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# The Synthesis and Characterization of the Macrocyclic and Ring-opened Complexes Formed in the Reaction of the Lanthanides with 2,6-diacetylpyridine and Hydrazine

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*Complexes, $[LnL^1(H_2O)_2](ClO_4)_3 \cdot 4H_2O$, where $L^1$ is 2,5,11,14-tetramethyl-3,4,12,13,19,20-hexaazatricyclo$[13.3.1.1.^{6,10}]$eicosa-1(19),2,4,6,8,10(20),11,13,15,17-decaene and Ln is Tb, Dy, Ho, Er, Tm, Yb or Lu, have been prepared by the condensation of 2,6-diacetylpyridine with hydrazine in the presence of metal-ion templates and characterized by spectral data, thermal and elemental analysis. They are proposed to have six-coordinate and octahedral geometry with four nitrogen donor atoms occupying the equatorial plane and two water molecules in the axial positions. In contrast, analogous reactions involving the lighter lanthanides yield ring-opened complexes $[LnL^2_2](ClO_4)_3 \cdot 2H_2O$, where $L^2$ is (6-acetyl-pyrid-2-yl)methyl ketone azine, Ln is La, Pr, Nd or Sm and $[LnL^2(H_2O)_2](ClO_4)_3 \cdot 2H_2O$, where Ln is Eu or Gd. In addition to the above major products small amounts of lanthanide complexes of 2,6-diacetylpyridine ($L^3$) have been isolated from the reaction and identified by spectral, thermal, and elemental analysis. These complexes are formulated as $[LnL^3_4](ClO_4)_3 \cdot 2H_2O$, where Ln is La, Pr, Nd or Sm, $[LnL^3_3(H_2O)](ClO_4)_3 \cdot 2H_2O$, where Ln is Eu or Gd, and $[LnL^3_3](ClO_4)_3 \cdot 3H_2O$, where Ln is Tb, Dy, Ho, Er, Tm, Yb or Lu.*

*Treatment of $[LnL^1(H_2O)_2](ClO_4)_3 \cdot 4H_2O$ with water yields complexes of the ring-opened ligand $L^2$ of general formula $[LnL^2(H_2O)_2](ClO_4)_3 \cdot 2H_2O$, where Ln is Tb, Dy, Ho, Er, Tm, Yb or Lu.*

## Introduction

The intense interest in synthetic macrocycles and their metal complexes depends on the fact that they may mimic naturally occurring macrocyclic molecules in their structural and functional features and on their rich chemical behavior [1]. The macrocyclic compounds show an extraordinary stability and peculiar ability to selectively bind certain cations in preference to others. The formation of macrocyclic complexes depends significantly on the dimension of the internal cavity, on the rigidity of the macrocycle, on the nature of its donor atoms, and on the complexing properties of the anion involved in the coordination [2]. The syntheses of macrocyclic compounds are generally carried out in the presence of a suitable salt, the cation of which is assumed to act as a template for the ring formation [3].

In previous papers we have described the template syntheses and characterization of magnesium, zinc, and scandium complexes containing 14-membered quadridentate hexaaza macrocyclic ligand [4]. As a continuation of these studies on the effectiveness of metal ions of varying radius and electron configuration in the synthesis of macrocylic compounds we extended investigations to the lanthanides [5].

The coordination of lanthanides by polyoxa and polyaza macrocycles has been little studied until recently [6]. Interest in the exploring of encapsulation of the lanthanide ions by macrocycles like crown ethers and cryptands has continually increased since they can be used for lanthanide separation, for stabilizing Ln(II) oxidation states, and for studying high coordination number of the rare earths [7]. The lanthanum and cerium ions have been found to be effective as templates for the synthesis of 18-membered hexadentate nitrogen donor macrocycles [5, 8]. This type of complexes might be of use as an aqueous nuclear magnetic resonance shift reagent [8]. In recent years the bioinorganic chemistry of the lanthanides has been a research subject. In view of the similarity between the ionic radius of calcium and of the trivalent rare earths and the remarkable multitude of spectroscopic and magnetic properties of the lanthanides they are considered to be useful for probing metal ion binding sites of macromolecules of biological interest including aminoacids, carbohydrates, nucleotides, sugar phosphates, porphyrins, nucleic acids, proteins and enzymes, phospholipides and membranes [9, 10].

