Available online at www.sciencedirect.com
SCIENCE DIRECT®
PERGAMON
Polyhedron 22 (2003) 2773–2779
POLYHEDRON
www.elsevier.com/locate/poly

# The template synthesis and characterization of pentaaza macrocyclic complexes of rare earth elements. The crystal structure of the 2,14-dimethyl-3,6,10,13,19-pentaazabicyclo[13.3.1]nonadeca-1(19),2,13,15,17-pentaene-dichlorolutetium(III)perchlorate

Wanda Radecka-Paryzek *, Violetta Patroniak, Maciej Kubicki

*Faculty of Chemistry, Adam Mickiewicz University, 60-780 Poznan, Poland*

Received 5 March 2003; accepted 3 June 2003

## Abstract

The yttrium and lanthanide ions were found to act as templates for the cyclic [1 + 1] condensation of 2,6-diacetylpyridine with 3,7-diazanonane-1,9-diamine to yield 16-membered pentadentate Schiff base macrocyclic complexes with an $N_5$ set of donor atoms. The complexes were characterized by spectral data (IR, luminescence, $^1$H NMR, FAB MS) and elemental analysis. The crystal structure of the lutetium complex was determined by single X-ray analysis providing the first example of the seven-coordination and pentagonal bipyramidal coordination geometry found among the lutetium macrocyclic compounds.

*Keywords:* Yttrium; Lanthanides; Macrocyclic Schiff base complexes; Template synthesis; X-ray structure

## 1. Introduction

The macrocyclic and macroacyclic yttrium and lanthanide complexes are currently attracting considerable attention because of their possibility of using as supramolecular devices, suitable bioinorganic probes for the active sites in metallobiomolecules, as contrast agents in magnetic resonance imaging, potential radioimmunopharmaceutical for monoclonal antibody technology and sensitizers for photodynamic therapy, as synthetic nucleases for in vivo application [1–17]. The Schiff base macrocyclic complexes of rare earth elements obtained by us [18–20] have found to be very effective catalysts for hydrolytic cleavage or transesterification of RNA phosphate diester backbone [21,22]. Unlike the lanthanide chelates of linear ligands, the macrocyclic complexes of rare earth elements are extremely rigid and display kinetic inertness towards metal release, whereas the exocyclic ligands (anion or water molecules) are labile and easy to change [23,24]. Many of the synthetic routes to Schiff base macrocycles involve the use of the metal ion template to orient the reacting groups of the substrates in the desired conformation for optimum ring closure [25–28]. The 4f cations have found to be very effective as template agents because they have little or no stereochemical requirements and can be accommodated by the particular stereochemical constrains enforced by the template process. In searching for new stable complexes of the rare earth elements in view of their potential applications and continuing our studies on the effectiveness of metal ions of varying radius and electron configuration in the synthesis of supramolecular macrocyclic and macroacyclic systems derived from biogenic and similar to biogenic diamines [29] we now report the template synthesis and characterization of the new yttrium and lanthanide complexes containing 16-membered pentaazadentate macrocyclic Schiff base ligand **L**, where **L** is 2,14-dimethyl-3,6,10,13,19-pentaazabicyclo[13.3.1]nonadeca-1(19),2,13,15,17-pentaene, formed in the metal-promoted cyclocondensation reac-

---

* Corresponding author. Tel.: +48-61-8291-356; fax: +48-61-8658-008.

*E-mail address:* wrp@amu.edu.pl (W. Radecka-Paryzek).

0277-5387/03/$ - see front matter © 2003 Published by Elsevier Ltd.
doi:10.1016/S0277-5387(03)00398-X

tion of 2,6-diacetylpyridine and 3,7-diazanonane-1,9-diamine. The crystal structure of the lutetium(III) macrocyclic complex has also been described.

## 2. Experimental

### 2.1. Preparation of the complexes. General procedures

All syntheses of the complexes were performed under similar conditions. To a mixture of appropriate metal salt (0.1 or 0.15 mmol) in methanol (10 $cm^3$) and 2,6-diacetylpyridine (0.1 mmol) in methanol (10 $cm^3$), 3,7-diazanonane-1,9-diamine (0.1 or 0.2 mmol) in methanol (10 $cm^3$) was added dropwise with stirring. The reactions were carried out for 3–6 h at ambient temperature. The solution volume was then reduced to 10 $cm^3$ by roto-evaporation and a yellow precipitate formed on addition of a small amount of diethyl ether. This was filtered off, washed with ether, and dried in vacuo. The yields were: 67–74% (42.2–60.3 mg).

### 2.2. Preparation of single crystals of $[LuLCl_2]ClO_4$

To a mixture of $LuCl_3 \cdot 6H_2O$ (0.2 mmol) and $Lu(ClO_4)_3 \cdot 6H_2O$ (0.1 mmol) in methanol (10 $cm^3$) and 2,6-diacetylpyridine (0.3 mmol) in methanol (10 $cm^3$), 3,7-diazanonane-1,9-diamine (0.3 mmol) in methanol (10 $cm^3$) was added dropwise with stirring. The reaction was carried out for 24 h under reflux at argon atmosphere. The solution volume was then reduced to 10 $cm^3$ by roto-evaporation and colorless crystals suitable for X-ray diffraction analysis were formed (yield 87%, 165 mg).

