

Structure of [LuCl₃(triethylene glycol)].OHMe*

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Abstract. 2,2'-[1,2-Ethanediybis(oxy)]bisethanol(tri-chloro)lutetium(III)-methanol (1/1), [LuCl₃(C₆H₁₄O₄).CH₃OH], $M_r = 463.5$, monoclinic, $P2_1/c$, $a = 7.421$ (2), $b = 14.299$ (5), $c = 14.178$ (8) Å, $\beta = 102.19$ (5)°, $V = 1471$ Å³, $Z = 4$, $D_x = 2.09$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 69.3$ cm⁻¹, $F(000) = 888$, $T = 293$ K, final $R = 0.040$ for 2282 observed [$F_o \geq 5\sigma(F_o)$] reflections. The Lu atom is seven-coordinate, pentagonal bipyramidal with two Cl atoms in axial positions. The two axial ligands [Lu-Cl_{ax} = 2.56 (1) Å average] are bent [Cl-Lu-Cl = 170.3 (1)°] away from the equatorial chlorine [Lu-Cl_{eq} = 2.536 (3) Å]. The alcoholic Lu-O separations [2.296 (7) Å, average] are shorter than the average Lu-O distance for the etheric oxygen atoms [2.357 (7) Å]. The formula units are hydrogen bonded into pairs of polymeric chains which propagate along a.

Introduction. We have recently structurally surveyed the complexation of triethylene glycol (EO3) to hydrated lanthanide chloride salts (Rogers, Voss & Etzenhouser, 1988). The early and mid lanthanides crystallize as nine-coordinate pentahydrates, [M(OH₂)₅(EO3)]Cl₃ ($M = \text{Nd, Eu, Gd, Dy}$ and Y have been structurally characterized). The smaller late lanthanides crystallize as very deliquescent seven-coordinate complexes of which we have structurally characterized [MCl₃(EO3)].CH₃CN ($M = \text{Ho, Lu}$), [MCl₃(EO3)].OHMe ($M = \text{Er, Yb}$) and [LuCl₃(EO3)]. Structural differences in the late-lanthanide complexes are related to very different hydrogen-bonding patterns. The characterization of the title complex now allows us to compare these subtle differences in the metal ion environment for a single metal in all three forms.

Experimental. The synthesis of the title complex has been reported (Rogers, Voss & Etzenhouser, 1988). Clear parallelepipeds grown from acetonitrile:methanol (3:1). D_m not determined. Crystal 0.45 × 0.65 × 0.80 mm. Enraf-Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$. Cell constants from setting angles of 25 reflections ($\theta > 23^\circ$). Corrections

for Lorentz-polarization effect and for absorption (empirical), range of relative transmission factors 66/100%. $\theta_{\text{max}} = 25^\circ$; h 0 to 8, k 0 to 17, l -16 to 16. 2884 reflections measured, 2282 independent observed reflections [$F_o \geq 5\sigma(F_o)$]. Structure solved *via* utilization of fractional coordinates from isostructural [ErCl₃(EO3)].OHMe (Rogers, Voss & Etzenhouser, 1988). Glycol H atoms placed 0.95 Å from the bonded C atom with a fixed isotropic thermal parameter $B = 5.5$ Å² and allowed to ride with the C-H distance fixed; remaining H atoms not included. Two disordered orientations were observed for the solvent O atom. The two O-atom positions were refined in alternate least-squares cycles at 50% occupancy. Scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974); structure refined with *SHELX76* (Sheldrick, 1976). $\sum w(|F_o| - |F_c|)^2$ minimized, weights = $[\sigma(F_o)]^{-1}$, 154 parameters varied. $R = 0.040$, $wR = 0.044$, $S = 4.0$. Δ/σ in final least-squares refinement cycle < 0.01 , $\Delta\rho < 1.9$ e Å⁻³ near Lu position in final difference map.†

Discussion. Fractional coordinates and U_{eq} values are given in Table 1, distances and angles in Table 2, and an *ORTEP* illustration (Johnson, 1976) of the atom labelling and hydrogen bonding in Fig. 1. The title complex is isostructural with [MCl₃(EO3)].OHMe ($M = \text{Er, Yb}$; Rogers, Voss & Etzenhouser, 1988). The Lu ion is seven-coordinate with all four O atoms and Cl(1) in the equatorial plane (planar to 0.022 Å) of a distorted pentagonal bipyramid. Cl(2) and Cl(3) are in axial positions bent away from Cl(1) [Cl(2)-Lu-Cl(3) = 170.3 (1)°]. In the recently determined [YbCl₂(15-crown-5)][AlCl₂Me₂] (Atwood, Bott & Atwood, 1987) a similar geometry was observed for Yb³⁺. The lack of a bulkier Cl atom in the equatorial plane results in a more nearly linear Cl-Yb-Cl angle of 178.4 (3)° for the axial ligands in the Yb complex.

† Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and least-squares-planes results have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44938 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

* *f*-Element/Crown Ether Complexes 24. Part 23: Rogers & Benning (1988).

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Table 1. *Final fractional coordinates for [LuCl₃(EO3)].OHMe*

	x	y	z	U_{eq}^*
Lu	0.15150 (6)	0.41352 (3)	0.19158 (3)	0.021
Cl(1)	0.2732 (4)	0.5758 (2)	0.1686 (2)	0.038
Cl(2)	0.0551 (5)	0.4500 (2)	0.3498 (2)	0.054
Cl(3)	0.2248 (4)	0.3493 (2)	0.0343 (2)	0.036
O(1)	0.453 (1)	0.3978 (5)	0.2716 (5)	0.035
O(2)	0.223 (1)	0.2619 (5)	0.2519 (5)	0.033
O(3)	-0.103 (1)	0.3106 (5)	0.1565 (5)	0.031
O(4)	-0.1069 (9)	0.4837 (5)	0.1018 (5)	0.032
C(1)	0.529 (2)	0.3090 (8)	0.3015 (9)	0.047
C(2)	0.377 (2)	0.2532 (8)	0.3352 (8)	0.046
C(3)	0.067 (2)	0.1995 (8)	0.2622 (9)	0.046
C(4)	-0.067 (2)	0.2112 (8)	0.1664 (9)	0.055
C(5)	-0.246 (2)	0.3345 (7)	0.0737 (8)	0.038
C(6)	-0.285 (1)	0.4348 (8)	0.0833 (9)	0.041
O(5)†	-0.323 (2)	0.532 (1)	0.332 (1)	0.049
O(5)'	-0.341 (2)	0.510 (1)	0.388 (1)	0.068
C(7)	-0.380 (2)	0.589 (1)	0.412 (1)	0.077

* U_{eq} is equal to $(U_{11} + U_{22} + U_{33})/3$.

† O(5) and O(5)' are disordered with 50% occupancy each.

Table 2. *Bond distances (Å) and angles (°) for [LuCl₃(EO3)].OHMe*

Lu-Cl(1)	2.536 (3)	Lu-Cl(2)	2.548 (3)
Lu-Cl(3)	2.574 (3)	Lu-O(1)	2.296 (7)
Lu-O(2)	2.350 (7)	Lu-O(3)	2.364 (7)
Lu-O(4)	2.297 (6)	O(1)-C(1)	1.42 (1)
O(2)-C(2)	1.47 (1)	O(2)-C(3)	1.49 (1)
O(3)-C(4)	1.45 (1)	O(3)-C(5)	1.45 (1)
O(4)-C(6)	1.47 (1)	C(1)-C(2)	1.53 (2)
C(3)-C(4)	1.51 (2)	C(5)-C(6)	1.48 (2)
O(5)-C(7)	1.53 (2)	O(5')-C(7)	1.23 (3)
Cl(1)-Lu-Cl(2)	95.7 (1)	Cl(1)-Lu-Cl(3)	93.95 (9)
Cl(2)-Lu-Cl(3)	170.3 (1)	Cl(1)-Lu-O(1)	79.4 (2)
Cl(2)-Lu-O(1)	90.6 (2)	Cl(3)-Lu-O(1)	91.8 (2)
Cl(1)-Lu-O(2)	146.3 (2)	Cl(2)-Lu-O(2)	87.2 (2)
Cl(3)-Lu-O(2)	85.1 (2)	O(1)-Lu-O(2)	67.0 (2)
Cl(1)-Lu-O(3)	146.4 (2)	Cl(2)-Lu-O(3)	87.2 (2)
Cl(3)-Lu-O(3)	84.4 (2)	O(1)-Lu-O(3)	134.1 (2)
O(2)-Lu-O(3)	67.1 (2)	Cl(1)-Lu-O(4)	78.9 (2)
Cl(2)-Lu-O(4)	92.4 (2)	Cl(3)-Lu-O(4)	88.9 (2)
O(1)-Lu-O(4)	158.3 (3)	O(2)-Lu-O(4)	134.6 (2)
O(3)-Lu-O(4)	67.6 (2)	Lu-O(1)-C(1)	121.2 (6)
Lu-O(2)-C(2)	116.7 (6)	Lu-O(2)-C(3)	117.9 (6)
C(2)-O(2)-C(3)	111.1 (8)	Lu-O(3)-C(4)	117.7 (7)
Lu-O(3)-C(5)	116.1 (6)	C(4)-O(3)-C(5)	113.6 (8)
Lu-O(4)-C(6)	120.4 (6)	O(1)-C(1)-C(2)	106.8 (9)
O(2)-C(2)-C(1)	101.8 (9)	O(2)-C(3)-C(4)	102.8 (9)
O(3)-C(4)-C(3)	105.7 (9)	O(3)-C(5)-C(6)	106.3 (8)
O(4)-C(6)-C(5)	106.8 (8)		

