Journal of Alloys and Compounds 275–277 (1998) 822–826

Lanthanide ions as templates for the synthesis of new dinuclear octadentate Schiff base complexes of podate type

Violetta Patroniak-Krzyminiewska, Wanda Radecka-Paryzek*

Faculty of Chemistry, Adam Mickiewicz University, 60-780 Poznań, Poland

---

Abstract

The template reactions of 2,6-diacetylpyridine with 1,12-diamine-4,9-dioxadodecane in the presence of lanthanide ions produce octadentate macroacyclic complexes of podate type with terminal acetylpyridyl groups and a N_4O_4 set of donor atoms as a result of [2+1] Schiff base condensation. The complexes were characterized by spectral data (IR, UV–vis, ^{1}H-NMR, FAB-MS) and thermogravimetric and elemental analysis.

Keywords: Lanthanides; Podate complexes; Schiff base complexes

---

1. Introduction

The design and synthesis of macroacyclic (podate) and macrocyclic (coronate) Schiff base dinuclear complexes of lanthanides have been the subject of an active research field of growing importance. These complexes are important in studying the molecular recognition processes which govern lanthanide dinucleation [1], for understanding the nature and application of lanthanide metal–metal interaction in lasers [2] and phosphors [3] and as spectroscopic probes for active sites in metalloproteins [4–6]. They are used for the efficient separation and purification of the lanthanides [7], as novel tunable photonic supramolecular devices [8,9] with potential application in biomedical diagnostics [10], as fluorescence labels [11], as paramagnetic contrast enhancing agents in magnetic resonance imaging [12], and as synthetic nucleases for efficient catalytic cleavage of RNA [13].

The effective method for the synthesis of Schiff base podate and coronate complexes involves the condensation reaction between suitable dicarbonyls and diprimary amines carried out in the presence of appropriate metal ions which serve as templates in directing the steric course of the reaction [14–16]. We have found the lanthanides to be very efficient as metal templates in the synthesis of complexes of this type [17–19]. Seeking new stable complexes of the lanthanides in view of their potential applications, we now report the template synthesis and characterization of new dinuclear octadentate complexes of podate type formed in the condensation reactions between 2,6-diacetylpyridine and 1,12-diamine-4,9-dioxadodecane in the presence of lanthanide ions. We have also found that, under different experimental conditions, these ions may act as effective templates in the synthesis of mononuclear complexes of 19-membered macrocyclic ligands with a N_3O_2 set of donor atoms, a product of a Schiff base cyclocondensation of one molecule of 2,6-diacetylpyridine with one molecule of 1,12-diamine-4,9-dioxadodecane [20].

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 and 1,12-diamine-4,9-dioxadodecane (Al-

---

*Corresponding author.

PII: S0925-8388(98)00469-1

Table 1
Analytical data for the complexes of **L**

Complex	Found (%)			Calculated (%)		
	C	H	N	C	H	N
$La_2\mathbf{L}(H_2O)_{10}(NO_3)_6\cdot 2H_2O$	24.09	4.45	10.47	24.72	4.59	10.29
$Pr_2\mathbf{L}(H_2O)_6(NO_3)_6\cdot 2H_2O$	25.29	4.16	10.56	26.02	4.21	10.84
$Nd_2\mathbf{L}(H_2O)_6(NO_3)_6\cdot 2H_2O$	28.86	4.55	9.89	25.89	4.19	10.78
$Nd_2\mathbf{L}(H_2O)_6Cl_6\cdot 5H_2O$	29.44	4.96	4.47	28.17	5.03	4.69
$Sm_2\mathbf{L}(H_2O)_6(NO_3)_6\cdot 2H_2O$	28.09	3.95	9.46	25.64	4.15	10.68
$Sm_2\mathbf{L}(H_2O)_6Cl_6\cdot 5H_2O$	28.72	5.22	4.81	27.88	5.01	4.64
$Gd_2\mathbf{L}(H_2O)_6Cl_6\cdot 2H_2O$	27.47	4.45	4.85	28.84	4.67	4.81
$Dy_2\mathbf{L}(H_2O)_4(NO)_6\cdot 2H_2O$	28.84	4.29	9.89	25.87	3.88	10.88
$Dy_2\mathbf{L}(H_2O)_6Cl_6$	28.23	4.27	5.25	29.49	4.39	4.91
$Ho_2\mathbf{L}(H_2O)_4(NO_3)_6\cdot 4H_2O$	25.40	3.90	9.40	25.09	4.06	10.44
$Ho_2\mathbf{L}(H_2O)_6Cl_6\cdot 6H_2O$	25.21	4.94	4.73	26.83	4.95	4.47
$Er_2\mathbf{L}(H_2O)_4(NO_3)_6\cdot 2H_2O$	24.78	3.74	9.92	25.69	3.85	10.69
$Er_2\mathbf{L}(H_2O)_6Cl_6$	29.85	4.54	4.96	29.25	4.35	4.87
$Er_2\mathbf{L}(H_2O)_4(ClO_4)_6\cdot 4H_2O$	23.23	3.59	3.62	21.42	3.47	3.57
$Tm_2\mathbf{L}(H_2O)_6Cl_6\cdot 4H_2O$	28.78	5.01	5.13	27.45	4.77	4.57
$Yb_2\mathbf{L}(H_2O)_6Cl_6\cdot 6H_2O$	26.07	5.21	4.61	26.49	4.92	4.41
$Lu_2\mathbf{L}(H_2O)_6Cl_6\cdot H_2O$	27.83	4.40	4.78	28.42	4.43	4.73