### 2.3. Measurements

IR spectra were recorded using CsI pellets in the range 4000–200 $cm^{-1}$ on a Perkin–Elmer 580 spectrophotometer. $^1H$ NMR spectra were run on a Varian Gemini 300 spectrometer using TMS as an internal reference. FAB mass spectra were obtained on an AMD-604 mass spectrometer with the nitrobenzyl alcohol/acetic acid as matrix. The corrected luminescence spectrum for the Eu(III) complex in methanol was registered using a Perkin–Elmer MPF-3 spectrofluorometer with the excitation wavelength of 290 nm at room temperature. All data reported refer to isolated materials judged to be homogenous by thin layer chromatography performed on precoated silica gel plates (0.2 mm 60 F-254 E. Merck) and visualized by UV light.

### 2.4. Crystal structure determination of $[LuLCl_2]ClO_4$

Diffraction data from a colorless crystal with dimensions $0.05 \times 0.15 \times 0.45$ mm, sealed in a glass capillary, were collected on a KUMA KM4CCD diffractometer [30] at room temperature, using graphite-monochromated Mo Ka radiation ($\lambda = 0.71073$ Å). The data collection was performed in four separate runs in order to cover the symmetry-independent part of the reciprocal space. The $\omega$-scan was used with a step of 0.55°, two reference frames were measured after every 50 frames, they did not show any systematical changes either in peaks positions or in their intensities. A total of 724 frames was collected, giving 15 133 reflections up to $2\theta = 60°$. The unit-cell parameters were determined by the least-squares treatment of the setting angles of 3611 highest-intensity reflections, chosen from the whole experiment. The Lorentz and polarization corrections were applied [31], and then the intensities were merged and corrected for absorption ($T_{min} = 0.52$, $T_{max} = 0.75$) with Sortav [32]. The merging procedure produced 5741 unique data with $R_{int}$ of 0.057.

The structure was solved by direct methods with SHELXS-97 program [33] and refined with full-matrix least-squares by SHELXS-97 [34]. The perchlorate anion was found in two alternative orientations with site occupation factors of 0.72(1) and 0.28(1), respectively. These disordered oxygen atoms were refined isotropically, all other non-hydrogen atoms were refined anisotropically, positions of hydrogen atoms were generated geometrically and these atoms were included in the refinement as a 'riding model' with $U_{iso}$ parameters set at 1.2 times $U_{eq}$ of the appropriate carrier atom. Selected geometric parameters are listed in Table 1. Atom labelling is shown in Fig. 1.

Crystallographic data: empirical formula $[Lu(C_{16}H_{25}N_5)Cl_2]^+ \cdot ClO_4^-$, monoclinic, space group $P2_1/c$, $a = 11.5485(7)$ Å, $b = 12.1929(7)$ Å, $c = 16.8202(10)$ Å, $\beta = 106.606(5)°$, $V = 2269.7(2)$ Å$^3$, $Z = 4$, $d_x = 1.85$ g $cm^{-3}$, $\mu$(Mo Ka) = 4.73 $mm^{-1}$, $F(0\,0\,0) = 1240$, 5741 data, 259 parameters; $R(F)[F_o > 4F_o] = 0.037$, $wR(F^2)[F_o > 4F_o] = 0.0451$, where $w^{-1} = [\sigma^2(F_o)^2 + (0.0096P)^2]^{-1}$, $P = (\mathrm{Max}(F_o^2, 0) + 2F_c^2/3)$, $S = 0.78$, $(\Delta/\sigma_{max}) = 0.001$ in the last cycle of refinement, $\Delta\rho_{max} = 1.04$ e Å$^{-3}$, $\Delta\rho_{min} = -0.87$ e Å$^{-3}$.

## 3. Results and discussion

The template reactions of 2,6-diacetylpyridine with 3,7-diazanonane-1,9-diamine in the presence of trivalent yttrium, praseodymium, europium, gadolinium, terbium, dysprosium, holmium, erbium and lutetium salts in the 1:1:1 or 1:2:1.5 molar ratio of starting materials produce the 16-membered macrocyclic complexes with an $N_5$ set of donor atoms as a result of [1 + 1] Schiff base

Table 1
Selected bond lengths (Å), bond angles (°) and torsion angles with e.s.d.'s in parentheses

