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# Lanthanide Complexes of Some Macrocyclic Schiff Bases Derived from Pyridine-2,6-dicarboxaldehyde and α,ω-Primary Diamines

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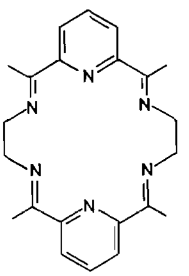
*The synthesis of macrocyclic lanthanide complexes via the reaction of pyridine-2,6-dicarboxaldehyde with 1,2-diaminoethane, 1,2-diaminopropane and 1,3-diaminopropane in the presence of lanthanide nitrates as templating agents is discussed together with the use of the lanthanum derivatives in transmetallation reactions with copper(II).*

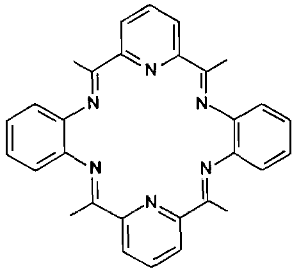
## Introduction

The use of alkaline earth metal cations as templating agents in the synthesis of tetraimine macrocycles derived from 1,1′-(2,6-pyridinediyl)-bis-ethanone (2,6-diacetylpyridine, pda), or pyridine-2,6-dicarboxaldehyde (2,6-diformylpyridine, pdf), and α,ω-primary diamines is now well-established [1]. In such syntheses it has been shown that the ionic potential and the ionic radius of the templating cation are important, particularly in dictating the size of the macrocycle formed. A consideration of both of these factors suggests that lanthanide cations should act as efficient templates and furthermore, through the lanthanide contraction, should act as monitors for any subtle changes in macrocycle formation.

There have been, however, few reports of the use of lanthanides as templating agents in the synthesis of macrocyclic tetraimine ligands. Hart *et al.* [2] and Radecka-Paryzek [3] have shown that pda and 1,2-diaminoethane (en) readily give the 18-membered hexaazamacrocycle (**1**) as its metal complex when La(NO$_3$)$_3$, La(ClO$_4$)$_3$ or Ce(NO$_3$)$_3$ are used as templates, and (**2**) is formed as its metal complex when pda and 1,2-diaminobenzene are reacted in the presence of La(NO$_3$)$_3$ [4]. The heavier lanthanide cations (Tb, Dy, Ho, Er, Tm, Yb, Lu) were found to be effective as templating agents in the synthesis of the smaller 14-membered hexaazamacrocycle, (**3**), from pda and hydrazine; the lighter lanthanide cations here only gave complexes of the acyclic ligand (**4**) [5]. Addition of water to the metal complexes of (**3**) also led to ring-opening. The macrocyclic complexes obtained were all of 1:1 stoichiometry, and had the general formula (m/c)M(anion)$_3$·nH$_2$O.



**1**



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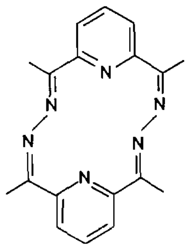

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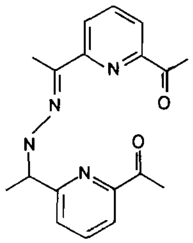
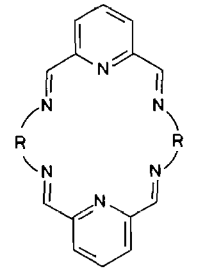


**4**

We report here the synthesis and properties of lanthanide (La$^{+++}$–Lu$^{+++}$, except Pm$^{+++}$) complexes



**5**, R = CH$_2$CH$_2$
**6**, R = CH$_2$CH(CH$_3$)
**7**, R = CH$_2$CH$_2$CH$_2$

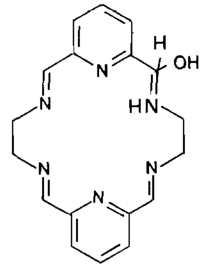


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TABLE I. Microanalytical Data.

