Inorganic Chemistry
including bioinorganic chemistry
Inorg. Chem., 1998, 37(7), 1637-1647, DOI:10.1021/ic971488g

Table S1. Crystallographic data[a]

Compound	$[C_{60}H_{90}LuN_8O_{12}](NO_3)_3 \cdot 3H_2O$
Formula	$C_{60}H_{96}LuN_{11}O_{24}P_6$
fw	1716.29
Color, habit	Colorless, prism
Crystal size, mm	0.12 x 0.15 x 0.25
Crystal system	Trigonal
Space group	$R\bar{3}\,c$
a, Å	19.060(1)
c, Å	36.395(3)
V, Å^3	11449(1)
Z	6
ρ_{calc}, g/cm^3	1.493
$F(000)$	5316
μ(Cu Kα), cm^{-1}	43.66
Transmission factors (rel)	0.82-1.00
Scan type	ω-2θ
Scan range, deg in ω	0.94 + 0.20 tan θ
Scan speed, deg/min	16 (up to 8 rescans)
Data collected	$+h, +k, +l$
$2\theta_{max}$, deg	155
Crystal decay, %	2.7
Total reflections	5671
Unique reflections	2964
R_{merge}	0.026

Reflections with $I \geq 3\sigma(I)$	2061
No. of variables	178
R	0.024
R_w	0.025
gof	1.57
Max Δ/σ (final cycle)	0.0005
Residual density, e/Å^3	-0.47, 0.58 (near Lu)

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[a] Temperature 294 K, Rigaku AFC6S diffractometer, Cu K_α (λ = 1.54178 Å) radiation, graphite monochromator, takeoff angle 6.0°, aperture 6.0 x 6.0 mm at a distance of 285 mm from the crystal, stationary background counts at each end of the scan (scan/background time ratio 2:1), $\sigma^2(F^2) = [S^2(C + 4B)]/Lp^2$ (S = scan rate, C = scan count, B = normalized background count), function minimized $\Sigma w(|F_o|-|F_c|)^2$ where $w = 4F_o^2/\sigma^2(F_o^2)$, $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $R_w = (\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2)^{1/2}$, and gof = $[\Sigma w(|F_o|-|F_c|)^2/(m-n)]^{1/2}$. Values given for R, R_w, and gof are based on those reflections with $I \geq 3\sigma(I)$.

Table S2. Atomic coordinates and B_{eq}

atom	x	y	z	B_{eq}	occ.
Lu(1)	0.00000	0.00000	0.50000	2.742(3)	1/6
P(1)	0.16357(4)	0.06103(4)	0.43892(2)	3.60(1)	
O(1)	0.1058(1)	0.0673(1)	0.46450(4)	4.00(4)	
O(2)	0.1326(1)	-0.0088(1)	0.41321(4)	4.42(4)	
O(3)	0.4571(8)	-0.0862(5)	0.4506(2)	9.6(2)	0.50
O(4)	0.4208(7)	-0.1654(5)	0.4084(2)	14.5(3)	0.50
O(5)	0.328(2)	-0.129(1)	0.4282(3)	16.8(6)	0.50
O(6)	0.197(1)	-0.247(1)	0.4004(3)	12.8(5)	0.50
N(1)	0.0000	0.0000	0.34601(8)	4.14(3)	1/3
N(2)	0.1476(1)	0.1580(1)	0.38648(5)	4.20(5)	
N(3)	0.4146(6)	-0.1196(5)	0.4277(2)	7.2(2)	0.50
C(1)	0.0628(2)	0.0792(2)	0.33203(6)	4.99(7)	
C(2)	0.1428(2)	0.1120(2)	0.35166(6)	4.75(6)	
C(3)	0.1698(2)	0.2437(2)	0.37831(8)	6.06(8)	
C(4)	0.2071(1)	0.1556(2)	0.41293(6)	4.34(5)	
C(5)	0.2473(1)	0.0707(2)	0.46510(6)	4.03(5)	
C(6)	0.2849(2)	0.0269(2)	0.45672(7)	5.20(7)	
C(7)	0.3486(2)	0.0342(2)	0.47767(10)	6.45(9)	
C(8)	0.3745(2)	0.0840(3)	0.5074(1)	7.01(10)	
C(9)	0.3381(2)	0.1276(2)	0.51653(9)	6.88(9)	
C(10)	0.2740(2)	0.1218(2)	0.49557(8)	5.37(7)	

$$B_{eq} = \frac{8}{3}\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos\gamma + 2U_{13}aa^*cc^*\cos\beta + 2U_{23}bb^*cc^*\cos\alpha)$$

