

## Metal-Ion-Directed Synthesis of Homo- and Heteronuclear Dimetallic Schiff Base Podates

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Homodinuclear complexes of lanthanum(III), zinc(II), cadmium(II) and mercury(II) ions and heterodinuclear complexes of lanthanum(II) and zinc(II) ions containing Schiff base open-chain ligands terminated by two carbonyl groups or one amine and one carbonyl group were prepared as a result of the partial Schiff base condensation reaction between 2,6-diacetylpyridine and 4-methyl-1,2-phenylenediamine or 2,6-diaminopyridine in the presence of the appropriate ions acting as templates. The complexes were characterized by spectroscopic methods (IR,  $^1\text{H}$  NMR, FAB-MS) and elemental analysis.

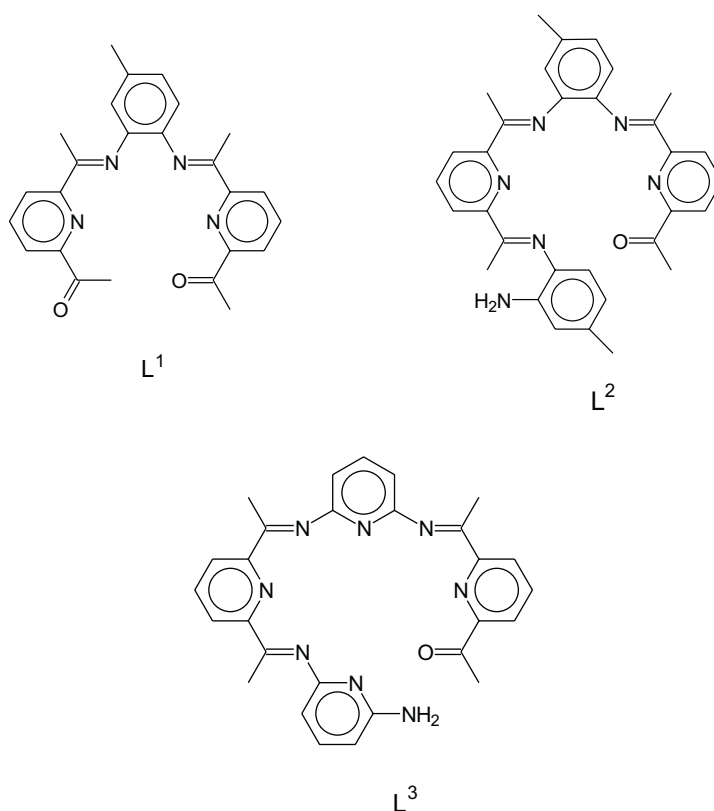
**Key words:** dinuclear complexes, Schiff base podates, lanthanum, zinc, cadmium, mercury, template synthesis

Schiffbase dinuclear complexes of lanthanides 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 [1]. The new applications involve the use of heterodinuclear complexes with predetermined properties as novel supramolecular tunable photonic light-converting devices [2–4] and as catalysts for hydrolytic cleavage or transesterification of RNA phosphate diester backbone [5]. The Schiff base complexes of lanthanides obtained by us [6–8] have found to be very effective catalysts with a high site selectivity for hydrolysis of tRNA [9,10]. Recently, it was found that the lanthanide(III) complexes promote cleavage more efficiently in the presence of a second metal ion [11]. It seems to be in accord with the general observation related to bioinorganic processes that the catalytic activity of dinuclear metal complexes is clearly higher. The novel applications of dinuclear zinc(II) complexes, for example, include the use as a host molecule capable of recognizing barbiturates [12] and the demonstration that dinuclear Schiff base zinc(II) complexes exhibit *in vitro* activity against the HIV virus [13]. Continuing our studies on the effectiveness of metal ions with varying radius and electron configuration as templates in the synthesis of Schiff base compounds, we extended our investigations to the dinuclear complexes. We have recently reported the template action of the rare earth metal ions in the synthesis of the new Schiff base podands, terminated