| Complex | Required | | | Found | | | Colour |
|---|---|---|---|---|---|---|---|
| | %C | %H | %N | %C | %H | %N | |
| $La(5)(NO_3)_3$ | 33.59 | 2.79 | 19.60 | 33.63 | 2.83 | 19.82 | pale pink |
| $Ce(5)(NO_3)_3$ | 33.56 | 2.76 | 19.57 | 33.70 | 2.88 | 20.05 | yellow |
| $Pr(5)(NO_3)_3$ | 33.48 | 2.76 | 19.50 | 33.44 | 2.85 | 18.84 | white |
| $Nd(5)(NO_3)_3 \cdot H_2O$ | 32.45 | 3.03 | 18.92 | 32.66 | 3.12 | 19.17 | white |
| $Sm(5)(NO_3)_3 \cdot H_2O$ | 32.23 | 2.93 | 18.90 | 33.01 | 2.96 | 19.37 | white |
| $Eu(5)(NO_3)_3 \cdot H_2O$ | 32.04 | 2.96 | 18.69 | 32.31 | 3.07 | 18.90 | milky |
| $Gd(5)(NO_3)_3 \cdot H_2O$ | 31.81 | 2.94 | 18.55 | 32.01 | 3.03 | 18.74 | white |
| $Tb(5)(NO_3)_3 \cdot 2H_2O$ | 30.90 | 3.14 | 17.99 | 30.81 | 3.04 | 17.59 | white |
| $Dy(5)(NO_3)_3 \cdot H_2O$ | 31.48 | 2.92 | 18.35 | 31.40 | 3.15 | 17.99 | white |
| $Ho(5)(NO_3)_3 \cdot 2H_2O$ | 30.63 | 3.12 | 17.89 | 30.68 | 3.10 | 18.26 | white |
| $Er(5)(NO_3)_3 \cdot 2H_2O$ | 30.55 | 3.11 | 17.82 | 30.84 | 3.19 | 17.75 | white |
| $Tm(5)(NO_3)_3 \cdot 2H_2O$ | 30.46 | 3.10 | 17.75 | 30.51 | 3.27 | 17.05 | white |
| $Yb(5)(NO_3)_3 \cdot 2H_2O$ | 30.29 | 3.08 | 17.65 | 30.38 | 2.84 | 17.07 | white |
| $Lu(5)(NO_3)_3 \cdot 4H_2O$ | 28.73 | 3.36 | 16.78 | 28.21 | 2.85 | 16.81 | white |
| $La(6)(NO_3)_3 \cdot 2H_2O$ | 33.91 | 3.39 | 17.80 | 33.74 | 3.25 | 16.83 | pale pink |
| $Ce(6)(NO_3)_3 \cdot 3H_2O$ | 33.04 | 3.83 | 17.34 | 32.75 | 3.25 | 17.04 | yellow |
| $Pr(6)(NO_3)_3 \cdot 2H_2O$ | 33.85 | 3.60 | 17.76 | 34.12 | 3.10 | 17.23 | white |
| $Nd(6)(NO_3)_3 \cdot 2H_2O$ | 33.75 | 3.65 | 17.69 | 34.04 | 3.35 | 17.23 | pale pink |
| $Sm(6)(NO_3)_3 \cdot 2H_2O$ | 33.37 | 3.60 | 17.51 | 33.02 | 3.11 | 17.01 | milky |
| $Eu(6)(NO_3)_3 \cdot H_2O$ | 34.15 | 3.41 | 17.91 | 34.56 | 3.34 | 17.65 | white |
| $Gd(6)(NO_3)_3 \cdot 2H_2O$ | 33.10 | 3.58 | 17.37 | 33.25 | 3.67 | 17.60 | white |
| $Tb(6)(NO_3)_3 \cdot 3H_2O$ | 32.21 | 3.74 | 16.90 | 32.47 | 3.51 | 16.73 | milky |
| $Dy(6)(NO_3)_3 \cdot 2H_2O$ | 33.67 | 3.37 | 17.65 | 34.17 | 3.64 | 16.99 | white |
| $Ho(6)(NO_3)_3 \cdot 2H_2O$ | 32.73 | 3.54 | 17.18 | 32.41 | 3.37 | 17.66 | pale grey |
| $Er(6)(NO_3)_3 \cdot 2H_2O$ | 32.65 | 3.53 | 17.14 | 32.39 | 3.48 | 17.25 | milky |
| $Tm(6)(NO_3)_3 \cdot 3H_2O$ | 31.76 | 3.65 | 16.57 | 31.69 | 3.22 | 16.08 | milky |
| $Yb(6)(NO_3)_3 \cdot 2H_2O$ | 32.38 | 3.50 | 17.00 | 32.53 | 3.45 | 16.69 | white |
| $Lu(6)(NO_3)_3 \cdot 2H_2O$ | 31.53 | 3.67 | 16.55 | 31.70 | 3.48 | 16.32 | white |
| $La(7)(NO_3)_3 \cdot H_2O$ | 34.83 | 3.48 | 18.25 | 34.76 | 3.38 | 17.61 | white |
| $Ce(7)(NO_3)_3 \cdot 2H_2O$ | 33.05 | 3.85 | 17.35 | 33.41 | 3.37 | 16.88 | orange |
| $Pr(7)(NO_3)_3 \cdot 2H_2O$ | 33.85 | 3.66 | 17.75 | 34.47 | 3.53 | 16.88 | milky |
| $Nd(7)(NO_3)_3 \cdot H_2O$ | 34.58 | 3.45 | 18.15 | 34.43 | 3.39 | 17.63 | white |
| $Sm(7)(NO_3)_3 \cdot 2H_2O$ | 33.37 | 3.61 | 17.41 | 33.71 | 3.41 | 16.81 | white |
| $Eu(7)(NO_3)_3 \cdot 2H_2O$ | 33.33 | 3.61 | 17.40 | 33.36 | 3.34 | 16.89 | white |
| $Gd(7)(NO_3)_3 \cdot 2H_2O$ | 33.03 | 3.57 | 17.30 | 33.39 | 3.38 | 16.94 | white |
| $Tb(7)(NO_3)_3 \cdot 4H_2O$ | 31.42 | 3.91 | 16.52 | 30.86 | 3.82 | 16.44 | milky |
| $Dy(7)(NO_3)_3 \cdot 2H_2O$ | 32.83 | 3.55 | 17.22 | 33.31 | 3.52 | 16.85 | white |
| $Ho(7)(NO_3)_3 \cdot H_2O$ | 33.60 | 3.35 | 17.61 | 34.07 | 3.50 | 16.89 | pale grey |
| $Er(7)(NO_3)_3 \cdot H_2O$ | 33.47 | 3.34 | 17.51 | 33.49 | 3.56 | 16.81 | white |
| $Tm(7)(NO_3)_3 \cdot 3H_2O$ | 31.80 | 3.68 | 16.67 | 32.00 | 3.42 | 16.62 | pale grey |
| $Yb(7)(NO_3)_3 \cdot 3H_2O$ | 31.62 | 3.67 | 16.60 | 31.82 | 3.43 | 15.96 | white |
| $Lu(7)(NO_3)_3 \cdot H_2O$ | 33.03 | 3.32 | 17.32 | 33.34 | 3.62 | 16.86 | milky |

