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Structural Chemistry of Dicyclopentadienidehalides of Lanthanides
Part 4*. Erbiumdicyclopentadienidechloride $[Er(C_5H_5)_2Cl]_2$

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Abstract

The crystal structure of erbiumdicyclopentadienidechloride $[Er(C_5H_5)_2Cl]_2$ has been determined from X-ray diffraction data. The compound crystallizes in space group $P2_1/c$ with $a = 11.056(3)$, $b = 8.015(1)$, $c = 12.154(3)$ Å, $\beta = 110.28(2)°$, $V = 1010.2(7)$ Å^3, $D_c = 2.189$ g cm^{-3} and $Z = 2$ dimers. The structure has been refined by full-matrix least-squares techniques to a conventional R factor of 0.027 for 2042 reflections (with $I > 2\sigma(I)$). In the unit cell centrosymmetric dimers of one type exist with bridging chlorine atoms and C_5H_5 groups bonded in η^5-fashion to the metal (mean Er–C 2.59 Å). The $[Er(C_5H_5)_2Cl]_2$-type is compared to the $[Sc(C_5H_5)_2Cl]_2$-type structure which is realized in several dicyclopentadienidebromides of the lanthanides.

Introduction

We are interested in the magnetic properties of polynuclear rare earth complexes. Compounds of the type $Ln(C_5H_5)_2X$ (with Ln = lanthanide and X = Br, Cl) would appear to be relevant to these investigations because of their expected dimeric nature. Meanwhile, this structure has been confirmed in the case of the bromides of gadolinium, dysprosium and erbium [1, 2] ($[Sc(C_5H_5)_2Cl]_2$-type [3]). For the gadolinium compound, however, a second modification with one-dimensional infinite polymers is observed [1], and in the case of the corresponding chlorine compounds our previous investigations have led to a new structure type with one-dimensional infinite polymers for $Dy(C_5H_5)_2Cl$ [4]. This is our report on the structural results concerning $Er(C_5H_5)_2Cl$.

Experimental

Preparation

$Er(C_5H_5)_2Cl$ was prepared by stoichiometric reaction of water-free sublimed $ErCl_3$ (purity of the starting material $ErCl_3 \cdot xH_2O$: 99.99%, Johnson–Matthey Company, U.K.) with colourless NaC_5H_5 in benzene, following standard methods [1]. The compound is very sensitive to air and moisture and therefore all procedures have been carried out under purified argon. Single crystals suitable for X-ray structure investigation were obtained by slow sublimation at a temperature of *ca.* 150 °C under low pressure.

Structural Investigations

Intensities for structure determination were collected by an Enraf-Nonius CAD 4 automatic diffractometer using graphite monochromated Ag Kα radiation ($\lambda = 0.56083$ Å; ω–2θ scan) at room temperature. Lattice parameters were determined by least-squares refinement of the setting angles of 25 computer-centered reflections in the range of $5° < \theta < 15°$. Three standard reflections were monitored every 150 reflections to check crystal stability. No decrease of intensity during data collection was observed. Specific details concerning crystal size, unit cell, density, number of reflections and absorption coefficients are presented in Table I. The calculations were performed on a VAX 11/730 computer (Digital Equipment Corporation) using the SDP plus program system [5]. Scattering factors for neutral atoms were taken from the International Tables of Crystallography [6]. For full-matrix least-squares refinements, reflections with $I > 2\sigma(I)$ were used. The positions of the hydrogen atoms were calculated with a C–H bond length of 0.95 Å. In final calculations the H atoms ride on the external bisectors of the C–C–C angles (SDP plus [5]). Atomic parameters are given in Table II; bond distances and bond angles in Table III[†].

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*For Part 3: see ref. 4.

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[†] See 'Supplementary Material'.

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TABLE I. $[Er(C_5H_5)_2Cl]_2$ Details and Results of Structural Investigation

Crystal size (mm)	0.15 × 0.32 × 0.25
θ range	$0.1 \leq \theta \leq 24°$
Space group	$P2_1/c$
a (Å)	11.056(3)
b (Å)	8.015(1)
c (Å)	12.154(3)
β (°)	110.28(2)
V (Å^3)	1010.2(7)
Z	2 (dimers)
D_c (g cm^{-3})	2.189
Number of reflections	3568
Number of unique reflections	3210
Number of reflections in the refinements	2042
Absorption coefficient μ(cm^{-1})	46.5
R	0.027
R_w [a]	0.033
e.s.d.	1.18

[a] $w = 1/(\sigma(|F_o|))^2$; $(\sigma(|F_o|))^2 = \{(\sigma(I))^2 + pF_o^2\}^2/(4F_o^2)$ with $p = 0.04$.

