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Structural Chemistry of Dicyclopentadienidehalides of Lanthanides. Part 3*. Dysprosiumdicyclopentadienidechloride $^1_\infty[Dy(C_5H_5)_2Cl]$

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Abstract

The crystal structure of dysprosiumdicyclopentadienidechloride $^1_\infty[Dy(C_5H_5)_2Cl]$ has been determined from X-ray diffraction data. The compound crystallizes in space group $P2_12_12_1$ with $a = 8.487(1)$, $b = 18.198(3)$, $c = 6.627(3)$ Å, $V = 1023.5(7)$ Å^3, $D_c = 2.129$ g cm^{-3} and $Z = 4$ formula units. The structure has been refined by full matrix least-squares techniques to a conventional R factor of 0.033 for 1989 reflections (with $I > 2\sigma(I)$). The compound has a chain structure similar to $^1_\infty[Gd(C_5H_5)_2Br]$ with bridging chlorine atoms (Dy–Cl 2.687 and 2.678 Å). The C_5H_5 groups are η^5-bonded to the metal atom (mean Dy–C 2.63 Å).

Introduction

The structural chemistry of the compounds $Ln(C_5H_5)_2Br$ (Ln = lanthanide) is more diverse than expected. Apart from the $[Sc(C_5H_5)_2Cl]_2$-type structure [1] with isolated dimers, which exists for gadolinium (modification **I** [2]), dysprosium and erbium [3], a polymeric structure is observed for $Gd(C_5H_5)_2Br$ (modification **II**) with a double chain arrangement of the heavy atoms [2]. We are mainly interested in the magnetochemistry of halides of this type and more especially of chlorides. Their crystal structures are unknown and therefore we started single crystal investigations on the dysprosium-, erbium- and gadolinium-dicyclopentadienidechlorides. The results with regard to $Dy(C_5H_5)_2Cl$ are reported in this work.

Experimental

Preparation

Due to the high sensitivity of the compound to air and moisture, all procedures have been carried out under purified argon [2]. $Dy(C_5H_5)_2Cl$ was prepared by stoichiometric reaction of water-free sublimed $DyCl_3$ (purity of the starting material $DyCl_3 \cdot xH_2O$ 99.99%, Johnson–Matthey Company, U.K.) with colourless NaC_5H_5 in benzene following standard methods [2, 4]. Single crystals suitable for X-ray structure investigation were obtained by slow sublimation at *ca.* 160 °C under low pressure.

Mass Spectroscopy

The compound was characterized by mass spectroscopy using the double-focusing Varian MAT CH 5 DF mass spectrometer with electron energies of 70 eV (temperature of the ion source 170 °C). The spectrum was consistent with the corresponding investigations on the analogous bromides [2, 3].

Structural Investigations

Weissenberg photographs (Fe Kα and Mo Kα radiations) were used to determine crystal quality, cell constants and systematic absences. 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 refinements 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 coefficient 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

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*Part 2: see ref. 3.

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TABLE I. ${}^{1}_{\infty}[\mathrm{Dy(C_5H_5)_2Cl}]$, Details and Results of Structural Investigations

Crystal size (mm)	0.67 × 0.10 × 0.15[a]
θ range	$0.01° \leqslant \theta \leqslant 30°$
Space group	$P2_12_12_1$
a (Å)	8.487(1)
b (Å)	18.198(3)
c (Å)	6.627(3)
V (Å^3)	1023.5(7)
Z	4
D_c (g cm^{-3})	2.129
Number of reflections	3188
Number of unique reflections	3076
Number of reflections in the refinements	1989
Absorption coefficient μ (cm^{-1})	36.9
R	0.033
R_w	0.040
e.s.d.	1.317
Major peak in final difference Fourier synthesis (e/Å^3)	1.4

[a] Empirical absorption correction was applied (PSI-scan, programs PSI and EAC, SDP plus [5]).