of the macrocycles (**5**, **6**, **7** and **8**) derived from the reactions of pdf with 1,2-diaminoethane (en), 1,2-diaminopropane (pn) and 1,3-diaminopropane (pd) in the presence of lanthanide templating agents.

## Experimental

Microanalysis was carried out by the University of Sheffield Microanalysis Service. Infra-red spectra were recorded in the 4000–600 $cm^{-1}$ region with a Perkin-Elmer 297 infra-red instrument, using KBr discs. $^1H$ NMR spectra were recorded at either 220 MHz using a Perkin-Elmer R34 spectrometer or 400.13 MHz using a Bruker WH 400 NMR spectrometer. $^{13}C-\{^1H\}$ NMR were recorded using a JEOL PFT-100 FT spectrometer at 25.15 MHz. Mass spectra were obtained using a Kratos MS25 mass spectrometer.

Pyridine-2,6-dicarboxaldehyde was prepared according to the literature method [6]. The diamines were used as purchased.

### *Condensation between Pyridine-2,6-dicarboxaldehyde and Primary Diamine in the Absence of Metal Ions*

Pyridine-2,6-dicarboxaldehyde (2 mmol, 0.270 g) was mixed with the primary diamine (2 mmol of 1,2-diaminoethane or 1,3-diaminopropane) in hot ethanol/methanol, the colour of the solution changed to yellow-orange, but no precipitates have been found. When the solutions have been evaporated on the rotary evaporator, deep brown oily compounds have been obtained, but no identifiable products could be isolated.

### *Reaction of Pyridine-2,6-dicarboxaldehyde and 1,2-Diaminoethane in the Presence of Lanthanide Ion*

Methanolic solutions (30 ml) of pyridine-2,6-dicarboxaldehyde (2 mmol, 0.270 g), 1,2-diaminoethane (2 mmol, 0.120 g) and $Ln(NO_3)_3$ (1 mmol) [Ln = La–Lu except Pm], were mixed and stirred at reflux for 3 hr. Fine powdery products have been obtained, filtered off, washed with methanol and dried under vacuum. The microanalytical data can be seen in Table I.

### *Reaction of Pyridine-2,6-dicarboxaldehyde and 1,2-Diaminopropane in the Presence of Lanthanide Ions*

2 mmol of pyridine-2,6-dicarboxaldehyde (0.270 g), 2 mmol of 1,2-diaminopropane (0.148 g) and 1 mmol of $Ln(NO_3)_3$ [Ln = La–Lu except Pm], were mixed in absolute ethanol (30 ml), stirred at reflux for 3 hr. The fine powdery product was filtered, washed with absolute ethanol and dried under vacuum. The microanalytical data can be seen in Table I.