Table S3. Anisotropic displacement parameters

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Lu(1)	0.03321(9)	0.03321	0.0378(1)	0.0166	0.0000	0.0000
P(1)	0.0372(3)	0.0483(3)	0.0466(3)	0.0178(2)	0.0043(2)	0.0028(2)
O(1)	0.0406(8)	0.054(1)	0.0552(8)	0.0220(7)	0.0110(7)	0.0073(7)
O(2)	0.052(1)	0.056(1)	0.0546(9)	0.0227(9)	-0.0016(8)	-0.0056(8)
O(3)	0.128(6)	0.089(5)	0.081(4)	0.005(4)	-0.037(6)	0.010(4)
O(4)	0.26(1)	0.138(7)	0.099(5)	0.062(7)	0.027(7)	-0.025(5)
O(5)	0.33(2)	0.24(1)	0.15(1)	0.20(1)	0.02(2)	0.02(1)
O(6)	0.137(9)	0.29(2)	0.102(8)	0.14(1)	-0.039(8)	-0.067(10)
N(1)	0.059(1)	0.0587	0.040(1)	0.0294	0.0000	0.0000
N(2)	0.052(1)	0.053(1)	0.050(1)	0.023(1)	0.0113(9)	0.0121(9)
N(3)	0.111(6)	0.061(4)	0.064(4)	0.015(4)	-0.008(4)	0.015(3)
C(1)	0.072(2)	0.069(2)	0.045(1)	0.032(2)	0.004(1)	0.011(1)
C(2)	0.061(2)	0.070(2)	0.048(1)	0.031(1)	0.015(1)	0.010(1)
C(3)	0.085(2)	0.052(2)	0.081(2)	0.026(2)	0.008(2)	0.021(1)
C(4)	0.041(1)	0.057(2)	0.055(1)	0.016(1)	0.007(1)	0.008(1)
C(5)	0.039(1)	0.059(1)	0.049(1)	0.020(1)	0.0052(10)	0.006(1)
C(6)	0.057(2)	0.084(2)	0.063(2)	0.041(2)	0.010(1)	0.013(1)
C(7)	0.062(2)	0.103(3)	0.093(2)	0.051(2)	0.008(2)	0.027(2)
C(8)	0.052(2)	0.109(3)	0.092(2)	0.031(2)	-0.004(2)	0.038(2)
C(9)	0.063(2)	0.099(3)	0.070(2)	0.017(2)	-0.016(2)	0.001(2)
C(10)	0.056(2)	0.068(2)	0.071(2)	0.024(1)	-0.007(1)	-0.008(1)

The general temperature factor expression:

$$\exp(-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$$

Table S4. Bond lengths (Å)

atom	atom	distance	atom	atom	distance
Lu(1)	O(1)	2.190(2)	P(1)	O(1)	1.492(2)
P(1)	O(2)	1.487(2)	P(1)	C(4)	1.826(3)
P(1)	C(5)	1.786(3)	O(3)	N(3)	1.12(1)
O(4)	N(3)	1.17(1)	O(5)	N(3)	1.56(3)
N(1)	C(1)	1.471(3)	N(2)	C(2)	1.518(3)
N(2)	C(3)	1.498(4)	N(2)	C(4)	1.506(3)
C(1)	C(2)	1.507(4)	C(5)	C(6)	1.381(4)
C(5)	C(10)	1.393(4)	C(6)	C(7)	1.380(4)
C(7)	C(8)	1.359(5)	C(8)	C(9)	1.363(5)
C(9)	C(10)	1.397(4)			

