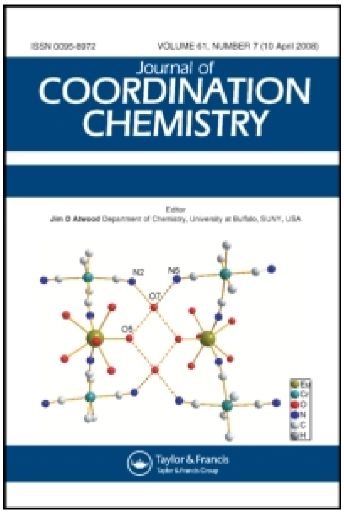

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

SYNTHESIS, CHARACTERIZATION AND CRYSTAL STRUCTURE OF DIAQUADI(2,2"-BIPYRIDINE)DI(DICHLOROACETATO)LANTHANIDE(III) MONODICHLOROACETATO

Lu Weimin[a]; Cheng Yiqiang[a]; Dong Nan[a]; Gu Jianming[a]; Chen Chenggang[a]
[a] Department of Chemistry, Hangzhou University, Hangzhou, P.R. China

To cite this Article Weimin, Lu , Yiqiang, Cheng , Nan, Dong , Jianming, Gu and Chenggang, Chen(1995) 'SYNTHESIS, CHARACTERIZATION AND CRYSTAL STRUCTURE OF DIAQUADI(2,2"-BIPYRIDINE)DI(DICHLOROACETATO)LANTHANIDE(III) MONODICHLOROACETATO', Journal of Coordination Chemistry, 35: 1, 51 — 59

To link to this Article: DOI: 10.1080/00958979508033085

URL: http://dx.doi.org/10.1080/00958979508033085

J. Coord. Chem., 1995, Vol 35, pp. 51–59
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SYNTHESIS, CHARACTERIZATION AND CRYSTAL STRUCTURE OF DIAQUADI(2,2'-BIPYRIDINE)DI(DICHLOROACETATO) LANTHANIDE(III) MONODICHLOROACETATO

LU WEIMIN,* CHENG YIQIANG, DONG NAN

Department of Chemistry, Hangzhou University, Hangzhou 310028, P.R. China

GU JIANMING and CHEN CHENGGANG

Department of Chemistry, Hangzhou University, Hangzhou 310028, P.R. China

(Received July 12, 1993; in final form October 20, 1994)

The title complexes, diaquadi(2,2"-bipyridine)di(dichloroacetato)lanthanide(III) monodichloroacetato $[Ln(CHCl_2COO)_2(2,2'\text{-bipy})_2(H_2O)_2]^+(CHCl_2COO)^-$ (Ln = Dy, Ho, Tm, Er, Yb], were obtained and characterized. $[Er(CHCl_2COO)_2(2,2'\text{-bipy})_2(H_2O)_2]^+(CHCl_2COO)^-$ crystallizes in the monoclinic space group $P2_1/n$ with $Z = 4$. Cell dimensions are $a = 15.886(9)$, $b = 13.758(2)$, $c = 16.343(4)$Å, $\beta = 113.31(3)°$, and the structure was refined to an R of 0.049 for 3415 observed reflections. The Er(III) ion exhibits a distorted, square antiprismatic configuration. Four N atoms of 2,2'-bipy and four O atoms from two dichloroacetato and two water ligands are coordinated. One dichloroacetato group lies outside the polyhedron and is connected with water ligands by hydrogen bonds.

KEYWORDS: lanthanide, erbium, dichloroacetato, 2,2'-bipyridine, X-ray structure

INTRODUCTION

Lanthanide dichloroacetate and corresponding ternary coordination compounds have been studied by earlier workers[1,2,3] particularly from the point of view of preparation. It is difficult to obtain complexes with bidentate heterocyclic amine ligands in aqueous media,[4] but in this paper we report complexes of lanthanide dichloroacetate (Ln = Dy, Ho, Er, Tm, Yb) with two 2,2'-bipyridines from H_2O and ethanol; we have determined the structure of $[Ln(CHCl_2COO)_2(2,2'\text{-bipy})_2(H_2O)_2]^+(CHCl_2COO)^-$ by X-ray diffraction methods and have obtained related complexes of lanthanide dichloroacetate with 1,10-phenanthroline.[5] The present work is a part of a continuing study of lanthanide complexes with heterocyclic amine ligands.