In the previous paper we reported the template action of lanthanide ion in the synthesis of a macro-

TABLE I. Yields and Analytical Data for the Lanthanide Complexes of $L^1$.

| Complex | Yield % | Calculated |  |  | Found |  |  |
|---|---|---|---|---|---|---|---|
|  |  | %C | %H | %N | %C | %H | %N |
| $[TbL^1(H_2O)_2](ClO_4)_3 \cdot 4H_2O$ | 42 | 24.44 | 3.42 | 9.51 | 24.21 | 3.26 | 9.38 |
| $[DyL^1(H_2O)_2](ClO_4)_3 \cdot 4H_2O$ | 44 | 24.34 | 3.41 | 9.47 | 24.18 | 3.32 | 9.41 |
| $[HoL^1(H_2O)_2](ClO_4)_3 \cdot 4H_2O$ | 45 | 24.28 | 3.40 | 9.44 | 24.36 | 3.34 | 9.31 |
| $[ErL^1(H_2O)_2](ClO_4)_3 \cdot 4H_2O$ | 43 | 24.21 | 3.39 | 9.42 | 24.32 | 3.48 | 9.61 |
| $[TmL^1(H_2O)_2](ClO_4)_3 \cdot 4H_2O$ | 48 | 24.18 | 3.38 | 9.40 | 24.03 | 3.33 | 9.52 |
| $[YbL^1(H_2O)_2](ClO_4)_3 \cdot 4H_2O$ | 55 | 24.06 | 3.37 | 9.36 | 24.25 | 3.41 | 9.21 |
| $[LuL^1(H_2O)_2](ClO_4)_3 \cdot 4H_2O$ | 54 | 24.00 | 3.36 | 9.34 | 23.81 | 3.26 | 9.17 |

TABLE II. Infrared ($cm^{-1}$) and Electronic (nm) Spectral Data for the Lanthanide Complexes of $L^1$.

| Complex | $\nu py$ | $\nu(CN)$ | $\nu(ClO_4^-)$ | $\nu(OH)$ | $\lambda$ |
|---|---|---|---|---|---|
| $[TbL^1(H_2O)_2](ClO_4)_3 \cdot 4H_2O$ | 1593, 1458, 630, 423 | 1570 | 1095, 625 | 3390, 865, 560 | 225, 255, 293, 315, 370 |
| $[DyL^1(H_2O)_2](ClO_4)_3 \cdot 4H_2O$ | 1596, 1460, 630, 425 | 1570 | 1100, 625 | 3400, 860, 560 | 226, 255, 290, 315, 372 |
| $[HoL^1(H_2O)_2](ClO_4)_3 \cdot 4H_2O$ | 1598, 1463, 630, 425 | 1568 | 1100, 625 | 3400, 860, 558 | 226, 255, 290, 316, 375 |
| $[ErL^1(H_2O)_2](ClO_4)_3 \cdot 4H_2O$ | 1597, 1458, 630, 430 | 1570 | 1090, 625 | 3390, 860, 560 | 228, 255, 293, 315, 380 |
| $[TmL^1(H_2O)_2](ClO_4)_3 \cdot 4H_2O$ | 1593, 1460, 635, 420 | 1565 | 1100, 630 | 3400, 855, 550 | 225, 255, 290, 315, 370 |
| $[YbL^1(H_2O)_2](ClO_4)_3 \cdot 4H_2O$ | 1599, 1455, 635, 428 | 1560 | 1085, 625 | 3410, 860, 560 | 225, 260, 300, 320, 380 |
| $[LuL^1(H_2O)_2](ClO_4)_3 \cdot 4H_2O$ | 1603, 1458, 635, 428 | 1560 | 1085, 625 | 3410, 865, 560 | 220, 260, 290, 315, 370 |

TABLE III. Analytical Data for the Lanthanide Complexes of $L^2$.

| Complex | Calculated |  |  | Found |  |  |
|---|---|---|---|---|---|---|
|  | %C | %H | %N | %C | %H | %N |
| $[LaL^2_2](ClO_4)_3 \cdot 2H_2O$ | 38.65 | 3.61 | 10.03 | 38.72 | 3.67 | 10.06 |
| $[PrL^2_2](ClO_4)_3 \cdot 2H_2O$ | 38.61 | 3.60 | 10.01 | 38.53 | 3.68 | 10.09 |
| $[NdL^2_2](ClO_4)_3 \cdot 2H_2O$ | 38.47 | 3.59 | 9.98 | 38.39 | 3.59 | 9.97 |
| $[SmL^2_2](ClO_4)_3 \cdot 2H_2O$ | 38.26 | 3.57 | 9.92 | 38.21 | 3.68 | 9.89 |
| $[EuL^2(H_2O)_2](ClO_4)_3 \cdot 2H_2O$ | 25.58 | 3.10 | 6.63 | 25.68 | 3.10 | 6.71 |
| $[GdL^2(H_2O)_2](ClO_4)_3 \cdot 2H_2O$ | 25.42 | 3.09 | 6.59 | 25.49 | 2.95 | 6.66 |
| $[TbL^2(H_2O)_2](ClO_4)_3 \cdot 2H_2O$ | 25.37 | 3.08 | 6.58 | 25.41 | 3.03 | 6.56 |
| $[DyL^2(H_2O)_2](ClO_4)_3 \cdot 2H_2O$ | 25.26 | 3.06 | 6.55 | 25.17 | 3.16 | 6.44 |
| $[HoL^2(H_2O)_2](ClO_4)_3 \cdot 2H_2O$ | 25.19 | 3.06 | 6.53 | 25.28 | 3.04 | 6.64 |
| $[ErL^2(H_2O)_2](ClO_4)_3 \cdot 2H_2O$ | 25.12 | 3.05 | 6.52 | 25.09 | 3.12 | 6.57 |
| $[TmL^2(H_2O)_2](ClO_4)_3 \cdot 2H_2O$ | 25.07 | 3.09 | 6.47 | 25.07 | 3.04 | 6.50 |
| $[YbL^2(H_2O)_2](ClO_4)_3 \cdot 2H_2O$ | 24.98 | 3.03 | 6.48 | 24.86 | 3.00 | 6.45 |
| $[LuL^2(H_2O)_2](ClO_4)_3 \cdot 2H_2O$ | 24.93 | 3.02 | 6.46 | 25.01 | 3.04 | 6.41 |

