Inorganica Chimica Acta, *155* (1989) 149–152

The Crystal Structure of the Eight-coordinated Erbium(III) Complex with the Tetradentate Ligand *N,N'*-Ethylene-bis(salicylaldimine)

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(Received June 4, 1988)

Abstract

The crystal structure of Er(III)(salen)$_2$(pipH) [salen = *N,N'*-ethylene-bis(salicylaldimine), pipH = piperidinium] has been determined by X-ray diffraction. The structure of the compound consists of [Er(salen)$_2$]$^{-1}$ anions and pipH$^+$ cations. In the complex anion the erbium(III) ion is eight-coordinated by the donor atoms of two tetradentate salen ligands, forming a distorted square antiprism with approximate D_2 symmetry. The Er–O and Er–N distances average respectively 2.270 and 2.511 Å. This is the first structural determination of a lanthanide element complex with a tetradentate ligand.

Introduction

The tetradentate ligand *N,N'*-ethylenebis(salicylideneimine) (salen) forms with 3d transition metals a series of complexes whose physico-chemical properties have been extensively studied [1]. The oxygen carrying properties of the cobalt(II) complex were discovered in 1938 [2]. Little attention, however, has been given to complexes of the f-block elements, the studies being limited to spectroscopic and structural investigations on some uranyl complexes [3]. We wish to report here the first crystal structure of the salen complex with an element of the lanthanide series.

Experimental

An aqueous solution of erbium(III) chloride hexahydrate (1 g) was added to a methanolic solution of *N,N'*-ethylene-bis(salicylaldimine) (1.6 g) and piperidine (0.4 g). The resulting solution was heated on a water bath at about 60 °C with stirring for about 1 h. The yellow precipitate formed was filtered, dried and then recrystallized from tetrahydrofuran–methanol, containing a small amount of piperidine. The pure crystalline product obtained was washed with ethyl ether. The magnetic moment at 295 K is 9.56 BM. *Anal.* Found: C, 56.43; H, 5.17; N, 8.98. Calc. for $C_{37}H_{40}N_5O_4Er$: C, 56.54; H, 5.13; N, 8.91%.

Cell constants were determined by least-squares fitting of 25 accurately centered reflections. Intensity data, collected on a Philips PW 1100 automatic diffractometer, were corrected for Lorentz, polarization and absorption effects. Absorption corrections were based on the numerical integration method, as included in SHELX-76 [4]. The intensities of three standard reflections were monitored periodically for stability control during data collection. The structure was solved by standard Patterson and Fourier technique and subsequently refined by blocked full-matrix least-squares technique. The function minimized was $\Sigma w(F_o - |F_c|)$ with weights $w = a/(\sigma^2(F) + bF^2)$ where a and b are adjustable parameters. Anisotropic temperature factors were used for all the atoms except for the hydrogen atoms which were included in calculated positions and the salicylaldimine benzene ring atoms which were refined as rigid groups (C–C = 1.395, C–H = 1.08 Å; C–C–C = 120°). All the calculations were performed with the SHELX-76 set of programs [4] which use the analytical approximation for the atomic scattering factors and anomalous dispersion corrections for all the atoms from the International Tables [5]. The molecular plots were produced by ORTEP [6] Crystal data are listed in Table 1. Table 2 shows the final atomic coordinates with estimated standard deviations from the least-squares inverse matrix.