drich Chemical Company) were used without further purification.

2.2. Preparation of the complexes. General procedures

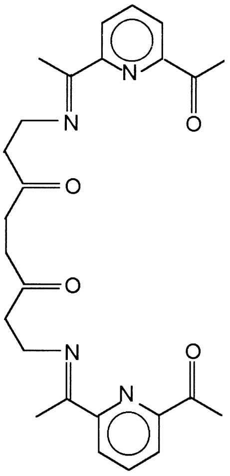
All complexes were prepared under similar conditions. To a mixture of the appropriate metal salt (0.2 mmol) in methanol (10 cm^3) and 2,6-diacetylpyridine (0.2 mmol) in methanol (10 cm^3), 1,12-diamine-4,9-dioxadodecane (0.1 mmol) in methanol (10 cm^3) was added dropwise with stirring. The reaction was carried out for 4 h 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. The yield was 67–72%. The results of elemental analyses of the complexes are listed in Table 1.

2.3. Measurements

IR spectra were recorded using CsI pellets in the range 4000–200 cm^{-1} on a Perkin-Elmer 580 spectrophotometer. Electronic spectra were recorded on a Shimadzu UV-160 spectrophotometer. ^1H-NMR spectra were run in DMSO-d_6 on a Varian Gemini 300 spectrometer using TMS as an internal reference. FAB-mass spectra were obtained on a AMD-604 mass spectrometer with glycerol as matrix. Thermogravimetric measurements were performed using a Shimadzu TGA-50 derivatograph.

3. Results and discussion

The new dinuclear lanthanide (III) ion complexes of the podand **L**, the product of a Schiff base condensation of two molecules of 2,6-diacetylpyridine with one molecule of 1,12-diamine-4,9-dioxadodecane, were prepared by the reaction of appropriate metal salts acting as template agents with diketone and diamine in a 2:2:1 molar ratio of starting materials.



L

The stoichiometry and the mode of coordination in the complexes were deduced by means of elemental and thermal analysis and spectral data (IR, UV–vis, ^{1}H-NMR, FAB-MS). The complexes appear to be orange, air-stable solids, moderately soluble in CH_3CN and DMSO.