| | | | |
|---|---|---|---|
| *Bond lengths* | | | |
| Lu(1)–N(3) | 2.373(5) | Lu(1)–N(6) | 2.429(5) |
| Lu(1)–N(10) | 2.397(4) | Lu(1)–N(13) | 2.372(5) |
| Lu(1)–N(19) | 2.383(4) | Lu(1)–Cl(2) | 2.5063(15) |
| Lu(1)–Cl(1) | 2.5515(14) | | |
| *Bond angles* | | | |
| N(13)–Lu(1)–N(3) | 134.09(17) | N(13)–Lu(1)–N(19) | 66.98(16) |
| N(3)–Lu(1)–N(19) | 67.13(16) | N(13)–Lu(1)–N(10) | 71.08(16) |
| N(3)–Lu(1)–N(10) | 154.22(17) | N(19)–Lu(1)–N(10) | 137.81(17) |
| N(13)–Lu(1)–N(6) | 154.70(16) | N(3)–Lu(1)–N(6) | 70.56(15) |
| N(19)–Lu(1)–N(6) | 137.43(16) | N(10)–Lu(1)–N(6) | 83.88(15) |
| N(13)–Lu(1)–Cl(2) | 94.57(11) | N(3)–Lu(1)–Cl(2) | 94.48(11) |
| N(19)–Lu(1)–Cl(2) | 99.79(10) | N(10)–Lu(1)–Cl(2) | 87.67(11) |
| N(6)–Lu(1)–Cl(2) | 87.78(11) | N(13)–Lu(1)–Cl(1) | 88.53(11) |
| N(3)–Lu(1)–Cl(1) | 89.13(11) | N(19)–Lu(1)–Cl(1) | 88.88(10) |
| N(10)–Lu(1)–Cl(1) | 85.67(11) | N(6)–Lu(1)–Cl(1) | 85.99(11) |
| Cl(2)–Lu(1)–Cl(1) | 171.32(5) | | |
| *Torsion angles* | | | |
| N(19)–C(1)–C(2)–N(3) | −5.2(7) | C(1)–C(2)–N(3)–C(4) | 179.4(5) |
| C(2)–N(3)–C(4)–C(5) | 162.4(5) | N(3)–C(4)–C(5)–N(6) | 52.5(7) |
| C(4)–C(5)–N(6)–C(7) | 173.5(5) | C(5)–N(6)–C(7)–C(8) | 176.4(6) |
| N(6)–C(7)–C(8)–C(9) | −76.4(7) | C(7)–C(8)–C(9)–N(10) | 78.4(7) |
| C(8)–C(9)–N(10)–C(11) | 176.5(5) | C(9)–N(10)–C(11)–C(12) | −175.3(5) |
| N(10)–C(11)–C(12)–N(13) | −51.0(7) | C(11)–C(12)–N(13)–C(14) | −163.2(5) |
| C(12)–N(13)–C(14)–C(15) | −177.5(5) | N(13)–C(14)–C(15)–N(19) | 7.2(7) |
| C(14)–C(15)–N(19)–C(1) | 174.2(5) | C(2)–C(1)–N(19)–C(15) | −176.1(5) |

Table 2
Analytical data for the complexes of **L**

| Complex | Found (%) | | | Calculated (%) | | |
|---|---|---|---|---|---|---|
| | C | H | N | C | H | N |
| $YL(NO_3)_3 \cdot 4H_2O$ | 29.4 | 5.0 | 17.6 | 30.3 | 5.2 | 17.7 |
| $PrL(ClO_4) \cdot 2H_2O$ | 26.4 | 4.0 | 9.1 | 25.2 | 3.8 | 9.2 |
| $GdLCl_3 \cdot 3H_2O$ | 31.6 | 5.5 | 12.3 | 31.8 | 5.2 | 11.6 |
| $EuL(CF_3SO_3)_3 \cdot 4H_2O$ | 19.8 | 3.5 | 6.7 | 20.1 | 3.5 | 7.3 |
| $TbL(NO_3)_3 \cdot 4H_2O$ | 29.2 | 4.7 | 15.7 | 27.3 | 4.7 | 15.9 |
| $DyL(NO_3)_3 \cdot 5H_2O$ | 28.4 | 5.1 | 15.9 | 26.7 | 4.9 | 15.4 |
| $HoL(NO_3)_3 \cdot 5H_2O$ | 25.6 | 4.6 | 14.9 | 26.4 | 4.8 | 15.4 |
| $HoL(ClO_4)_3 \cdot 2H_2O$ | 23.7 | 3.7 | 9.1 | 24.4 | 3.7 | 8.9 |
| $ErLCl_3 \cdot 4H_2O$ | 29.5 | 5.3 | 11.2 | 29.5 | 5.4 | 10.8 |
| $ErL(NO_3)_3 \cdot 3H_2O$ | 28.7 | 4.6 | 15.6 | 27.7 | 4.5 | 16.1 |
| $LuLCl_3 \cdot 6H_2O$ | 30.7 | 5.3 | 11.5 | 28.4 | 5.5 | 12.4 |
| $LuL(ClO_4)_3 \cdot 3H_2O$ | 24.2 | 3.9 | 8.6 | 23.6 | 3.8 | 8.6 |

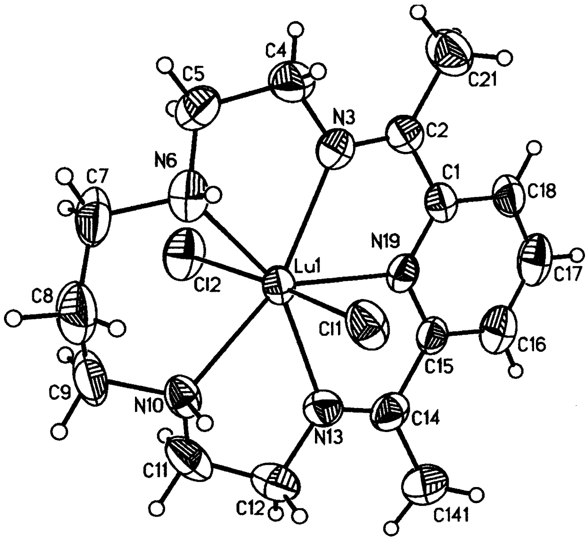
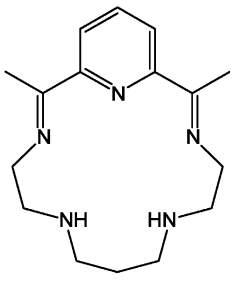