Table S5. Bond angles (°)*

atom	atom	atom	angle	atom	atom	atom	angle
O(1)	Lu(1)	O(1)a	88.72(6)	O(1)	Lu(1)	O(1)b	180.0
O(1)	Lu(1)	O(1)c	91.28(6)	O(1)	P(1)	O(2)	119.1(1)
O(1)	P(1)	C(4)	103.5(1)	O(1)	P(1)	C(5)	108.41(10)
O(2)	P(1)	C(4)	109.8(1)	O(2)	P(1)	C(5)	111.3(1)
C(4)	P(1)	C(5)	103.5(1)	Lu(1)	O(1)	P(1)	145.2(1)
C(1)	N(1)	C(1)	108.7(2)	C(2)	N(2)	C(3)	111.5(2)
C(2)	N(2)	C(4)	110.2(2)	C(3)	N(2)	C(4)	110.7(2)
O(3)	N(3)	O(4)	123(1)	O(3)	N(3)	O(5)	118(1)
O(4)	N(3)	O(5)	114(1)	N(1)	C(1)	C(2)	113.4(2)
N(2)	C(2)	C(1)	113.1(2)	P(1)	C(4)	N(2)	112.6(2)
P(1)	C(5)	C(6)	121.8(2)	P(1)	C(5)	C(10)	119.5(2)
C(6)	C(5)	C(10)	118.6(3)	C(5)	C(6)	C(7)	120.9(3)
C(6)	C(7)	C(8)	120.3(3)	C(7)	C(8)	C(9)	120.2(3)
C(8)	C(9)	C(10)	120.6(3)	C(5)	C(10)	C(9)	119.4(3)

*Symmetry operations: (a) -y, x-y, z (b) -x, -y, 1-z (c) y, -x+y, 1-z.

Table S6. Torsion angles (°)

atom	atom	atom	atom	angle	atom	atom	atom	atom	angle
Lu(1)	O(1)	P(1)	O(2)	38.6(2)	Lu(1)	O(1)	P(1)	C(4)	160.7(2)
Lu(1)	O(1)	P(1)	C(5)	-89.9(2)	P(1)	O(1)	Lu(1)	O(1)a	-116.8(1)
P(1)	O(1)	Lu(1)	O(1)d	-28.0(2)	P(1)	O(1)	Lu(1)	O(1)c	63.2(1)
P(1)	O(1)	Lu(1)	O(1)e	152.0(2)	P(1)	C(4)	N(2)	C(2)	-80.9(2)
P(1)	C(4)	N(2)	C(3)	155.2(2)	P(1)	C(5)	C(6)	C(7)	-178.9(2)
P(1)	C(5)	C(10)	C(9)	178.4(2)	O(1)	P(1)	C(4)	N(2)	-71.1(2)
O(1)	P(1)	C(5)	C(6)	143.5(2)	O(1)	P(1)	C(5)	C(10)	-34.4(2)
O(2)	P(1)	C(4)	N(2)	57.0(2)	O(2)	P(1)	C(5)	C(6)	10.7(2)
O(2)	P(1)	C(5)	C(10)	-167.2(2)	N(1)	C(1)	C(2)	N(2)	-85.3(3)
N(2)	C(4)	P(1)	C(5)	175.8(2)	C(1)	N(1)	C(1)a	C(2)a	-76.2(3)
C(1)	N(1)	C(1)d	C(2)d	165.7(2)	C(1)	C(2)	N(2)	C(3)	-82.7(3)
C(1)	C(2)	N(2)	C(4)	154.0(2)	C(4)	P(1)	C(5)	C(6)	-107.1(2)
C(4)	P(1)	C(5)	C(10)	75.0(2)	C(5)	C(6)	C(7)	C(8)	1.1(5)
C(5)	C(10)	C(9)	C(8)	0.1(5)	C(6)	C(5)	C(10)	C(9)	0.4(4)
C(6)	C(7)	C(8)	C(9)	-0.6(5)	C(7)	C(6)	C(5)	C(10)	-1.0(4)
C(7)	C(8)	C(9)	C(10)	0.0(5)					

*Symmetry operations: (a) -y, x-y, z (b) -x, -y, 1-z (c) y, -x+y, 1-z

(d) -x+y, -x, z (e) x-y, x, 1-z.