0020-1693/89/$3.50

TABLE 1. Crystal Data

Formula	$C_{37}H_{39}N_5O_4Er_1$
Molecular weight	784.2
Space group	$P2_1/a$
a (Å)	16.867(4)
b (Å)	19.876(4)
c (Å)	10.238(3)
β (°)	100.37(4)
V (Å^3)	3376.2
Z	4
D_c (g cm^{-3})	1.54
μ(Mo Kα) (cm^{-1})	23.9
Crystal dimensions (mm)	0.33 × 0.27 × 0.27
μ(Mo Kα) (Å)	0.7107 (graphite monochromator)
Scan type	θ–2θ
Scan width (°)	1.0
Scan speed (°/s)	0.025
range (°)	4.0–50.0
Total unique data	5949
Observed data ($I > 3.5\sigma$)	3792
No. parameters	261
$R_F = \Sigma F_o - \lvert F_c\rvert/\Sigma F_o$	0.082
R_{wF} $[\Sigma w(F_o - \lvert F_c\rvert)^2/\Sigma w F_o{}^2]^{1/2}$	0.083

TABLE 2. Interatomic Distances (Å) and Angles (°)[a]

Metal coordination			
Er–O1	2.35(1)	N1–Er–O1	69.4(5)
Er–O2	2.23(1)	N1–Er–O2	140.8(5)
Er–O3	2.28(1)	N1–Er–O3	78.4(5)
Er–O4	2.22(1)	N1–Er–O4	85.8(4)
Er–N1	2.52(2)	N2–Er–O1	134.7(5)
Er–N2	2.52(1)	N2–Er–O2	74.2(5)
Er–N3	2.53(1)	N2–Er–O3	74.3(4)
Er–N4	2.48(1)	N2–Er–O4	76.5(4)
		N2–Er–N1	67.0(5)
O1–Er–O2	149.7(4)	N3–Er–O1	73.4(5)
O1–Er–O3	108.0(4)	N3–Er–O2	86.6(5)
O2–Er–O3	86.5(5)	N3–Er–O3	72.5(4)
O1–Er–O4	89.1(4)	N3–Er–O4	136.7(4)
O2–Er–O4	90.4(4)	N3–Er–N1	121.8(6)
O3–Er–O4	150.4(4)	N3–Er–N2	142.4(5)
N4–Er–O1	72.3(5)	N4–Er–N1	135.4(5)
N4–Er–O2	78.8(5)	N4–Er–N2	137.6(5)
N4–Er–O3	136.0(4)	N4–Er–N3	65.4(5)
N4–Er–O4	71.6(4)		
Ligand			
C1–O1	1.34(2)	C1–O1–Er	124.8(8)
C10–O2	1.33(2)	C10–O2–Er	136.9(9)
C17–O3	1.35(2)	C17–O3–Er	126.8(9)
C26–O4	1.33(2)	C26–O4–Er	132.2(9)
C7–N1	1.24(3)	C7–N1–Er	126.1(1.3)
C8–N1	1.47(2)	C8–N1–Er	114.9(1.3)
C9–N2	1.39(3)	C8–N1–C7	117.3(1.7)
C16–N2	1.35(3)	C9–N2–Er	118.9(1.2)
C23–N3	1.37(2)	C16–N2–Er	123.3(1.2)

(continued)