The infrared spectra of these complexes recorded in the region 4000–200 cm^{-1} are all very similar except for anion vibrational modes (Table 2) and provide some information regarding the bonding in the complexes. The presence of a band in the 1645–1620 cm^{-1} region for all complexes attributable to C=N stretching modes confirms the Schiff base condensation. The spectra exhibit medium to strong bands at 1601–1579 cm^{-1} as expected for 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 1031–992 cm^{-1} and 680–660 cm^{-1} attributable to the ring breathing frequency and the low energy pyridine ring vibrations, respectively [19]. The C–O–C stretching mode occurs at 1142–1085 cm^{-1}, indicating ether oxygen coordination [21]. An important feature common to all the complexes is the occurrence of a strong absorption band in the 1695–1653 cm^{-1} region assigned to the C=O stretching vibration, indicating the formation of an open-chain product containing terminal acetylpyridyl groups. The shift of this band from 1705 cm^{-1} in uncomplexed 2,6-diacetylpyridine to lower wavenumbers strongly suggests coordination through oxygen atoms, because the involvement of metal ions in the coordination moiety causes a decrease of the bond order in C=O groups, owing to the donation of electron density to the two metal ions [22]. The complexes show a broad diffuse band centered at ca. 3430–3390 cm^{-1} due to the stretching and bending modes of the lattice and/or coordinated water. In addition, weak bands are detectable in the 875–820 cm^{-1} region which may be assigned to rocking or wagging modes of water molecules interacting with the metal ion [23]. The presence of water bound in two different ways is confirmed by the results of thermogravimetric analysis. The complexes lose the water molecules in two steps (except for the dysprosium and erbium chloride complexes): below 80°C and above 150°C corresponding to the lattice and coordinated water molecules, respectively. The number of these two kinds of water molecules per mole of metal ion was calculated from the weight loss observed for the complexes at these two temperatures. Information on the bonding mode of the counterions in these complexes may also be obtained from IR spectra [24]. In the spectra of nitrate complexes, the ν(N–O) stretching frequency is observed as a very strong broad band centered at 1380 cm^{-1}. In addition, two medium bands at 825 and 818–815 cm^{-1} are also observed. Comparison of the infrared spectral data for the various nitrate complexes with known X-ray crystal structures reveals that the broadening or splitting of these bands is characteristic of the presence of both coordinated and ionic nitrates [25–28]. The spectra of the chloride complexes show medium absorption bands in the 270–226 cm^{-1} region attributable to the M–Cl frequency, indicating the interaction of at least some of the chloride counterions with the metal. The IR spectrum of the erbium perchlorate complex exhibits a strong absorption band centered at 1080 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 (1200–950 cm^{-1}) of the higher energy band suggests, similarly to the nitrate complexes, that the perchlorate counterions are partially involved in the coordination sphere of the metal ion [24,25]. However, the

Table 2
Infrared spectral data (cm^{-1}) for the complexes of **L**

Complex	OH	C=O	C=N	Py	C–O–C	Anion
$La_2\mathbf{L}(H_2O)_{10}(NO_3)_6\cdot 2H_2O$	3400, 855	1660	1630	1585, 1030, 975, 680	1090	1500–1350, 825, 818
$Pr_2\mathbf{L}(H_2O)_6(NO_3)_6\cdot 2H_2O$	3420, 855	1665	1635	1590, 1015, 995,670	1110	1500–1350, 825,818
$Nd_2\mathbf{L}(H_2O)_6(NO_3)_6\cdot 2H_2O$	3400, 830	1665	1635	1590, 1010, 965, 665	1090	1550–1300, 825, 818
$Nd_2\mathbf{L}(H_2O)_6Cl_6\cdot 5H_2O$	3420, 820	1690	1635	1590, 990, 665	1105	255
$Sm_2\mathbf{L}(H_2O)_6(NO_3)_6\cdot 2H_2O$	3438, 833	1666	1630	1595, 1031, 991, 668	1092	1500–1330, 825, 815
$Sm_2\mathbf{L}(H_2O)_6Cl_6\cdot 5H_2O$	3400, 820	1690	1620	1590, 1015, 665	1120	255
$Dy_2\mathbf{L}(H_2O)_4(NO_3)_6\cdot 2H_2O$	3425, 865	1670	1620	1595, 1010, 990, 670	1090	1500–1350, 825, 815
$Dy_2\mathbf{L}(H_2O)_6Cl_6$	3420, 820	1670	1640	1595, 1010, 665	1100	270
$Ho_2\mathbf{L}(H_2O)_4(NO_3)_6\cdot 4H_2O$	3390, 856	1666	1630	1579, 992, 668	1110	1500–1300, 817
$Ho_2\mathbf{L}(H_2O)_6Cl_6\cdot 6H_2O$	3420, 820	1680	1635	1590, 1010, 660	1100	260
$Er_2\mathbf{L}(H_2O)_4(NO_3)_6\cdot 2H_2O$	3410, 875	1669	1630	1601, 1014, 665	1085	1506–1293, 825, 813
$Er_2\mathbf{L}(H_2O)_6Cl_6$	3420, 860	1660	1640	1590, 1015, 670, 655	1090	270
$Er_2\mathbf{L}(H_2O)_4(ClO_4)_6\cdot 4H_2O$	3400, 860	1665	1620	1595, 1015, 670	1120	1200–950, 625
$Tm_2\mathbf{L}(H_2O)_6Cl_6\cdot 4H_2O$	3400, 866	1695	1635	1590, 1015, 1003, 655	1142	260
$Yb_2\mathbf{L}(H_2O)_6Cl_6\cdot 6H_2O$	3410, 820	1695	1645	1595, 1025, 990, 670	1110	255
$Lu_2\mathbf{L}(H_2O)_6Cl_6\cdot H_2O$	3405, 848	1653	1634	1595, 1019, 995, 668	1104	226

