Pergamon

0277-5387(95)00067-4

Polyhedron Vol. 14, No. 17–18, pp. 2451–2454, 1995

0277-5387/95 $9.50+0.00

SYNTHESIS OF LANTHANIDE COMPLEXES WITH L-ISOLEUCINE: X-RAY CRYSTAL STRUCTURE OF $[Nd_2(Ileu)_4(H_2O)_8](ClO_4)_6$

JIAN-JUN ZHAO, WEI-CHUN YANG, XIAO-QING WANG and TIAN-ZHU JIN*

Research Centre of Rare Earth Chemistry, Peking University, Beijing, 100871, China

(*Received* 21 *November* 1994; *accepted* 18 *January* 1995)

Abstract—Two lanthanide complexes, $Ln_2(Ileu)_4(ClO_4)_6 \cdot 8H_2O$, were synthesized in aqueous solution (where Ln = Nd or Er, Ileu = L-isoleucine). The crystal structure of the neodymium complex was determined by X-ray diffraction. The complex is a binuclear molecule, each neodymium ion is coordinated by four carboxylic oxygen atoms from four L-isoleucine and four oxygen atoms from H_2O, forming a square antiprism coordination polyhedron.

Lanthanide ions are often used as spectroscopic probes as surrogates for calcium ions in studies of biological systems, as well as promoters in the textile dyeing industry and diagnostic agents in clinical medicine.[1–3] Since lanthanide ions can substitute for calcium ions in living systems, studies of the bonding modes and structures of lanthanide complexes with some amino acids are of interest. Studies on lanthanide complexes with some amino acids in solution have been carried out using NMR, luminescence and titration methods to determine the thermodynamic stability constants.[4–6] Crystallographic studies on these complexes in the solid state have also appeared recently. However, they are limited to glycine, alanine, glutamic acid, proline, etc.[7–10] In this paper, a novel neodymium complex with L-isoleucine is synthesized and its crystal structure determined by X-ray analysis.

EXPERIMENTAL

Preparation

The complexes were prepared by dissolving L-isoleucine in an aqueous solution of $Nd(ClO_4)_3$ or $Er(ClO_4)_3$ at pH 4–5 with the molar ratio 1 : 1. A single crystal was obtained by slow evaporation at room temperature. After washing with water and air-drying, the composition of these crystals was determined by elemental analysis. The formulae and elemental analysis data are listed in Table 1. The water contents are a little higher than the calculated compositions of the complexes because of insufficient air-drying of the crystal before elemental analysis.

X-ray analysis

A reddish coloured crystal of the neodymium compound with dimensions $0.2 \times 0.3 \times 0.3$ mm was mounted in a thin capillary for structure determination. The reflection data were collected on an Enraf–Nonius CAD4 diffractometer with graphite-monochromated Mo-K_α radiation in the ω–2θ scan mode. Cell parameters were calculated by the least-squares method; 2241 independent reflections were collected, of which 1977 reflections with $I \geqslant 3\sigma(I)$ were used in the analysis. Intensities were treated by Lorentz polarization and absorption corrections. The calculations were performed using the SDP-PLUS system. The structure was determined by direct methods (MULTAN 82) and difference-Fourier synthesis, and then refined by full-matrix

*Author to whom correspondence should be addressed.

Table 1. Formulae and elemental analysis data (calculated values in parentheses)

Complex	N (%)	C (%)	H (%)
$Nd(Ileu)_2(ClO_4)_3 \cdot 5H_2O$	3.4 (3.5)	17.9 (18.1)	4.3 (4.6)
$Er(Ileu)_2(ClO_4)_3 \cdot 5H_2O$	3.0 (3.4)	17.2 (17.6)	4.3 (4.4)

least-squares method to final R and R_w values of 0.056 and 0.060, respectively. Crystal data, details of data collection and refinement are listed in Table 2.

