The First Example of μ-η^2:η^2-Peroxo-Bridged Macrocyclic Lanthanide Complex. The Crystal Structure of [Lu$_2${Me$_2$pyo[16]trieneN$_5$}$_2$(μ-η^2:η^2-O$_2$)Cl$_2$](ClO$_4$)$_2$ Dioxane Solvate

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Abstract

The crystal structure of [Lu$_2${Me$_2$pyo[16]trieneN$_5$}$_2$(μ-η^2:η^2-O$_2$)Cl$_2$](ClO$_4$)$_2$ (**1**), where Me$_2$pyo[16]trieneN$_5$ is 2,14-dimethyl-3,6,10,13,19-pentaazabicyclo[13.3.1]nonadeca-1(19),2,13,15,17-pentaene reveals the biologically significant – unprecedented among the lanthanide macrocyclic complexes – planar side-on μ-η^2:η^2 coordination mode of the peroxide as a result of [1 + 1] template Schiff base cyclocondensation of 2,6-diacetylpyridine with 3,7-diazanonane-1,9-diamine in the presence of mixed lutetium chloride and perchlorate salts followed by slow crystallization process.

Introduction

The design, synthesis and detailed physicochemical investigations of synthetic model complexes have contributed greatly to the understanding of dioxygen binding and activation by metal ions in biological and other catalytic systems. Most of the impetus for research in this area has arisen from the desire to understand and mimic the coordination chemistry at the active sites of hemocyanin and tyrosinase [1]. The use of appropriately positioned, highly hindered tris(pyrazolyl)borate ligands made it possible to establish structurally the novel coordination mode of the peroxide in d-block element complexes referred to as planar μ-η^2:η^2 [2]. These μ-η^2:η^2-peroxo dinuclear copper(II) complexes prepared either by low-temperature direct dioxygen addition to monomeric copper(I) complexes or by H$_2$O$_2$ treatment of bis(μ-hydroxo)copper(II) complexes were found to have physicochemical properties strikingly similar to those of oxyhemocyanin. Subsequently, the crystal structure of oxyhemocyanin from horseshoe crab (*Limulus polyphemus*) has been solved, revealing the presence of precisely this type of μ-η^2:η^2-peroxide moiety [3]. In this case the accurate structural model compounds preceded the determination of the protein structure. This mode of bonding of dioxygen was discussed for understanding of the mechanism of catalytic activity of the cofacial dicobalt porphyrins which is extremely

sensitive to the catalyst geometry [4]. Based on reports involving binuclear Cu(II) peroxo species, the formation of μ-η^2:η^2-peroxo intermediate has been proposed as an attractive novel possibility for the mechanism of water oxidation and O$_2$ evolution during photosynthesis catalyzed by tetranuclear manganese clusters, although no such Mn complex has been synthesized yet [5].

The first solid evidence for the formation of entirely novel planar μ-η^2:η^2 structure of peroxide ligand was found in [La$_2${N(SiMe$_3$)$_2$}$_4$(O$_2$)(PPh$_3$O)$_2$] dinuclear species obtained either by the action of the excess of PPh$_3$O on the tris(silylamide) under anaerobic conditions or by the treatment with a (Ph$_3$PO)$_2$·H$_2$O$_2$ [6] and till the end of 2002 remained the only known structurally characterized example of such a coordination mode of O$_2^{2-}$ in lanthanide chemistry. Here, we wish to report the successful synthesis and definitive identification of peroxo centrosymmetric dimeric lutetium(III) complex of formula [Lu$_2${Me$_2$pyo[16]trieneN$_5$}$_2$O$_2$Cl$_2$](ClO$_4$)$_2$ (**1**), where Me$_2$pyo[16]trieneN$_5$ is 2,14-dimethyl-3,6,10,-13,19-pentaazabicyclo[13.3.1]nonadeca-1(19),2,13,15,17-pentaene, containing the biologically significant – unprecedented among the lanthanide macrocyclic complexes – planar side-on μ-η^2:η^2 coordination mode of the peroxide. This complex is a result of metal-directed [1 + 1] Schiff base cyclocondensation of 2,6-diacetyl-pyridine with 3,7-diazanonane-1,9-diamine followed by slow crystallization process. When the structure of our peroxo lutetium complex was solved, the ytterbium analogue of the first lanthanum peroxo complex [6] of formula [Yb$_2${N(SiMe$_3$)$_2$}$_4$(O$_2$)(thf)$_2$] was obtained as the minor product during the experiments involving the

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investigation of the low-coordinated lanthanide organyls [7].