### *Reaction of Pyridine-2,6-dicarboxaldehyde and 1,3-Diaminopropane in the Presence of Lanthanide Ions*

Pyridine-2,6-dicarboxaldehyde (2 mmol, 0.270 g), 1,3-diaminopropane (2 mmol, 0.148 g) and $Ln(NO_3)_3$ [Ln = La–Lu except Pm], were mixed in absolute ethanol (30 ml). The mixture was stirred at reflux for 3 hr. A fine powdery product was obtained, filtered off, washed with absolute ethanol and dried. The microanalytical data are listed in Table I.

All microanalytical data is presented in terms of macrocycles **5**, **6** and **7**. The carbinolamine complexes are delineated in the text.

### *Transmetallation with La(7)(NO₃)₃*

1 mmol of $Cu(ClO_4)_2$ in warm ethanol was added to a warm ethanol solution of 0.5 mmol $La(7)(NO_3)_3$ (0.345 g). The mixture (about 50 ml) was stirred at reflux for 4 hr. A light blue precipitate was obtained, filtered off, washed with ethanol and dried. If the same reaction was carried out but with 3 mmol of $Cu(ClO_4)_2$ instead of 1 mmol, a deep blue precipitate was obtained (complex 2 below). $Cu_2(7)(ClO_4)_2(OH)_2 \cdot 3H_2O$. Found: 31.08% C, 3.35% H, 12.05%, N, 9.33% Cl. Required: 31.53% C, 3.24% H, 11.15% N, 9.32% Cl. $Cu_2(7)(ClO_4)_3(OH)$. Found: 31.01% C, 3.24% H, 10.53% N, 11.97% Cl. Required: 30.41% C, 3.03% H, 10.63% N, 13.05% Cl.

### *Transmetallation with La(5)(NO₃)₃*

The copper complex was obtained by reaction of $Cu(ClO_4)_2$ (3 mmol) in warm ethanol with $La(5)(NO_3)_3$ (0.5 mmol) in hot ethanol. The mixture (about 50 ml) was stirred at reflux for 6 hr. A green precipitate was obtained, filtered off, washed with ethanol and dried. $Cu_2(5)(ClO_4)_3(OH) \cdot 2H_2O$. Found: 26.91% C, 2.58% H, 9.51% N, 12.41% Cl. Required: 27.06% C, 2.85% H, 10.50% N, 13.11% Cl.

## Results and Discussion

The products of the condensation reactions between pdf and α,ω-alkanediamines carried out in the presence of $Ln(NO_3)_3$ (Ln = La–Lu, except Pm), in 2:2:1 stoichiometric ratio in methanol analysed as having the general formula $Ln(m/c)(NO_3)_3 \cdot xH_2O$, (m/c = **5**, **6**, **7**). That macrocyclisation had occurred was evidenced by the presence of an imine band in the IR, and the absence of carbonyl and amine stretching frequencies, together with the absence of a $-C(H)=O$ proton in the $^1H$ NMR spectra of the $La^{+++}$ complexes, and the presence of the peak of highest abundance corresponding to the molecular weight of the macrocycle in those species volatile enough to allow the recording of the mass spectrum. In the absence of the templating cation only viscous oils were recovered indicating the organisational role of the metal.

### *Complexes of 5*

The complexes derived from pdf and en were fine powders of formula $Ln(5)(NO_3)_3 \cdot xH_2O$ (x = 0, La–Pr; 1, Nd–Gd and Dy; 2, Tb, Ho–Yb and 4, Lu). Inspection of the IR spectra revealed two types of complex. The first group (La–Pr, Eu) gave spectra in which the imine bands were seen *ca.* 1650 $cm^{-1}$,

TABLE II. Major Infrared Bands, $cm^{-1}$, KBr Disc.