RESULTS AND DISCUSSION

The crystal structure of the $[Nd_2(Ileu)_4(H_2O)_8](ClO_4)_6$ complex and its coordination polyhedron are shown in Figs 1 and 2, respectively. Selected bond lengths and bond angles are listed in Table 3.

The complex exists as dimeric molecules. Two neodymium ions are connected by four bridging carboxyl groups from four isoleucine molecules. Each central ion is also coordinated by four oxygen atoms from H_2O. The coordination number is 8, and the coordination polyhedron is a distorted

Table 2. Crystal data, data collection details and refinement

Empirical formula	$C_{24}H_{68}Cl_6N_4Nd_2O_{40}$
Colour	Reddish
Crystal size (mm)	$0.2 \times 0.3 \times 0.3$
Crystal system	Monoclinic
Space group	C_2
a (Å)	21.703(4)
b (Å)	10.435(2)
c (Å)	15.200(3)
β (°)	120.26(2)
V (Å^3)	2973(2)
Z	2
M	1554.01
D_c (g cm^{-3})	1.736
Absorption coefficient (cm^{-1})	21.016
$F(000)$	1564
λ (Å) (Mo-K_α)	0.71073
Monochromator	Graphite
Scan type	ω–2θ
2θ range (°)	4.0–46.0
Scan speed (° min^{-1})	0.92–5.49
Standard reflections	1/100
Index range h, k, l	−23 to 23; 0–11; 0–16
Reflections collected	2241
Independent reflections	2024 (R_{int} = 2.4%)
Observed reflections	1977 [$I \geqslant 3\sigma(I)$]
Absorption correction	Empirical absorption correction[a]
Quantity minimized	$\Sigma w(\|F_o\| - \|F_c\|)^2$
Number of parameters refined	352
Final R	0.056
Final R_w	0.060
Good-of-fit	5.04
Maximum Δ/σ	0.81
Max. residual peak (e Å^{-3})	0.94

[a] Ref. 12.

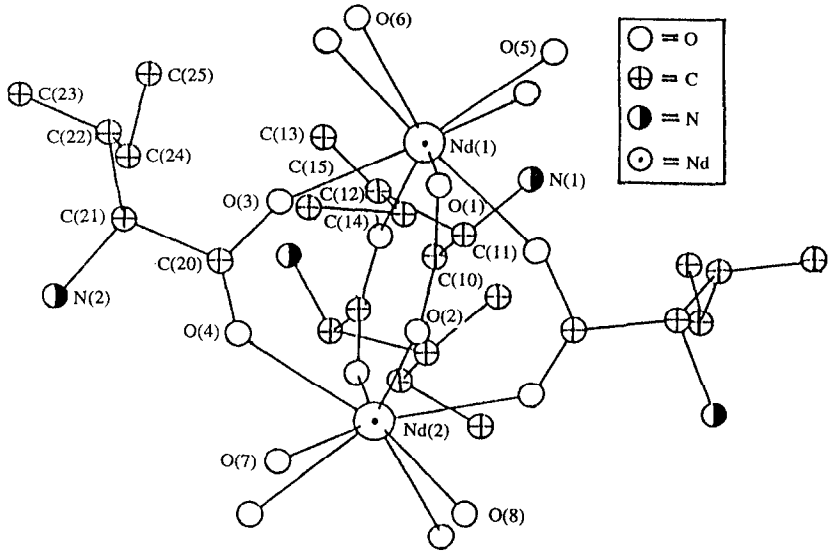

Fig. 1. Structure of $[Nd_2(Ileu)_4(H_2O)_8](ClO_4)_6$.

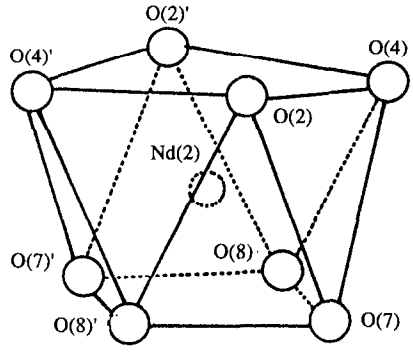

Fig. 2. Coordination polyhedron of $[Nd_2(Ileu)_4(H_2O)_8](ClO_4)_6$.