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with two carbonyl groups, which are able to encapsulate two metal ions irrespective of the ionic radius size of the central atoms [14,15]. The present paper is concerned with the preparation and characterization of novel dinuclear complexes of open-chain (podand) Schiff base ligands terminated by two carbonyl groups or amino and carbonyl groups formed in the metal-promoted condensation reaction between 2,6-diacetylpyridine with 4-methyl-1,2-phenylenediamine ( $L^1$ ,  $L^2$  complexes) or 2,6-diaminopyridine ( $L^3$  complexes). In view of the new potential applications of the homo- and heterodinuclear complexes and the possibility of using the lanthanide metal ion complexes as informative spectroscopic probes for binding sites of biometals, which do not show the remarkable multitude of spectroscopic and magnetic properties, we used lanthanum(III), zinc(II), cadmium(II) and mercury(II) ions as template agents for the synthesis of these macrocyclic systems.



## EXPERIMENTAL

The hydrated lanthanum(III) salts were prepared by dissolving the 99.99% oxides (Fluka) in a slight excess of the appropriate acid. The solutions were evaporated and precipitates recrystallized from methanol. 2,6-Diacetylpyridine (Aldrich Chemical Company), 2,6-diaminopyridine (Sigma), zinc, cadmium and mercury nitrates (Merck) were used without further purification. 4-Methyl-1,2-phenylenediamine (Merck) was purified by recrystallization from n-heptane.

**Preparation of the  $L^1$  complexes. General procedures:** All complexes were performed under similar conditions. To a mixture of appropriate metal nitrate (0.2 mmol for homodinuclear complexes or 0.1 mmol lanthanum(III) nitrate and 0.1 mmol zinc nitrate for heterodinuclear complex) in methanol (10 cm<sup>3</sup>) and 2,6-diacetylpyridine (0.2 mmol) in methanol (10 cm<sup>3</sup>), 4-methyl-1,2-phenylenediamine (0.1 mmol) in methanol (10 cm<sup>3</sup>) was added dropwise with stirring. The reactions were carried out for 6 h in the case of homodinuclear complexes or 24 h for heterodinuclear complexes. The solution volume was then reduced to 10 cm<sup>3</sup> 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*.

**Preparation of the homodinuclear  $L^2$  and  $L^3$  complexes. General procedures:** All complexes were prepared under similar conditions. To a mixture of appropriate metal salt (0.2 mmol) in methanol (10 cm<sup>3</sup>) and 2,6-diacetylpyridine (0.2 mmol) in methanol (10 cm<sup>3</sup>), 4-methyl-1,2-phenylenediamine (0.2 mmol) or 2,6-diaminopyridine (0.2 mmol) in methanol (10 cm<sup>3</sup>) was added dropwise with stirring. The reactions were carried out for 6 h. The solution volume was then reduced to 10 cm<sup>3</sup> by roto-evaporation and a yellow precipitate formed on addition of a small amount of diethyl ether. This was filtered off, washed with ether and dried *in vacuo*.

**Preparation of the heterodinuclear  $L^3$  complex:** To a mixture of lanthanum chloride (0.1 mmol) and zinc chloride in methanol (10 cm<sup>3</sup>) with 2,6-diacetylpyridine (0.2 mmol) in methanol (10 cm<sup>3</sup>), 2,6-diaminopyridine (0.2 mmol) in methanol (10 cm<sup>3</sup>) was added dropwise with stirring. After 1 h of stirring at 65° ammonium hexafluorophosphate in methanol was added. The reaction was carried out for 24 h at room temperature. The solution volume was then reduced to 10 cm<sup>3</sup> by roto-evaporation and a yellow precipitate formed on addition of a small amount of diethyl ether. This was filtered off, washed with ether and dried *in vacuo*.

**Measurements:** IR spectra were recorded using CsI pellets in the range 4000–200 cm<sup>-1</sup> on a Perkin-Elmer 580 spectrophotometer. <sup>1</sup>H NMR spectra were run in DMSO-d<sub>6</sub> on a Varian Gemini 300 spectrometer using TMS as an internal reference. 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 homogeneous by thin layer chromatography performed on precoated silica gel plates (0.2 mm 60 F-254 E. Merck) and visualized by UV light.