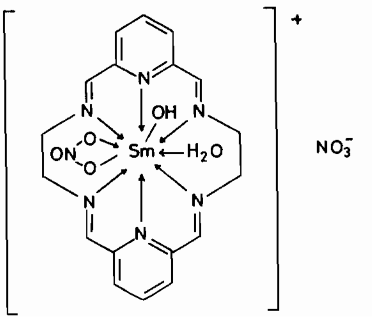
| Complex | $\nu$(>N–H) | $\nu$(>C=N) | $\nu$(>C=N) pyridine | $\nu(NO_3)$ | Other bands |
|---|---|---|---|---|---|
| $La(5)(NO_3)_3$ | – | 1652s | 1590s | 1380m, 1035s, 812m | 1440, 1320, 1160 |
| $Ce(5)(NO_3)_3$ | – | 1650s | 1588s | 1382m, 1038s, 816m | 1442, 1330, 1162 |
| $Pr(5)(NO_3)_3$ | – | 1655s | 1590s | 1380sh, 1040s, 808m | 1450, 1335, 1161 |
| $Nd(5)(NO_3)_3$ | 3200sh | 1660s | 1598s | 1380m, 1078s, 820m | 1495, 1270, 1160 |
| $Sm(5)(NO_3)_3 \cdot H_2O$ | 3210sh | 1658s | 1592s | 1380m, 1075s, 815m | 1495, 1278, 1160 |
| $Eu(5)(NO_3)_3 \cdot H_2O$ | – | 1655s | 1590s | 1380m, 1030s, 810m | 1500, 1280, 1160 |
| $Gd(5)(NO_3)_3 \cdot H_2O$ | 3200sh | 1658s | 1595s | 1380m, 1075s, 812m | 1498, 1275, 1160 |
| $Tb(5)(NO_3)_3 \cdot 2H_2O$ | 3250sh | 1660s | 1598s | 1385s, 1070s, 810m | 1512, 1268, 1162 |
| $Dy(5)(NO_3)_3 \cdot H_2O$ | 3250sh | 1655s | 1595s | 1382s, 1066s, 806m | 1505, 1270, 1160 |
| $Ho(5)(NO_3)_3 \cdot 2H_2O$ | 3255sh | 1660s | 1596s | 1380s, 1070s, 810m | 1510, 1275, 1161 |
| $Er(5)(NO_3)_3 \cdot 2H_2O$ | 3260sh | 1658s | 1592s | 1378s, 1068, 808m | 1508, 1272, 1160 |
| $Tm(5)(NO_3)_3 \cdot 2H_2O$ | 3260sh | 1660s | 1598s | 1382, 1070s, 810m | 1515, 1278, 1160 |
| $Yb(5)(NO_3)_3 \cdot 2H_2O$ | 3250sh | 1660s | 1598s | 1385m, 1075s, 808m | 1520, 1280, 1160 |
| $Lu(5)(NO_3)_3 \cdot 4H_2O$ | 3200sh | 1660s | 1600s | 1383s, 1080s, 810m | 1510, 1280, 1160 |
| $La(6)(NO_3)_3 \cdot 2H_2O$ | – | 1650s | 1592s | 1383m, 1042m, 818s | 1460, 1320, 1165, 736 |
| $Ce(6)(NO_3)_3 \cdot 3H_2O$ | – | 1650s | 1595s | 1385m, 1045s, 820s | 1456, 1325, 1161, 735 |
| $Pr(6)(NO_3)_3 \cdot 2H_2O$ | – | 1652s | 1593s | 1380m, 1044s, 817m | 1460, 1280, 1165, 752 |
| $Nd(6)(NO_3)_3 \cdot 2H_2O$ | 3240bd | 1655s | 1596s | 1384m, 1050s, 820m | 1490, 1278, 1162, 738 |
| $Sm(6)(NO_3)_3 \cdot 2H_2O$ | 3240bd | 1652s | 1595s | 1382m, 1050s, 818m | 1500, 1280, 1160, 740 |
| $Eu(6)(NO_3)_3 \cdot H_2O$ | 3240bd | 1654s | 1594s | 1380m, 1048s, 816s | 1500, 1278, 1160, 740 |
| $Gd(6)(NO_3)_3 \cdot 2H_2O$ | 3240bd | 1660s | 1598s | 1382m, 1082s, 812s | 1505, 1280, 1162, 738 |
| $Tb(6)(NO_3)_3 \cdot 3H_2O$ | 3240bd | 1656s | 1595s | 1382s, 1050s, 815s | 1500, 1280, 1162, 740 |
| $Dy(6)(NO_3)_3 \cdot 2H_2O$ | 3240bd | 1656s | 1592s | 1382m, 1055s, 816s | 1500, 1280, 1162, 741 |
| $Ho(6)(NO_3)_3 \cdot 2H_2O$ | 3240bd | 1660s | 1598s | 1382m, 1086s, 812s | 1510, 1280, 1165, 742 |
| $Er(6)(NO_3)_3 \cdot 2H_2O$ | 3230bd | 1658s | 1596s | 1380m, 1088s, 810s | 1512, 1278, 1160, 744 |
| $Tm(6)(NO_3)_3 \cdot 3H_2O$ | 3240bd | 1660s | 1598s | 1380s, 1052s, 810s | 1506, 1280, 1165, 741 |
| $Yb(6)(NO_3)_3 \cdot 2H_2O$ | 3240bd | 1658s | 1595s | 1380m, 1054, 810s | 1508, 1282, 1160, 745 |
| $Lu(6)(NO_3)_3 \cdot 3H_2O$ | 3250bd | 1652s | 1594s | 1382m, 1048s, 816s | 1502, 1290, 1164, 741 |
| $La(7)(NO_3)_3 \cdot H_2O$ | – | 1650s | 1590s | 1384m, 1098s, 820s | 1430, 1320, 1170, 732 |
| $Ce(7)(NO_3)_3 \cdot 3H_2O$ | – | 1648s | 1590s | 1382m, 1096s, 818s | 1460, 1285, 1160, 730 |
| $Pr(7)(NO_3)_3 \cdot 2H_2O$ |  | 1646s | 1588s | 1380m, 1097s, 819s | 1475, 1280, 1160, 735 |
| $Nd(7)(NO_3)_3 \cdot H_2O$ |  | 1650s | 1592s | 1381s, 1100s, 820s | 1465, 1284, 1160, 738 |
| $Sm(7)(NO_3)_3 \cdot 2H_2O$ |  | 1652s | 1595s | 1385s, 1100s, 818s | 1480, 1282, 1164, 740 |
| $Eu(7)(NO_3)_3 \cdot 2H_2O$ |  | 1650s | 1590s | 1382m, 1098s, 819s | 1482, 1280, 1160, 738 |
| $Gd(7)(NO_3)_3 \cdot 2H_2O$ |  | 1651s | 1592s | 1380s, 1099s, 819s | 1500, 1282, 1160, 740 |
| $Tb(7)(NO_3)_3 \cdot 4H_2O$ |  | 1655s | 1594s | 1382s, 1100s, 820s | 1486, 1286, 1160, 741 |
| $Dy(7)(NO_3)_3 \cdot 2H_2O$ |  | 1653s | 1596s | 1380s, 1098s, 818s | 1484, 1286, 1160, 741 |
| $Ho(7)(NO_3)_3 \cdot H_2O$ |  | 1652s | 1597s | 1384s, 1100s, 820s | 1485, 1285, 1163, 742 |
| $Er(7)(NO_3)_3 \cdot H_2O$ |  | 1650s | 1595s | 1382s, 1095s, 817s | 1486, 1286, 1160, 740 |
| $Tm(7)(NO_3)_3 \cdot 3H_2O$ |  | 1658s | 1598s | 1381s, 1097s, 816s | 1496, 1292, 1160, 748 |
| $Yb(7)(NO_3)_3 \cdot 3H_2O$ |  | 1657s | 1596s | 1383s, 1098s, 818s | 1492, 1290, 1160, 743 |
| $Lu(7)(NO_3)_3 \cdot H_2O$ |  | 1658s | 1596s | 1382s, 1094s, 817s | 1500, 1290, 1160, 744 |