Table S7. Non-bonded contacts out to 3.60Å

atom	atom	distance	ADC	atom	atom	distance	ADC
O(3)	O(6)	0.90(2)	23	O(3)	C(3)	3.046(10)	24
O(3)	C(1)	3.309(9)	54430	O(3)	C(8)	3.54(1)	65607
O(3)	C(3)	3.555(8)	54430	O(4)	O(6)	1.33(1)	23
O(4)	O(4)	2.72(3)	54522	O(4)	O(6)	2.93(2)	65503
O(4)	C(1)	3.343(9)	54533	O(4)	C(9)	3.477(9)	55416
O(4)	C(2)	3.527(9)	54533	O(4)	N(3)	3.54(1)	54522
O(5)	O(6)	2.54(3)	23	O(5)	O(6)	2.59(4)	1
O(5)	C(7)	3.45(1)	1	O(6)	N(3)	0.99(2)	23
O(6)	O(6)	3.08(4)	44524	O(6)	C(3)	3.44(1)	3
O(6)	C(1)	3.48(1)	54533	O(6)	C(9)	3.51(1)	55608
O(6)	C(8)	3.51(2)	44417	N(3)	C(1)	3.408(7)	54430
C(6)	C(6)	3.325(5)	23	O(3)	H(13)	2.57	65607
O(3)	H(8)	2.63	24	O(3)	H(7)	2.83	54430
O(3)	H(3)	2.84	54430	O(3)	H(12)	2.93	1
O(4)	H(2)	2.48	54533	O(4)	H(14)	2.71	55416
O(4)	H(2)	2.90	54430	O(5)	H(12)	2.71	1
O(5)	H(4)	2.83	54430	O(6)	H(13)	2.54	44417
O(6)	H(14)	2.67	55608	O(6)	H(8)	2.87	3
N(3)	H(14)	2.70	55416	N(3)	H(2)	2.84	54430
C(6)	H(11)	2.92	23	C(7)	H(6)	3.00	54430
C(8)	H(6)	3.00	54430	H(6)	H(13)	2.61	55418
H(6)	H(12)	2.62	55418	H(11)	H(11)	2.61	23

The ADC (atom designator code) specifies the position of an atom in a crystal. The 5-digit number

shown in the table is a composite of three one-digit numbers and one two-digit number: TA (first digit) + TB (second digit) + TC (third digit) + SN (last two digits). TA, TB and TC are the crystal lattice translation digits along cell edges a, b and c. A translation digit of 5 indicates the origin unit cell. If TA = 4, this indicates a translation of one unit cell length along the a-axis in the negative direction. Each translation digit can range in value from 1 to 9 and thus ±4 lattice translations from the origin (TA=5, TB=5, TC=5) can be represented.

The SN, or symmetry operator number, refers to the number of the symmetry operator used to generate the coordinates of the target atom. A list of symmetry operators relevant to this structure are given below.

For a given intermolecular contact, the first atom (origin atom) is located in the origin unit cell and its position can be generated using the identity operator (SN=1). Thus, the ADC for an origin atom is always 55501. The position of the second atom (target atom) can be generated using the ADC and the coordinates of the atom in the parameter table. For example, an ADC of 47502 refers to the target atom moved through symmetry operator two, then translated -1 cell translations along the a axis, +2 cell translations along the b axis, and 0 cell translations along the c axis.

An ADC of 1 indicates an intermolecular contact between two fragments (eg. cation and anion) that reside in the same asymmetric unit.

Symmetry Operators:

(1)	x,	y,	z	(2)	-y,	x-y,	z
(3)	-x+y,	-x,	z	(4)	-y,	-x,	1/2+z
(5)	x,	x-y,	1/2+z	(6)	-x+y,	y,	1/2+z
(7)	-x,	-y,	-z	(8)	y,	-x+y,	-z
(9)	x-y,	x,	-z	(10)	y,	x,	1/2-z
(11)	-x,	-x+y,	1/2-z	(12)	x-y,	-y,	1/2-z
(13)	2/3+x,	1/3+y,	1/3+z	(14)	2/3-y,	1/3+x-y,	1/3+z