## RESULTS AND DISCUSSION

The homodinuclear acyclic complexes of lanthanum(III), zinc(II), cadmium(II) and mercury(II) ions and heterodinuclear complexes of lanthanum(III) and zinc(II) ions – products of a Schiff base condensation of two molecules of 2,6-diacetylpyridine with one ( $L^1$  complexes) or two molecules of 4-methyl-1,2-phenylenediamine ( $L^2$  complexes) or two molecules of 2,6-diaminopyridine ( $L^3$  complexes) were prepared by the reaction of appropriate metal salts acting as template agents with diketone and diamine in the stoichiometric molar ratios of starting materials.

The formulations of these complexes as La<sub>2</sub>L<sup>1</sup>(NO<sub>3</sub>)<sub>6</sub>·3H<sub>2</sub>O, LaZnL<sup>1</sup>(NO<sub>3</sub>)<sub>5</sub>·3H<sub>2</sub>O, Zn<sub>2</sub>L<sup>1</sup>(NO<sub>3</sub>)<sub>4</sub>·3H<sub>2</sub>O, Hg<sub>2</sub>L<sup>1</sup>(NO<sub>3</sub>)<sub>4</sub>·2H<sub>2</sub>O, Zn<sub>2</sub>L<sup>2</sup>(NO<sub>3</sub>)<sub>4</sub>·4H<sub>2</sub>O, Cd<sub>2</sub>L<sup>2</sup>(NO<sub>3</sub>)<sub>4</sub>, La<sub>2</sub>L<sup>3</sup>(NO<sub>3</sub>)<sub>6</sub>·6H<sub>2</sub>O, La<sub>2</sub>L<sup>3</sup>Cl<sub>6</sub>·6H<sub>2</sub>O, LaZnL<sup>3</sup>Cl<sub>2</sub>(PF<sub>6</sub>)<sub>3</sub>·18H<sub>2</sub>O, Zn<sub>2</sub>L<sup>3</sup>(NO<sub>3</sub>)<sub>4</sub>·4H<sub>2</sub>O and Cd<sub>2</sub>L<sup>3</sup>(NO<sub>3</sub>)<sub>4</sub>·5H<sub>2</sub>O follow from spectroscopic data (IR, FAB-MS, <sup>1</sup>H NMR) and elemental analysis, being consistent with the above formulas. The  $L^1$  podates are terminated by two carbonyl groups, whereas the  $L^2$  and  $L^3$  complexes are terminated by one carbonyl group and one amine group. The complexes are air stable solids, soluble in DMSO.

The infrared spectra of these complexes taken in the region 4000–200 cm<sup>-1</sup> (Table) provide some information regarding the bonding in the complexes. The important feature, common to all the complexes, is the occurrence of a strong absorption band at

Table. Selected infrared and FAB mass spectral data for L<sup>1</sup>, L<sup>2</sup> and L<sup>3</sup> complexes.

