

Metal-Ion-Directed Synthesis of Homo- and Heteronuclear Dimetallic Schiff Base Podates. II.*

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Homodinuclear complexes with magnesium(II), calcium(II), and barium(II) ions and heterodinuclear complexes with calcium(II) or cadmium(II) and lanthanide(III) ions containing Schiff base open-chain ligand terminated by 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 in the presence of the appropriate ions acting as templates. The complexes were characterized by spectroscopic methods (IR, ¹H NMR, FAB-MS), thermogravimetric and elemental analyses.

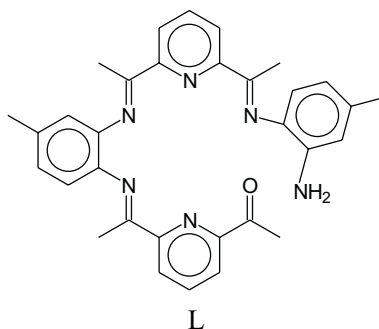
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New fascinating potential applications of the polynuclear Schiff base lanthanide complexes as contrast agents for medical resonance imaging, luminescent stains for fluoroimmunoassays, catalysts for the selective cleavage for RNA and DNA, tunable photonic light-converting devices has prompted us to extend our investigation on the coordination template effect in generating the Schiff bases to the homo- and heterodinuclear complexes [1]. Because of the similarity in ionic radii, coordination chemistry and binding behaviour between the lanthanide(III) cations and alkaline earth metal cations and the remarkable multitude of spectroscopic and magnetic properties, the lanthanides have been broadly used as presumed isomorphous replacements for calcium and, to a lesser degree, other biometals, and serve as informative spectroscopic probes of metal binding sites of macromolecules of biological interest. The latest suggestion of possible future employment of lanthanides as therapeutic agent in the treatment of inflammation, arthritis and atherosclerosis are based on the ability of lanthanide ions to antagonize the calcium-dependent processes [2–9]. It seemed, therefore, to be of interest for us to relate the template action of lanthanides and biologically important ions in the synthesis of the Schiff base systems [10–12].

This work has now been extrapolated to the synthesis and characterization of the homo- and heterodinuclear complexes, containing open-chain (podand) Schiff base ligand L formed in the metal-promoted condensation reaction between 2,6-diacetylpyridine and 4-methyl-1,2-phenylenediamine. Such ligand is able to encapsulate two alkaline earth metal ions or two different metal ions: calcium ion and lanthanide ion or cadmium ion and lanthanide ion.

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EXPERIMENTAL

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 formed precipitates were recrystallized from methanol. 2,6-Diacetylpyridine (Aldrich Chemical Company), magnesium, calcium, barium and cadmium salts (Merck) were used without further purification. 4-Methyl-1,2-phenylenediamine (Merck) was purified by recrystallization from n-heptane.

Preparation of the homodinuclear L complexes. General procedures. To a mixture of magnesium, calcium or barium perchlorate (0.2 mmol) in methanol (10 cm³) and 2,6-diacetylpyridine (0.2 mmol) in methanol (10 cm³), 4-methyl-1,2-phenylenediamine (0.2 mmol) in methanol (10 cm³) was added dropwise with stirring. The reactions were carried out for 48 h. The solution volume was then reduced to 10 cm³ by roto-evaporation and a yellow precipitate formed on addition of a small amount of diethyl ether. This solid was filtered off, washed with ether, and dried *in vacuo*.

Preparation of the heterodinuclear L complexes. General procedures. To a mixture of calcium or cadmium salt (0.1 mmol) in methanol (10 cm³) and appropriate lanthanide salt (0.1 mmol) in methanol (10 cm³), 2,6-diacetylpyridine (0.2 mmol) in methanol (10 cm³) and 4-methyl-1,2-phenylenediamine (0.2 mmol) in methanol (10 cm³) was added dropwise with stirring. The reaction were carried out for 24–48 h at room temperature. The solution volume was then reduced to 10 cm³ by roto-evaporation and a yellow precipitate formed on addition of a small amount of diethyl ether. This precipitate was filtered off, washed with ether, and dried *in vacuo*.

