

THE TEMPLATE SYNTHESIS AND CHARACTERIZATION OF NEW MONO- AND DINUCLEAR PODAND SCHIFF BASE COMPLEXES OF SCANDIUM GROUP ELEMENTS

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The partial Schiff base condensation reactions between 2,6-diacetylpyridine and 1,3-phenylenediamine in the presence of scandium(III), yttrium(III) and lanthanum(III) ions as template agents afford new mono- and dinuclear hexadentate complexes of podate type, depending on the molar ratio of starting materials used in the synthesis. They were characterized by IR, UV-VIS, ^1H NMR, and mass spectral data as well as by thermogravimetric and elemental analyses.

Key words: Chelates; Complexes of Schiff bases; Template synthesis; Lanthanides; Scandium(III), yttrium(III) and lanthanum(III) complexes; Infrared spectra.

Interest in the chelation of metal ions by Schiff base ligands of coronand and podand type has continually increased¹⁻⁴ owing to the recognition of the role played by these structures in metalloproteins. The synthetic mono- and polynuclear Schiff base complexes may serve as models for biologically important, naturally occurring ionophores. The new uses for complexes of the scandium group element with Schiff bases involve the clinical use of radioactive metal ion bond to proteins in monoclonal antibody technology⁵⁻⁷, as catalysts for cleavage of RNA (ref.⁸), structural probes for metal ion binding sites in macromolecules of biological interest⁹⁻¹³, and as novel tunable photonic devices in biomedical diagnostics¹⁴.

As a continuation of our studies on the effectiveness of metal ions with varying radius and electron configuration as templates in the synthesis of Schiff base ligands, we have recently reported the synthesis of the macrocyclic coronate¹⁵⁻¹⁷ and/or podate complexes of scandium group elements¹⁸. The present work is concerned with the preparation and characterization of new mono- and dinuclear hexadentate Schiff base complexes of podate type formed in the partial condensation reaction of scandium, yttrium and lanthanum ions with 2,6-diacetylpyridine and 1,3-phenylenediamine.

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EXPERIMENTAL

The hydrated scandium(III), yttrium(III) and lanthanum(III) salts were prepared by dissolving the appropriate oxide (99.99%, Fluka) in a slight excess of appropriate acid. The solutions were evaporated until crystalline precipitates formed; they were filtered off and recrystallized from methanol. 2,6-Diacetylpyridine and 1,3-phenylenediamine (Aldrich) were used without further purification.

Preparation of the Complexes. General Procedure

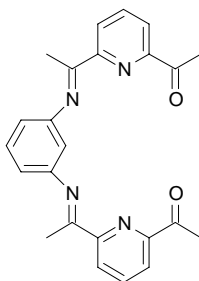
All complexes were prepared under similar conditions. To a solution of 2,6-diacetylpyridine (0.02 mol) in methanol (10 cm³), 1,3-phenylenediamine (0.01 mol) in methanol (10 cm³) and an appropriate metal salt (0.01 or 0.02 mol) in methanol (10 cm³) were added slowly with stirring. The reactions were carried out for 8 h. The resulting yellow precipitates were filtered off, washed with ether, and dried *in vacuo*. Yields: 83–88%. Table I reports analytical data of the complexes.

Measurements

IR spectra were recorded in the range 4 000–200 cm⁻¹ on a Perkin-Elmer 580 spectrophotometer using CsI pellets. Electronic spectra were measured in the range 200–500 nm on a Shimadzu UV-160 spectrophotometer. ¹H NMR spectra were run in (CD₃)₂SO on a Varian Gemini 300 spectrometer using TMS as an internal reference. Low resolution mass spectra were recorded on a Jeol-JMS D100 mass spectrometer operating on electron impact (EI, 70 eV, 300 μA, ion source temperature 200 °C) conditions. Thermogravimetric measurements were performed using Shimadzu TGA-50 derivatograph (up to 250 °C, heating rate 10 °C min⁻¹, on air).

RESULTS AND DISCUSSION

The new mononuclear and dinuclear scandium(III), yttrium(III) and lanthanum(III) complexes of the acyclic open-chain ligand L – product of the Schiff base condensation of two molecules of 2,6-diacetylpyridine with one molecule of 1,3-phenylenediamine – were prepared by the reaction of appropriate metal ions acting as template agents with the diketone and diamine. The two kinds of complexes with metal–ligand stoichiometry equal to 1 : 1 or 2 : 1 were isolated depending upon the molar ratio of the metal ion to linear precursors used in the synthesis (M : ketone : amine = 1 : 2 : 1 or 2 : 2 : 1, respectively).



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These complexes are formulated as $\text{ScL}(\text{H}_2\text{O})_5(\text{ClO}_4)_3$, $\text{YL}(\text{H}_2\text{O})_4(\text{ClO}_4)_3$, $\text{LaL}(\text{H}_2\text{O})_4(\text{NO}_3)_3$, $\text{Sc}_2\text{L}(\text{H}_2\text{O})_{15}(\text{ClO}_4)_6$, $\text{Y}_2\text{L}(\text{H}_2\text{O})_8(\text{NO}_3)_6$ and $\text{La}_2\text{L}(\text{H}_2\text{O})_7(\text{NO}_3)_6$ on the basis of spectral data (IR, UV-VIS, ^1H NMR, EI-MS) and thermogravimetric and elemental analyses (Table I). The complexes are yellow air-stable solids, moderately soluble in CH_3CN and $(\text{CH}_3)_2\text{SO}$.