Alcoholic oxygen O(4) is hydrogen bonded to axial Cl(3) [O(4)⋯Cl(3) = 3.078 (7) Å] in a symmetry-related formula unit ($-x, 1-y, -z$) and Cl(3) in the original asymmetric unit accepts a hydrogen bond from O(4) in the latter, forming a dimer of formula units. These dimers are bridged in polymeric chains along *a* via the disordered solvent molecule. Alcoholic O(1) donates a hydrogen bond to O(5), O(5)' ($1+x, y, z$) [O(1)⋯O(5), O(5)' = 2.56 (2) Å] and O(5), O(5)' donate hydrogen bonds to axial Cl(2) [O(5)⋯Cl(2) = 3.00 (2) Å, O(5)'⋯Cl(2) = 3.21 (2) Å]. As a result

of the hydrogen bonding, pairs of parallel polymeric chains propagate along *a*.

The hydrogen-bonding patterns are the only structural differences between the title complex, [LuCl₃(EO3)].CH₃CN, and [LuCl₃(EO3)]. In the unsolvated complex the alcoholic O atoms donate to axial Cl atoms, with each axial Cl accepting one such interaction. The Lu-Cl_{ax} separations [2.584 (2) Å] are equivalent by symmetry (twofold axis). The equatorial Lu-Cl distance is 2.547 (2) Å. The acetonitrile solvate is more complex. Again each alcoholic O donates one hydrogen bond to an axial Cl atom; however, each such Cl has close contacts with the solvent methyl group suggesting an acidic C-H⋯Cl interaction. The Lu-Cl axial separations are nearly the same [2.573 (2) and 2.563 (2) Å] and the Lu-Cl equatorial distance is 2.537 (2) Å.

In the title complex, the hydrogen bonding to the axial chlorines is quite different and so too are the Lu-Cl separations, 2.548 (3) Å for Cl(2) and 2.574 (3) Å for Cl(3). The Lu-Cl(1) equatorial distance is 2.536 (3) Å. The shorter Lu-Cl(2) separation probably reflects the weaker hydrogen-bonding interaction from one of the disordered positions of the solvent oxygen. [O(5)'⋯Cl(2)] is a rather long 3.21 (2) Å.]

The average Lu-O alcoholic and Lu-O etheric distances in the title complex [2.296 (7), 2.357 (7) Å, respectively] are slightly longer than observed for the previous two complexes: 2.278 (8) and 2.350 (2) Å in [LuCl₃(EO3)].CH₃CN and 2.279 (5) and 2.351 (5) Å in [LuCl₃(EO3)]. The bonding in the glycol is normal: O-C = 1.46 (2) Å average, C-C = 1.51 (2) Å average, C-O-C = 112 (1)° average, and C-C-O = 105 (2)° average. The O-C-C-O torsion angles alternate $g^+(60^\circ)$, g^- , g^+ and the C-C-O-C angles are all *anti* (180°).

