that the $\mathbf{L}^{3}$ complexes are less stable in comparision with the complexes containing $\mathbf{L}^{1}$ and $\mathbf{L}^{2}$ ligands.

The positive-ion FAB mass spectra (Table 1) offer additional structural information on these complexes. The peaks which may be assigned to the species containing two

Table 1
FAB mass spectral data for complexes of $\mathbf{L}^{1}$, $\mathbf{L}^{2}$ and $\mathbf{L}^{3}$

Complex	*m/z* and assignment
$Eu_2\mathbf{L}^{1}Cl_6\cdot 7H_2O$	918.3 $[Eu_2\mathbf{L}^{1}Cl_3\cdot 4H_2O]^+$
$Tb_2\mathbf{L}^{1}Cl_6\cdot 8H_2O$	901.9 $[Tb_2\mathbf{L}^{1}Cl_6\cdot 6H_2O]^+$; 865.3 $[Tb_2\mathbf{L}^{1}Cl_3\cdot 4H_2O]^+$
$Ho_2\mathbf{L}^{1}Cl_6\cdot 12H_2O$	1071.1 $[Ho_2\mathbf{L}^{1}Cl_6\cdot 5H_2O]^+$; 1020.2 $[Ho_2\mathbf{L}^{1}Cl_5\cdot 4H_2O]^+$; 439.5 $[\mathbf{L}^{1}]^+$
$Lu_2\mathbf{L}^{1}Cl_6\cdot 4H_2O$	1004.8 $[Lu_2\mathbf{L}^{1}Cl_6\cdot 4H_2O]^+$; 790.8 $[Lu_2\mathbf{L}^{1}]^+$; 441.0 $[\mathbf{L}^{1}]^+$
$Y_2\mathbf{L}^{2}(ClO_4)_6\cdot 6H_2O$	766.0 $[Y_2\mathbf{L}^{2}\cdot 5H_2O]^+$; 596.0 $[Y\mathbf{L}^{2}\cdot H_2O]^+$
$Y_2\mathbf{L}^{3}Cl_6\cdot 5H_2O$	975.9 $[Y_2\mathbf{L}^{3}Cl_6\cdot 4H_2O]^+$; 921.9 $[Y_2\mathbf{L}^{3}Cl_6\cdot H_2O]^+$; 885.1 $[Y_2\mathbf{L}^{3}Cl_5\cdot H_2O]^+$; 851.5 $[Y_2\mathbf{L}^{3}Cl_4\cdot H_2O]^+$; 721.3 $[Y_2\mathbf{L}^{3}Cl]^+$
$Pr_2\mathbf{L}^{3}Cl_6\cdot 4H_2O$	958.2 $[Pr_2\mathbf{L}^{3}Cl_4\cdot H_2O]^+$; 824.2 $[Pr_2\mathbf{L}^{3}Cl]^+$; 509.8 $[\mathbf{L}^{3}]^+$
$Nd_2\mathbf{L}^{3}Cl_6\cdot 4H_2O$	1050.8 $[Nd_2\mathbf{L}^{3}Cl_6\cdot 2H_2O]^+$; 939.6 $[Nd_2\mathbf{L}^{3}Cl_4]^+$; 511.2 $[\mathbf{L}^{3}]^+$
$Sm_2\mathbf{L}^{3}Cl_6\cdot 4H_2O$	919.4 $[Sm_2\mathbf{L}^{3}Cl_3]^+$; 883.4 $[Sm_2\mathbf{L}^{3}Cl_2]^+$; 509.8 $[\mathbf{L}^{3}]^+$
$Gd_2\mathbf{L}^{3}Cl_6\cdot 6H_2O$	1095.7 $[Gd_2\mathbf{L}^{3}Cl_6\cdot 3H_2O]^+$; 988.7 $[Gd_2\mathbf{L}^{3}Cl_4\cdot H_2O]^+$; 915.3 $[Gd_2\mathbf{L}^{3}Cl_2\cdot H_2O]^+$; 860.9 $[Gd_2\mathbf{L}^{3}Cl]^+$
$Dy_2\mathbf{L}^{3}Cl_6\cdot 4H_2O$	1067.6 $[Dy_2\mathbf{L}^{3}Cl_6\cdot H_2O]^+$; 1044.0 $[Dy_2\mathbf{L}^{3}Cl_6]^+$; 975.8 $[Dy_2\mathbf{L}^{3}Cl_4]^+$; 835.1 $[Dy_2\mathbf{L}^{3}]^+$
$Ho_2\mathbf{L}^{3}Cl_6\cdot 6H_2O$	1179.8 $[Ho_2\mathbf{L}^{3}Cl_6\cdot 7H_2O]^+$; 1120.8 $[Ho_2\mathbf{L}^{3}Cl_6\cdot 4H_2O]^+$; 1071.9 $[Ho_2\mathbf{L}^{3}Cl_6\cdot H_2O]^+$; 1020.7 $[Ho_2\mathbf{L}^{3}Cl_5]^+$; 984.8 $[Ho_2\mathbf{L}^{3}Cl_4]^+$
$Er_2\mathbf{L}^{3}Cl_6\cdot 8H_2O$	1130.8 $[Er_2\mathbf{L}^{3}Cl_6\cdot 4H_2O]^+$; 1079.0 $[Er_2\mathbf{L}^{3}Cl_6\cdot H_2O]^+$; 967.3 $[Er_2\mathbf{L}^{3}Cl_4]^+$; 917.4 $[Er_2\mathbf{L}^{3}Cl_3]^+$
$Yb_2\mathbf{L}^{3}Cl_6\cdot 6H_2O$	1180.0 $[Yb_2\mathbf{L}^{3}Cl_6\cdot 6H_2O]^+$; 1123.9 $[Yb_2\mathbf{L}^{3}Cl_6\cdot 3H_2O]^+$; 1068.0 $[Yb_2\mathbf{L}^{3}Cl_6]^+$; 960.0 $[Yb_2\mathbf{L}^{3}Cl_3]^+$