Complex	IR (cm <sup>-1</sup> )							m/z	FAB Assignments	
	OH	NH <sub>2</sub>	C=O	C=N	Pyridine	Anions				
La <sub>2</sub> L <sup>1</sup> (NO <sub>3</sub> ) <sub>6</sub> ·3H <sub>2</sub> O	3369	–	1675	1627	1592, 1032, 934, 736, 615	1748, 1738, 1384–1362, 815	1099.1 1061.0 879.8 811.8 724.6 413.2	La <sub>2</sub> L <sup>1</sup> (NO <sub>3</sub> ) <sub>6</sub> ·2H <sub>2</sub> O La <sub>2</sub> L <sup>1</sup> (NO <sub>3</sub> ) <sub>6</sub> La <sub>2</sub> L <sup>1</sup> (NO <sub>3</sub> ) <sub>3</sub> La <sub>2</sub> L <sup>1</sup> (NO <sub>3</sub> ) <sub>2</sub> La <sub>2</sub> L <sup>1</sup> ·2H <sub>2</sub> O L <sup>1</sup>		
	LaZnL <sup>1</sup> (NO <sub>3</sub> ) <sub>5</sub> ·3H <sub>2</sub> O	3342	–	1661	1625	1595, 1031 735, 616	1761, 1433–1321, 1384, 816	942.2 835.3 742.3	LaZnL <sup>1</sup> (NO <sub>3</sub> ) <sub>5</sub> ·H <sub>2</sub> O LaZnL <sup>1</sup> (NO <sub>3</sub> ) <sub>3</sub> ·2H <sub>2</sub> O LaZnL <sup>1</sup> (NO <sub>3</sub> ) <sub>2</sub>	
		Zn <sub>2</sub> L <sup>1</sup> (NO <sub>3</sub> ) <sub>4</sub> ·3H <sub>2</sub> O	3400	–	1650	1623	1595, 1026, 748, 620 1384, 813	1768, 1425–1330, 1384, 813	846.8 809.8 749.7 683.0 641.8	Zn <sub>2</sub> L <sup>1</sup> (NO <sub>3</sub> ) <sub>4</sub> ·3H <sub>2</sub> O Zn <sub>2</sub> L <sup>1</sup> (NO <sub>3</sub> ) <sub>4</sub> ·H <sub>2</sub> O Zn <sub>2</sub> L <sup>1</sup> (NO <sub>3</sub> ) <sub>3</sub> ·H <sub>2</sub> O Zn <sub>2</sub> L <sup>1</sup> (NO <sub>3</sub> ) <sub>2</sub> ·H <sub>2</sub> O Zn <sub>2</sub> L <sup>1</sup> (NO <sub>3</sub> )·2H <sub>2</sub> O
			Hg <sub>2</sub> L <sup>1</sup> (NO <sub>3</sub> ) <sub>4</sub> ·2H <sub>2</sub> O	3305	–	1695	1635	1582, 1035, 713, 598	1748, 1740, 1383–1321, 822	950.2 875.7 817.7
	Zn <sub>2</sub> L <sup>2</sup> (NO <sub>3</sub> ) <sub>4</sub> ·4H <sub>2</sub> O	3400		3300, 3151	1680	1623	1599, 1029, 937, 743, 648	1766, 1435–1370, 1384, 813	935.5 787.0 747.9 709.4 685.2	Zn <sub>2</sub> L <sup>2</sup> (NO <sub>3</sub> ) <sub>4</sub> ·2H <sub>2</sub> O Zn <sub>2</sub> L <sup>2</sup> (NO <sub>3</sub> ) <sub>2</sub> ·H <sub>2</sub> O Zn <sub>2</sub> L <sup>2</sup> (NO <sub>3</sub> )·2H <sub>2</sub> O Zn <sub>2</sub> L <sup>2</sup> (NO <sub>3</sub> ) Zn <sub>2</sub> L <sup>2</sup> ·2H <sub>2</sub> O

$\text{Cd}_2\text{L}^2(\text{NO}_3)_4$	3380	3321, 3267	1690	1622	1585, 1014, 980, 777, 667	1760, 1440–1332, 1383, 808	960.6, 935.5, 919.8, 864.9	$\text{Cd}_2\text{L}^2(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$ $\text{Cd}_2\text{L}^2(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ $\text{Cd}_2\text{L}^2(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$ $\text{Cd}_2\text{L}^2\text{NO}_3$
							519.5	$\text{L}^2$
							1248.4	$\text{La}_2\text{L}^3(\text{NO}_3)_6 \cdot 6\text{H}_2\text{O}$
							1079.1	$\text{La}_2\text{L}^3(\text{NO}_3)_5$
$\text{La}_2\text{L}^3(\text{NO}_3)_6 \cdot 6\text{H}_2\text{O}$	3450, 3400, 879	3336, 3213, 1632	1680	1626	1605, 1030, 992, 734, 615	1780, 1750, 1458–1305, 1384, 817	1018.3, 954.8, 893.8, 831.9, 769.8, 491.8	$\text{La}_2\text{L}^3(\text{NO}_3)_4$ $\text{La}_2\text{L}^3(\text{NO}_3)_3$ $\text{La}_2\text{L}^3(\text{NO}_3)_2$ $\text{La}_2\text{L}^3(\text{NO}_3)$ $\text{La}_2\text{L}^3$ $\text{L}^3$
							872.9	$\text{La}_2\text{L}^3\text{Cl}_3$
							769.1	$\text{La}_2\text{L}^3$
							490.2	$\text{L}^3$
							1347.9	$\text{LaZnL}^3\text{Cl}_2(\text{PF}_6)_3 \cdot 8\text{H}_2\text{O}$
							1234.7	$\text{LaZnL}^3\text{Cl}_2(\text{PF}_6)_3 \cdot 2\text{H}_2\text{O}$
							946.8	$\text{Zn}_2\text{L}^3(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$
$\text{Zn}_2\text{L}^3(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$	3455, 870	3327, 3208	1680	1640	1568, 1025, 991, 784, 598	1770, 1740, 1462–1310, 830	869.3, 555.0, 490.2	$\text{Zn}_2\text{L}^3(\text{NO}_3)_4$ $\text{Zn}_2\text{L}^3$ $\text{L}^3$
							1091.0	$\text{Cd}_2\text{L}^3(\text{NO}_3)_4 \cdot 7\text{H}_2\text{O}$
							983.3	$\text{Cd}_2\text{L}^3(\text{NO}_3)_4 \cdot \text{H}_2\text{O}$
$\text{Cd}_2\text{L}^3(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$	3461, 880	3330, 3208, 1653	1682	1645	1594, 1014, 991, 743, 668	1767, 1730, 1457–1300, 833		

