

# THE YTTRIUM ION AS A TEMPLATE IN THE SYNTHESIS OF THE MACROCYCLIC AND ACYCLIC COMPLEXES FORMED IN THE REACTIONS WITH 2,6-DIACETILPYRIDINE AND HYDRAZINE\*

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**Abstract**—The macrocyclic tetradentate NNNN donor yttrium nitrate complex of formula  $[\text{YL}^1(\text{NO}_3)_3] \cdot 2\text{H}_2\text{O}$ , where  $\text{L}^1$  is 2,5,11,14-tetramethyl-3,4,12,13,19,20-hexaazatricyclo[13.3.1.1<sup>6,10</sup>]eicosa-1(19),2,4,6,8,10(20),11,13,15,17-decaene, has been prepared by the condensation of 2,6-diacetylpyridine with hydrazine in the presence of a metal ion template and characterized by spectral and analytical data. Different experimental conditions (the type of counterion, ratio of starting materials) lead to the isolation of acyclic tetradentate NNNO or terdentate NNN donor complexes of yttrium with uncondensed carbonyl or amino groups. They are formulated as  $[\text{YL}^2(\text{H}_2\text{O})_2]\text{Cl}_3 \cdot 2\text{H}_2\text{O}$  and  $[\text{YL}^2(\text{H}_2\text{O})_2](\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$ , where  $\text{L}^2$  is (6-acetyl-pyrid-2-yl)methyl ketone azine, and  $[\text{YL}^3(\text{NO}_3)_3] \cdot 2\text{H}_2\text{O}$ ,  $[\text{YL}^3]\text{Cl}_3 \cdot 2\text{H}_2\text{O}$  and  $[\text{YL}^3](\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$ , where  $\text{L}^3$  is 2,6-diacetylpyridinedihydrazone. The 2,6-diacetylpyridine (L) complexes isolated as minor products, are regarded as possible intermediates in the formation of macrocyclic  $\text{L}^1$  and ring-opened  $\text{L}^2$  complexes of yttrium.

Interest in exploring the encapsulation of the rare earth elements by polyoxa- and polyaza-macrocycles like coronands and cryptands, has continually increased since they can be used for lanthanide separation, for the stabilization of unusual oxidation states, for the systematic investigation of the coordinating properties of these elements and for probing the metal ion binding sites of biological macromolecules.<sup>1</sup>

The coordination of yttrium by polyoxa-macrocycles has been little studied. The synthetic and structural results of research on complexation of yttrium with crown ethers were recently reported.<sup>2</sup>

In previous papers we reported the preparation and characterization of scandium and heavier lanthanide (Tb–Lu) complexes containing the 14-membered tetradentate hexaaza macrocyclic ligand.<sup>3</sup> The lighter lanthanides (La–Gd) have been found to be ineffective as templates for the synthesis of this macrocycle under similar

conditions, but effective in the synthesis of N donor macrocycles with greater ring size.<sup>4</sup> We have concluded that the important factor which must be taken into account in the synthesis of the macrocyclic compounds with the aid of a metal ion is the ratio of cation diameter to ligand cavity size. As a continuation of our studies on the effectiveness of metal ions of varying radius and electron configuration in the synthesis of polyaza-macrocyclic compounds with different ring size, we extended our investigations to the yttrium ion, which has not so far been examined in this respect. We now report what we believe to be the first example of the template action of yttrium ion (which is similar in size to Dy and Ho) in the synthesis of a macrocyclic compound. We have found that different experimental conditions lead to the isolation of macrocyclic (coronate) or acyclic (podate) complexes of yttrium.