Measurements. IR spectra were recorded using CsI pellets in the range 4000–200 cm⁻¹ on a Perkin-Elmer 580 spectrophotometer. ¹H NMR spectra were run in DMSO-d₆ 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 homogenous 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 magnesium(II), calcium(II) and barium(II) ions and heterodinuclear complexes of calcium(II) or cadmium(II) ion and lanthanide ion (La³⁺, Gd³⁺, Dy³⁺ or Lu³⁺) – products of a Schiff base condensation of two molecules of 2,6-diacetylpyridine with two molecules of 4-methyl-1,2-phenylenediamine 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 $\text{Mg}_2\text{L}(\text{ClO}_4)_4 \cdot 4\text{H}_2\text{O}$, $\text{Ca}_2\text{L}(\text{ClO}_4)_4 \cdot 2\text{H}_2\text{O}$, $\text{Ba}_2\text{L}(\text{ClO}_4)_4 \cdot 2\text{H}_2\text{O}$, $\text{CaLaL}(\text{NO}_3)_5 \cdot 4\text{H}_2\text{O}$, $\text{CaGdL}(\text{ClO}_4)_4 \cdot 4\text{H}_2\text{O}$, $\text{CaDyL}(\text{NO}_3)_5 \cdot 8\text{H}_2\text{O}$, $\text{CdLaL}(\text{NO}_3)_5 \cdot \text{H}_2\text{O}$, $\text{CdGdL}(\text{NO}_3)_5 \cdot 4\text{H}_2\text{O}$, $\text{CdDyL}(\text{NO}_3)_5 \cdot 2\text{H}_2\text{O}$ and $\text{CdLuL}(\text{NO}_3)_5 \cdot 4\text{H}_2\text{O}$ follow from spectroscopic data (IR, FAB-MS, ^1H NMR), thermogravimetric and elemental analysis. Chemical analyses confirm the compositions indicated. The L podates 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 $4000\text{--}200\text{ cm}^{-1}$ (Table 1) provide some information regarding the bonding in the complexes. The important feature is the occurrence of strong absorption band at $1700\text{--}1679\text{ cm}^{-1}$ assigned to the C=O stretching vibration, indicating the formation of the open-chain product containing terminal acetylpyridyl group. The shift of this band from 1705 cm^{-1} in uncomplexed 2,6-diacetylpyridine to lower wavenumbers suggests coordination through the oxygen atom. The comparison of the spectra of cadmium(II) [1], magnesium(II), calcium(II) and barium(II) homodinuclear complexes with heterodinuclear complexes of cadmium or calcium ions with lanthanide ions reveals that in the heterodinuclear complexes the $\nu(\text{C}=\text{O})$ exhibits considerable lower frequency than that in the corresponding homodinuclear complexes. The involvement of the lanthanide ion as 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 two different metal ions. The spectra of all complexes exhibit a strong doublet at $3359\text{--}2968\text{ cm}^{-1}$ and $3270\text{--}2866\text{ cm}^{-1}$, which may be attributed to the asymmetric and symmetric --NH_2 stretching vibrations and a weak intensity band at $1658\text{--}1645\text{ cm}^{-1}$ characteristic of --NH_2 bending mode suggesting the coordination of the nitrogen atoms of the primary amine group to the metal ion. All the spectra confirm the Schiff base condensation by the presence of a strong band at $1635\text{--}1605\text{ cm}^{-1}$ characteristic of C=N stretching modes. The spectra show medium to strong bands at $1594\text{--}1359\text{ cm}^{-1}$ 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 $1191\text{--}934\text{ cm}^{-1}$ and $747\text{--}613\text{ cm}^{-1}$ corresponding to the ring breathing frequency and the low energy pyridine ring vibrations, respectively. The complexes show the broad diffuse band centered at *ca* $3446\text{--}3346\text{ cm}^{-1}$ due to the stretching and bending modes of lattice and coordinated water. In addition, in the homodinuclear complexes and heterodinuclear calcium and lanthanide complexes very weak bands occur at $893\text{--}870\text{ cm}^{-1}$ region, which may be assigned to rocking or wagging modes of water molecules interacting with the metal ion. The presence of coordinated water molecules is supported by the results of thermogravimetric analysis. All these complexes lose their water molecules at $140\text{--}170^\circ\text{C}$ except for heterodinuclear complex with calcium and dysprosium ions, which shows the loss of eight water molecules in two steps: four below 100°C and four above 150°C corresponding to the lattice and coordinated water molecules, respectively. The number of water molecules per mol of metal ion was calculated from the weight loss observed for the complexes at the respective temperature ranges.

Table 1. Selected infrared and FAB mass spectral data for the complexes of L.