1695–1650  $\text{cm}^{-1}$  assigned to the C=O stretching vibration, indicating the formation of the open-chain products, containing terminal acetylpyridyl groups. The shift of this band from 1705  $\text{cm}^{-1}$  in uncomplexed 2,6-diacetylpyridine to lower wavenumbers strongly suggests coordination through the oxygen atoms. In the dinuclear complexes of  $L^1$  ligand terminated by two carbonyl groups  $\nu(\text{C}=\text{O})$  lies at a considerable lower frequency than in the dinuclear complexes of  $L^2$  and  $L^3$  ligands, terminated by one carbonyl and one amino group, 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 [14–16]. The spectra of  $L^2$  and  $L^3$  complexes exhibit a strong doublet at 3336–3300  $\text{cm}^{-1}$  and 3267–3054  $\text{cm}^{-1}$ , attributable to the asymmetric and symmetric  $-\text{NH}_2$  stretching vibrations and a weak intensity band at 1653–1652  $\text{cm}^{-1}$  characteristic of  $-\text{NH}_2$  bending mode, suggesting the coordination of the nitrogen atoms of the primary groups to the metal ion. All the spectra confirm the Schiff base condensation by the presence of a strong band at 1645–1622  $\text{cm}^{-1}$  characteristic of C=N stretching modes. The spectra show medium to strong bands at 1605–1568  $\text{cm}^{-1}$  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 band at 1045–934  $\text{cm}^{-1}$  and 784–613  $\text{cm}^{-1}$ , attributable to the ring breathing frequency and the low energy pyridine ring vibrations, respectively. The complexes show the broad diffuse band centered at *ca* 3461–3305  $\text{cm}^{-1}$  due to the stretching and bending modes of lattice and coordinated water. In addition, very weak bands are detectable at 892–870  $\text{cm}^{-1}$  region, which may be assigned to rocking or wagging modes of water molecules interacting with the metal ion. Information about the bonding mode of the counterions in these complexes may also be obtained from IR spectra. In the spectra of the nitrate complexes  $\nu(\text{N}-\text{O})$  stretching frequency is observed as a very strong broad band centered at *ca* 1380  $\text{cm}^{-1}$ . In addition, medium bands at 1780–1730  $\text{cm}^{-1}$  and 845–808  $\text{cm}^{-1}$  are also detectable. The broadening and splitting of the bands characteristic of nitrate groups is typical of the presence of coordinated nitrates. The spectra of the chloride complexes show medium absorption bands at 292 and 248  $\text{cm}^{-1}$  attributable to the M–Cl frequency indicating the interaction of at least part of the chloride counterions with the metal.