## EXPERIMENTAL

The hydrated yttrium salts (chloride, perchlorate or nitrate) were prepared by dissolving the 99.99%  $\text{Y}_2\text{O}_3$  in the appropriate acid. The solutions were

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Table 1. Analytical data for L<sup>1</sup>, L<sup>2</sup>, L<sup>3</sup> and L complexes of yttrium

Compound	Calculated			Found		
	%C	%H	%N	%C	%H	%N
[YL <sup>1</sup> (NO <sub>3</sub> ) <sub>3</sub> ]·2H <sub>2</sub> O	34.3	3.5	20.0	34.2	3.5	20.0
[YL <sup>2</sup> (H <sub>2</sub> O) <sub>2</sub> ]Cl <sub>3</sub> ·2H <sub>2</sub> O	36.6	4.4	9.5	36.4	4.5	9.3
[YL <sup>2</sup> (H <sub>2</sub> O) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>3</sub> ·2H <sub>2</sub> O	27.6	3.3	7.2	27.6	3.3	7.0
[YL <sup>3</sup> (NO <sub>3</sub> ) <sub>3</sub> ]·2H <sub>2</sub> O	21.5	3.4	22.3	21.4	3.4	22.2
[YL <sup>3</sup> ]Cl <sub>3</sub> ·2H <sub>2</sub> O	35.2	4.9	22.8	35.0	4.9	22.7
[YL <sup>3</sup> ](ClO <sub>4</sub> ) <sub>3</sub> ·2H <sub>2</sub> O	26.8	3.7	17.4	26.7	3.7	17.2
[YL(NO <sub>3</sub> ) <sub>3</sub> ]·2H <sub>2</sub> O	22.8	2.8	11.8	22.4	2.7	11.3
[YL <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]Cl <sub>3</sub> ·2H <sub>2</sub> O	36.4	4.4	4.7	37.1	4.3	4.9
[YL <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>3</sub> ·2H <sub>2</sub> O	27.5	3.8	3.6	27.4	3.8	3.5

evaporated and precipitates recrystallized from methanol.

#### Preparation of the yttrium complexes. General procedure

The complexes were prepared by the template synthesis of the yttrium chloride, perchlorate or nitrate with 2,6-diacetylpyridine and hydrazine in ethanol, in the reactant ratios 2:1:1, 1:1:2, 1:2:4 and 1:3:6. The reaction mixtures were heated under reflux with stirring for 24 h. The resulting precipitates were filtered off, washed with hot ethanol and ether, and dried under vacuum.

The macrocyclic complex of L<sup>1</sup> is formed only in the reaction of yttrium nitrate with 2,6-diacetylpyridine and hydrazine in the 2:1:1 molar ratio of starting materials. Under the same reaction conditions, yttrium chloride and perchlorate gave the acyclic 1:1 complexes (6-acetyl-pyrid-2-yl)methyl ketone azine (L<sup>2</sup>). Small amounts of yttrium nitrate, chloride or perchlorate complexes of 2,6-diacetylpyridine (L) were also obtained from these reactions.

From the reactions of yttrium nitrate, chloride and perchlorate with 2,6-diacetylpyridine and hydrazine in the molar ratios 1:1:2, 1:2:4 and 1:3:6, the 2,6-diacetylpyridinedihydrazone (L<sup>3</sup>) complexes were isolated with the metal-to-ligand stoichiometry of 1:1 for nitrate and 1:2 for chloride and perchlorate as counteranions, irrespective of the molar proportions of starting materials.

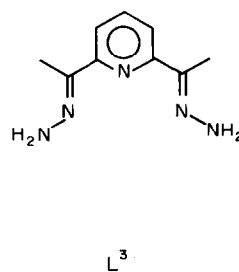
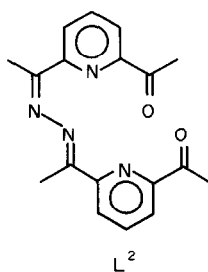
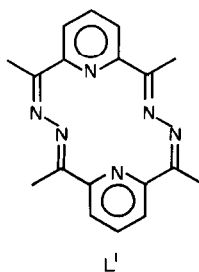


Table 1 reports analytical data of the compounds.