C–O–C stretching mode for the polyether chain also falls in this region. The FAB mass spectrum of the erbium perchlorate complex provides strong evidence for the formation of a dinuclear complex with the podand **L** as a product of the template condensation of two molecules of diketone with one molecule of diamine and confirms the presence of perchlorate anions and water molecules in both the inner and outer sphere of the complex. The highest peak of the spectrum observed at m/z 1183.4 corresponds to $[\mathrm{Er_2}\mathbf{L}(\mathrm{H_2O})_3(\mathrm{ClO_4})_3]^+$. This species loses the perchlorate groups and water molecules resulting in the formation of fragments $[\mathrm{Er_2}\mathbf{L}(\mathrm{H_2O})_3(\mathrm{ClO_4})_2]^+$ and $[\mathrm{Er_2}\mathbf{L}(\mathrm{H_2O})(\mathrm{ClO_4})]^+$ at m/z 1084.3 and 949.1. The peak at m/z 800.8 and the most intense peak at m/z 712.0 correspond to the mononuclear fragments $[\mathrm{Er}\mathbf{L}(\mathrm{H_2O})_2(\mathrm{ClO_4})]^+$ and $[\mathrm{Er}\mathbf{L}(\mathrm{H_2O})_3]^+$. The spectrum also exhibits a peak due to the free ligand at m/z 494.

The electronic spectra of the complexes for solutions in acetonitrile show similar features, containing three intense and medium bands with maxima at 215–218, 272–275 and 300–310 nm which may be assigned to a transition of the $\pi \rightarrow \pi^*$ type located on the C=N groups and to a $n \rightarrow \pi^*$ transition of the C=O groups, respectively [18,19].

The ^{1}H-NMR spectrum of the DMSO-d_6 solution of the diamagnetic lutetium complex exhibits three multiplets in the ratio 1:1:2 – the protons α to nitrogen give rise to a triplet at δ 2.83 (4H) ($J=7.4$), the protons β to nitrogen to a quintet at δ 1.77 (4H) ($J=7.2$) and the protons adjacent to the oxygen to a triplet at δ 3.43 (8H) ($J=7.2$). The remaining protons of the $-\mathrm{OCH_2C}H_2\mathrm{C}H_2\mathrm{CH_2O}-$ chain occur at δ 1.53 (4H). The pyridine protons are observed at δ 8.3–7.8 (6H) and the methyl protons of the two $\mathrm{CH_3CO}$ and two $\mathrm{CH_3CN}$ groups at δ 3.15 (6H) and δ 2.51 (6H), 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.

On the basis of the available evidence it can be concluded that lanthanide ions are effective templates for the synthesis of Schiff base dinuclear podate complexes, in which the podand with a $\mathrm{N_4O_4}$ set of donor atoms acts as octadentate ligand. The high coordination number characteristic of these ions is achieved by the incorporation of water molecules and counterions in the coordination sphere of the complexes. The final products of the template process appear not to be affected by the size match selectivity parameter. The flexible ligand of podand type can easily adopt the conformation that generates the specific coordination moiety and thus is able to encapsulate two metal ions irrespective of the ionic radius of the central atoms.

Acknowledgements

Financial support from the Committee of Scientific Research (grant 3T09A 13109) is gratefully acknowledged.

References

[1] K.D. Matthews, I.A. Kahwa, D.J. Williams, Inorg. Chem. 33 (1994) 1382, and references therein.