cyclic compound [5]. The present study is concerned with the preparation and characterization of the macrocyclic and open-chain complexes formed in the reaction of the lanthanides with 2,6-diacetylpyridine and hydrazine.

## Experimental

The hydrated lanthanide perchlorates were prepared by dissolving the appropriate 99.99% oxide ($Ln_2O_3$, except for $Pr_6O_{11}$ and $Tb_4O_7$) in a slight

TABLE IV. Infrared (cm$^{-1}$) and Electronic (nm) Spectra of (6-acetyl-pyrid-2-yl)methyl Ketone Azine (L$^2$) and Its Complexes with Lanthanides.

| Compound | ν(CO) | ν(CN) | νpy | ν($ClO_4^-$) | ν(OH) | λ |
|---|---|---|---|---|---|---|
| $L^2$ | 1695 | 1600 | 1570, 1440, 1400, 593, 405 | | | 232, 288 |
| $[LaL_2^2](ClO_4)_3 \cdot 2H_2O$ | 1697, 1670 | 1575 | 1617, 1455, 1425, 630, 420 | 1080, 620 | 3400 | 235, 255, 292 |
| $[PrL_2^2](ClO_4)_3 \cdot 2H_2O$ | 1700, 1675 | 1570 | 1617, 1460, 1430, 630, 420 | 1080, 620 | 3420 | 238, 258, 295 |
| $[NdL_2^2](ClO_4)_3 \cdot 2H_2O$ | 1700, 1670 | 1572 | 1612, 1460, 1435, 635, 420 | 1100, 622 | 3400 | 238. 260, 298 |
| $[SmL_2^2](ClO_4)_3 \cdot 2H_2O$ | 1697, 1670 | 1575 | 1615, 1460, 1430, 632, 420 | 1080, 622 | 3420 | 236, 258, 297 |
| $[EuL^2(H_2O)_2](ClO_4)_3 \cdot 2H_2O$ | 1700, 1665 | 1570 | 1615, 1465, 1440, 633, 425 | 1090, 622 | 3400, 860, 555 | 235, 260, 300 |
| $[GdL^2(H_2O)_2](ClO_4)_3 \cdot 2H_2O$ | 1700, 1660 | 1565 | 1615, 1460, 1430, 635, 425 | 1100, 620 | 3400, 865, 550 | 238, 260, 300 |
| $[TbL^2(H_2O)_2](ClO_4)_3 \cdot 2H_2O$ | 1700, 1663 | 1565 | 1617, 1458, 1428, 632, 423 | 1100, 620 | 3400, 868, 552 | 239, 258, 298 |
| $[DyL^2(H_2O)_2](ClO_4)_3 \cdot 2H_2O$ | 1700, 1664 | 1568 | 1615, 1460, 1428, 635, 423 | 1095, 625 | 3420, 865, 550 | 239, 257, 297 |
| $[HoL^2(H_2O)_2](ClO_4)_3 \cdot 2H_2O$ | 1700, 1660 | 1565 | 1615, 1463, 1430, 632, 420 | 1100, 625 | 3400, 865, 550 | 240, 257 296 |
| $[ErL^2(H_2O)_2](ClO_4)_3 \cdot 2H_2O$ | 1700, 1661 | 1564 | 1617, 1463, 1433, 635, 420 | 1080, 625 | 3420, 867, 550 | 238, 255, 295 |
| $[TmL^2(H_2O)_2](ClO_4)_3 \cdot 2H_2O$ | 1698, 1660 | 1565 | 1619, 1465, 1430, 635, 425 | 1080, 625 | 3400, 865, 550 | 239, 258, 297 |
| $[YbL^2(H_2O)_2](ClO_4)_3 \cdot 2H_2O$ | 1699, 1658 | 1563 | 1620, 1463, 1435, 635, 425 | 1100, 625 | 3420, 867, 552 | 240, 258, 299 |
| $[LuL^2(H_2O)_2](ClO_4)_3 \cdot 2H_2O$ | 1700, 1655 | 1563 | 1615, 1460, 1430, 635, 420 | 1100, 625 | 3420, 865, 550 | 240, 260, 300 |

excess of 70% perchloric acid. The solutions were evaporated on a water bath until crystalline precipitates formed; they were filtered off and recrystallized from methanol.