Experimental

Chemicals

The hydrated lutetium(III) chloride and perchlorate salts were prepared from Lu_2O_3 by treating 1 g of this oxide with $10 \, cm^3$ of appropriate acid. 2,6-Diacetylpyridine and 3,7-diazanonane-1,9-diamine (Aldrich Chemical Company) were used as received.

Synthesis of 1

To a mixture of $LuCl_3 \cdot 6H_2O$ (25.7 mg, 0.067 mmol) and $Lu(ClO_4)_3 \cdot 6H_2O$ (19.4 mg, 0.033 mmol) in methanol (10 mL) and 2,6-diacetylpyridine (16 mg, 0.1 mmol) in methanol (10 mL), 3,7-diazanonane-1,9-diamine (17 µL, 0.1 mmol) in methanol (10 mL) was added dropwise with stirring. The reactions were carried out for 3 h at room temperature. The solution volume was then reduced to 10 mL 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* (72%). ^1H NMR (300 MHz, DMSO-d_6, 25°, TMS): $\delta = 1.30$ (2H; NH), 1.62 (m, $J = 6.7 \, Hz$, 2H; CH_2), 2.56 (s, 6H; CH_3CN), 2.67 (t, $J = 6.7 \, Hz$, 4H; CH_2), 2.76 (t, $J = 6.1 \, Hz$, 4H; CH_2), 2.87 (t, $J = 6.1 \, Hz$, 4H; CH_2), 8.52 (d, $J = 7.5 \, Hz$, 2H; py), 8.63 (t, $J = 7.5 \, Hz$, 1H; py); FAB-MS (NBA): $m/z = 462.0$ [LuMe$_2$pyo[16]trieneN$_5$ + H$^+$], 289.2 [Me$_2$pyo[16]triene N$_5$ + H$^+$]; IR (CsI): $v = 3433$ (OH), 2957 (NH), 1611 (CN), 1530 (py), 1100 (ClO$_4^-$), 668 (py), 624 (ClO$_4^-$), 441 (py), 293 (Cl$^-$) cm^{-1}; elemental analysis (%) calcd for a powder solid $C_{16}H_{25}N_5O_4Cl_3Lu \cdot 6H_2O$ (740.92): C, 25.93; H, 5.09; N, 9.45. Found: C, 25.33; H, 5.26; N, 11.17. The single crystal of **1** suitable for X-ray diffraction analysis was obtained by slow diffusion of 1,4-dioxane into a solution of powder solid in methanol over a period of 5 months. FAB-MS (NBA): $m/z = 1225.8$ [(LuMe$_2$pyo[16]trieneN$_5$)$_2$O$_2$Cl$_2$(ClO$_4$)$_2$ + H$^+$], 514.3 [LuMe$_2$pyo[16]trieneN$_5$OCl + H$^+$], 497.1 [LuMe$_2$pyo[16]trieneN$_5$Cl + H$^+$], 461.2 [LuMe$_2$pyo[16]-trieneN$_5$ + H$^+$], 288.3 [Me$_2$pyo[16]trieneN$_5$ + H$^+$]; IR (CsI): $v = 2925$ (NH), 1590 (CN), 1559, 668, 436 (py), 1092, 620 (ClO$_4^-$), 881 (O—O), 287 (Cl$^-$) cm^{-1}.

Measurements

IR spectra were recorded using CsI pellets in the range 4000–200 cm^{-1} on a Perkin-Elmer 580 spectrophotometer. ^1H NMR spectrum was run on a Varian Gemini 300 spectrometer using TMS as an internal reference. Positive ion FAB-mass spectra were obtained on an AMD-604 mass spectrometer with the nitrobenzyl as matrix. Elemental analysis was carried out on Elementar Vario EL III microanalyzer.