[2] S.A. Pollack, D.B. Chang, J. Appl. Phys. 64 (1988) 2885.

[3] G. Blasse, Recl. Trav. Chim. Pays-Bas 105 (1986) 143.

[4] C.H. Evans, in: E. Frieden (Ed.), Biochemistry of Lanthanides, Plenum Press, New York, 1990, chapt. 9.

[5] M.F. Tweedle, in: J.-C. Bünzli, G.R. Choppin (Eds.), Lanthanide Probes in Life, Chemical and Earth Sciences, Elsevier, Amsterdam, 1989, chapt. 5.

[6] J.-C. Bünzli, P. Froidevaux, C. Piguet, New J. Chem. 19 (1995) 661, and references therein.

[7] R.M. Izatt, R.L. Bruening, M.L. Bruening, B.J. Tarbet, K.E. Krakowiak, J.S. Bradshaw, J.S. Christensen, J. Anal. Chem. 60 (1988) 1825.

[8] C. Piguet, J.-C. Bünzli, G. Bernardinelli, G. Hopfgartner, S. Petoud, O. Schaad, J. Am. Chem. Soc. 118 (1996) 6681, and references therein.

[9] R. Ziessel, M. Maestri, L. Prodi, V. Balzani, A. Van Dorsselaer, Inorg. Chem. 32 (1993) 1237.

[10] J.P. Desvergne, F. Fages, H. Bouas-Laurent, P. Marsau, Pure Appl. Chem. 64 (1992) 1231.

[11] V. Balzani, R. Ballardini, Photochem. Photobiol. 52 (1990) 409.

[12] C. Géze, C. Mouro, F. Hindré, M. Le Plouzennec, C. Moinet, R. Rolland, L. Alderighi, A. Vacca, G. Simonneaux, Bull. Chem. Soc. Chim. Fr. 133 (1966) 267, and references therein.

[13] S. Amin, J.R. Morrow, C.H. Lake, M.R. Churchill, Angew. Chem. Int. Ed. Engl. 33 (1994) 773, and references therein.

[14] D.S. Kumar, V. Alexander, Inorg. Chim. Acta 238 (1995) 63, and references therein.

[15] B. Dietrich, P. Viout, J.-M. Lehn, Macrocyclic Chemistry, VCH Verlagsgesellschaft, Weinheim, 1993.

[16] E.C. Constable, Metals and Ligand Reactivity, VCH Verlaggesellschaft, Weinheim, 1996.

[17] W. Radecka-Paryzek, Inorg. Chim. Acta 109 (1985) L21, and references therein.

[18] W. Radecka-Paryzek, V. Patroniak, Polyhedron 10 (1991) 683.

[19] W. Radecka-Paryzek, V. Patroniak, Polyhedron 13 (1994) 2125.

[20] W. Radecka-Paryzek, V. Patroniak-Krzyminiewska, H. Litkowska, Polyhedron (in press).

[21] R. Bandin, R. Bastida, A. de Blas, P. Castro, D.E. Fenton, A. Macias, A. Rodriguez, T. Rodriguez, J. Chem. Soc., Dalton Trans. (1994) 1185.

[22] U. Casellato, D. Fregona, S. Sitran, S. Tamburini, P.A. Vigato, P. Zanello, Inorg. Chim. Acta 95 (1984) 279.

[23] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Wiley-Interscience, New York, 1978.

[24] W. Radecka-Paryzek, E. Jankowska, E. Luks, Polyhedron 7 (1988) 439, and references therein.

[25] R. Bastida, A. de Blas, P. Castro, D.E. Fenton, A. Macias, R. Rial, A. Rodriguez, T. Rodriguez-Blas, J. Chem. Soc., Dalton Trans. (1996) 1493.

[26] W. Radecka-Paryzek, M. Gdaniec, Polyhedron 16 (1997) 3861, and references therein.

[27] K. Wieghardt, M. Kleine-Boymannn, B. Nuber, J. Weiss, L. Zsolnai, G. Huttner, Inorg. Chem. 25 (1986) 1647.

[28] R.E. Cramer, K.A. Mitchell, A.Y. Hirazumi, S.L. Smith, J. Chem. Soc., Dalton Trans. (1994) 563.