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* Author for correspondence.

EXPERIMENTAL

Synthesis

Lanthanide dichloroacetates were prepared following a method reported in a previous publication[6] and recrystallized from H_2O/CH_3CH_2OH (1:1 volume ratio). Lanthanide dichloroacetate (0.2 mmol) was dissolved in 4 cm^3 of mixed solvent and mixed with a solution of 2,2'-bipyridine (0.4 mmol) in the same solvent. The resulting solution was set aside at room temperature and single crystals suitable for X-ray work were obtained after about one month. Compositions were determined as $C_{26}H_{23}Cl_6LnN_4O_8$ by analysis (Table 1).

IR spectra of the complexes were recorded using a Perkin Elmer 683 IR spectrometer (KBr or CsI discs). Electrolytic conductances were measured at 25°C (0.3×10^{-6} M) in methanol.

Crystal Structure Determination

A crystal of the erbium complex was mounted on an Enraf-Nonius CAD4 diffractometer. A unique data set was measured in conventional $\omega/2\theta$ scan mode at room temperature with MoKα radiation (λ = 0.7107 Å). Final lattice parameters and crystal orientations were calculated from least-squares refinement within the 2θ range 10°–12°.

During the collection of crystal data, three reflections were monitored periodically. The intensities were corrected for Lorentz polarization effects and absorption based on intensity measurements at different azimnthal angles. A total of 5800 independent reflections were measured within the limit $2\theta max$ = 50°; 3415 with $I > 3\ \sigma(I)$ were included in the refinement.

The structure was solved by the heavy atom method. All non-hydrogen atoms were located by difference Fourier syntheses and refined by full-matrix least-squares methods with anisotropic temperature factors. All H atoms were located by using the same method but given fixed temperature factor Beq = 4.0 $Å^2$ and not refined. Scattering factors for neutral atoms were taken from International Tables For X-ray Crystallography (Vol IV, 1974) and were included in the program package. The final refinement factors are R = 0.049 and R_w = 0.054. All calculations were performed on a VAX II computer using the Structure Determination Package program system.[7] Details are given in Table 2, and complete data are available from the authors upon request.

Table 1 Analytical Data (%) For The Complexes.

Complex	C%		H%		N%		RE%	
	calc.	found	calc.	found	calc.	found	calc.	found
$C_{26}H_{23}Cl_6DyN_4O_8$	34.91	34.80	2.59	2.51	6.26	6.14	18.16	18.22
$C_{26}H_{23}Cl_6HoN_4O_8$	34.82	34.75	2.59	2.49	6.25	6.05	18.39	18.24
$C_{26}H_{23}Cl_6ErN_4O_8$	34.72	34.70	2.58	2.37	6.23	6.44	18.60	18.73
$C_{26}H_{23}Cl_6TmN_4O_8$	34.66	34.63	2.57	2.50	6.22	6.03	18.75	18.63
$C_{26}H_{23}Cl_6YbN_4O_8$	34.51	34.43	2.56	2.37	6.19	5.93	19.12	19.16

Table 2 Crystal and data collection parameters for the $[Er(CHC_2COO)_2(2,2'\text{-bipy})_2(H_2O)_2]^+$ $(CHCl_2COO)^-$ complex.

Chemical formula	$C_{26}H_{23}Cl_6ErN_4O_8$
Molecular weight	899.45
Crystal system	monoclinic
Space group	$P2_1/n$
Crystal size cell dimension	0.54 × 0.3 × 0.12
a(Å)	15.886(9)
b(Å)	13.758(3)
c(Å)	16.343(4)
β(°)	113.31(3)
V(Å^3)	3280(1)
Z	4
F(000)	1764
D_{calc}(g/cm^3)	1.820
μ (cm^{-1})	31.34
Absorption correction (T_{min}, T_{max})	0.764, 0.999
Intensity Variation	0.039
h min, max.	0, 18
k min, max.	0, 16
l min, max.	-19, 19
R	0.049
R_w	0.054
Weighting scheme	unit weights
(Δ/σ)max	0.06
(Δ ρ)min., max. (e/A^3)	-0.804, 0.930
GOF	4.46