The infrared spectra of these complexes provide some information regarding the bonding in the complexes (Table II) in all the complexes. The presence of the band at *ca* $1\,630\text{ cm}^{-1}$ attributable to C=N stretching modes confirms the Schiff base condensation.

The profile of the pyridine ring vibrations observed in the $1\,600\text{--}1\,450\text{ cm}^{-1}$ region together with the weak bands around $1\,000\text{ cm}^{-1}$ and 670 cm^{-1} is typical of metal bonding to the pyridine nitrogen atom. The important feature common to all the complexes is the occurrence of strong absorption band at $1\,695\text{--}1\,660\text{ cm}^{-1}$ assigned to the C=O stretching vibration, indicating the formation of the open-chain product containing terminal acetylpyridyl groups. The shift of this band from $1\,705\text{ cm}^{-1}$ in uncomplexed 2,6-diacetylpyridine to lower wavenumbers strongly suggests coordination through the oxygen atoms. Comparison of the spectra of mononuclear and dinuclear complexes in this region can add useful information about the chelation of the one or two metal ions by the donor sites of the multidentate ligand. In the dinuclear complexes, the

TABLE I
Analytical data for the Schiff base complexes

Compound	Calculated/Found		
	% C	% H	% N
$\text{ScL}(\text{H}_2\text{O})_5(\text{ClO}_4)_3$	34.65	6.73	3.87
	34.72	6.63	4.00
$\text{YL}(\text{H}_2\text{O})_4(\text{ClO}_4)_3$	33.56	6.52	3.52
	34.73	6.88	3.69
$\text{LaL}(\text{H}_2\text{O})_4(\text{NO}_3)_3$	36.23	12.32	3.80
	36.09	11.98	3.49
$\text{Sc}_2\text{L}(\text{H}_2\text{O})_{15}(\text{ClO}_4)_6$	21.71	4.13	3.86
	21.14	4.14	3.87
$\text{Y}_2\text{L}(\text{H}_2\text{O})_8(\text{NO}_3)_6$	26.33	12.79	3.49
	28.93	12.46	3.56
$\text{La}_2\text{L}(\text{H}_2\text{O})_7(\text{NO}_3)_6$	24.54	11.92	3.08
	24.42	10.95	3.18

$\nu(\text{C}=\text{O})$ lie at considerable lower wavenumber than in the corresponding mononuclear complexes because the involvement of the second metal in the coordination moiety causes a decrease in the bond order of the $\text{C}=\text{O}$ groups, owing to a stronger donation of electron density towards the two metal ions¹⁹. Information about the bonding mode of the counterions in these complexes may also be obtained from IR spectra²⁰. The spectra of the perchlorate complexes do not exhibit absorptions characteristic of coordinated anions. The presence of uncoordinated perchlorates is inferred from the broad band centered at $1\ 100\ \text{cm}^{-1}$ and the sharp band of medium intensity at *ca* $620\ \text{cm}^{-1}$. The IR spectra of the lanthanum(III) and yttrium(III) nitrate complexes show nitrate vibrations indicative of coordinated nitrate groups. The bands characteristic of ionic nitrates are split and replaced by the two bands associated with the asymmetric stretch at $1\ 480\text{--}1\ 470\ \text{cm}^{-1}$ and $1\ 300\ \text{cm}^{-1}$. The range of splitting along with the appearance of the band at $818\text{--}815\ \text{cm}^{-1}$ is typical of the binding of the nitrate groups in the bidentate fashion. The separation of the combination frequencies in the $1\ 800\text{--}1\ 700\ \text{cm}^{-1}$ which is used to differentiate between bidentate and monodentate coordination of nitrates, is $40\ \text{cm}^{-1}$ and confirm the bidentate chelating behaviour of counterions in these complexes. The complexes show the broad diffuse band centered at *ca* $3\ 450\ \text{cm}^{-1}$ due to the stretching and bending modes of water. In addition, weak bands are detectable at $890\text{--}870\ \text{cm}^{-1}$ (except for the mononuclear lanthanum complex) which may be assigned to rocking or wagging modes of water molecules interacting with the metal ion. This is confirmed by the results of thermogravimetric analysis. The mononuclear complexes of scandium and yttrium lose