TABLE II. Atomic Parameters for $[Er(C_5H_5)_2Cl]_2$ (all atoms in general positions)

Atom	x	y	z
Er	0.19293(2)	0.01940(3)	0.05799(2)
Cl	−0.0073(1)	0.1548(2)	0.0987(1)
C1	0.4027(6)	−0.1020(9)	0.2066(6)
C2	0.3328(7)	−0.0476(8)	0.2732(6)
C3	0.2287(6)	−0.1468(9)	0.2518(6)
C4	0.2308(8)	−0.2638(8)	0.1689(7)
C5	0.3410(6)	−0.2336(8)	0.1418(6)
C6	0.1967(7)	0.163(1)	−0.1324(6)
C7	0.3149(6)	0.106(1)	−0.0785(6)
C8	0.3707(6)	0.1923(8)	0.0178(6)
C9	0.2863(7)	0.3054(8)	0.0314(6)
C10	0.1723(6)	0.2876(9)	−0.0677(6)
H1	0.482	−0.056	0.206
H2	0.355	0.045	0.325
H3	0.166	−0.138	0.288
H4	0.169	−0.349	0.135
H5	0.369	−0.294	0.088
H6	0.139	0.120	−0.204
H7	0.355	0.017	−0.105
H8	0.456	0.176	0.070
H9	0.301	0.383	0.094
H10	0.095	0.350	−0.085

Structural Results and Discussion

TABLE III. $[Er(C_5H_5)_2Cl]_2$: Bond Distances (Å) and Angles (°)

Er–Er	4.0142(3)		
Cl–Cl	3.493(2)		
Er–Cl	2.661(2)	Er–Cl–Er	97.94(5)
Er–Cl	2.660(1)	Cl–Er–Cl	82.06(4)
Next-but-one erbium neighbour			
Er–Er	7.1129(3)		
Er–C1	2.585(6)	Er–C6	2.596(8)
Er–C2	2.592(6)	Er–C7	2.569(8)
Er–C3	2.614(7)	Er–C8	2.587(7)
Er–C4	2.599(7)	Er–C9	2.580(7)
Er–C5	2.583(6)	Er–C10	2.601(7)
C1–C2	1.37(1)	C5–C1–C2	108.6(6)
C2–C3	1.35(1)	C1–C2–C3	108.4(6)
C3–C4	1.38(1)	C2–C3–C4	108.2(7)
C4–C5	1.39(1)	C3–C4–C5	107.0(6)
C5–C1	1.351(9)	C4–C5–C1	107.8(7)
C6–C7	1.32(1)	C10–C6–C7	109.2(6)
C7–C8	1.32(1)	C6–C7–C8	109.6(8)
C8–C9	1.35(1)	C7–C8–C9	109.4(6)
C9–C10	1.417(9)	C8–C9–C10	106.1(6)
C10–C6	1.36(1)	C9–C10–C6	105.6(6)

$Er(C_5H_5)_2Cl$ forms pink-coloured lamella-like crystals with nearly hexagonal shape. The structure was solved using Patterson and Fourier techniques which led to the location of all non-hydrogen atoms. Refinements on the basis of 2042 reflections converged to a final conventional R factor of 0.027 (R_w = 0.033, $w = 1/(\sigma(|F_o|))^2)$*; estimated standard deviation of an observation of unit weight: 1.18). In much the same manner as the $[Sc(C_5H_5)_2Cl]_2$-type structure, $Er(C_5H_5)_2Cl$ consists of binuclear units. The geometry of the dimers is illustrated in Fig. 1. The C_5H_5 rings are nearly planar and η^5-bonded to the metal with Er–C distances ranging from 2.57 to 2.61 Å.

Comparing the $[Er(C_5H_5)_2Cl]_2$-type structure with the previously investigated organolanthanides of the type $Ln(C_5H_5)_2X$, it is worth mentioning that the metal coordination hardly differs with regard to cyclopentadienide; *i.e.* in all compounds the same geometry of C_5H_5 rings and $Ln(C_5H_5)_2$ arrangements are found. There are variations, however, in the coordination of the metal with respect to the halide [1, 3] which have far-reaching structural consequences. Examples are the dicyclopentadienidechlorides of dysprosium and erbium (one-dimensional infinite polymers in the former, dimers in the latter).