whereas the second group (Nd–Lu except Eu) gave the imine band *ca.* 1660 $cm^{-1}$ and also a secondary amine band *ca.* 3220 $cm^{-1}$ (in all of the complexes a broad band at *ca.* 3450 $cm^{-1}$ was observed and assigned to coordinated or lattice water; major IR bands are given in Table II).

In accordance with the IR the $^1H$ NMR and $^{13}C-\{^1H\}$ NMR of the $La^{+++}$ and $Lu^{+++}$ complexes were quite different. The $^1H$ NMR of the $La^{+++}$ complex was run in $d_6$-dmso and showed the expected simple spectrum ($\delta$ = 8.93 (s, 4H, C*H*N), 8.45 (t, 2H, $H_4$(pyr)), 8.17 (d, 4H, $H_3$(pyr)) and 4.07 (s, 8H,

$-CH_2CH_2-$) p.p.m.) and the $^{13}C\{^1H\}$ NMR gave peaks at 165.1 (imine-C), 150.1 ($C_1$ pyridine), 142.3 ($C_3$ pyridine), 129.1 ($C_2$ pyridine) and 59.4 (ethylene bridge C's) p.p.m. The corresponding spectra for the $Lu^{+++}$ compound are more complex and indicate an equilibrium in solution between $Lu(5)(NO_3)_3$ and $Lu(8)(NO_3)_3$. There are four singlet signals at $\delta$ = 9.10, 9.02, 8.98 and 8.93 p.p.m. which correspond to the three $-CH{=}N$ protons in 8 and to the single $-CH{=}N$ proton in 5. Furthermore the pyridine region shows seven signals and there are additional multiplets in the region for the ethylenic bridge protons. A doublet is observed at $\delta$ = 5.60 p.p.m. (J = 10.3 Hz) assignable to the carbinolamine signal ($>CHOH$ in 8) and a broad singlet is found at $\delta$ = 7.48 p.p.m. due to the $>NH$ proton in 8. Addition of $D_2O$ removes the latter signal and collapses the doublet to a singlet as coupling with the $>NH$ is removed. The $^{13}C$ NMR spectrum is again more complex and indicates two types of macrocycle are present; one set of signals corresponds to those described for the $La^{+++}$ complex of 5 and there are further peaks for the non-symmetrical macrocycle at 164.5, 164.3 and 163.9 p.p.m. (imine C's), 162.4, 152.1, 152.0, 140.8, 128.9, 128.8, 126.8 and 124.9 p.p.m. (pyridine C's), 80.8 p.p.m. ($>CHOH$) and 59.0, 58.9 and 57.5 p.p.m. (ethylenic bridge C's).