X-ray data collection, structure determination and refinement

Diffraction data were collected at 100(1) K on a KUMA KM4CCD diffractometer [8] using graphite-monochromated MoK$_\alpha$ radiation ($\lambda = 0.71073$ Å). The data collection was performed in six separate runs in order to cover the symmetry-independent part of the reciprocal space. The ω-scan was used with the step of 0.75°, two reference frames were measured after every 50 frames, they did not show any systematical changes neither in the peak position nor in their intensities. Total of 782 frames was collected. The unit-cell parameters were determined by least-squares treatment of the setting angles of 12,774 highest-intensity reflections, chosen from the whole experiment. The Lorentz and polarization corrections were applied [9] as well as the absorption correction with SORTAV [10]. Relevant crystallographic data, together with data collection and structure refinement details, are listed in Table 1. The structure was solved by direct methods with SHELXS-97 program [11], and refined by full-matrix least squares on F^2, using SHELXL-97 [12]. Scattering factors incorporated in SHELXL-97 were used. The function $\sum w(|F_o|^2 - |F_c|^2)^2$ was minimized, with $w^{-1} = [\sigma^2(F_o)^2 + 0.0351 \cdot P^2]$ ($P = [\text{Max} \, (F_o^2, 0) + 2F_c^2]/3$). Non-hydrogen atoms were refined anisotropically, positions of all hydrogen atoms were calculated assuming the ideal geometry and were refined as a 'riding model' with U_{iso} values set at 1.2 times the U_{eq} value of an appropriate carrier atom. Final difference Fourier map contained two peaks of ca. 2.7 e Å^{-3}; they might be caused by absorption which is not accounted for or by small imperfectness of the crystal.

Results and discussion

In the course of our investigation of the coordination template effect in generating of the supramolecular mono- and dinuclear Schiff base macrocyclic and acyclic complexes of rare earth elements [13] in view of their new fascinating biomedical and technological applications we have carried out the template reaction of 2,6-diacetylpyridine with 3,7-diazanonane-1,9-diamine in the presence of mixed lutetium chloride and perchlorate salts. The isolated powder solid was characterized by spectroscopic, mass spectrometric and analytical data and appeared to be the expected 16-membered macrocyclic complex with N_5 set of donor atoms formulated as LuMe$_2$pyo[16]trieneN$_5$Cl$_2$(ClO$_4$)·6H$_2$O – a product of metal-promoted [1 + 1] Schiff base cyclocondensation. After numerous attempts the preparation of single crystals was finally accomplished by slow diffusion of 1,4-dioxane into a solution of the powder product in

Table 1. Crystal data and structure refinement for **1**

| Empirical formula	$C_{36}H_{58}Cl_4Lu_2N_{10}O_{12}$
Formula weight	1314.66
Temperature, K	100(1)
Crystal system	Monoclinic
Space group	C2/c
$a/Å$	$a = 18.2173(5)$
$b/Å$	$b = 21.8664(7)$
$c/Å$	$c = 11.6899(4)$
$\beta/°$	95.537(3)
$V/Å^3$	4634.9(3)
Z	8
$D_c/\text{g cm}^{-3}$	1.884
μ/mm^{-1}	4.535
$F(000)$	2600
Crystal size	$0.15 \times 0.15 \times 0.1 \text{ mm}^3$
θ range for data collection	3.43 to 26.02°
Index ranges	$-22 \leq h \leq 22, -26 \leq k \leq 26, -14 \leq l \leq 14$
Reflections collected	18,212
Independent reflections	4564 [$R_{\text{int}} = 0.060$]
Completeness to $\theta = 25.99°$	99.8
Absorption correction	Ψ-scan
Max and min transmission	0.59 and 0.46
Data/restraints/parameters	4564/0/289
Goodness-of-fit on F^2	1.123
Final R indices [$I > 2\sigma(I)$]	$R(F) = 0.0372, wR(F^2) = 0.0733$
R indices (all data)	$R(F) = 0.0481, wR(F^2) = 0.0775$
Largest diff. peak and hole	2.778 and $-1.271\,\text{e Å}^{-3}$
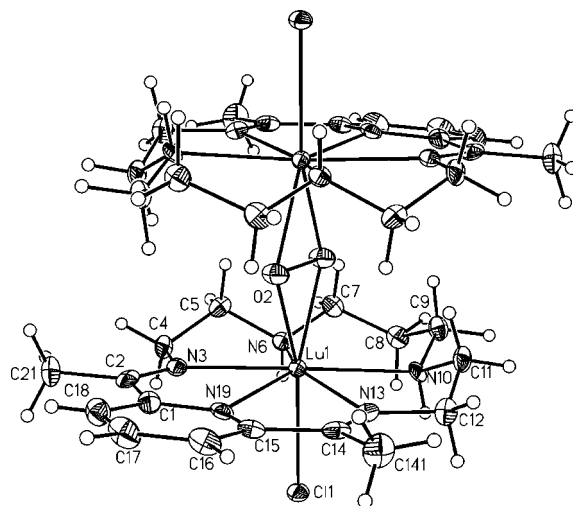
Figure 1. ORTEP diagram [15] of complex **1** showing thermal ellipsoids at the 50% probability level; hydrogen atoms are depicted as spheres with arbitrary radii. For clarity, the symmetry-related part of the complex was not labeled (symmetry operator: $1/2-x$, $1/2-y$, $2-z$). Selected bond lengths [Å] and angles [°]: Lu—X1 2.059(1), Lu—O2 2.203(3), Lu—O2^i 2.188(3), Lu—N3 2.418(4), Lu—N6 2.434(4), Lu—N10 2.433(4), Lu—N13 2.421(4), Lu—N19 2.413(4), Lu—Cl1 2.6379(12), O2—O2^i 1.527(7) ; N3—Lu—N19 66.28(14), N13—Lu—N19 66.54(14), N6—Lu—N10 70.80(14), N10—Lu—N13 70.64(14); O2—Lu—Cl1 162.41(9), O2^i—Lu—Cl1 156.89(9) < X1—Lu—N > 94.4, < Cl1—Lu—N > 85.7, X1—Lu—Cl1 177.28(3), Lu—X1—Lu^i 180. X1 denotes the midpoint of O2—O2^i bond; it lies at the center of symmetry at 1/4,1/4,1. Symmetry code: $^i 1/2-x$, $1/2-y$, $2-z$.