RESULTS AND DISCUSSION

Solubility, Molar Conductivity and IR Spectra

The complexes are soluble in dimethylformamide and pyridine, and slightly soluble in methanol, acetone; they are insoluble in ether, benzene, chloroform, nitromethane, carbon tetrachloride and ethyl acetate. Molar conductivity values are 64 to 78 S cm^2 mol^{-1}, which indicates 1:1 electrolyte behaviour[8] and shows that one dichloroacete anion is not coordinated. This is confirmed in the crystal structure.

IR spectra of $[Ln(CHCl_2COO)_2(2,2'\text{-bipy})_2(H_2O)_2]^+(CHCl_2COO)^-$ complexes are similar to each other. The υas(COO$^-$) and υs(COO$^-$) in the complexes have absorptions at ~1648 cm^{-1} and ~1378 cm^{-1} respectively. The Δv values are ~270 cm^{-1}, larger than that in $CHCl_2COONa$ (240 cm^{-1}).[9] The direction of shifts in the υas(COO$^-$) and υs(COO$^-$) is higher and lower, respectively, and the separation (Δ) between the v(CO_2) frequencies is increased compared with those of $CHCl_2COONa$ (Table 3). Dca groups in the complexes can behave as unidentates.[10,11]

The characteristic ring stretching vibration of 2,2'-bipy at 990 cm^{-1} [12] is increased to ~1020 cm^{-1} for the complexes and the strong C-H out-of-plane

Table 3 Characteristic IR data (cm^{-1}), for the complexes

	$CHCl_2COONa$	Dy	Ho	Er	Tm	Yb
υas(COO$^-$)	1640	1650	1647	1647	1648	1648
υs(COO$^-$)	1399	1400	1379	1375	1376	1380
Δv	241	250	268	272	272	268

bending absorption appearing at 760 cm^{-1} splits into several bands; this is evidence of 2,2'-bipy coordinating with lanthanide atoms. Weak ν(Ln-O) and ν(Ln-N) frequencies appear at ~450 cm^{-1} and ~275 cm^{-1}, respectively. Water absorptions appear at ~3450 cm^{-1}.

Crystal Structure Analysis

Final atomic coordinates and equivalent temperature factors for non-hydrogen atoms are given in Table 4. Selected bond distances and angles are listed in Table 5. Figure 1 shows an ORTEP diagram of the molecular structure and the numbering scheme for the erbium complex. Figure 2 and Figure 3 illustrate the coordination geometry of the erbium atom and the molecular packing arrangement in the unit cell, respectively.

The crystal is composed of $[Er(CHCl_2COO)_2(2,2'\text{-bipy})_2(H_2O)_2]^+$ cations and $CHCl_2COO^-$ anions, which is quite different to the case of $Pr(CCl_3COO)_3$ $(bipy)_2$ $(H_2O)_2$.[13] The erbium(III) atom is eight-coordinate (by four oxygen atoms and four nitrogen atoms) in a distorted square antiprism. Two oxygen atoms of the unidentate dca and water ligands and two nitrogen atoms respectively coming from the two 2,2'-bipy ligands occupy the ligand sites of each square face of the antiprism; deviation of all these atoms from their least-squares planes is negligible (max. dev. 0.05(1)Å for N(3)). The least-squares planes of the square faces of the antiprism are essentially parallel to each other (dihedral angle about 2°). The distance of the erbium atom to the two square faces of the antiprism is nearly the same (1.300(1) and 1.316(1)Å respectively). For an undistorted square antiprism, with identical ligands, the angle α between the four-fold axis of the square antiprism and the Ln-L bond is 59.26° for a structure with minimum repulsion energy based on the hard sphere model.[14] In this molecular structure, the values (Table 5) for nitrogen atoms are nearly the same or smaller than the idea value, but values for oxygen atoms are larger. This is caused by the ring composed of the erbium atom, two bidentate nitrogen atoms and two carbon atoms of 2,2'-bipy; the distance between bidentate nitrogen atoms is shorter than the O-O and O-N distances in the square faces of the antiprism.