Table 3. Selected bond lengths (Å) and bond angles (°)

Nd(1)—O(1)	2.49(2)	Nd(2)—O(2)	2.24(1)
Nd(1)—O(3)	2.33(2)	Nd(2)—O(4)	2.41(1)
Nd(1)—O(5)	2.47(1)	Nd(2)—O(7)	2.51(1)
Nd(1)—O(6)	2.52(1)	Nd(2)—O(8)	2.58(1)
O(1)—Nd(1)—O(1)′	128.7(6)	O(2)—Nd(2)—O(2)′	119.6(6)
O(1)—Nd(1)—O(3)	79.5(4)	O(2)—Nd(2)—O(4)	79.9(4)
O(1)—Nd(1)—O(3)′	71.7(4)	O(2)—Nd(2)—O(4)′	78.0(4)
O(1)—Nd(1)—O(5)	80.4(4)	O(2)—Nd(2)—O(7)	74.9(4)
O(1)—Nd(1)—O(5)′	135.5(3)	O(2)—Nd(2)—O(7)′	139.9(5)
O(1)—Nd(1)—O(6)	75.3(4)	O(2)—Nd(2)—O(8)	74.3(4)
O(1)—Nd(1)—O(6)′	139.2(4)	O(2)—Nd(2)—O(8)′	149.0(4)
O(3)—Nd(1)—O(3)′	109.9(6)	O(4)—Nd(2)—O(4)′	135.4(4)
O(3)—Nd(1)—O(5)	152.8(3)	O(4)—Nd(2)—O(7)	67.6(4)
O(3)—Nd(1)—O(5)′	80.5(4)	O(4)—Nd(2)—O(7)′	139.7(3)
O(3)—Nd(1)—O(6)	83.8(4)	O(4)—Nd(2)—O(8)	133.0(3)
O(3)—Nd(1)—O(6)′	140.8(4)	O(4)—Nd(2)—O(8)′	76.2(3)
O(5)—Nd(1)—O(5)′	101.8(5)	O(7)—Nd(2)—O(7)′	119.8(6)
O(5)—Nd(1)—O(6)	73.6(3)	O(7)—Nd(2)—O(8)	68.1(3)
O(5)—Nd(1)—O(6)′	63.3(4)	O(7)—Nd(2)—O(8)′	77.8(3)
O(6)—Nd(1)—O(6)′	109.1(6)	O(8)—Nd(2)—O(8)′	108.8(4)

A prime means that the symmetry operation is: 2-x, y, 1-z.

Table 4. Least square fitting equations of planes containing co-planar atoms

Plane 1	Equation	$-0.0002\,x+1.0000\,y+0.0004\,z=-4.8584$			
	Atoms	O(7)	O(8)	O(8)′	O(7)
	P (Å)	0.1207	−0.1224	−0.1224	0.1241
Plane 2	Equation	$0.0002\,x+1.0000\,y+0.0002\,z=-2.4519$			
	Atoms	O(4)	O(2)	O(2)′	O(4)′
	P (Å)	−0.1052	0.1038	0.1052	−0.1039
Plane 3	Equation	$-0.0003\,x-1.0000\,y+0.0019\,z=0.2246$			
	Atoms	O(1)	O(3)	O(3)′	O(1)′
	P (Å)	−0.1333	0.1272	0.1335	−0.1275
Plane 4	Equation	$-0.0004\,x-1.0000\,y-0.0003\,z=-2.5105$			
	Atoms	O(6)	O(5)′	O(5)	O(6)′
	P (Å)	0.0476	−0.0476	−0.0476	0.0475

P is the distance of the atoms from the plane.

square antiprism. Four oxygen atoms from water molecules form the lower plane and four carboxyl atoms form the upper plane (Table 4).