#### Measurements

These were as previously described.<sup>2</sup>

## RESULTS AND DISCUSSION

The 14-membered hexaaza-macrocyclic complex of yttrium has been prepared via template condensation of 2,6-diacetylpyridine with hydrazine in the presence of Y(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O in the ratio of reactants 1:1:2. Less than the stoichiometric amounts of 2,6-diacetylpyridine and hydrazine were required to prevent the formation of 2,6-diacetylpyridinedihydrazone. The formulation of this complex as [YL<sup>1</sup>(NO<sub>3</sub>)<sub>3</sub>]·2H<sub>2</sub>O follows from spectral data (IR, UV-vis, <sup>1</sup>H NMR and MS) and thermal and elemental analysis. The complex is a yellow air-stable solid, soluble in CH<sub>3</sub>CN and DMSO.

The IR spectrum of this complex in the 4000–200 cm<sup>-1</sup> region confirms the formation of the macrocyclic compound by the absence of uncondensed functional group (NH<sub>2</sub>, C=O) stretching modes of starting materials and the appearance of a strong absorption band at 1620 cm<sup>-1</sup>, attributable to the coordinated C=N stretching frequencies. The high and low energy pyridine bands are observed at 1575, 1460, 630 and 420 cm<sup>-1</sup> suggesting coordination of pyridine.<sup>5</sup> A broad diffuse band of strong intensity in the 3700–3200 cm<sup>-1</sup> region may be assigned to the O—H stretching vibration for lattice water. The

absorption characteristic of coordinated water does not appear. The thermogravimetric analysis confirms this observation indicating the loss of two molecules of water at 40–70°C.

The IR spectrum of this complex demonstrates the presence of coordinated nitrates. The band characteristic of ionic nitrates at 1390  $\text{cm}^{-1}$  does not appear. The two new bands associated with the asymmetric stretch appear near 1320 and 1495  $\text{cm}^{-1}$ . The magnitude of the separation (175  $\text{cm}^{-1}$ ) is typical of bidentate bonding of the nitrates.<sup>6</sup>

The electronic spectra of acetonitrile solution of the complex exhibit bands at *ca* 268 and 333 nm, attributable to the  $\pi \rightarrow \pi^*$  transitions of coordinated macrocycle.

The  $^1\text{H}$  NMR spectrum of the yttrium complex of  $L^1$  obtained in  $\text{DMSO-d}_6$  solution shows the pyridine protons at  $\delta$  7.9–8.2 and methyl protons at  $\delta$  2.28 and 2.56. The integrated relative intensities are in good agreement with the required ratio 1 : 1 : 1, consistent with the proposed formulation of this complex.

The mass spectrum of this complex provides strong evidence for the presence of a macrocyclic compound showing the highest fragment at  $m/z$  318, corresponding to the molecular weight of the uncoordinated macrocycle.

On the basis of the spectral data and thermogravimetric analysis, along with molecular model inspection, it seems reasonable to assign the tentative coordination number of 10 for the yttrium ion in this complex. The metal ion is presumably coordinated to the four nitrogen atoms of the hexaaza 14-membered macrocycle and to oxygen atoms of three bidentate nitrate groups. The synthesis and crystal structure of the 12-membered crown ether complex of yttrium nitrate with such a high coordination number was recently reported.<sup>7</sup>

Attempts to prepare this macrocyclic compound with the aid of yttrium chloride or perchlorate was unsuccessful. In the reactions in which 2,6-diacetylpyridine was allowed to react with hydrazine in the presence of yttrium chloride or perchlorate, the ring closure did not occur. Instead, the ring-opened complexes of (6-acetylpyrid-2-yl)methyl ketone azine ( $L^2$ ) were formed. The complexes are yellow solids, moderately soluble in acetonitrile. They have the composition  $[\text{YL}^2(\text{H}_2\text{O})_2]\text{Cl}_3 \cdot 2\text{H}_2\text{O}$  and  $[\text{YL}^2(\text{H}_2\text{O})_2](\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$ .