In the mixed-ligand Er(III) complex, being different to the 1,10-phenanthroline complexes[15] or 2,2'-bipy in the copper complex,[16] the atoms of two 2,2'-bipy groups are removed from least-squares planes, especially C(8), C(13), C(15), C(18) and C(25) atoms (max. dev. 0.144(1)Å for C(25)), as the rings of coordinated 2,2'-bipy are bent. Er(III) is displaced out of the mean planes of the bidentate nitrogen heterocycles (0.545(1) and 0.629(1)Å, respectively).

The angle between the least-squares planes of the faces of the two 2,2'-bipy rings is 25.9(5)°. The average bond distances are Er-O(dca) 2.297, Er-O(H_2O) 2.323 and Er-N 2.504 Å, which do not differ significantly from other similar complexes.[15] Bond distances and angles for the dca groups are nearly the same as those in the free dichloroacetic anion.

As shown in Figure 1, and Table 5, the non-coordinated $CHCl_2COO^-$ anion is connected with two water molecules by hydrogen bonds. Besides this, water ligands also form intramolecular hydrogen bonds with the uncoordinated O atoms of the dca ligands. Hydrogen bonds play an important role in the stability of the molecular structure and crystal packing.

IR spectra and molar conductivities of $[Ln(CHCl_2COO)_2(2,2'\text{-bipy})_2(H_2O)_2]^+$

Table 4 Fractional coordinates and equivalent isotropic temperature factors (Å^2) of the non-H atoms.

Atom	*x/a*	*y/b*	*z/c*	*B*eq
Er	0.25247(4)	0.43962(4)	0.49420(3)	3.225(9)
Cl(1)	0.1871(3)	-0.0575(4)	0.4209(3)	8.2(1)
Cl(2)	0.2840(3)	-0.0838(3)	0.6100(3)	8.3(1)
Cl(3)	0.3225(4)	0.6837(3)	0.7356(3)	7.6(1)
Cl(4)	0.4507(4)	0.5425(4)	0.8467(4)	10.2(2)
Cl(5)	0.0305(3)	0.4589(4)	0.1282(3)	8.8(2)
Cl(6)	0.1150(5)	0.6331(3)	0.2223(3)	11.2(2)
O(1)	0.2606(8)	0.1244(7)	0.5769(6)	7.1(3)
O(2)	0.3178(7)	0.1258(7)	0.4711(6)	6.5(3)
O(3)	0.2798(6)	0.5096(6)	0.6303(4)	4.2(2)
O(4)	0.2930(9)	0.4055(7)	0.7357(6)	7.8(3)
O(5)	0.2135(8)	0.3728(7)	0.2544(5)	6.6(3)
O(6)	0.2085(6)	0.4857(6)	0.3484(4)	4.2(2)
O(7)	0.2485(6)	0.3123(6)	0.5851(5)	4.3(2)
O(8)	0.2903(6)	0.3079(6)	0.4256(5)	4.4(2)
N(1)	0.1251(6)	0.5564(8)	0.4688(5)	3.7(2)
N(2)	0.0946(7)	0.3719(8)	0.4177(6)	4.4(3)
N(3)	0.3474(7)	0.5858(7)	0.4980(6)	3.9(2)
N(4)	0.4227(7)	0.4202(8)	0.5839(6)	4.3(2)
C(1)	0.2900(9)	0.0903(9)	0.5223(8)	5.0(3)
C(2)	0.2891(9)	-0.0266(9)	0.5159(8)	5.6(4)
C(3)	0.2989(9)	0.4850(9)	0.7084(8)	4.2(3)
C(4)	0.3362(9)	0.5664(9)	0.7804(7)	4.7(2)
C(5)	0.1900(8)	0.4508(9)	0.2723(7)	4.3(3)
C(6)	0.1327(9)	0.5148(9)	0.1918(8)	5.1(4)
C(7)	0.1422(9)	0.6484(9)	0.5012(7)	4.5(3)
C(8)	0.0754(9)	0.7205(9)	0.4809(8)	5.1(3)
C(9)	-0.0117(9)	0.6986(9)	0.4225(9)	6.1(4)
C(10)	-0.0297(9)	0.6052(9)	0.3897(9)	5.7(4)
C(11)	0.0414(8)	0.5374(9)	0.4133(7)	4.4(3)
C(12)	0.0224(8)	0.4335(9)	0.3827(7)	4.6(3)
C(13)	-0.0633(9)	0.4004(9)	0.3241(9)	6.7(5)
C(14)	-0.0754(9)	0.3022(9)	0.3069(9)	7.6(5)
C(15)	-0.0033(9)	0.2401(9)	0.3467(9)	5.8(4)
C(16)	0.0794(9)	0.2783(9)	0.4010(8)	5.3(4)
C(17)	0.3113(9)	0.6632(9)	0.4467(7)	4.4(3)
C(18)	0.3579(9)	0.7499(9)	0.4548(8)	4.7(3)
C(19)	0.4421(9)	0.7594(9)	0.5196(9)	5.9(4)
C(20)	0.4824(9)	0.6795(9)	0.5728(9)	5.4(4)
C(21)	0.4327(8)	0.5916(9)	0.5585(7)	4.2(3)
C(22)	0.4752(8)	0.5023(9)	0.6071(8)	4.3(3)
C(23)	0.5641(9)	0.4994(9)	0.6717(9)	5.8(4)
C(24)	0.5989(9)	0.4111(9)	0.7076(9)	6.3(4)
C(25)	0.5451(8)	0.3271(9)	0.6808(8)	5.3(4)
C(26)	0.4591(9)	0.3366(9)	0.6183(8)	4.9(3)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $Beq = (4/3)[a^2B_{11} + b^2 B_{22} + c^2 B_{33} + ab(\cos\gamma) B_{12} + ac(\cos\beta) B_{13} + bc(\cos\alpha)B_{23}]$.