Complex	IR(cm^{-1})				C=N	py	X ⁻	FAB	
	OH	NH ₂	C=O	m/z				Assignment	
$\text{Mg}_2\text{L}(\text{ClO}_4)_4 \cdot 4\text{H}_2\text{O}$	3346, 870	2973, 2908, 1658	1700	1605	1566, 1361, 1012, 993, 940, 746, 669	1143, 1109, 1089, 641, 627	979.9	$[\text{Mg}_2\text{L}(\text{ClO}_4)_4 \cdot \text{H}_2\text{O}]^+$	
							884.3	$[\text{Mg}_2\text{L}(\text{ClO}_4)_3 \cdot \text{H}_2\text{O}]^+$	
							765.2	$[\text{Mg}_2\text{L}(\text{ClO}_4)_2]^+$	
							562.3	$[\text{Mg}_2\text{L}]^+$	
							541.0	$[\text{MgL}]^+$	
							514.4	$[\text{L}]^+$	
$\text{Ca}_2\text{L}(\text{ClO}_4)_4 \cdot 2\text{H}_2\text{O}$	3375, 870	2979, 2906, 1654	1698	1606	1566, 1361, 1013, 993, 940, 747, 672	1144, 1111, 1089, 636, 627	1030.4	$[\text{Ca}_2\text{L}(\text{ClO}_4)_4 \cdot 2\text{H}_2\text{O}]^+$	
							930.4	$[\text{Ca}_2\text{L}(\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}]^+$	
							748.6	$[\text{Ca}_2\text{L}(\text{ClO}_4)_3 \cdot \text{H}_2\text{O}]^+$	
							717.5	$[\text{Ca}_2\text{L}(\text{ClO}_4 \cdot \text{H}_2\text{O})]^+$	
							593.5	$[\text{Ca}_2\text{L}]^+$	
							552.1	$[\text{CaL}]^+$	
							514.5	$[\text{L}]^+$	
$\text{Ba}_2\text{L}(\text{ClO}_4)_4 \cdot 2\text{H}_2\text{O}$	3412, 871	2962, 2923, 1645	1695	1615	1582, 1359, 995, 937, 660	1133, 1104, 1083, 636, 625	1228.9	$[\text{Ba}_2\text{L}(\text{ClO}_4)_4 \cdot 2\text{H}_2\text{O}]^+$	
							1192.1	$[\text{Ba}_2\text{L}(\text{ClO}_4)_4]^+$	
							991.3	$[\text{Ba}_2\text{L}(\text{ClO}_4)_2]^+$	
							759.0	$[\text{Ba}_2\text{L}]^+$	
							653.1	$[\text{BaL}]^+$	
							520.4	$[\text{L}]^+$	
$\text{CaLaL}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$	3387, 870	3228, 3075, 1653	1680	1623	1584, 1082, 992, 736, 615	1765 1490–1305 1384, 835, 816	938.1	$[\text{CaLaL}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}]^+$	
							884.7	$[\text{CaLaL}(\text{NO}_3)_3 \cdot \text{H}_2\text{O}]^+$	
							675.4	$[\text{CaLaL}]^+$	
							514.5	$[\text{L}]^+$	

CaGdL(ClO ₄) ₄ ·4H ₂ O	3373, 890	3214, 3075, 1657	1679	1621	1568, 992, 745, 617	1146, 1111, 1088, 636, 626	1162.9 1062.6 848.6 748.8 751.0	[CaGdL(ClO ₄) ₄ ·3H ₂ O] ⁺ [CaGdL(ClO ₄) ₃ ·3H ₂ O] ⁺ [CaGdL(ClO ₄) ₂ ·2H ₂ O] ⁺ [CaGdL·2H ₂ O] ⁺ [CaGdL] ⁺			
	CaDyL(NO ₃) ₅ ·8H ₂ O	3411, 893	2968, 2866, 1658	1692	1627	1594, 1084, 1013, 994, 746, 667	1763 1487–1256 1384, 824, 817	1067.2 999.2 845.3 780.6 721.2 659.2 514.0	[CaDyL(NO ₃) ₅ ·2H ₂ O] ⁺ [CaDyL(NO ₃) ₄ ·2H ₂ O] ⁺ [CaDyL(NO ₃) ₃] ⁺ [CaDyL(NO ₃) ₂] ⁺ [CaDyLNO ₃] ⁺ [CaDyL] ⁺ [L] ⁺		
		CdLaL(NO ₃) ₅ ·H ₂ O	3446	3359, 3267	1685	1635	1590, 1034 1017, 976 613	1768, 1384 1456–1318 817	957.5 895.6 766.2	[CdLaL(NO ₃) ₃] ⁺ [CdLaL(NO ₃) ₂] ⁺ [CdLaL] ⁺	
			CdGdL(NO ₃) ₅ ·H ₂ O	3441	3318, 3262	1685	1621	1589, 1080 1039, 1007 934	1765, 1384 1412–1301 806	1057.6 969.8	[CdGdL(NO ₃) ₄ ·H ₂ O] ⁺ [CdGdL(NO ₃) ₃] ⁺
				CdDyL(NO ₃) ₅ ·H ₂ O	3415	3322, 3270	1689	1627	1544, 1511, 1103, 1016, 616	1767, 1420–1380, 1384, 1318, 807	968.7 851.9 797.3 685.5
CdLuL(NO ₃) ₅ ·4H ₂ O	3439	3073, 3150	1684		1634	1590, 1191, 1120, 1016, 616	1765, 1731, 1430–1290, 1384, 839, 810	1186.1 1135.0 1054.1 930.4 806.2	[CdLuL(NO ₃) ₅ ·4H ₂ O] ⁺ [CdLuL(NO ₃) ₅ ·H ₂ O] ⁺ [CdLuL(NO ₃) ₄] ⁺ [CdLuL(NO ₃) ₂] ⁺ [CdLuL] ⁺		