It should be noted, here, that ligand  $L^2$  appears to be identical with the compound isolated earlier, as an intermediate in the preparative route to the free  $L^1$  macrocycle.<sup>8</sup>

The IR spectra of the two complexes of  $L^2$  are very similar and analysed similarly to that of the free ligand. The band characteristic of the  $\text{C}=\text{N}$

stretching mode, indicating the partial condensation reaction, is shifted by *ca* 30  $\text{cm}^{-1}$  from 1600  $\text{cm}^{-1}$  in the free ligand to lower frequencies, suggesting the coordination by the nitrogen atom. The profile of the pyridine ring vibration observed in the 1600–1400  $\text{cm}^{-1}$  region and the strong band at 1000  $\text{cm}^{-1}$  are characteristic of coordinated pyridine. An important feature is the occurrence of the medium absorption bands at 1700 and 1670  $\text{cm}^{-1}$ , assigned to the  $\text{C}=\text{O}$  stretching modes. In the IR spectrum of the free ligand this absorption appears at 1695  $\text{cm}^{-1}$ . The shift of this band to lower frequencies in the complexes indicates the coordination through the oxygen atom. The position of the other  $\text{C}=\text{O}$  band at a slightly higher frequency than in the free ligand suggests that one of the two carbonyl groups remain uncoordinated.

The  $^1\text{H}$  NMR spectra of these complexes in acetonitrile- $\text{d}_3$  solution confirm this observation. The appearance of two methyl proton signals of the  $\text{CH}_3\text{CO}$  groups at  $\delta$  2.72 and 2.85, instead of one signal observed at  $\delta$  2.72 for the free ligand, and the small downfield shift of the  $\text{CH}_3\text{CN}$  methyl and pyridine proton resonances from  $\delta$  2.4 and 7.7–8.3, respectively, in the free azine to  $\delta$  2.45 and 7.9–8.4 in the complexes, is assumed to be a consequence of coordination of the ligand to the yttrium ion through the three nitrogen donor atoms and one oxygen atom of the two carbonyl groups.<sup>9</sup>

The presence of uncoordinated perchlorates is inferred from the absence of the degenerate stretching and bending modes of  $\text{ClO}_4^-$  at 1100  $\text{cm}^{-1}$ . A broad diffuse band in the 3500–3200  $\text{cm}^{-1}$  region and weak absorptions at 860 and 540  $\text{cm}^{-1}$  suggest the presence of lattice and coordinated water. This is supported by the results of the thermogravimetric analysis, which indicates a loss of two molecules of water at 35–65°C and two water molecules at 140–190°C for these complexes.

The electronic spectra of yttrium chloride and perchlorate complexes of  $L^2$ , for solutions in acetonitrile, consist of three bands at 238–240, 258–262 and 296–300 nm. The differences in the spectra of the complexes and free ligand can be attributed to changes in energy levels of the ligand orbitals on coordination.

The tentative coordination number of six is proposed for podate yttrium chloride and perchlorate complexes of (6-acetylpyrid-2-yl)methyl ketone azine. The coordination sphere is filled by the tetradentate NNNO donor ligand with sufficient interaction of two water molecules.

The failure of the 2,6-diacetylpyridine and hydrazine system to undergo complete condensation and cyclization, in the presence of yttrium chloride and perchlorate, is presumably attributed to the greater

flexibility of the podands than coronands and to the different complexing properties of the counterions involved in the template synthesis. The nitrate ions, contrary to the chlorides and perchlorates, are known to be very good complexing agents towards the rare earth elements. The yttrium ion has therefore been found to be effective for the synthesis of the 14-membered hexaaza-macrocyclic ligand, but the interaction between the metal ion and the counteranion seems to play the decisive role in the stabilization of the macrocyclic complex.