### *Preparation of Tb, Dy, Ho, Er, Tm, Yb and Lu complexes of L$^1$ and of La, Pr, Nd, Sm, Eu and Gd complexes of L$^2$. General procedure*

A mixture of metal salt (4 mmol) in ethanol (50 ml) and 2,6-diacetylpyridine (2 mmol) in ethanol (25 ml) was heated at 80 °C under reflux with stirring. To this solution, hydrazine (2 mmol) in ethanol (25 ml) was added dropwise. Less than the stoichiometric amounts of 2,6-diacetylpyridine and hydrazine are required to prevent the formation of 2,6-diacetylpyridinedihydrazone. The reaction was carried out for 48 hours. The small amount of microcrystalline product, which turned out to be the lanthanide complex of 2,6-diacetylpyridine was removed by filtration. The filtrate volume was then reduced to 15 ml by rotoevaporation. The precipitates formed on cooling the solution or by addition of small amounts of anhydrous diethyl ether; they were filtered off, washed with ether, and dried under vacuum over $P_2O_5$.

### *Preparation of Tb, Dy, Ho, Er, Tm, Yb and Lu complexes of L$^2$. General procedure*

The appropriate lanthanide perchlorate complex of L$^1$ (0.2 mmol) was dissolved in hot acetonitrile (30 ml). To this solution water (10 ml) was added. The resulting yellow precipitate was filtered, washed with ether, and dried under vacuum over $P_2O_5$.

Tables I, III and V report analytical data of the compounds.

### *Measurements*

The infrared spectra were recorded on KBr pellets in the range 4000–300 cm$^{-1}$ using a Perkin-Elmer 580 infrared spectrophotometer. The electronic spectra were measured on a Beckman 25 spectrophotometer. The diffuse reflectance spectra of the solids were determined on a Unicam SP 700 ultraviolet and visible spectrophotometer fitted with SP 735 reflectance attachment. The nuclear magnetic resonance spectra were run on a Varian EM-360 60 MHz spectrometer for solutions in acetonitrile-d$_3$ (except for the compound L$^2$ in deuteriochloroform) using tetramethylsilane as the internal standard. Thermogravimetric measurements were performed using the Derivatograph OD-102, MOM.

## Results and Discussion

The 14-membered hexaaza macrocyclic complexes of heavier lanthanides have been prepared via template condensation of 2,6-diacetylpyridine with

TABLE V. Analytical Data for the Lanthanide Complexes of $L^3$.

| Complex | Calculated | | | Found | | |
|---|---|---|---|---|---|---|
| | %C | %H | %N | %C | %H | %N |
| $[LaL^3_4](ClO_4)_3 \cdot 2H_2O$ | 38.36 | 3.67 | 4.98 | 38.33 | 3.71 | 4.96 |
| $[PrL^3_4](ClO_4)_3 \cdot 2H_2O$ | 38.32 | 3.58 | 4.97 | 38.51 | 3.67 | 4.98 |
| $[NdL^3_4](ClO_4)_3 \cdot 2H_2O$ | 38.19 | 3.56 | 4.95 | 38.44 | 3.41 | 5.12 |
| $[SmL^3_4](ClO_4)_3 \cdot 2H_2O$ | 37.98 | 3.54 | 4.92 | 37.92 | 3.48 | 4.79 |
| $[EuL^3_3(H_2O)](ClO_4)_3 \cdot 2H_2O$ | 32.60 | 3.35 | 4.23 | 32.71 | 3.37 | 4.25 |
| $[GdL^3_3(H_2O)](ClO_4)_3 \cdot 2H_2O$ | 32.43 | 3.33 | 4.21 | 32.40 | 3.16 | 3.94 |
| $[TbL^3_3](ClO_4)_3 \cdot 3H_2O$ | 32.37 | 3.32 | 4.20 | 32.32 | 3.29 | 4.18 |
| $[DyL^3_3](ClO_4)_3 \cdot 3H_2O$ | 32.26 | 3.31 | 4.18 | 32.09 | 3.27 | 4.05 |
| $[HoL^3_3](ClO_4)_3 \cdot 3H_2O$ | 32.18 | 3.30 | 4.17 | 32.13 | 3.30 | 4.24 |
| $[ErL^3_3](ClO_4)_3 \cdot 3H_2O$ | 32.10 | 3.30 | 4.16 | 32.02 | 3.33 | 4.20 |
| $[TmL^3_3](ClO_4)_3 \cdot 3H_2O$ | 32.05 | 3.29 | 4.16 | 32.09 | 3.25 | 4.13 |
| $[YbL^3_3](ClO_4)_3 \cdot 3H_2O$ | 31.92 | 3.28 | 4.14 | 32.01 | 3.27 | 4.16 |
| $[LuL^3_3](ClO_4)_3 \cdot 3H_2O$ | 31.85 | 3.27 | 4.13 | 31.84 | 3.15 | 4.04 |