The complexes were studied by  $^1\text{H}$  NMR and homonuclear correlation spectroscopy (COSY) experiments. The  $^1\text{H}$  NMR spectra of DMSO- $d_6$  solutions of the complexes of  $L^1$  exhibit the expected splitting patterns and chemical shifts for acetylpyridine ring protons (6H) at  $\delta$  8.0–8.6 for  $\text{La}_2$ ,  $\delta$  7.8–8.6 for  $\text{LaZn}$ ,  $\delta$  7.8–8.7 for  $\text{Zn}_2$  and  $\delta$  8.0–8.7 for  $\text{Hg}_2$ . The protons corresponding to the phenylene ring occur as three signals: a doublet (1H) at  $\delta$  6.81 ( $J=7.2$ ) for  $\text{La}_2$ ,  $\delta$  6.71 ( $J=7.3$ ) for  $\text{LaZn}$ ,  $\delta$  6.63 ( $J=7.4$ ) for  $\text{Zn}_2$  and  $\delta$  7.06 ( $J=7.0$ ) for  $\text{Hg}_2$ , singlet (1H) at  $\delta$  6.52 for  $\text{La}_2$ ,  $\delta$  6.60 for  $\text{LaZn}$ ,  $\delta$  6.52 for  $\text{Zn}_2$  and  $\delta$  6.78 for  $\text{Hg}_2$  and another doublet (1H) at  $\delta$  6.45 ( $J=7.2$ ) for  $\text{La}_2$ ,  $\delta$  6.55 ( $J=7.3$ ) for  $\text{LaZn}$ ,  $\delta$  6.21 ( $J=7.4$ ) for  $\text{Zn}_2$  and  $\delta$  6.67 ( $J=7.0$ ) for  $\text{Hg}_2$ . These two latter signals are definitely assigned to the protons close to the methyl substituent, because they show COSY cross peaks to the same signal observed as singlet (3H) at  $\delta$  2.02 for  $\text{La}_2$ ,  $\delta$  2.05 for  $\text{LaZn}$ ,  $\delta$  2.05 for  $\text{Zn}_2$  and  $\delta$  2.08 for  $\text{Hg}_2$ , thus, corresponding to the protons of this methyl

group. The methyl protons of the two  $\text{CH}_3\text{C}=\text{O}$  groups and two  $\text{CH}_3\text{C}=\text{N}$  groups occur at  $\delta$  2.72–2.73 (6H) and  $\delta$  2.41–2.43 (6H), respectively, for all these complexes. The  $^1\text{H}$  NMR spectra of  $\text{DMSO-d}_6$  solutions of the complexes of  $\text{L}^2$  were analysed in a similar fashion to that discussed above. They show acetylpyridine ring protons (6H) at  $\delta$  8.0–8.6 for  $\text{Zn}_2$  and  $\delta$  8.05–8.6 for  $\text{Cd}_2$  complexes. The protons corresponding to the two phenylene rings occur as three signals: a doublet (2H) at  $\delta$  6.39 ( $J=7.4$ ) for  $\text{Zn}_2$  and  $\delta$  6.38 ( $J=7.7$ ) for  $\text{Cd}_2$ , singlet (2H) at  $\delta$  6.32 for  $\text{Zn}_2$  and  $\delta$  6.32 for  $\text{Cd}_2$  and another doublet (2H) at  $\delta$  6.19 ( $J=7.4$ ) for  $\text{Zn}_2$  and  $\delta$  6.18 ( $J=7.7$ ) for  $\text{Cd}_2$ . These two latter signals are definitely assigned to the protons close to the methyl substituent, because they show COSY cross peaks to the same signal observed as singlet (6H) at  $\delta$  2.05 for  $\text{Zn}_2$  and  $\delta$  2.05 for  $\text{Cd}_2$ , thus, corresponding to the protons of this methyl group. The methyl protons of the one  $\text{CH}_3\text{C}=\text{O}$  groups and three  $\text{CH}_3\text{C}=\text{N}$  groups occur at  $\delta$  2.73 (3H) and  $\delta$  2.41–2.42 (9H), respectively, for these two complexes. The signals at  $\delta$  4.19 (1H) and  $\delta$  4.34 (1H) for  $\text{Zn}_2$  and  $\delta$  4.20 (1H) and  $\delta$  4.34 (1H) for  $\text{Cd}_2$  are assigned to the protons of primary amine group and confirm the proposed formulations of these two  $\text{L}^2$  complexes. The  $^1\text{H}$  NMR spectra of  $\text{DMSO-d}_6$  solutions of the complexes of  $\text{L}^3$  show the resonances of acetylpyridine ring protons (6H) at  $\delta$  7.6–8.2 for  $\text{La}_2$ ,  $\delta$  7.8–8.2 for  $\text{LaZn}$ ,  $\delta$  7.7–8.2 for  $\text{Zn}_2$  and  $\delta$  7.7–8.3 for  $\text{Cd}_2$ . The protons of two aminopyridine rings give rise to a triplet (2H) at  $\delta$  7.03 ( $J=7.7$ ) for  $\text{La}_2$ ,  $\delta$  7.18 ( $J=8.2$ ) for  $\text{LaZn}$ ,  $\delta$  7.09 ( $J=7.8$ ) for  $\text{Zn}_2$  and  $\delta$  7.02 ( $J=7.6$ ) for  $\text{Cd}_2$  and to the doublet (4H) at  $\delta$  5.62 ( $J=7.7$ ) for  $\text{La}_2$ ,  $\delta$  5.62 ( $J=8.2$ ) for  $\text{LaZn}$ ,  $\delta$  5.72 ( $J=7.8$ ) for  $\text{Zn}_2$  and  $\delta$  5.61 ( $J=7.6$ ) for  $\text{Cd}_2$ . These signals are correlated with each other in COSY spectra. The methyl protons of the one  $\text{CH}_3\text{C}=\text{O}$  groups (3H) and three  $\text{CH}_3\text{C}=\text{N}$  groups (9H) occur at  $\delta$  2.73 and  $\delta$  2.55 for  $\text{La}_2$ ,  $\delta$  2.72 and  $\delta$  2.56 for  $\text{LaZn}$ ,  $\delta$  2.73 and  $\delta$  2.56 for  $\text{Zn}_2$  and  $\delta$  2.7 and  $\delta$  2.56 for  $\text{Cd}_2$ , respectively. The broad signal centered at  $\delta$  5.44 for  $\text{La}_2$ ,  $\delta$  5.41 for  $\text{LaZn}$ ,  $\delta$  5.28 for  $\text{Zn}_2$  and  $\delta$  5.31 for  $\text{Cd}_2$  is assigned to the two protons of primary amine group and consistent with the proposed formulations of  $\text{L}^3$  complexes.