Information about the bonding mode of the counterions in these complexes may also be obtained from IR spectra. 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. In the perchlorate complexes three maxima are observed: at 1146–1133, 1111–1104 and 1089–1083 cm^{-1} . These bands along with two bands at 641–625 cm^{-1} indicate the interaction of these anions with the metal ions. In the spectra of the nitrate complexes $\nu(\text{N–O})$ stretching frequency is observed as splitted bands at 1768–1731, 1490–1256 and 817–806 cm^{-1} ranges. The magnitude of the separation provides evidence for the chelating behaviour of the nitrate groups. The occurrence of a strong absorption at 1384 cm^{-1} , in addition to the above bands, points on the presence of both ionic and coordinated nitrates in the complexes.

The heterodinuclear diamagnetic complexes of L were studied by ^1H NMR and homonuclear correlation spectroscopy (COSY) experiments. The ^1H NMR spectra of DMSO- d_6 solutions of the complexes exhibit the expected splitting patterns and chemical shifts for acetylpyridine ring protons (6H) at δ 7.9–8.3 for CaLaL and δ 7.9–8.5 for CdLa and CdLu complexes. The methyl protons of the one $\text{CH}_3\text{C=O}$ groups and three $\text{CH}_3\text{C=N}$ groups occur at δ 2.72–2.74 (3H) and δ 2.41–2.42 (9H), respectively. The signals at δ 4.71 (2H) for CaLaL, δ 4.67 (2H) for CdLaL and δ 4.61 (2H) for CdLuL complexes are assigned to the protons of primary amine group. The protons corresponding to the two phenylene rings occur as three signals: a doublet (2H) at δ 6.76 ($J=6.7$) for CaLaL, δ 6.54 ($J=7.7$) for CdLaL and δ 6.55 ($J=7.6$) for CdLuL, singlet (2H) at δ 6.51 for CaLaL, δ 6.41 for CdLaL and CdLuL and another doublet (2H) at δ 6.36 ($J=6.7$) for CaLaL, δ 6.27 ($J=7.7$) for CdLaL and δ 6.22 ($J=7.6$) for CdLuL. 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 δ 2.27 for CaLaL, δ 2.20 for CdLaL and δ 2.19 for CdLuL, thus corresponding to the protons of this methyl group.

FAB spectroscopy offers additional structural information on these complexes. The FAB mass spectra (Table 1) 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 ligand as a result of demetallation of the species under FAB conditions supporting the formation of the complexes of podate type with ligand L as product of [2+2] (dicarbonyl and diamine) template condensation process.

The results discussed in this paper extend the number of homo- and heterodimetallic Schiff base s- and f-element complexes formed in the presence of metal ions acting as templates. It is worth noting that stoichiometric [2+2] templated condensation does not lead to the 2+2 macrocyclic product. Instead [2+2] open-chain complexes terminated by one carbonyl group and one amino group arise. The formation of these products seems to be dictated by the stereochemical requirements of the two central atoms coordinating flexible ligand in such conformation, which decreases the probability of

interaction between the amine nitrogen and oxygen atom of the carbonyl group and stabilizes the open-chain product once formed.

These findings lead to the conclusion that alkaline and rare earth metal ions may act as effective templates in the synthesis of the same Schiff bases and coordinate in similar manner. The ability of lanthanide ions to substitute the biologically important metal ions seems to be of interest in view of the possible biochemical applications based mainly upon their close physical and chemical similarities aided by some useful spectroscopic differences.

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