Fig. 1. ORTEP diagram [36] of $[LuLCl_2]^+$ complex cation with the numbering scheme. The thermal ellipsoids are drawn at the 50% probability level, hydrogen atoms are depicted as the spheres of arbitrary radii.

cyclocondensation. Reaction conditions (molar ratio and the method of adding starting materials, reaction time, range of temperatures) were employed to prevent the formation of acyclic products. The formulation of these complexes as $YL(NO_3)_3 \cdot 4H_2O$, $PrL(ClO_4)_3 \cdot 2H_2O$, $EuL(CF_3SO_3)_3 \cdot 4H_2O$, $GdLCl_3 \cdot 3H_2O$, $TbL(NO_3)_3 \cdot 4H_2O$, $DyL(NO_3)_3 \cdot 5H_2O$, $HoL(NO_3)_3 \cdot 5H_2O$, $HoL(ClO_4)_3 \cdot 2H_2O$, $ErLCl_3 \cdot 4H_2O$, $ErL(NO_3)_3 \cdot 3H_2O$, $LuLCl_3 \cdot 6H_2O$, $LuL(ClO_4)_3 \cdot 3H_2O$ and $LuLCl_2ClO_4$ follow from spectral data (IR, $^1H$ NMR, FAB MS) and elemental analyses (Table 2). The complexes are yellow air stable solids, moderately soluble in $CH_3CN$, $CH_3OH$ and DMSO.



**L**

All the complexes give very similar infrared spectra (Table 3) indicating the presence of the same ligand throughout the series. The occurrence of the band at 1645–1590 $cm^{-1}$ attributable to C=N stretching modes which is diagnostic for the Schiff base condensation and the absence of bands characteristic of carbonyl groups confirm the formation of the macrocyclic compounds. The spectra contain medium to strong bands at 1590–1507 $cm^{-1}$ as expected for the high energy ring vibrations of the coordinated pyridine. The bonding of

Table 3
Selected infrared and FAB mass spectral data for **L** complexes

| Complex | IR ($cm^{-1}$) | | | | | FAB | |
|---|---|---|---|---|---|---|---|
| | OH | NH | CN | py | Counterions | $m/z$ | Assignments |
| $YL(NO_3)_3 \cdot 4H_2O$ | 3345, 880 | 3034 | 1592 | 1570, 1082, 667, 430 | 1749, 1450–1260, 1382, 824 | 635.2<br>538.0<br>412.9 | $[YL(NO_3)_2 \cdot 4H_2O]^+$<br>$[YL(NO_3)_2 \cdot 2H_2O]^+$<br>$[YL]^+$ |
| $PrL(ClO_4)_3 \cdot 2H_2O$ | 3420, 850 | 2930 | 1630 | 1590, 1010, 670 | 1090, 625 | 766.7<br>527.0<br>427.0<br>289.0 | $[PrL(ClO_4)_3 \cdot 2H_2O]^+$<br>$[PrL(ClO_4)]^+$<br>$[PrL]^+$<br>$[L]^+$ |
| $EuL(CF_3SO_3)_3 \cdot 4H_2O$ | 3410 | 2927 | 1645 | 1517, 607, 470 | 1263, 1233, 1163, 1039, 760, 644, 580, 515 | 922.9 | $[EuL(CF_3SO_3)_3 \cdot 2H_2O]^+$ |
| $GdLCl_3 \cdot 3H_2O$ | 3419, 833 | 2978 | 1593 | 1045, 1013, 613, 434 | 285, 272, 235 | 539.4<br>482.1 | $[GdLCl_3]^+$<br>$[GdLCl]^+$ |
| $TbL(NO_3)_3 \cdot 4H_2O$ | 3446 | 2942 | 1558 | 1507, 1085 | 1763, 1384, 825 | 634.7 | $[TbL(NO_3)_3]^+$ |
| $DyL(NO_3)_3 \cdot 5H_2O$ | 3446 | 2981 | 1559 | 1507, 1083 | 1763, 1384, 825 | 725.8<br>663.5 | $[Dy(NO_3)_3 \cdot 5H_2O]^+$<br>$[Dy(NO_3)_3 \cdot 5H_2O]^+$ |
| $HoL(NO_3)_3 \cdot 5H_2O$ | 3421 | 2962 | 1590 | 1506, 1089, 668 | 1763, 1384, 825 | 490.2<br>454.2 | $[HoL \cdot 2H_2O]^+$<br>$[HoL]^+$ |
| $HoL(ClO_4)_3 \cdot 2H_2O$ | 3482, 851 | 2949 | 1635 | 1507, 1095 | 1090, 625 | 489.8<br>288.9 | $[HoL \cdot 2H_2O]^+$<br>$[L]^+$ |
| $ErLCl_3 \cdot 4H_2O$ | 3431, 833 | 2962 | 1595 | 1507, 1100, 614 | 279, 248 | 633.0<br>596.2<br>454.2 | $[ErLCl_3 \cdot 4H_2O]^+$<br>$[ErLCl_3 \cdot 2H_2O]^+$<br>$[ErL]^+$ |
| $ErL(NO_3)_3 \cdot 3H_2O$ | 3437 | 2924 | 1593 | 664, 491 | 1400–1299, 1384, 825 | 599.7 | $[ErL(NO_3)_2 \cdot H_2O]$ |
| $LuLCl_3 \cdot 6H_2O$ | 3444, 833 | 2985 | 1595 | 1017, 632, 439 | 273, 237 | 499.0 | $[LuLCl]^+$ |
| $LuL(ClO_4)_3 \cdot 3H_2O$ | 3460, 833 | 3040 | 1597 | 1513, 673, 453 | 1101, 625 | 716.0<br>563.1<br>462.0<br>289.2 | $[Lu(ClO_4)_2 \cdot 3H_2O]^+$<br>$[LuL(ClO_4)]^+$<br>$[LuL]^+$<br>$[L]^+$ |
| $LuLCl_2ClO_4$ | | 2957 | 1611 | 1530, 668, 441 | 1100, 624, 293 | 462.0<br>289.2 | $[LuL]^+$<br>$[L]^+$ |