FAB spectroscopy offers additional structural information on these complexes. The FAB mass spectra (Table) provide strong evidence for the formation of the complexes containing two metal ions. The presence of the counterions and water molecules in inner sphere of the complexes is confirmed by the stepwise loss of these species, which appears to be a common route of fragmentation. The spectra exhibit peaks due to the free ligands as a result of demetalation of the species under FAB conditions, supporting the formation of the complexes of podate type with  $\text{L}^1$ ,  $\text{L}^2$  and  $\text{L}^3$  ligands as products of [2+1] or [2+2] (dicarbonyl and diamine) template condensation process.

It is worth noting that the open-chain complexes, terminated by two carbonyl groups or one carbonyl group and one amino group, are known to be intermediates in the template synthesis of Schiff base macrocyclic compounds derived from dicarbonyl compounds and diprimary amines [17–19]. In this study the potential intermediates occur to be the final products. It seems reasonable to assume that the encapsulation of the two metal ions requires such orientation of the terminal  $>\text{C}=\text{O}$  and  $-\text{NH}_2$  groups, which

makes impossible the bringing these functional groups to the distance necessary for intra- or intermolecular condensation leading to the ring closure. Moreover, the strong coordination of the  $-NH_2$  group to the metal ion decreases the probability of the nucleophilic attack of the coordinated amine nitrogen on carbon atom of the carbonyl group and stabilizes the open-chain product once formed. Thus, it can be concluded that in this case the formation of the complexes containing two metal ions requires the existence of the more flexible ligand of the podand type, which can easily adapt the conformation that generates the specific coordination cavity. The results discussed in this paper, along with our earlier investigations concerning the mechanism of the formation of mono- and dinuclear podate complexes instead of the expected macrocyclic products [14,15,20], demonstrate that the structure and coordination mode of potential intermediates are the factors, which prove to be of importance in determining the preferred pathway of the metal-ion-templated condensation in the Schiff base systems and must be taken into account in the design and synthesis of the desired products.

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