$(CHCl_2COO)^-$ [Ln = Dy, Ho, Tm and Yb] are all similar and the composition of the complexes are in fair agreement with analyses. The complexes may, therefore, be isomorphous.

Table 5 Relevant bond distances (Å), bond angles (°).

Eu-O(3)	2.302(2)	C(3)-C(4)	1.561(8)
Eu-O(6)	2.293(3)	C(4)-Cl(3)	1.749(7)
Eu-O(7)	2.314(2)	C(4)-Cl(4)	1.741(9)
Eu-O(8)	2.332(2)	C(5)-C(6)	1.545(8)
Eu-N(1)	2.486(5)	C(6)-Cl(5)	1.725(8)
Eu-N(2)	2.499(6)	C(6)-Cl(6)	1.757(8)
Eu-N(3)	2.500(5)	C(7)-C(8)	1.394(9)
Eu-N(4)	2.530(5)	C(8)-C(9)	1.368(9)
O(1)-C(1)	1.251(8)	C(9)-C(10)	1.378(9)
O(2)-C(1)	1.193(9)	C(10)-C(11)	1.397(9)
O(3)-C(3)	1.236(7)	C(11)-C(12)	1.505(9)
O(4)-C(3)	1.198(7)	C(12)-C(13)	1.396(9)
O(5)-C(5)	1.209(7)	C(13)-C(14)	1.378(9)
O(6)-C(5)	1.254(6)	C(14)-C(15)	1.370(9)
N(1)-C(7)	1.357(8)	C(15)-C(16)	1.367(9)
N(1)-C(11)	1.306(9)	C(17)-C(18)	1.383(8)
N(2)-C(12)	1.357(5)	C(18)-C(19)	1.344(9)
N(2)-C(16)	1.317(4)	C(19)-C(20)	1.391(9)
N(3)-C(17)	1.336(5)	C(20)-C(21)	1.411(9)
N(3)-C(21)	1.327(5)	C(21)-C(22)	1.473(9)
N(4)-C(22)	1.365(5)	C(22)-C(23)	1.391(9)
N(4)-C(26)	1.309(5)	C(23)-C(24)	1.366(9)
C(1)-C(2)	1.610(9)	C(24)-C(25)	1.401(9)
C(2)-Cl(1)	1.796(7)	C(25)-C(26)	1.350(9)
C(2)-Cl(2)	1.759(7)		
O(7)-H(71)	1.137(9)	O(8)-H(81)	1.008(6)
O(7)-H(72)	0.945(7)	O(8)-H(82)	0.996(8)