the pyridine nitrogen atom is also shown by the presence of the band at 1082–1010 $cm^{-1}$ and 673–430 $cm^{-1}$ attributable to the ring breathing frequency and the low energy pyridine ring vibrations, respectively. The band at 3040–2924 $cm^{-1}$ region suggests the coordination of the nitrogen atoms of the secondary amino groups. The complexes show the broad diffuse band centered at 3421–3345 $cm^{-1}$ due to the stretching and bending modes of lattice and coordinated water. In addition, weak bands are detectable at 890–825 $cm^{-1}$ region which may be assigned to rocking or wagging modes of water molecules interacting with the metal ion. The appearance of the considerable broadening of the IR bands associated with nitrate and perchlorate vibrations suggests that the counterions are partially involved in the coordination sphere of the metal ions. The medium absorption bands at 293–235 $cm^{-1}$ region observed in the IR spectra of the chloride complexes attributable to the M–Cl frequency demonstrate the interaction of at least part of the chloride counterions with the metal. The vibrational modes for the triflate anion are split suggesting the presence of coordinated species [35]. These features are consistent with the FAB MS fragmentation mode (Table 3). The positive FAB mass spectra confirm the presence of the counterions and water molecules in inner sphere of the complexes. The stepwise loss of these species appears to be a common route of fragmentation. The spectra exhibit a peak due to the free ligand at $m/z$ 289 as a result of demetallation of the species under FAB conditions providing strong evidence for the formation of the complexes with macrocycle **L** as a [1+1] product of the template cyclocondensation of one molecule of diketone with one molecule of diamine.

The luminescence spectrum of Eu(III) shows three intense lines at $\lambda_{em} = 595$, 618 and 697 nm associated with the $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_4$, respectively. The luminescence intensity of the Eu(III) complex has been analyzed to determine the ratio parameter $\eta = I_{615}/I_{590}$. The value of $\eta = 2.3$ provides information on the complex formation. The emission was observed in Eu(III) complex when the system was excited with wavelength of 290 nm.

The $^1$H NMR spectra of DMSO-$d_6$ solution of the diamagnetic yttrium and lutetium complexes strongly suggest the presence of the macrocyclic ligand. Three well-resolved multiplets of the methylene protons are observed in the 1:1:1 ratio. The proton signals of two methylene groups of the $NCH_2CH_2N$ chain appear as two triplets at $\delta$ 2.85 (4H) ($J = 5.9$ Hz) and $\delta$ 2.72 (4H) ($J = 5.9$ Hz) for yttrium complex and $\delta$ 2.87 (4H) ($J = 6.1$ Hz) and $\delta$ 2.76 (4H) ($J = 6.1$ Hz) for lutetium complex. The $\alpha$ to nitrogen methylene protons of the propylene bridge give the third triplet at $\delta$ 2.63 (4H) ($J = 7.0$ Hz) for yttrium complex and at $\delta$ 2.67 (4H) ($J = 6.7$ Hz) for lutetium complexes. The remaining protons of the propylene bridge occur as quintet at $\delta$ 1.60 (2H) ($J = 6.9$ Hz) for yttrium complex and at $\delta$ 1.62 (2H) ($J = 6.7$ Hz) for lutetium complexes. The signal at $\delta$ 1.23 (2H) for yttrium complex and at $\delta$ 1.30 (2H) for lutetium complexes is due to protons of the secondary amino groups. The pyridine protons are observed at $\delta$ 7.9–8.1 (3H) for yttrium complex and as a doublet at 8.52 (2H) ($J = 7.5$ Hz) and triplet at 8.63 (1H) ($J = 7.5$ Hz) for lutetium complexes. The methyl protons of the $CH_3C{=}N$ groups occur as singlets at $\delta$ 2.56 (6H) for yttrium complex and at $\delta$ 2.51 (6H) for lutetium complexes (6H). The integrated relative intensities of the above signals are in good agreement with the required ratios consistent with the proposed formulations of the complexes. The DMSO with strong donor properties is known to compete for the coordination sphere of the metal ions. The competition between the solvent and the ligand for the lanthanide ion could result in removal of the metal ion from the macrocycle, followed by ligand breakdown. The stability of the complexes in DMSO solution is demonstrated by the absence of any additional signals. Hence, it is evident that no metal–solvent interaction occurs.