In addition to the ring-closed and ring-opened complexes discussed above, a small number of 2,6-diacetylpyridine (L) complexes were isolated from the reactions of 2,6-diacetylpyridine with hydrazine in the presence of yttrium nitrate, chloride and perchlorate in the reactant ratio 1 : 1 : 2. They are yellow microcrystalline compounds, soluble in polar solvents. The complexes have the compositions  $[\text{YL}(\text{NO}_3)_3] \cdot 2\text{H}_2\text{O}$ ,  $[\text{YL}_2(\text{H}_2\text{O})_2]\text{Cl}_3 \cdot 2\text{H}_2\text{O}$  and  $[\text{YL}_2(\text{H}_2\text{O})_2](\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$ .

The evidence for the coordination of the carbonyl oxygen atoms and pyridine nitrogen atom to the yttrium ion comes from the IR and  $^1\text{H}$  NMR spectra of the complexes.

The most diagnostic feature is the shifting of the  $\text{C}=\text{O}$  absorption band to lower wavenumbers by about  $40\text{ cm}^{-1}$  relative to the ligand ( $1700\text{ cm}^{-1}$ ), resulting from a decrease in the  $\text{C}=\text{O}$  double bond character owing to coordination. The band assigned to the pyridine ring vibrations are shifted to higher frequencies, which is a good indication of the coordination of the heterocyclic nitrogen atom.

The signals of methyl protons at  $\delta$  2.75 and pyridine protons at  $\delta$  8.18 observed in the  $^1\text{H}$  NMR spectrum of 2,6-diacetylpyridine appear at  $\delta$  2.88–2.90 and  $\delta$  8.2–8.6 in the spectra of yttrium complexes.

The IR spectra of the complexes indicate the presence of ionic perchlorate and chloride (unsplit band at  $1100\text{ cm}^{-1}$  and absence of the band at *ca*  $230\text{ cm}^{-1}$  characteristic of  $\text{Ln}-\text{Cl}$  interaction) and coordinated bidentate nitrato groups (bands at  $1310$  and  $1465\text{ cm}^{-1}$ ).

The absorptions characteristic of lattice water at  $3700$ – $3200\text{ cm}^{-1}$  occur in the IR spectra of nitrate, chloride and perchlorate complexes of yttrium. In addition, in the spectrum of the nitrate complex, a weak absorption is found at *ca*  $880$  and  $540\text{ cm}^{-1}$  as expected for coordinated water. The thermogravimetric analysis confirms this observation indicating the loss of two molecules of water at  $40$ – $80^\circ\text{C}$  for all the complexes and, additionally, in the case of the chloride and perchlorate complexes, the loss of two water molecules at  $150$ – $190^\circ\text{C}$ .

Treatment of the yttrium complexes of L with

hydrazine in ethanol at  $75^\circ\text{C}$  for 24 h leads to isolation of the  $\text{L}^1$  complex of yttrium nitrate and  $\text{L}^2$  complexes of yttrium chloride and perchlorate. Thus the yttrium complexes of 2,6-diacetylpyridine are regarded as possible intermediates in the partial or total condensation reaction leading to the formation of coronate  $\text{L}^1$  or podate  $\text{L}^2$  complexes. The coordination of the metal ion to the pyridine nitrogen and the two oxygen atoms of the carbonyl groups makes the carbonyl more susceptible to nucleophilic attack by the hydrazine nitrogen atom.

From the reaction of yttrium nitrate, chloride and perchlorate with 2,6-diacetylpyridine and hydrazine in 1 : 1 : 2, 1 : 2 : 4 and 1 : 3 : 6 molar ratios of starting materials, the yellow air-stable complexes of 2,6-diacetylpyridinedihydrazone ( $\text{L}^3$ ) were isolated. They are formulated as  $[\text{YL}^3(\text{NO}_3)_3] \cdot 2\text{H}_2\text{O}$ ,  $[\text{YL}^3]\text{Cl}_3 \cdot 2\text{H}_2\text{O}$  and  $[\text{YL}^3](\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$ .