O(3)-Er-O(6)	138.85(9)	O(8)-Er-N(2)	82.4(1)
O(3)-Er-O(7)	74.84(9)	O(8)-Er-N(3)	111.6(1)
O(3)-Er-O(8)	143.50(8)	O(8)-Er-N(4)	77.1(1)
O(3)-Er-N(1)	73.8(1)	N(1)-Er-N(2)	64.4(1)
O(3)-Er-N(2)	114.0(1)	N(1)-Er-N(3)	85.9(2)
O(3)-Er-N(3)	76.0(1)	N(1)-Er-N(4)	141.1(1)
O(3)-Er-N(4)	74.5(1)	N(2)-Er-N(3)	142.1(1)
O(6)-Er-O(7)	143.37(9)	N(2)-Er-N(4)	151.9(1)
O(6)-Er-O(8)	75.20(8)	N(3)-Er-N(4)	64.8(2)
O(6)-Er-N(1)	75.8(1)	Er-O(3)-C(3)	139.3(3)
O(6)-Er-N(2)	75.5(1)	Er-O(6)-C(6)	141.3(3)
O(6)-Er-N(3)	74.7(1)	Er-N(1)-C(7)	120.9(5)
O(6)-Er-N(4)	116.6(1)	Er-N(1)-C(11)	121.6(4)
O(7)-Er-O(8)	78.4(1)	Er-N(2)-C(12)	119.5(4)
O(7)-Er-N(1)	111.6(1)	Er-N(2)-C(16)	122.2(4)
O(7)-Er-N(2)	76.2(1)	Er-N(3)-C(17)	121.3(4)
O(7)-Er-N(3)	139.7(1)	Er-N(3)-C(21)	119.7(4)
O(7)-Er-N(4)	80.9(1)	Er-N(4)-C(22)	117.9(4)
O(8)-Er-N(1)	140.3(1)	Er-N(4)-C(26)	122.1(4)
	hydrogen-bond geometry		
O(1)-H(72)-O(7)	2.598(5)	O(1)---H(72)-O(7)	142.8(5)
O(4)-H(71)-O(7)	2.613(3)	O(4)---H(71)-O(7)	117.2(5)
O(5)-H(81)-O(8)	2.723(3)	O(5)---H(81)-O(8)	153.6(6)
O(2)-H(82)-O(8)	2.600(6)	O(2)---H(82)-O(8)	159.6(7)

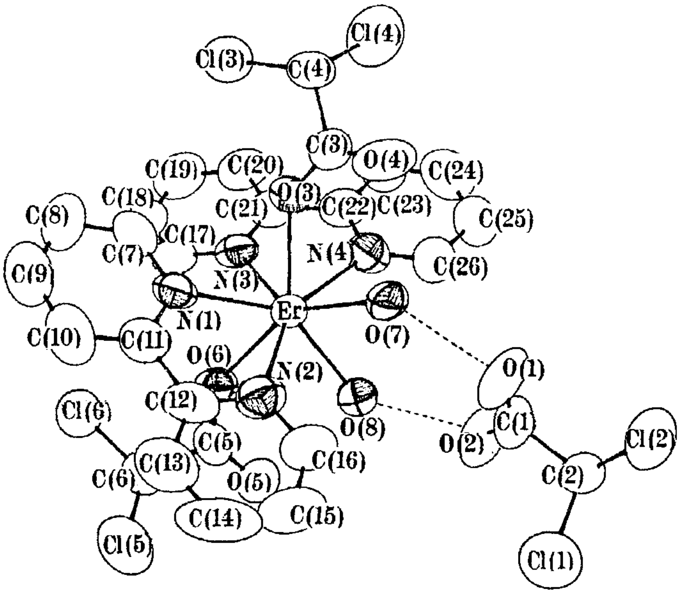

Figure 1 The molecular structure and numbering scheme for the erbium complex. Displacement ellipsoids are shown at the 50% probability level.