Satisfactory spectroscopic, mass spectrometric and analytical data were thus obtained for all new compounds, but in the absence of detailed structural studies the exact mode of coordination remained somewhat speculative. After numerous unsuccessful attempts the preparation of single crystals suitable for X-ray analysis was finally achieved for the lutetium(III) complex isolated from the template reaction of 2,6-diacetylpyridine with 3,7-diazanonane-1,9-diamine carried out in the presence of mixed lutetium chloride and perchlorate salts in argon with the argon atmosphere maintained during the crystallization process. The X-ray structure is shown in Fig. 1.

The central Lu(III) ion is in seven-coordinate environment with the N3, N6, N10, N13 and N19 donor atoms of the macrocycle occupying the equatorial plane and the axial position being filled with chlorine atoms. An uncoordinated perchlorate anion balances the ionic charge of the complex cation. The coordination polyhedron is close to a pentagonal bipyramid. Five nitrogen atoms of the macrocycle are almost coplanar (maximum deviation from the least squares plane is 0.030(3) Å) and the Lu ion is only slightly (0.104(2) Å) tilted out of this plane. This value is smaller than in very closely related dimeric $\mu$-$\eta^2$:$\eta^2$ peroxo analogue of this complex (0.190 Å), isolated and definitely identified recently [37]. To our knowledge, just one example of structurally characterized pentaaza macrocyclic lutetium(III) complex has been reported previously [38]. By comparison, in this pentadentate texaphyrin lutetium(III) complex—regarded as an example of near-to-complete in-plane metal-coordination—the eight-coordinate metal center is found to be 0.269 Å above the mean plane of the macrocycle and the maximum deviation from planarity is 0.072 Å.

The 16-membered macrocyclic ring has approximate $C_2$ symmetry, the twofold axis passes through C8 and N19 atoms. The small value of an asymmetry parameter $\Delta C_2^8$ [39], of 1.90°, shows that the deviations from the ideal symmetry are almost negligible. The bond lengths and angles have typical values; the Lu–N bonds follow the same pattern as the Fe–N bonds in very similar structure of 2,14-dimethyl-3,6,10,13,19-pentaazabicyclo[13.3.1]nonadeca-1(19),2,13,15,17-pentaene-diisothiocyanatoiron(III)perchlorate [40], but they are slightly shorter than those found in the 18-membered hexaazadentate nine-coordinate lutetium(III) macrocyclic Schiff base complex (2.55 Å) [41].

In the crystal structure the complexes form centrosymmetric dimers connected by means of N10–H10··· Cl1 hydrogen bonds (Fig. 2).

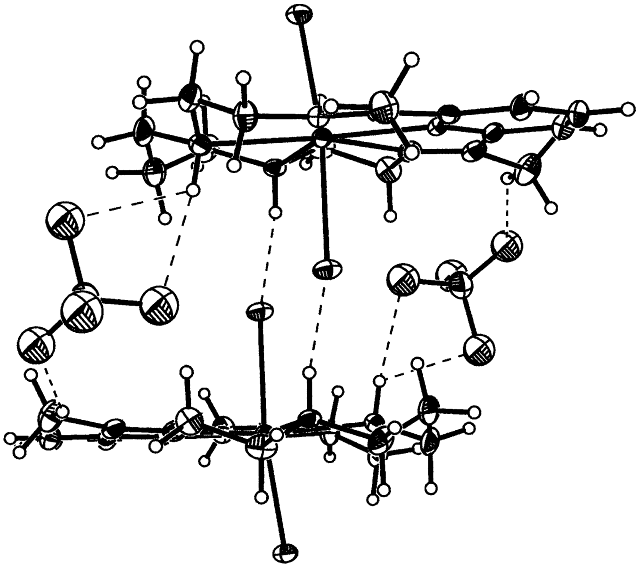


Fig. 2. Centrosymmetric hydrogen-bonded dimer. Hydrogen bonds are drawn as the dashed lines. The disordered perchlorate anions are represented by those of higher occupancy.

Table 4
Hydrogen bond data (Å and °)