The IR spectra of these complexes were analysed in comparison with that of the free ligand, which was prepared and described previously.<sup>10</sup> These three complexes all give very similar spectra except for anion and water vibrational modes, but they are different from the spectra of the free ligand. The  $\text{C}=\text{N}$  absorption band observed in the spectrum of the ligand at  $1600\text{ cm}^{-1}$  is shifted by  $50$ – $60\text{ cm}^{-1}$  to lower wavenumbers upon complexation, suggesting the involvement of the nitrogen lone pair in coordination with the yttrium ion. The  $\text{N}-\text{N}$  frequency found at  $1150\text{ cm}^{-1}$  in the free ligand, increased by  $50\text{ cm}^{-1}$  in the complexes. It may be explained by the coordination of one of the nitrogen atoms from each  $\text{N}-\text{N}$  bond to the metal.<sup>11</sup> Bonding of the pyridine nitrogen atom is shown by the increase in frequency of higher and lower energy pyridine ring vibrations ( $1570$ ,  $950$ ,  $640$ ,  $400\text{ cm}^{-1}$ ) by about  $20$ – $45\text{ cm}^{-1}$  in the complexes. The non-bonding of the  $\text{NH}_2$  nitrogen atom is confirmed by the persistence of the  $\text{NH}_2$  vibration occurring at  $1635\text{ cm}^{-1}$  in the free ligand, and the shifting of the antisymmetric and symmetric stretching vibrations of the  $\text{NH}_2$  groups from  $3360$  and  $3200\text{ cm}^{-1}$  to higher frequencies in the metal complexes. The weak absorption band at  $375$ – $385\text{ cm}^{-1}$  may be assigned to the metal–nitrogen stretching vibrations.

The  $^1\text{H}$  NMR spectra of these complexes indicate the bonding mode discussed above, showing a small downfield shift of the methyl and pyridine proton resonances from  $\delta$  2.25 and 7.82, respectively, in the free ligand, to  $\delta$  2.32–2.38 and  $\delta$  8.12–8.25 in the complexes.

The broad diffuse band in the  $3600$ – $3500\text{ cm}^{-1}$  region is observed for all these complexes and is assigned to the stretching and bending modes for lattice water. The thermogravimetric analysis in-

dicates for yttrium complexes of 2,6-diacetylpyridinedihydrazone, loss of two molecules of water at 30–60°C.

The spectra of the chloride and perchlorate complexes of  $L^3$  do not show absorption bands characteristic of coordinated counterions. An IR absorption attributable to the  $ClO_4^-$  anion occurs as unsplit bands at 1100 and 626  $cm^{-1}$ . The spectrum of the yttrium nitrate complex of  $L^3$  indicates the presence of the nitrate groups coordinating in a bidentate fashion by the appearance of two bands at 1310 and 1480  $cm^{-1}$ , instead of one band at 1390  $cm^{-1}$  typical for ionic nitrates.

The electronic spectra of  $L^3$  complexes of yttrium recorded in acetonitrile, show similar features and contain intense and medium absorption bands with maxima at 285–287 nm and 352–360 nm. The free ligand shows an intense band at 273 nm with a shoulder at 305 nm. The differences between the spectra of the complexes and free ligand can be attributed to the metal–ligand interaction.

On the basis of available evidence, it can be concluded that 2,6-diacetylpyridinedihydrazone acts as a terdentate NNN donor ligand. The stoichiometry of the complexes depends on the type of counterion. The coordination number of six is assigned for the yttrium complex of hydrazone with non-coordinating chlorides and perchlorates, assuming that the coordination sphere is filled by two molecules of ligand. With the small but strongly coordinating nitrates as counterions, the yttrium forms a complex with a 1:1 metal to hydrazone ratio, and the coordination number of nine is achieved by the in-

corporation of three bidentate nitrate groups into the coordination sphere.

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