methanol over a period of a 5 months. To our surprise, X-ray diffraction analysis reveals the dimeric [Lu$_2${Me$_2$pyo[16]trieneN$_5$}$_2$(O$_2$)Cl$_2$](ClO$_4$)$_2$ complex **1** containing μ-η^2:η^2-peroxo bridge – the unprecedented species in coordination chemistry of macrocyclic lanthanide complexes. The IR spectrum of **1** shows a weak band at 881 cm^{-1} which is not present in the spectrum of powder sample and may be assigned to the ν(O—O). The highest mass peak in the FAB-mass spectrum and the fragmentation pattern corresponds to the indicated formulation.

It is worth noticing that the template reaction carrying out in argon with the argon atmosphere maintained during the crystallization yields the colorless crystals of monomeric 16-membered pentaaza macrocyclic complex of formula [LuMe$_2$pyo[16]trieneN$_5$Cl$_2$]-ClO$_4$ – first example of the seven-coordinate Lu(III) macrocyclic complex with the pentagonal bipyramidal coordination geometry [14]. This complex appears to be quite analogous to the initial LuMe$_2$pyo[16]trieneN$_5$Cl$_2$(ClO$_4$)·6H$_2$O powder solid except for the lack of water molecules.

The X-ray structure of **1** is shown in Figure 1.

In the solid state the complex resides at the special position of the space group C2/c with the center of symmetry lying at the midpoint of O—O bond. Regarding this point as the coordination site X1, the geometry around lutetium ion is best described as close to the pentagonal bipyramid; two such bipyramids with a common axial apex formed by the symmetrical peroxo bridge constitute the whole complex molecule. All the Lu—O bond lengths are equivalent within experimental error, clearly proving the planar side-on μ-η^2:η^2 coordination mode of the peroxide. Each lutetium center is coordinated to the N3, N6, N10, N13 and N19 donor atoms of the macrocycle occupying the equatorial plane. The outer axial position is filled by chlorine atom. Two uncoordinated perchlorate anions balance the ionic charge of the dimeric complex cation. The crystal structure also contains the dioxane molecules (which occupy another center of symmetry at 0,0,0) and perchlorate anions. Dioxane molecules connect – by means of N—H···O hydrogen bonds – the neighboring complexes into chains along [1 0 1] direction (Figure 2) and these chains are interconnected by N—H···Cl hydrogen bonds. Perchlorate anions are involved in a number of weak C—H···O interactions.