There is a C_2 symmetry axis in the binuclear molecule and two neodymium ions were located on the C_2 axis. Alkyl groups of the L-isoleucine were arranged around the C_2 axis. The unit cell contains two molecules.

The crystal structure of the isoleucine complex has some similarities with those of alanine and phenylalanine complexes reported previously.[11] For example, they are all dimeric molecules, eight-coordinated and have a C_2 symmetry axis. The average Er—O(carboxyl) and Er—O(water) bond lengths of the complex are 2.37 and 2.52 Å, respectively.

The perchlorate anions reside in the cavities of the crystal and stabilize the crystal packing by forming hydrogen bonds.

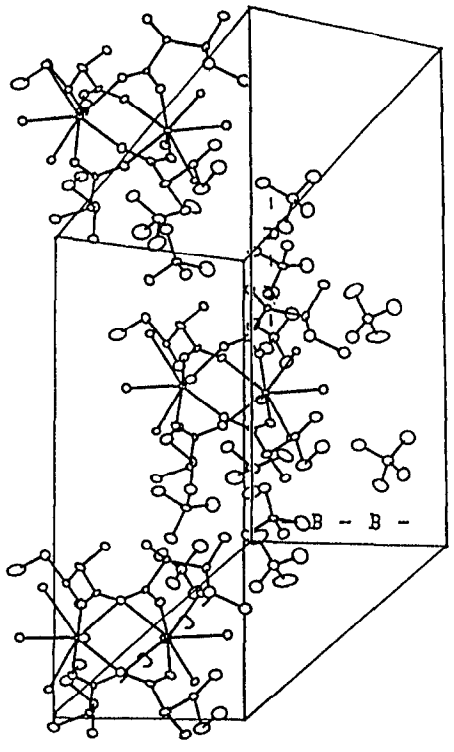

Fig. 3. Arrangement of $[Nd_2(Ileu)_4(H_2O)_8](ClO_4)_6$ in unit cell.

Acknowledgement—This work was supported by Climbing Program, a National Key Project for Fundamental Research.

REFERENCES

1. H. B. Brittain, F. S. Richardson and R. B. Martin, *J. Am. Chem. Soc.* 1978, **98**, 8255.
2. W. De. W. Horrocks Jr and D. R. Sudnick, *J. Am. Chem. Soc.* 1979, **101**, 334.
3. H. G. Brittain, *Inorg. Chem.* 1979, **18**, 1740.
4. A. Aziz, S. J. Lyle and J. E. Newbery, *J. Inorg. Nucl. Chem.* 1979, **33**, 1975.
5. A. D. Sherry, C. Yoshida, E. R. Birnbaun and D. W. Darnall, *J. Am. Chem. Soc.* 1973, **95**, 3011.
6. J. Legendziewicz, E. Huskowska, G. Y. Argay and A. Waskowska, *Inorg. Chim. Acta* 1984, **95**, 57.
7. T. Z. Jin, S. Gao, C. H. Huang, Y. Z. Han and G. X. Xu, *Chem. J. Chin. Univ.* 1989, **10**, 118.
8. T. Z. Jin, S. Gao, C. H. Huang, Y. Z. Han and G. X. Xu, *J. Chin. RE Soc.* 1987, **5**, 1.
9. I. Gsoregh, M. Gzugler, P. Kierkegaard, J. Legengziewicz and E. Huskowska, *Acta Chem. Scand.* 1989, **43**, 735.
10. J. Legendziewicz, T. Glowiak, E. Huskowska and D. C. Ngoan, *Polyhedron* 1989, **8**, 2139.
11. Q. R. Jin, X. Q. Wang, T. Z. Jin, S. W. Zhang and G. X. Xu, *J. Alloys and Compounds* 1994, **207/208**, 400.
12. N. Walker and D. Stuart, *Acta Cryst.* 1983 **A39**, 159.