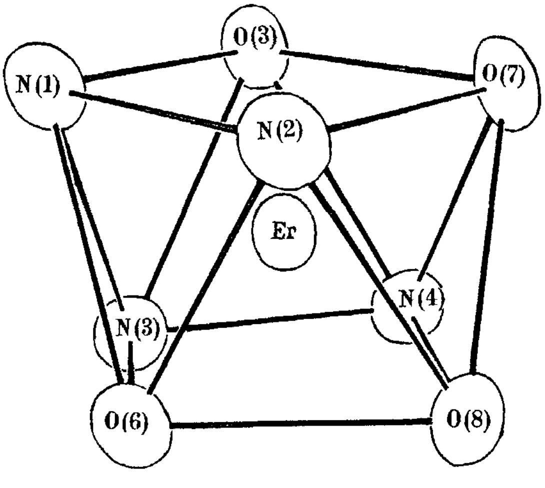

Figure 2 Coordination geometries of the central Er atom.

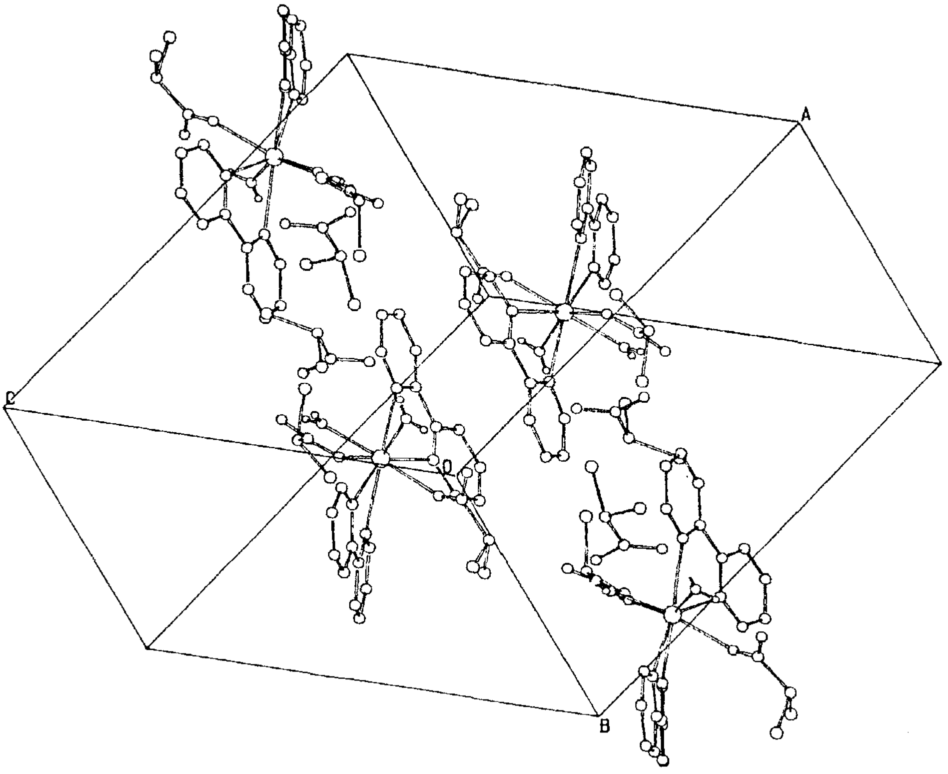

Figure 3 Molecular packing in the unit cell.

Table 6 Structural parameters for the square antiprismatic configuration of the erbium complex.

atoms	α°	Atom 1	Atom 2	Distance (Å)
O(3)	58.24(4)	O(3)	–O(7)	2.803(4)
O(6)	61.97(3)	O(3)	–N(1)	2.855(4)
O(7)	66.81(9)	O(6)	–O(8)	2.803(4)
O(8)	61.34(3)	O(6)	–N(3)	2.891(4)
N(1)	45.49(9)	O(7)	–N(2)	2.974(5)
N(2)	55.97(5)	O(8)	–N(4)	3.035(4)
N(3)	50.10(3)	N(1)	–N(8)	2.673(5)
N(4)	54.40(3)	N(3)	–N(4)	2.674(5)

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