(15)	2/3-x+y,	1/3-x,	1/3+z	(16)	2/3-y,	1/3-x,	5/6+z
(17)	2/3+x,	1/3+x-y,	5/6+z	(18)	2/3-x+y,	1/3+y,	5/6+z
(19)	2/3-x,	1/3-y,	1/3-z	(20)	2/3+y,	1/3-x+y,	1/3-z
(21)	2/3+x-y,	1/3+x,	1/3-z	(22)	2/3+y,	1/3+x,	5/6-z
(23)	2/3-x,	1/3-x+y,	5/6-z	(24)	2/3+x-y,	1/3-y,	5/6-z
(25)	1/3+x,	2/3+y,	2/3+z	(26)	1/3-y,	2/3+x-y,	2/3+z
(27)	1/3-x+y,	2/3-x,	2/3+z	(28)	1/3-y,	2/3-x,	1/6+z
(29)	1/3+x,	2/3+x-y,	1/6+z	(30)	1/3-x+y,	2/3+y,	1/6+z
(31)	1/3-x,	2/3-y,	2/3-z	(32)	1/3+y,	2/3-x+y,	2/3-z
(33)	1/3+x-y,	2/3+x,	2/3-z	(34)	1/3+y,	2/3+x,	1/6-z
(35)	1/3-x,	2/3-x+y,	1/6-z	(36)	1/3+x-y,	2/3-y,	1/6-z

Table S8. Least squares planes

Plane number 1

Atoms defining plane	Distance
C(5)	0.003(2)
C(6)	-0.005(3)
C(7)	0.004(3)
C(8)	0.000(3)
C(9)	-0.003(4)
C(10)	-0.001(3)
Additional Atoms	**Distance**
P(1)	-0.039

Plane number 2

Atoms defining plane	Distance
O(3)	-0.036(8)
O(4)	-0.046(8)
O(5)	-0.09(1)
N(3)	0.071(7)

Summary

plane	mean deviation	χ^2
1	0.0026	6.7
2	0.0602	205.9

Dihedral angles between planes (°)

plane	1
2	17.6

Table S9. +LSIMS Mass Spectral Data for $[LnL_2]^{3+}$ (L = H_3ppma) Complexes

	$[ML_2\text{-}2H]^+$	$[ML\text{-}2H]^+$	$[ML_2\text{-}2H]^{2+}$
Lu*	1473	823	778
Yb*	1472	822	737
Tm	1467	817	734
Er	1466	816	733
Ho	1463	813	733
Dy	1462	812	731
Tb	1457	807	729
Gd	1456	806	728
Eu	1451	801	726
Sm	1450	800	726

* Identical spectrum obtained for trihydrate and pentahydrate

Table S10. Infrared Data (cm^{-1}) for $[Ln(H_3ppma)_2](X)_3 \cdot YH_2O$ (X = NO_3 or Cl†; Y = 3 or 5‡).

	$\nu_{OH/NH}$	δ_{NH}	ν_{NO_3}	ν_{PO}	$\nu_{PC/PPh}$
Lu	3435, 2614	1642	1386	1194, 1136, 1065	745, 720, 579, 560
Lu‡	3431, 2426	1643	1385	1182, 1137, 1062	740, 719, 580, 553
Yb	3455, 2621	1644	1385	1193, 1135, 1062	743, 718, 579, 559
Yb‡	3429, 2441	1643	1384	1181, 1136, 1062	741, 720, 580, 553
Tm	3429, 2615	1644	1386	1194, 1135, 1063	745, 718, 580, 559
Er	2454, 2614	1641	1386	1192, 1134, 1061	743, 718, 578, 559
Ho†‡	3442, 2413	1644		1183, 1134, 1060	740, 719, 580, 553
Dy‡	3431, 2426	1644	1364	1181, 1134, 1058	741, 718, 580, 555
Tb‡	3429, 2410	1643	1386	1180, 1034, 1058	740, 718, 580, 553
Gd‡	3423, 2445	1644	1384	1180, 1035, 1057	740, 718, 580, 553
Eu†‡	3443, 2445	1643		1180, 1035, 1055	740, 718, 580, 553
Sm†‡	3418, 2460	1650		1180, 1133, 1054	741, 717, 580, 559

Figure S1. ORTEP representation of the cation in $[Lu(H_3ppma)_2](NO_3)_3 \cdot 3H_2O$ (25% probability thermal ellipsoids). View approximately down the threefold axis.