TABLE 2. *(continued)*

C24–N3	1.35(2)	C16–N2–C9	117.3(1.5)
C25–N4	1.49(2)	C23–N3–Er	118.9(1.2)
C32–N4	1.29(3)	C24–N3–Er	118.9(1.1)
C6–C7	1.48(2)	C24–N3–C23	121.0(1.4)
C8–C9	1.57(3)	C32–N4–Er	128.3(1.2)
C15–C16	1.41(2)	C32–N4–C25	117.0(1.6)
C22–C23	1.46(2)	C2–C1–O1	118.5(0.9)
C24–C25	1.51(3)	C6–C1–O1	121.4(1.1)
C31–C32	1.46(2)	C7–C6–C1	123.9(1.2)
		C11–C10–O2	117.0(1.0)
C7–C6–C5	115.9(1.1)	C6–C7–N1	123.5(1.7)
C9–C8–N1	109.8(1.6)	C8–C9–N2	109.6(1.5)
C15–C10–O2	122.9(1.1)	C16–C15–C10	124.3(1.2)
C16–C15–C14	115.1(1.1)	C15–C16–N2	128.4(1.4)
C18–C17–O3	120.7(1.0)	C22–C17–O3	119.3(1.0)
C23–C22–C17	124.7(1.1)	C23–C22–C21	115.1(1.1)
C25–C24–N3	108.9(1.6)	C24–C25–N4	108.0(1.4)
C27–C26–O4	119.1(1.0)	C31–C26–O4	120.9(1.1)
C32–C31–C26	124.2(1.2)	C32–C31–C30	115.7(1.2)
C31–C32–N4	123.5(1.6)		
Piperidinium cation			
Np–Cp1	1.47(2)	Cp5–Np–Cp1	110.9(1.6)
Cp1–Cp2	1.52(3)	Cp2–Cp1–Np	111.5(1.6)
Cp2–Cp3	1.45(4)	Cp3–Cp2–Cp1	111.8(2.3)
Cp3–Cp4	1.47(4)	Cp4–Cp3–Cp2	109.8(2.2)
Cp4–Cp5	1.51(3)	Cp5–Cp4–Cp3	111.8(1.9)
Np–Cp5	1.44(3)	Cp4–Cp5–Np	111.9(2.0)

[a] e.s.d.s given in parentheses.

TABLE 3. Atomic Coordinates for Er(salen)$_2$(pipH)[a] (× 10^4)

Atom	x	y	z
Er	1239(1)	2307(1)	3242(1)
O(1)	2396(6)	2644(6)	2436(13)
O(2)	0509(7)	2310(6)	4853(13)
O(3)	0146(7)	2784(5)	1933(14)
O(4)	1903(7)	1401(6)	4123(11)
N(1)	1279(9)	1766(8)	1030(18)
N(2)	0226(8)	1372(7)	2684(17)
N(3)	1354(9)	3567(7)	3565(19)
N(4)	2259(8)	2667(7)	5170(16)
C(1)	2392(7)	2932(6)	1250(9)
C(2)	2848(7)	3514(6)	1195(9)
C(3)	2817(7)	3851(6)	−0008(9)
C(4)	2330(7)	3606(6)	−1157(9)
C(5)	1875(7)	3024(6)	−1103(9)
C(6)	1906(7)	2687(6)	0101(9)
C(7)	1451(10)	2050(9)	0038(21)
C(8)	0878(11)	1107(9)	0827(22)
C(9)	0075(11)	1119(9)	1400(24)
C(10)	0127(7)	1856(5)	5474(11)
C(11)	0008(7)	2019(5)	6750(11)
C(12)	−0342(7)	1551(5)	7489(11)
C(13)	−0571(7)	0920(5)	6953(11)
C(14)	−0452(7)	0758(5)	5677(11)

(continued)

TABLE 3. *(continued)*

Atom	*x*	*y*	*z*
C(15)	-0102(7)	1226(5)	4938(11)
C(16)	-0107(10)	1044(8)	3605(21)
C(17)	0153(7)	3240(5)	0954(11)
C(18)	-0328(7)	3151(5)	-0292(11)
C(19)	-0317(7)	3629(5)	-1288(11)
C(20)	0175(7)	4195(5)	-1037(11)
C(21)	0656(7)	4284(5)	0210(11)
C(22)	0645(7)	3807(5)	1206(11)
C(23)	1125(11)	3978(9)	2494(20)
C(24)	1776(11)	3809(8)	4710(19)
C(25)	2520(12)	3383(9)	5120(26)
C(26)	2094(7)	1181(6)	5368(10)
C(27)	1996(7)	0500(6)	5630(10)
C(28)	2176(7)	0262(6)	6931(10)
C(29)	2453(7)	0704(6)	7971(10)
C(30)	2551(7)	1385(6)	7709(10)
C(31)	2371(7)	1623(6)	6408(10)
C(32)	2542(10)	2332(9)	6232(23)
NP	3747(9)	2596(9)	7028(23)
CP(1)	3323(11)	1307(10)	2102(25)
CP(2)	3785(14)	0645(11)	2314(28)
CP(3)	3944(16)	0448(12)	3701(30)
CP(4)	4375(14)	0992(13)	4512(30)
CP(5)	3918(12)	1651(10)	4313(24)

[a]e.s.d.s given in parentheses.