metal ions coordinated to the ligand were found in all these complexes. However, the appearance of a set of peaks due to the different isotopes of the metal and extra or fewer protons on the ligands accounts for the slight ambiguities in making assignment. Moreover, the lanthanide ions are known to display tendency to form polyanions. In the case of the complexes with the stoichiometry metal:ligand 2:1 one may expect the formation of cationic species containing the ligand coordinated to metal ion in the ratio 1:1 and polyanionic species with inorganic anion coordinated to the trivalent metal ion. This situation manifests itself in significantly smaller shift of the $\upsilon C=O$ in IR spectra and the appearance of the peaks in FAB mass spectra corresponding to polyanionic fragments. No peaks attributable to these species were observed in the FAB mass spectra of all these complexes. The presence of the counterions and water molecules in inner sphere of the complexes is confirmed by the stepwise loss of these species which seems to be a common route of fragmentation. The spectra exhibit a peaks due to the free ligands as a result of demetallation of the species under FAB conditions supporting the formation of the complexes of podate type with $\mathbf{L^1}$, $\mathbf{L^2}$ and $\mathbf{L^3}$ ligands as products of [2+1] (dicarbonyl and diamine) template condensation process.

It is worth noting that the formation of the dinuclear $\mathbf{L^1}$ complexes of the heavier (smaller) lanthanides occurs even in the lower than stoichiometric amount of metal ion used as template, whereas the reactions performed under the same experimental conditions in the presence of the lighter lanthanides (with greater ionic radius) have led to the mononuclear $\mathbf{L^1}$ complexes [19]. Thus, the ability of encapsulating two rare earth elements by $\mathbf{L^1}$ Schiff base appears to be depend upon the the size match selectivity parameter. In contrast, the $\mathbf{L^2}$ podand has found to be able to form the dinuclear complexes of yttrium and all the lanthanide ions (La^{3+}–Lu^{3+}) [16], however, under different experimental conditions (1:1:1 molar ratio of starting materials) these rare earth metal ions may act as effective templates in the synthesis of mononuclear complexes of 19-membered macrocyclic ligand with N_2O_3 set of donor atoms [20]. The dinuclear open-chain $\mathbf{L^3}$ complexes of lanthanides are formed irrespective on the molar ratio of starting materials.

Reactions conducted in different experimental conditions (various molar ratios and the method of adding starting materials, reaction time, range of temperatures) in the absence of the metal salt yielded amorphous solids, oils or gums. The importance of metal ion in promoting the condensation process is thus apparent.

Acknowledgements

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