hydrazine in the presence of the metal perchlorate. The complexes are yellow air stable compounds, moderately soluble in $CH_3CN$ and DMSO and insoluble in other common organic solvents.

The infrared spectra of the complexes $[LnL^1(H_2O)_2](ClO_4)_3 \cdot 4H_2O$, where Ln = Tb to Lu (Table II), are all very similar to one another and provide some information regarding the bonding in the complexes. The absence of any bands which might be assigned to the $-NH_2$ or C=O stretching frequencies and the appearance of a strong band at 1560–1570 $cm^{-1}$ which is attributed to the coordinated $>$C=N stretching mode suggest the formation of a macrocyclic compound [11]. All the spectra exhibit medium to strong bands at 1593–1603 $cm^{-1}$ and 1455–1463 $cm^{-1}$ as expected for the two high energy pyridine ring vibrations. The low frequency pyridine modes are observed at 630–635 $cm^{-1}$ and 423–430 $cm^{-1}$ suggesting the coordination of pyridine nitrogen [12].

Infrared absorptions attributable to the anion $ClO_4^-$ occur as unsplit bands at *ca.* 1100 $cm^{-1}$ and 625 $cm^{-1}$ as expected for these anions in the ionic state [13]. Perchlorate anions are known to coordinate under special conditions, but such interactions normally manifest themselves by a splitting of the antisymmetric Cl–O stretching mode due to reduced symmetry of the coordinated species. No such splitting of the $ClO_4^-$ absorption band at 1100 $cm^{-1}$ was observed.

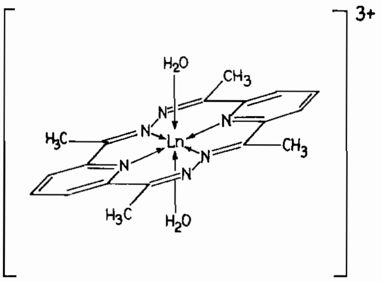
All the complexes of $L^1$ show the broad diffuse band centered at *ca.* 3400 $cm^{-1}$ due to the stretching and bending modes of water. In addition, weak bands are detectable at around 860 and 560 $cm^{-1}$, which may be assigned to rocking or wagging modes of water molecules coordinated to the metal ions [14, 15].

The thermogravimetric analysis indicates for lanthanide perchlorate complexes of $L^1$ loss of four molecules of water at 30–60 °C and two water molecules at 140–180 °C.

Electronic spectra of the solid complexes of $L^1$ and their acetonitrile solutions were taken in the range 220–700 nm. The complexes in the solid state exhibit closely similar spectra to those of their acetonitrile solutions. This observation may suggest, in agreement with other data, that axial ligands are water molecules [15].

The nuclear magnetic resonance spectrum of the diamagnetic lutetium complex of $L^1$ shows methyl protons of $CH_3\dot{C}{=}N{-}$ groups at $\delta$ 2.28 and 2.6 and pyridine protons at $\delta$ 7.7–8.3. The integrated relative intensities are in good agreement with the required ratio 1:1:1, consistent with the proposed formulation of this complex.

All these data along with molecular model analysis constitute evidence for the presence of 14-membered hexaaza $L^1$ macrocycle in the complexes of trivalent ions of Tb, Dy, Ho, Er, Tm, Yb and Lu and for its function as quadridentate ligand. A tentative coordination number of six in these complexes can be assigned. It seems therefore reasonable to assume that these complexes of general formula $[LnL^1(H_2O)_2]^{3+}$ have a six-coordinate octahedral structure (I) with the four nitrogen donor atoms of macrocycle occupying the equatorial plane and the axial position being filled with water. This structure is highly stabilized by the formation of two five- and two six-membered chelate rings upon coordination. The inner ring of the macrocycle is fully conjugated and incorporates

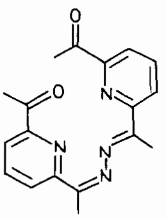


I

(4n + 2)π electrons satisfying the Hückel criterion, and is therefore expected to be planar.