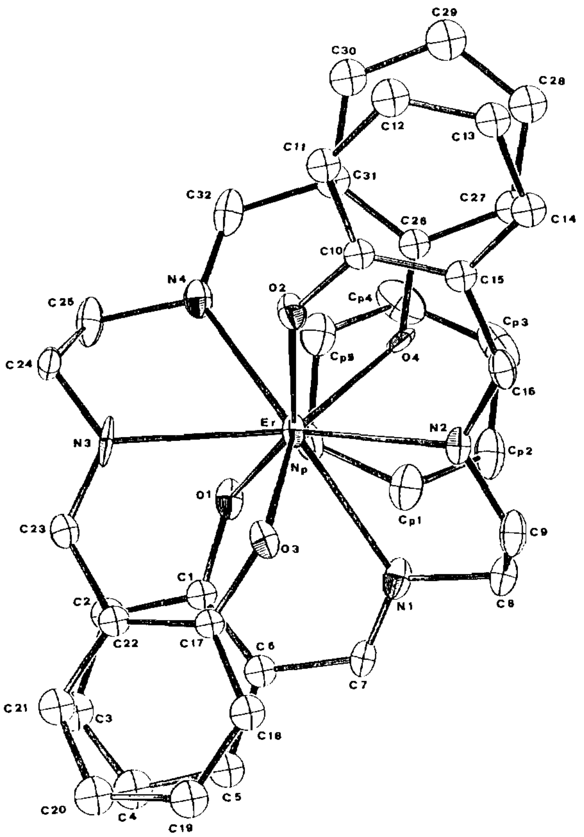

Fig. 1. ORTEP drawing of Er(salen)$_2$(pipH). Thermal ellipsoids for non-hydrogen atoms at 30% probability.

Results and Discussion

The structure of the compound consists of $[ErL_2]^{-1}$ anions and $pipH^+$ cations. In the complex anion the erbium(III) ion is eight-coordinated by the donor atoms of two tetradentate salen ligands, forming a distorted square antiprism with approximate D_2 symmetry. Bond lengths and angles around the erbium ion are reported in Table 3. A perspective drawing of one complex anion and of the piperidinium cation is shown in Fig. 1. The mode of binding of the tetradentate ligand and the coordination polyhedron around the metal atom are shown schematically in Fig. 2. The two sets of atoms forming the two bases of the square antiprism (*i.e.* N(1), O(1), N(4), O(4) and N(2), O(2), N(3), O(3)) are not strictly coplanar, the maximum deviation from the least-squares planes being 0.48 Å. The erbium ion is located approximately half way between the basal planes, the mean distance from them being 1.24 Å. The Er–O and Er–N distances average respectively 2.270 and 2.511 Å in agreement with analogous values from eight-coordinated erbium complexes [7]. The piperidinium cation is in the common chair conformation and forms with O(1) and O(3) two strong hydrogen bonds (N(P)···O(1) = 2.746 and N(P)···O(3) = 2.832 Å).

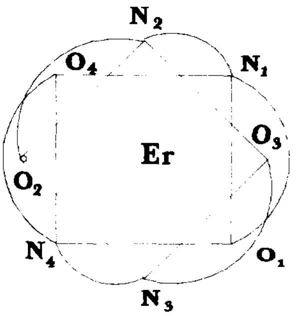

Fig. 2. Schematic drawing showing the coordination polyhedron around the erbium ion and the mode of binding of the salen ligand.

Supplementary Material

Tables of observed and calculated structure factors, thermal parameters, and hydrogen coordinates can be obtained from the author upon request.

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