The 16-membered macrocyclic ring has an approximate C_s symmetry with a mirror plane passing through N19 and C8 atoms. Five nitrogen donor atoms are almost perfectly coplanar (maximum deviation from the least-squares plane of 0.026(3) Å) defining a circular cavity with a center-to-nitrogen radius ca. 2.42 Å. The Lu atom is only slightly but statistically significantly tilted out of this plane (deviation of 0.190(2) Å) towards the O$_2$ group. This value is greater than in closely related monomeric analogue of this complex (0.104 Å), isolated from the template reaction in the argon atmosphere and
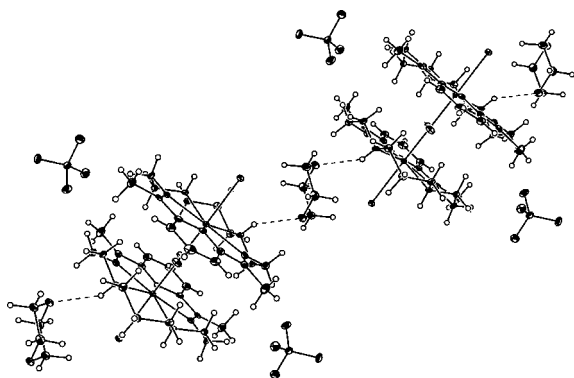
Figure 2. Packing diagram of **1** showing the ~**1**~dioxane~**1**~dioxane~ chains and the neighbouring ClO_4 anions. The ellipsoids are drawn at the 30% probability level. Selected hydrogen bond data [Å and °]: H10···O1S 2.30, N10···O1S 3.034(6), N10—H10···O1S 147; H6···Cl1^i 2.65, N6···Cl1^i 3.376(4), N6-H6···Cl1^i 143 (^{i} $-x$, y, $3/2-z$).

definitely identified recently (*vide supra*) [14]. Interestingly enough, in a single, to our knowledge, structurally characterized and reported previously pentaaza macrocyclic 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 texaphyrin macrocycle and the maximum deviation from planarity is 0.072 Å [16].

The O—O bond distance with the value of 1.527(7) Å is consistent with the peroxo formulation of the O_2 ligand and close to the 1.40–1.50 Å range usually observed for this kind of compounds [17] including dinuclear Cu(II) μ-η^2:η^2-peroxide bridges species, of interest as oxyhaemocyanin and oxytyrosinase models [2]. By comparison, in previously cited $[La_2\{N(SiMe_3)_2\}_4(\mu$-$\eta^2$:$\eta^2$-$O_2)(PPh_3O)_2]$ complex the O—O distance was found to be extremely large (1.65 Å), probably due to the artificial elongation caused by the effects of crystal decomposition [6].

To summarize, the results reported here can provide an interesting complement to the existing rich coordination chemistry of lanthanide Schiff base macrocycles generated by the template coordination effect [18]. The curious feature is the unprecedented so far, facile isolation of the polyaza macrocyclic lanthanide complex containing the peroxo bridge of symmetrical side-on bonding type in view of the utilizing this particular coordination mode to bind or activate dioxygen by biological systems. The driving force substantiating this unusual behavior may be attributable to the stabilizing effect provided by specific steric arrangement of the two macrocycles. It seems worth noting that the syntheses of the two lanthanide peroxo derivatives of bis(trimethylsilyl)-amido species reported previously [6, 7] and the peroxo copper(II) complexes [2] regarded as models for hemocyanin and tyrosinase require severe conditions: action of the excess of PPh_3O and H_2O_2 under anaerobic conditions or treatment with H_2O_2 or low-temperature (ca. $-70\,°C$) direct dioxygen addition. In our case the macrocyclic lutetium peroxo complex is a result of the template synthesis followed by slow crystallization on the air which seems to be important for the formation of this peroxo species. The isolation and structural characterization of the μ-η^2:η^2-peroxo-bridged dinuclear lutetium(III) species expands the unique series of compounds containing the biologically significant planar M_2O_2 moiety and confirms the efficiency of specially designed macrocycles with rigidity sufficient enough to present a donor set with a defined geometry in imposing unusual coordination arrangement around the metal ion.

Acknowledgement

Supplementary data

CCDC-198196 contains the supplementary crystallographic data for this paper. This data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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