The lanthanide complexes derived from pdf and en and containing Nd–Lu, except Eu, are therefore assigned the structure $M(8)(NO_3)_3$ in the solid state. Attempts were made to obtain crystals for X-ray analysis and in the case of the samarium complex were successful. However the band present in the IR of the bulk sample at 3210 $cm^{-1}$ had disappeared and a new band was present at 3560 $cm^{-1}$. This band can be assigned to a Sm–OH group, and the crystal structure shows that the complex analysed is $Sm(5)(OH)(NO_3)_2 \cdot H_2O$ [7]. The samarium cation is enclosed in the cyclic ligand and coordinated to the six nitrogen atoms as well as to a bidentate nitrate anion, a water molecule and a hydroxide anion. The coordination geometry is best described as an irregular antiprism capped on its 'square' faces by the pyridinyl-nitrogen atoms. The structure is depicted schematically as:



For the lighter, and larger, lanthanide cations the preferred products are those involving the tetraimine 5, whereas for the heavier and smaller lanthanide cations the modified ligand 8 is preferred. It is possible that in order to incorporate these latter ions the cavity size must be contracted to accompany the lanthanide contraction and this is done by making the ligand more flexible by addition of water, thus allowing it to bend round the cation. This effect has been noted in d-block transition metal chemistry [8].

The isolation of the dicarbinolamine complexes also suggests that it is probable that the formation of the tetraimine complexes could proceed *via* the formation of a carbinolamine intermediate prior to any elimination of water occurs to yield the tetraimine [9]. In this instance the isolation of the complexes of 8 represents the stabilisation of a reaction intermediate *via* the facile coordination of that species to the smaller lanthanide ions. On dissolution of these complexes in water prior to recrystallisation a higher temperature is reached than in the original reaction in ethanol, and this facilitates moving the reaction on to completion and, as in the samarium case, the tetraimine macrocyclic complex is recovered.

The samarium complex is also hydrolysed on recrystallisation from $Sm(8)(NO_3)_3$ to $Sm(5)(OH)(NO_3)_2$. If, on prolonged exposure to water, some dissociation of the complex occurs to give the free ligand and aquated $Sm^{+++}$ then it is plausible that the following sequence occurs [10],

$$SmL(NO_3)_3 \xrightarrow{H_2O} [Sm(H_2O)_n]^{3+} + L + 3NO_3^-$$

$$[Sm(H_2O)_n]^{3+} \rightleftharpoons [Sm(OH)(H_2O)_{n-1}]^{2+} + H_3O^+$$

It is not immediately obvious why the $[Sm(OH)(NO_3)(H_2O)]^{2+}$ unit should be stabilised by the macrocycle. The seemingly facile hydrolysis of $Ln(NO_3)_3$ complexes has been observed by us in related systems which contain compartmental ligands [11].

### *Complexes with 6 and 7*

The reaction of pdf with pn in the presence of $Ln(NO_3)_3$ in EtOH in 2:2:1 stoichiometry gave powdery products of constitution $Ln(6)(NO_3)_3 \cdot xH_2O$ (x = 1, Eu; 2, La, Pr–Sm, Gd–Er, Yb; 3, Ce, Tb, Tm, Lu). The IR spectra (Table II) of the complexes from Nd–Lu all show a broad band at *ca.* 3240 $cm^{-1}$ of varying intensity which suggests the likelihood that these are also carbinolamine containing species. The $^1H$ NMR of the $La^{+++}$ complex shows the expected simple spectrum – although some multiplicity of signal indicates the likely existence of isomers ($\delta$ = 8.90 (d, 4H, $CHN$), 8.41 (t, 2H, $H_4$(pyr)), 8.18 (d, 4H, $H_3$(pyr)), 4.28 (bd, m, 4H, $CH_2$-N), 3.80 (bd, t, 2H, $CH(CH_3)$) and 1.36 (bd, s, 6H,

TABLE III. Major Infrared Bands of Copper Macrocyclic Complexes, $cm^{-1}$, KBr Disc.[a]

| Complex | $\nu$(OH) | $\nu$(>C=N) | $\nu$(>C=N pyridine) | $\nu(ClO_4)$ |
|---|---|---|---|---|
| $Cu_2(5)(ClO_4)_3(OH)\cdot 2H_2O$ | 3500bd | 1638m | 1594s | 1082s, 630s |
| $Cu_2(7)(ClO_4)_2(OH)_2\cdot 3H_2O$ | 3550s, 3325s | 1648m | 1590s | 1085s, 625s |
| $Cu_2(7)(ClO_4)_3(OH)$ | 3550s | 1650m | 1590s | 1080s, 624s |

[a] s = sharp, m = medium, bd = broad.