Under the same reaction conditions the lighter lanthanides have found to be ineffective as templates for the synthesis of this 14-membered macrocycle. In the reactions in which the 2,6-diacetylpyridine is allowed to react with hydrazine in the presence of trivalent ions of La, Pr, Nd, Sm, Eu or Gd the ring closure does not occur. Instead, the ring-opened complexes of (6-acetyl-pyrid-2-yl)methyl ketone azine ($L^2$) (II) are formed. Similar complexes of the heavier lanthanides (Tb to Lu) can be obtained by treatment of the $L^1$ complexes with water. They do not undergo further hydrolysis. The complexes are yellow air stable solids, moderately soluble in acetonitrile. They have the composition $[\mathrm{LnL}^2_2](\mathrm{ClO_4})_3 \cdot 2\mathrm{H_2O}$ for Ln = La to Sm, and $[\mathrm{LnL_2}(\mathrm{H_2O})_2](\mathrm{ClO_4})_3 \cdot 2\mathrm{H_2O}$ for Ln = Eu to Lu.

II



It should be noted here that free (6-acetyl-pyrid-2-yl)methyl ketone azine is an intermediate in the preparative route to the free $L^1$ macrocycle and was isolated in the manner described earlier [4].

The infrared spectra of the $L^2$ complexes of the lanthanides (Table IV) are very similar except for water vibration modes indicating the presence of the same ligand throughout the series. The most diagnostic absorption band is the C=N stretching mode indicating the partial condensation reaction. This band observed in the spectrum of the ligand at 1600 $cm^{-1}$ is shifted to lower frequencies by 25–37 $cm^{-1}$ upon complex formation suggesting that the double bond character of C=N decreases as a consequence of the coordination by nitrogen [16]. An important feature common to all $L^2$ complexes is the occurrence of two medium absorption bands at 1697–1700 $cm^{-1}$ and 1655–1675 $cm^{-1}$ assigned to C=O stretching vibration. In the infrared spectrum of the free ligand this vibration appears at 1695 $cm^{-1}$. The shift of this band to lower frequency in the complexes clearly indicates coordination through the oxygen atom [17, 18]. The position of the other νC=O band at a slightly higher frequency than in the free ligand suggests that one of the two carbonyl groups remains uncoordinated [19]. Bonding of the pyridine ring is shown by the increase in the frequency of the higher and lower energy pyridine ring vibrations by about 15–50 $cm^{-1}$ in the complexes relative to the ligand. Such changes indicate the coordination of pyridine nitrogen [12, 20]. All infrared spectra show a very strong band around 1100 $cm^{-1}$ and another band at *ca.* 625 $cm^{-1}$; neither of each has undergone any splitting, indicating the presence of ionic perchlorate. The νOH band appears in all complexes as a broad absorption at *ca.* 3400 $cm^{-1}$. Additionally, the complexes of Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu show bands at *ca.* 550 $cm^{-1}$ and 860 $cm^{-1}$ assigned to rocking and wagging modes of coordinated water. The presence of water bound in two different ways is supported by the results of a thermogravimetric analysis. In the case of La, Pr, Nd and Sm perchlorate complexes of $L^2$ the loss of two molecules of water is observed at 50–80 °C, whereas the complexes of Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu indicate the loss of two water molecules at 40–70 °C and two molecules of water at 150–200 °C.

The electronic spectra of lanthanide complexes of (6-acetyl-pyrid-2-yl)methyl ketone azine taken in the range 220–700 nm for solution in acetonitrile consist of three bands at 235–240 nm, 255–260 nm and 292–300 nm. The free ligand exhibits two bands at 232 and 288 nm. The differences in the spectra can be attributed to changes in energy levels of the ligand orbitals in coordination [16].

The nuclear magnetic resonance spectra of the ligand $L^2$ and its diamagnetic lanthanum and lutetium complexes afford further information on the mode of coordination. The $^1H$ n.m.r. spectrum of (6-acetyl-pyrid-2-yl)methyl ketone azine shows methyl protons of $CH_3-\overset{|}{C}=N-$ groups at δ 2.4, methyl protons of $CH_3-\overset{|}{C}=O$ groups at δ 2.72 and pyridine protons at δ 7.7–8.3. Integrated intensities of the above signals are in the ratio 1:1:1. In the $^1H$ n.m.r. spectra of lanthanum and lutetium complexes of $L^2$ the methyl protons of $CH_3-\overset{|}{C}=N-$ groups occur as broad signals centered at δ 2.43 (for La) and δ 2.45 (for Lu). The methyl protons of $CH_3-\overset{|}{C}=O$ groups are observed at δ 2.72 and δ 2.83 (for La) and δ 2.72 and δ 2.85 (for Lu). The integrated relative intensities are in good agreement with the required ratios. The appearance of two signals assigned to methyl protons attached to carbonyl groups instead of one signal observed in the spectrum of free $L^2$ ligand may suggest that one of the two carbonyl groups is uncoordinated to the metal ion and remains unchanged. A downfield shift of the proton resonances in the diamagnetic complexes compared to the ligand itself is assumed to be a consequence of coordination of the ligand to the metal ion through three nitrogen donor atoms and the oxygen atom of one of the two carbonyl groups [21, 22].