| D–H···A | *d*(D–H) | *d*(H···A) | *d*(D···A) | ∠(DHA) |
|---|---|---|---|---|
| N(10)–H(10)···Cl(1)$^{i}$ | 0.91 | 2.44 | 3.263(4) | 150.6 |
| N(6)–H(6)···O(22S)$^{ii}$ | 0.91 | 2.38 | 3.13(2) | 139.8 |
| N(6)–H(6)···O(14S)$^{ii}$ | 0.91 | 2.71 | 3.235(10) | 117.6 |
| C(4)–H(4A)···Cl(2)$^{iii}$ | 0.97 | 3.04 | 3.585(6) | 116.9 |
| C(5)–H(5A)···O(14S)$^{ii}$ | 0.97 | 2.53 | 3.205(10) | 126.5 |
| C(5)–H(5A)···O(24S)$^{ii}$ | 0.97 | 2.58 | 3.19(3) | 120.8 |
| C(7)–H(7B)···O(22S)$^{ii}$ | 0.97 | 2.73 | 3.19(2) | 110.4 |
| C(7)–H(7B)···O(14S)$^{ii}$ | 0.97 | 2.70 | 3.390(10) | 128.2 |
| C(141)–H(14B)···Cl(2)$^{iv}$ | 0.96 | 2.99 | 3.875(6) | 154.2 |
| C(141)–H(14C)···O(21S)$^{v}$ | 0.96 | 2.50 | 3.246(17) | 134.2 |
| C(141)–H(14C)···O(12S)$^{v}$ | 0.96 | 2.75 | 3.424(10) | 128.2 |
| C(16)–H(16)···Cl(2)$^{iv}$ | 0.93 | 3.17 | 3.567(6) | 107.8 |
| C(17)–H(17)···O(21S)$^{vi}$ | 0.93 | 2.45 | 3.358(15) | 165.6 |
| C(17)–H(17)···O(13S)$^{vi}$ | 0.93 | 2.61 | 3.474(10) | 154.6 |
| C(18)–H(18)···Cl(1)$^{vii}$ | 0.93 | 2.78 | 3.598(6) | 147.9 |
| C(21)–H(21C)···Cl(1)$^{vii}$ | 0.96 | 3.06 | 3.726(5) | 128.1 |
| C(21)–H(21A)···Cl(2)$^{iii}$ | 0.96 | 2.71 | 3.621(6) | 159.2 |
| C(21)–H(21B)···O(14S)$^{viii}$ | 0.96 | 2.50 | 3.220(10) | 131.7 |

Symmetry transformations used to generate equivalent atoms: $^{i}-x+1, -y, -z+1$; $^{ii}-x+1, y-(1/2), -z+(1/2)$; $^{iii}-x, y-(1/2), -z+1$; $^{iv}x, -y+1/2, z+(1/2)$; $^{v}-x+1, y+(1/2), -z+(1/2)$; $^{vi}x-1, -y+(1/2), z+(1/2)$; $^{vii}-x, -y, -z+1$; $^{viii}x-1, y, z$.

The oxygen atoms from perchlorate anion are involved in a number of weak N–H···O and C–H···O hydrogen bonds and also—to some extent—take part in formation of the dimers. The dimers are connected by much weaker C–H···Cl2 hydrogen bonds. Interestingly, the chlorine atom involved in the stronger hydrogen bond has a longer Lu–Cl bond distance. Hydrogen bond data are listed in Table 4.

Unlike the majority of the polyaza macrocyclic complexes of lanthanides this complex show no tendency to include solvent molecules in either the metal coordination sphere or the crystal lattice. The electronic and steric requirements of the central metal atom appear to be fully satisfied by coordination to the five nitrogen donors of the macrocycle and two chlorine donors. The stabilization of seven-coordination and pentagonal bipyramidal geometry in this complex, relatively uncommon in the lanthanide series, seems to be a consequence of the 'best fit' between the size of lutetium(III) cation and the cavity of the macrocycle generated during the template process. To the best of our knowledge this result constitutes the first structurally documented instance of such a structure among the lutetium macrocyclic compounds.

The results discussed in this paper along with our earlier investigations lead to the conclusion that the yttrium(III) and lanthanide(III) ions may act as templates in the synthesis of the nitrogen donor macrocycles. The cavity of the pentadentate 16-membered macrocyclic product of the template process with $N_5$ set of donor atoms appears to be sufficiently large to enclose the yttrium and lanthanides irrespective on the ionic radius size of central atoms. It is worth noting however that in some cases the successful synthesis of the macrocyclic systems requires nonstoichiometric amounts of reactants in order to prevent the formation of acyclic products. Our earlier studies reveal that these open-chain chelates considered as potential intermediates in the template process may occur to be the final products [42–44]. The formation of these compounds instead of the expected macrocycles seems to be dictated by the stereochemical requirements of the central atoms coordinating more flexible ligands of podand type in such conformation which decreases the probability of interaction between the amine nitrogen and oxygen atom of the carbonyl group and stabilizes the open-chain product once formed. Our investigations concerning the mechanism of the formation of Schiff base complexes demonstrate that the structure and coordination mode of potential intermediates is one of the factors which prove to be of importance in determining the preferred pathway of the metal-ion-templated condensation in the systems of this type and must be taken into account in the design and synthesis of the desired macrocyclic products.

## 4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 201909. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

## Acknowledgements

This work was supported by the Polish State Committee for Scientific Research (grant 4T09A 056 24). The authors thank Dr. Zbigniew Hnatejko for luminescence measurements.

## References

[1] Y. Bretonnière, R. Wietzke, C. Lebrun, M. Mazzanti, J. Pécaut, Inorg. Chem 39 (2000) 3499.
[2] D. Parker, Coord. Chem. Rev. 205 (2000) 109.
[3] T. Gunnlaugsson, D.A. Mac Dónaill, D. Parker, J. Am. Chem. Soc. 123 (2001) 12866.
[4] L. Thunus, R. Lejeune, Coord. Chem. Rev. 184 (1999) 125.
[5] K. Wang, R. Li, Y. Cheng, B. Zhu, Coord. Chem. Rev. 190–192 (1999) 297.
[6] M.K. Moi, C.F. Meares, J. Am. Chem. Soc. 110 (1988) 6224.

[7] C.D. Hall, J.H. Tucker, A. Sheridan, Y.F. Chu, D.J. Williams, J. Chem. Soc., Dalton Trans. (1992) 3133.

[8] M. Botta, Eur. J. Inorg. Chem. (2000) 399.