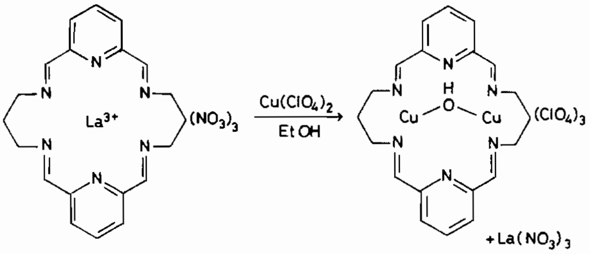
$CH_3$) p.p.m.). The MS of the $La^{+++}$ and $Nd^{+++}$ complex gave peaks of highest molecular weight at m/e = 364, corresponding to the free tetramine macrocycle and suggesting facile loss of water from the proposed carbinolamine structure in the latter case.

With pd and pdf macrocyclic complexes of the type $Ln(7)(NO_3)_3\cdot xH_2O$ (x = 1, La, Nd, Ho, Er, Lu; 2, Pr, Sm–Gd, Dy, 3, Ce, Tm, Yb; and 4, Tb) were obtained. A broad band *ca.* 3450 $cm^{-1}$ was detected in the IR but no obvious secondary amine band was found and so tetraimine structures are proposed throughout. The MS of the $La^{+++}$ complex gave a peak of highest molecular weight at m/e = 346 corresponding to the free macrocycle and the $^1H$ NMR of $La(7)(NO_3)_3$ run in $d_6$-dmso gave the expected simple spectrum ($\delta$ = 8.92 (s, 4H, C*H*N), 8.45 (t, 2H, $H_4$(pyr)), 8.18 (d, 4H, $H_3$(pyr)), 3.96 (m, 8H, $CH_2N$) and 3.78 (m, 4H, $CH_2$) p.p.m.). In these macrocycles it is probable that there is an increased flexibility inherent in the system due to the extended bridge unit and this helps facilitate incorporation of all of the lanthanide cations.

### *Copper Macrocyclic Complexes obtained from Transmetallation Reactions with Lanthanide Complexes*

Due to the general instability of the macrocyclic Schiff base ligands in the uncomplexed state, it seems that the synthesis of metal macrocyclic complexes is often restricted to those of metals which are effective as templates. In spite of that, it has been found that this class of complexes are usually kinetically labile and that the complexed template ion could be exchanged in very many cases with other metal ions present in solution [1]. Since that observation attention has been focused on the synthesis of macrocyclic complexes by transmetallation reactions to obtain complexes of metal ions, which were not effective if used in the direct template route. Furthermore, when some metal ions were used in the transmetallation reactions new types of macrocyclic ligand arising from ring expansions or contractions were obtained. This was dependent on the demands and the size of the transmetallating ion [1, 12, 13].

There is a considerable literature concerning the synthesis of copper macrocyclic complexes by transmetallation reactions [14–16], and most of these reactions were carried out using alkaline earth complexes, and in particular barium complexes as the starting material. We report here the synthesis of copper macrocyclic complexes formed by transmetallation reactions with lanthanum complexes.



When $Cu(ClO_4)_2$ and $La(7)(NO_3)_2$ were mixed in ethanol with 2:1 mol ratio and stirred at reflux for 4 hr, a fine light-blue powdery product of macrocyclic complex of the type $Cu(7)(ClO_4)_2(OH)_2\cdot 3H_2O$, was obtained. When the mol ratio was changed to 6:1 under the same reaction conditions a fine deep-blue powdery product of macrocyclic complex of the type $Cu_2(7)(ClO_4)_3(OH)$ was obtained. It has been found that with $La(5)(NO_3)_3$, a longer time of reflux was needed (about 7 hr), with the mol ratio of 6:1 to obtain a fine green powdery product of macrocyclic complex of the type $Cu_2(5)(ClO_4)_3(OH)\cdot 2H_2O$. The IR spectra of the dinuclear copper(II) products are similar to one another and the salient features are recorded in Table III. All show absorptions corresponding to the imine linkage and bands *ca.* 1090 $cm^{-1}$ and 625 $cm^{-1}$ assignable to the perchlorate group. The complexes derived from 7 show a sharp band at 3550 $cm^{-1}$ ascribed to the –OH bridging limit. It was not possible to identify an –OH band in the IR of the complex derived from 5 in which a broad band was detected centred on 3500 $cm^{-1}$.

The lanthanide complexes are therefore sufficiently kinetically labile for transmetallation reactions to occur with copper(II), and gave essentially the same results as had previously been found using the corresponding barium complexes [15].

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