On the basis of available evidence a tentative coordination number of eight in the La, Pr, Nd and Sm complexes of (6-acetyl-pyrid-2-yl)methyl ketone azine and six in the heavier lanthanide (Eu to Lu) complexes can be assigned. In the complexes of La, Pr, Nd and Sm the metal and the $L^2$ ligand are in the ratio 1:2. The heavier lanthanides form 1:1 (metal:ligand) complexes and the coordination number of six is achieved by incorporation of two water molecules in the coordination sphere. The decrease in the metal:ligand ratio for heavier lanthanides is clearly a consequence of decrease in ionic radii due to the lanthanide contraction.

The failure of La, Pr, Nd, Sm, Eu and Gd systems to undergo complete cyclization is presumably attributed to the larger radius of these ions compared to the heavier lanthanides which are found to be effective in the template synthesis of 14-membered $L^1$ macrocycle. Examination of molecular models of this compound reveals that its cavity is too small to enclose the lighter lanthanides. It is noteworthy that the europium and gadolinum ions, although ineffective as templates in the synthesis of 14-membered macrocyclic compounds, can form the open-chain (6-acetyl-pyrid-2-yl)methyl ketone azine complexes with similar geometry as proposed for the complexes of heavier lanthanides. The open-chain $L^2$ ligand is expected to be more flexible than $L^1$ macrocycle and thus able to coordinate a relatively large metal ion. Being more flexible it can form complexes with different geometries and can adopt itself to the specific features of the coordinated metal ion.

In addition to the ring-opened and ring-closed complexes discussed above, 2,6-diacetylpyridine ($L^3$) complexes of the lanthanides were isolated from reaction of 2,6-diacetylpyridine with hydrazine in the presence of metal ions (see Experimental) and identified by spectral data and thermal and elemental analysis. These complexes appear to be identical with those prepared in the direct synthesis in which the appropriate lanthanide perchlorate reacts with 2,6-diacetylpyridine in refluxing ethanol for 24 hours. Treatment of the lanthanide complexes of $L^3$ with hydrazine in acetonitrile at 65 °C for 20 hours leads to isolation of the $L^2$ complexes of La, Pr, Nd, Sm, Eu and Gd and $L^1$ complexes of Tb, Dy, Ho, Er, Tm, Yb and Lu. Thus the lanthanide complexes of 2,6-diacetylpyridine are regarded as possible intermediates in the formation of macrocyclic $L^1$ and ring-opened $L^2$ complexes. The presence of pyridine group between the two carbonyl functions in 2,6-diacetylpyridine probably assures initial chelation of the metal ion through the pyridine nitrogen and two oxygen atoms. Such a coordination mode makes the carbonyl more susceptible to hydrazine nitrogen donor attack.

The lanthanide complexes of 2,6-diacetylpyridine are yellow microcrystalline compounds soluble in acetonitrile.

The infrared spectra of these complexes (Table VI) are analysed in comparison with that of the free ligand. These data give evidence for the coordination of 2,6-diacetylpyridine to metal ion via carbonyl oxygen atoms and pyridine nitrogen. As is seen in Table VI, The C=O absorption band is shifted to lower wavenumbers by about 23–45 $cm^{-1}$ in all complexes relative to the ligand, resulting from a decrease in C=O double bond character owing to coordination. The bands assigned to the pyridine ring vibrations are shifted to higher frequencies as a good indication of the coordination of the heterocyclic nitrogen. The presence of uncoordinated perchlorates is inferred from the broad band centered at 1100 $cm^{-1}$ and the sharp medium band at 625 $cm^{-1}$. No splitting of Cl–O stretching mode is observed as would be expected for coordinated perchlorate. A broad diffuse band at *ca.* 3400 $cm^{-1}$ is observed in the infrared spectra of all $L^3$ lanthanide complexes and assigned to the O–H stretching modes for lattice water. In addition, in the infrared spectra of Eu and Gd complexes a weak absorption is found at 535 $cm^{-1}$ as expected for coordinated water. The thermogravimetric analysis confirms this observation indicating the loss of two or three molecules of water at 40–90 °C for all the complexes and, additionally, in the case of europium and gadolinium complexes, the loss of one water molecule at 130–200 °C.

Electronic spectra of lanthanide complexes with 2,6-diacetylpyridine in acetonitrile contain four bands at 215–220 nm, 238–240 nm, 277–285 nm, and 313–324 nm. The free ligand shows three bands at 211 nm, 236 nm, and 274 nm. The shift of all three bands and the occurrence of a new band in the complexes relative to the free ligand may be explained by the metal–ligand interaction.