[9] S. Rigault, C. Piguet, J. Am. Chem. Soc. 122 (2000) 9304.

[10] M. Woods, S. Aime, M. Botta, J.A.K. Howard, J.M. Moloney, M. Navet, D. Parker, M. Port, O. Rousseaux, J. Am. Chem. Soc. 122 (2000) 9781.

[11] L. Xu, S. Rettig, Ch. Orvig, Inorg. Chem. 40 (2001) 3734.

[12] F. Alhaique, I. Bertini, M. Fragai, M. Carafa, C. Luchinat, G. Parigi, Inorg. Chim. Acta 331 (2002) 151.

[13] S. Aime, L. Frullano, S.G. Crich, Angew. Chem., Int. Ed. 41 (2002) 1017.

[14] M.K. Thompson, M. Vuchokv, I.A. Kahwa, Inorg. Chem. 40 (2001) 4332.

[15] S. Arndt, T.P. Spaniol, J. Okuda Chem. Commun. (2002) 896.

[16] R. Häner, J. Hall, Antisense Nucleic Acid Drug Dev. 7 (1997) 423.

[17] S.W.A. Bligh, N. Choi, E.G. Evagorou, M. McPartlin, K.N. White, J. Chem. Soc., Dalton Trans. (2001) 3169.

[18] W. Radecka-Paryzek, Inorg. Chim. Acta 45 (1980) L147.

[19] W. Radecka-Paryzek, Inorg. Chim. Acta 54 (1981) L251.

[20] W. Radecka-Paryzek, Inorg. Chim. Acta 109 (1985) L21.

[21] J.R. Morrow, L.A. Buttrey, V.M. Shelton, K.A. Berback, J. Am. Chem. Soc. 114 (1992) 1903.

[22] N. Hayashi, N. Takeda, T. Shiiba, M. Yashiro, K. Watanabe, M. Komiyama, Inorg. Chem. 32 (1993) 5889.

[23] D.A. Voss, Jr., L.A. Butterey-Thomas, T.S. Janik, M.R. Churchill, J.R. Morrow, Inorg. Chim. Acta 317 (2001) 149.

[24] K.K. Fonda, L.M. Vallarino, Inorg. Chim. Acta 334 (2002) 403.

[25] N.V. Gerbeleu, V.B. Arion, J. Burges, Template Synthesis of Macrocyclic Compounds, Wiley-VCH, Weinheim, 1999.

[26] B. Dietrich, P. Viout, J.-M. Lehn, Macrocyclic Chemistry, VCH Verlagsgesellschaft, Weinheim, 1993.

[27] E.C. Constable, Metals and Ligand Reactivity, VCH Verlagsgesellschaft, Weinheim, 1996.

[28] J.R. Fredericks, A.D. Hamilton, in: A.D. Hamilton (Ed.), Supramolecular Control of Structure and Reactivity, Wiley, Chichester, 1996 (Chapter 1).

[29] W. Radecka-Paryzek, H. Litkowska, J. Alloys Comp. 300–301 (2000) 435.

[30] CrysAlisCCD, User Guide vers. 168, Kuma Diffraction, Wroclaw, Poland, 1999.

[31] CrysAlisRed, Program for Reduction of the Data from Kuma CCD Diffractometer, Kuma Diffraction, Wroclaw, Poland, 1999.

[32] R.H. Blessing, J. Appl. Crystallogr. 22 (1989) 396.

[33] G.M. Sheldrick, Acta Crystallogr., Sect. A 46 (1990) 467.

[34] G.M. Sheldrick, SHELXS-97, in: Program for the Refinement of Crystal Structures, University of Göttingen, Göttingen, Germany, 1997, p. 1997.

[35] G. Muller, J.-C. Bünzli, K.J. Schenk, C. Piguet, G. Hopgartner, Inorg. Chem. 40 (2001) 2642.

[36] Siemens, Stereochemical Workstation Operation Manual, Release 3.4, Siemens Analytical X-ray Instruments Inc., Madison, WI, USA, 1989.

[37] V. Patroniak, W. Radecka-Paryzek, M. Kubicki, J. Inclusion Phenom. Macrocyclic Chem., submitted for publication.

[38] J. Sessler, T.D. Mody, G.W. Hemmi, V. Lynch, Inorg. Chem. 32 (1993) 3175.

[39] W.L. Duax, D.A. Norton, Atlas of Steroid Structure, vol. 1, Plenum, New York, 1975.

[40] M.G.B. Drew, A.H. bin Othman, P.D.A. McIlroy, S.M. Nelson, J. Chem. Soc., Dalton Trans. (1975) 2507.

[41] G. Bombieri, F. Benetollo, A. Polo, L. de Cola, D.L. Smailes, L.M. Vallarino, Inorg. Chem. 25 (1986) 1127.

[42] W. Radecka-Paryzek, M. Kaczmarek, V. Patroniak, I. Pospieszna-Markiewicz, J. Alloys Comp. 323–324 (2001) 173.

[43] W. Radecka-Paryzek, M. Kaczmarek, I. Pospieszna-Markiewicz, Polish J. Chem. 76 (2002) 679.

[44] W. Radecka-Paryzek, M. Kaczmarek, V. Patroniak, I. Pospieszna-Markiewicz, Inorg. Chem. Commun. 6 (2003) 26.