$[Er(C_5H_5)_2Cl]_2$ and $[Er(C_5H_5)_2Br]_2$, on the other hand, show structural differences with respect to the packing of the dimers. For future discussion of various structure determining factors in this class of compounds, comparison of the arrangement of the dimers in the two structure types might be useful.

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*$(\sigma(|F_o|))^2 = \{(\sigma(I))^2 + pF_o^2\}^2/(4F_o^2)$ with $p = 0.04$.

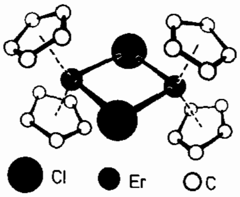

Fig. 1. Molecular structure of $[Er(C_5H_5)_2Cl]_2$.

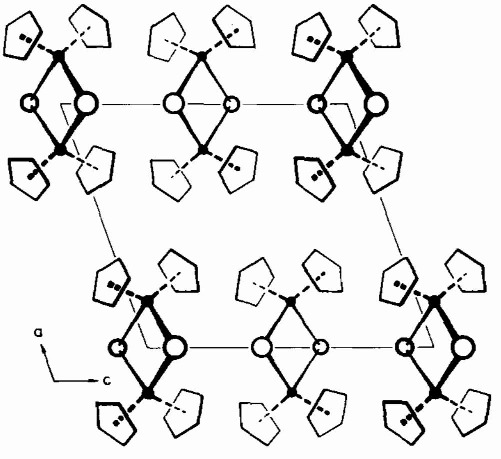

Fig. 2. $[Er(C_5H_5)_2Cl]_2$: [010] projection of the unit cell; dimers in $0, \frac{1}{2}, \frac{1}{2}$ are drawn in thin lines.

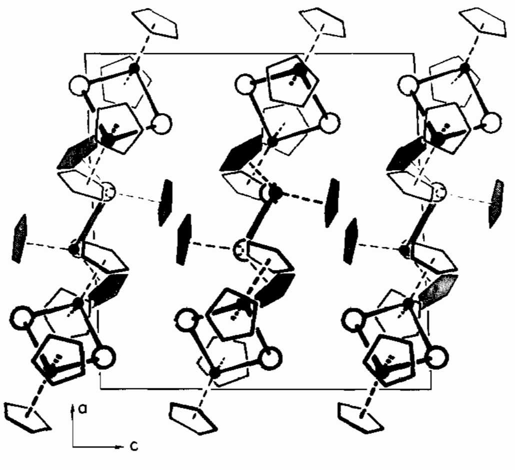

Fig. 3. $[Er(C_5H_5)_2Br]_2$: [010] projection of the unit cell; centro-symmetric dimers are dark shade $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and light shade $(\frac{1}{2}, 0, 0)$; symmetry-less dimers are drawn in bold lines $(y \approx \frac{3}{4})$ and thin lines $(y \approx \frac{1}{4})$.

In both compounds the principles in the packing of the dimers can be outlined by simple models. In the case of the chloride, the habit of the crystals (hexagonal lamella-like) is typical of a layer structure, the arrangement of which becomes obvious from the [010] projection of the unit cell (see Fig. 2): the centrosymmetric (and equivalent) dimers are 'close-packed' in the b–c plane with the Er_2Cl_2 units nearly perpendicular to the plane. The layers are stacked in terms of cubic closest-packing. In $[Er(C_5H_5)_2Br]_2$ (space group $P2_1/c$ [2]) the two types of dimers are 'closest-packed' in a plane perpendicular to [102] with the longest molecular axis within the plane (see Fig. 3). The molecules differ in orientation: the Er_2Br_2 units lie either in the plane (centrosymmetric dimers) or perpendicular to the plane (symmetry-less dimers). Representing each binuclear species by its centre of gravity, the planar network can be subdivided: (i) in a distorted 6^3 net (resulting from the symmetry-less dimers); and (ii) in a distorted 3^6 net (resulting from the centrosymmetric dimers). The two networks fit together with the vertices of the latter centering the hexagons of the former*. The stacking sequence of the layers is obtained by applying the 2_1 axis.

Supplementary Material

Details of the refinements (tables of anisotropic thermal parameters, listings of observed *versus* calculated structure factors) can be obtained from the authors on request.

Acknowledgements

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*This combination of networks is often observed in intermetallics (e.g. in the $CaCu_5$-type structure [7]).