Further evidence for the coordination of the pyridine nitrogen and carbonyl oxygen atoms comes from the nuclear magnetic resonance spectra of 2,6-diacetylpyridine and the diamagnetic complexes of lanthanum and lutetium. The $^1H$ n.m.r. spectrum of 2,6-diacetylpyridine contains the signal of methyl protons at $\delta$ 2.75 and pyridine protons at $\delta$ 8.18. A downfield shift of the proton resonances in the complexes of lanthanum and lutetium to $\delta$ 2.83

TABLE VI. Infrared (cm$^{-1}$) and Electronic (nm) Spectra of 2,6-Diacetylpyridine (L$^3$) and Its Complexes with Lanthanides.

| Compound | $\nu$(CO) | $\nu$py | $\nu$($ClO_4^-$) | $\nu$(OH) | $\lambda$ |
|---|---|---|---|---|---|
| $L^3$ | 1705 | 1580, 1410, 603, 415 | | | 211, 236, 274 |
| $[LaL^3_4](ClO_4)_3 \cdot 2H_2O$ | 1682 | 1585, 1455, 1415, 630, 418 | 1100, 620 | 3430 | 218, 240, 277, 313 |
| $[PrL^3_4](ClO_4)_3 \cdot 2H_2O$ | 1680 | 1585, 1453, 1420, 630, 420 | 1100, 620 | 3400 | 220, 238, 276, 315 |
| $[NdL^3_4](ClO_4)_3 \cdot 2H_2O$ | 1680 | 1585, 1455, 1420, 632, 420 | 1100, 620 | 3400 | 220, 238, 276, 314 |
| $[SmL^3_4](ClO_4)_3 \cdot 2H_2O$ | 1678 | 1585, 1455, 1420, 632, 420 | 1100, 625 | 3400 | 219, 239, 276, 316 |
| $[EuL^3_3(H_2O)](ClO_4)_3 \cdot 2H_2O$ | 1668 | 1598, 1455, 1420, 635, 425 | 1100, 623 | 3400, 535 | 217, 238, 278, 311 |
| $[GdL^3_3(H_2O)](ClO_4)_3 \cdot 2H_2O$ | 1665 | 1598, 1465, 1430, 635, 425 | 1100, 620 | 3400, 535 | 220, 238, 278, 324 |
| $[TbL^3_3](ClO_4)_3 \cdot 3H_2O$ | 1665 | 1597, 1468, 1430, 640, 430 | 1100, 620 | 3420 | 216, 240, 279, 318 |
| $[DyL^3_3](ClO_4)_3 \cdot 3H_2O$ | 1668 | 1598, 1468, 1440, 640, 435 | 1100, 625 | 3400 | 215, 238, 280, 320 |
| $[HoL^3_3](ClO_4)_3 \cdot 3H_2O$ | 1668 | 1598, 1468, 1440, 640, 435 | 1100, 625 | 3400 | 215, 238, 279, 319 |
| $[ErL^3_3](ClO_4)_3 \cdot 3H_2O$ | 1668 | 1599, 1465, 1440, 640, 430 | 1100, 620 | 3400 | 220, 238, 285, 320 |
| $[TmL^3_3](ClO_4)_3 \cdot 3H_2O$ | 1668 | 1598, 1465, 1440, 640, 433 | 1100, 625 | 3420 | 216, 238, 280, 320 |
| $[YbL^3_3](ClO_4)_3 \cdot 3H_2O$ | 1665 | 1605, 1465, 1440, 640, 430 | 1080, 625 | 3400 | 216, 240, 285, 320 |
| $[LuL^3_3](ClO_4)_3 \cdot 3H_2O$ | 1660 | 1600, 1468, 1440, 640, 435 | 1080, 625 | 3420 | 218, 240, 280, 318 |

and $\delta$ 8.2–8.56 and $\delta$ 2.95 and $\delta$ 8.2–8.8, respectively, indicates the bonding mode discussed above.

Changes in coordination number through the series La to Lu are expected to be a result of the lanthanide contraction.

Earlier investigations provide the evidence for the possibility of using the lanthanum ion in promoting the synthesis of macrocyclic ligands with greater ring size [5, 8, 23]. The results discussed in this paper along with our earlier findings lead to the conclusion that the lanthanide ions may act as templates for the synthesis of nitrogen donor atom macrocycles and that the important factor which must be taken into account in the planning of the synthesis of macrocyclic compounds with the aid of metal ion is the ratio of cation diameter to ligand cavity size. The differences in complexing behaviour of the macrocycles observed among the lanthanides may provide the basis for a novel means of separating these closely related metals.

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