TABLE II
Infrared spectral data (cm^{-1}) for the Schiff base complexes

Compound	OH	C=O	C=N	Pyridine	Anions
$\text{ScL}(\text{H}_2\text{O})_5(\text{ClO}_4)_3$	3 500–3 400 br, 870 w	1 695 s	1 635 m	1 600 m, 1 450 m, 995 w, 670 w	1 180–1 140 br, 620 m
$\text{YL}(\text{H}_2\text{O})_4(\text{ClO}_4)_3$	3 500–3 400 br, 890 w	1 685 s	1 630 m	1 590 m, 990 w, 670 w	1 170–1 050 br, 620 m
$\text{LaL}(\text{H}_2\text{O})_4(\text{NO}_3)_3$	3 500 br	1 685 s	1 630 m	1 590 m, 1 005 w, 995 w, 670 w	1 780 w, 1 740 w, 1 470 s, 1 300 s, 818 m
$\text{Sc}_2\text{L}(\text{H}_2\text{O})_{15}(\text{ClO}_4)_6$	3 500–3 400 br, 870 w	1 665 s	1 630 m	1 570 m, 1 030 w, 970 w, 670 w	1 130–1 085 br, 628 m
$\text{Y}_2\text{L}(\text{H}_2\text{O})_8(\text{NO}_3)_6$	3 500–3 400 br, 875 w	1 660 s	1 630 m	1 600 m, 1 030 w, 1 010 w, 990 w, 670 w	1 780 w, 1 740 w, 1 480 s, 1 300 s, 815 w
$\text{La}_2\text{L}(\text{H}_2\text{O})_7(\text{NO}_3)_6$	3 440 br, 875 w	1 660 s	1 630 m	1 580 m, 1 030 w, 1 000 w, 990 w, 670 w	1 780 w, 1 740 w, 1 480 s, 1 300 s, 815 w

three lattice water molecules at 68 °C and two or one water molecules, respectively, coordinated to metal ion at 150 °C, whereas in the case of lanthanum complex a weight loss is observed only at 65 °C corresponding to four lattice water molecules. The dinuclear scandium(III), yttrium(III) and lanthanum(III) complexes indicate the loss of five, eight and five water molecules, respectively, in the temperature range 62–84 °C and ten (for Sc(III)) or two (for La(III)) water molecules at 143 °C, thus supporting the presence of water bound in two different ways.

The electronic spectra of the complexes in acetonitrile solution contain intense and medium bands with maxima at 217–230 and 255–266 nm attributable to the $\pi \rightarrow \pi^*$ transition of the coordinated ligand²¹.

The ¹H NMR spectra of (CD₃)₂SO solution of all the complexes show similar features. The resonances of pyridine protons occur at δ 8.3–7.8 (6-H) and the benzene protons at δ 7.3–6.7 (4-H). The methyl protons of the two CH₃C=O and two CH₃C=N groups appear as singlets at δ 2.8–2.7 (6-H) and δ 2.4–2.2 (6-H), respectively. The integrated relative intensities of the above signals are in the ratio 3 : 2 : 3 : 3, respectively. This is consistent with the proposed formulations of the complexes.

These results are supported by the mass spectra obtained for the lanthanum(III) complexes. The fragment with 100% intensity observed at *m/z* 398 corresponds to the molecular weight of the free ligand – product of a Schiff base condensation of two molecules of 2,6-diacetylpyridine with one molecule of 1,3-phenylenediamine.

Reactions conducted in the absence of the metal salt yielded amorphous yellow materials of low solubility and indefinite composition which gave broad, poorly resolved infrared spectra. The importance of metal ion in promoting the condensation process is thus apparent.

Attempts to effect ring closure by treatment of these open-chain [2+1] complexes with a further equivalent of the 1,3-phenylenediamine in order to span of the two terminal groups were also unsuccessful. The coordination of the pyridine nitrogen and two carbonyl groups to the metal ions indicated by the infrared spectra should encourage the nucleophilic attack of amine nitrogen atoms at the carbon atoms of carbonyl moieties. The employment of different experimental conditions (various molar ratios and the method of adding starting materials, reaction time, range of temperatures) have not led to the macrocyclic [2+2] condensation product. The products isolated were amorphous solids, oils or gums. The open-chain complexes with two terminal carbonyl groups are known to be intermediates in the template synthesis of [2+2] Schiff base complexes derived from dicarbonyl compounds and diprimary amines²². Whether the dicarbonyl species is able to react with the next molecule of diamine to give the macrocyclic product is expected to depend on the conformation of this intermediate, which might be such that the C=O groups are not in the necessary cis relationship for the intramolecular linkage with diamine. The failure of podate Schiff base complexes of scandium group elements derived from 2,6-diacetylpyridine and 1,3-phenylenediamine

to undergo complete condensation and cyclization is presumably attributed to unfavourable positions of the two carbonyl groups. These results demonstrate that the structure and coordination mode of potential intermediates is one of the factors which prove to be important in determining the preferred pathway of the metal-ion-templated condensation of the Schiff base systems and must be taken into account in the design and synthesis of the desired products.

On the basis of available evidence it can be concluded that the scandium group ions are effective templates for the synthesis of Schiff base mononuclear and dinuclear complexes of open-chain podate type, in which the podand with an N_4O_2 set of donor atoms acts as hexadentate ligand. The high coordination number characteristic of these ions is achieved by the incorporation of water molecules or nitrate counterions in the coordination sphere of the complexes. The final products of the template process do not appear to be effected by the size match selectivity parameter. The flexible ligand of the podand type can easily adopt the conformation that generates the specific coordination moiety and thus is able to chelate one or two metal ions irrespective of the ionic radius size of the atom center.

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