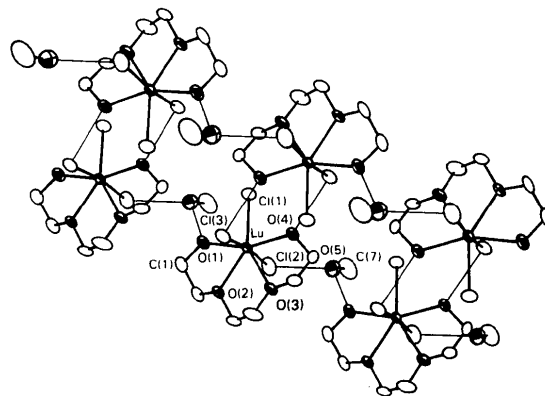


Fig. 1. Pairs of polymeric chains of the formula unit propagate along *a*. 50% probability ellipsoids for thermal motion. Disordered position O(5)' and H atoms omitted.

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Structure of [OC-6-33]-{1,1-Bis(diphenylphosphinomethyl)-1-[(diphenylphosphine oxide)methyl]ethane}tricarbonylchlororhenium(I) Monohydrate

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Abstract. [ReCl(CO)₃(C₄₁H₃₉OP₃)].H₂O, $M_r = 964.05$, monoclinic, $P2_1/c$, $a = 21.309$ (5), $b = 8.771$ (2), $c = 21.530$ (6) Å, $\beta = 96.54$ (2)°, $V = 3997.9$ (18) Å³, $Z = 4$, $D_x = 1.602$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.70930$ Å, $\mu = 0.344$ cm⁻¹, $F(000) = 2019.64$, $T = 298$ K, $R = 0.036$ for 3160 reflections with $I > 2.5\sigma(I)$. The Re atom is octahedrally coordinated by one Cl atom, two phosphine moieties, and three carbonyl ligands with the three carbonyl ligands occupying a face. The six-membered ring formed by Re, P1, P2, C4, C5 and C7 adopts a boat form. The phosphoranyl O and the water molecule are strongly hydrogen bonded such that inversion-related molecules are paired in the crystalline state.

Introduction. The reaction between an organometallic cluster compound and a multidentate phosphine ligand has been studied with interest because it is believed that the multidentate phosphine ligand is able to maintain the integrity of the metal cluster under severe reaction conditions and may serve as a template in the synthesis of new cluster compounds. Hence, we have investigated the reaction of a tripod ligand, 1,1,1-tris(diphenylphosphinomethyl)ethane (tdppme) with Re₂(CO)₁₀ under photolytic conditions.

Experimental. A slight excess of tdppme tripod ligand (560 mg, 0.90 mmol) was stirred with Re₂(CO)₁₀ (528 mg, 0.81 mmol) in dichloromethane (30 ml) under photolyzing conditions for 8 h using a 450 W Hg lamp. After evaporating the solvent, the residue was separated by thin-layer chromatography using dichloromethane/*n*-hexane mixed solvent (2:1). The major product was found to be [OC-6-33]-[ReCl(CO)₃(tdppme)] (Lin, Cheng, Lee, Lee & Peng, 1986). The minor product was investigated with single-crystal X-ray diffraction studies and the results are reported here.

Nonius CAD-4 diffractometer with graphite monochromator, $2 < 2\theta < 50^\circ$, Mo $K\alpha$, $\omega-2\theta$ scan method with speed $0.9-6.7^\circ \text{ min}^{-1}$, $2(0.7^\circ + 0.35^\circ \tan\theta)$ around maximum, h 0 to 25, k 0 to 10, l -25 to 25. 25 reflections ($9.63-11.83^\circ$) used for lattice parameters. Data-crystal dimensions ca $0.25 \times 0.25 \times 0.40$ mm. Three standard reflections ($1, \bar{2}, \bar{1}0$, $\bar{1}, 2, 10$ and $44\bar{6}$) recollected after every 7200 s, no decay or decomposition found. Intensity variations within 2%. Absorption correction applied, min. and max. transmission factors 0.738 and 0.999. 7062 unique reflections measured, 3160 observed with $I > 2.5\sigma(I)$. Structure solved with Patterson and Fourier methods. Structure refined by full-matrix least squares minimizing $\sum w(|F_o| - |F_c|)^2$, w from counting statistics only. Calculations with anisotropic non-H and isotropic H. H only calculated

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