TABLE II. Atomic Parameters of ${}^{1}_{\infty}[\mathrm{Dy(C_5H_5)_2Cl}]$ (all atoms in general position)

Atom	x	y	z
Dy	0.67030(3)	0.41350(1)	0.76188(4)
Cl	0.2962(3)	0.9583(1)	0.3542(3)
C1	0.3911(9)	0.3549(5)	0.7387(14)
C2	0.4159(9)	0.3850(5)	0.5491(12)
C3	0.4205(10)	0.4582(5)	0.5709(15)
C4	0.3912(8)	0.4741(5)	0.7674(17)
C5	0.3758(9)	0.4089(5)	0.8752(14)
C6	0.2830(13)	0.2198(4)	0.1834(21)
C7	0.4043(11)	0.1760(5)	0.1316(16)
C8	0.4588(9)	0.1423(5)	0.3034(16)
C9	0.3660(13)	0.1672(5)	0.4545(14)
C10	0.2521(12)	0.2124(5)	0.3884(20)
H1	0.3836	0.3043	0.7731
H2	0.4287	0.3576	0.4283
H3	0.4402	0.4918	0.4640
H4	0.3855	0.5223	0.8216
H5	0.3562	0.4053	1.0161
H6	0.2313	0.2506	0.0884
H7	0.4451	0.1677	0.0001
H8	0.5413	0.1072	0.3142
H9	0.3825	0.1554	0.5926
H10	0.1686	0.2364	0.4577

Table II, bond distances and bond angles in Table III*.

Structural Results and Discussion

$\mathrm{Dy(C_5H_5)_2Cl}$ forms pale yellow column-shaped crystals. The structure was solved using Patterson and Fourier techniques which led to the location of all non-hydrogen atoms. Refinements using 1989 reflections converged to a final conventional R factor of 0.033 ($R_w = 0.040$, $w = 1/(\sigma(|F_o|))^2$; estimated standard deviation of an observation of unit weight: 1.317). Major peaks in the final difference Fourier synthesis did not exceed 1.4 e/Å^3. The $\mathrm{Dy(C_5H_5)_2Cl}$ units are condensed to one-dimensional infinite chains which are similar to the linkage of the $\mathrm{Gd(C_5H_5)_2Br}$ units (modification **II** [2]). The geometry of the polymers and their packing are illustrated in two projections of the crystal structure along the a and c axes (see Fig. 1). The chains are orientated in the direction of the shortest crystallographic axis c which is identical with the long column axis. Along this direction the crystals are easily cleaved. Within the chains the arrangements of dysprosium and chlorine are planar. The $\mathrm{C_5H_5}$ rings are nearly planar and η^5-bonded with Dy–C distances ranging from 2.59 to 2.69 Å (mean 2.63 Å).

TABLE III. Bond Distances (Å) and Angles (°) of ${}^{1}_{\infty}[\mathrm{Dy(C_5H_5)_2Cl}]$

Dy–Dy	4.766(1)		
Cl–Cl	3.727(3)		
		Cl–Dy–Cl	61.42(5)
Dy–Cl	2.678(2)	Cl–Dy–Cl	88.01(6)
Dy–Cl	2.687(2)	Dy–Cl–Dy	85.21(4)
Dy–Cl	4.173(2)	Dy–Cl–Dy	125.35(7)
Next but one dysprosium neighbour			
Dy–Dy	6.627(1)		
Dy–C1	2.60(1)	Dy–C6	2.63(1)
Dy–C2	2.63(1)	Dy–C7	2.66(1)
Dy–C3	2.60(1)	Dy–C8	2.69(1)
Dy–C4	2.61(1)	Dy–C9	2.64(1)
Dy–C5	2.61(1)	Dy–C10	2.59(1)
C1–C2	1.39(1)	C5–C1–C2	110(1)
C2–C3	1.34(1)	C1–C2–C3	107(1)
C3–C4	1.36(1)	C2–C3–C4	108(1)
C4–C5	1.39(1)	C3–C4–C5	109(1)
C5–C1	1.34(1)	C4–C5–C1	106(1)
C6–C7	1.35(1)	C10–C6–C7	110(1)
C7–C8	1.37(1)	C6–C7–C8	108(1)
C8–C9	1.35(1)	C7–C8–C9	106(1)
C9–C10	1.34(1)	C8–C9–C10	113(1)
C10–C6	1.39(2)	C9–C10–C6	104(1)

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*See Supplementary Material.

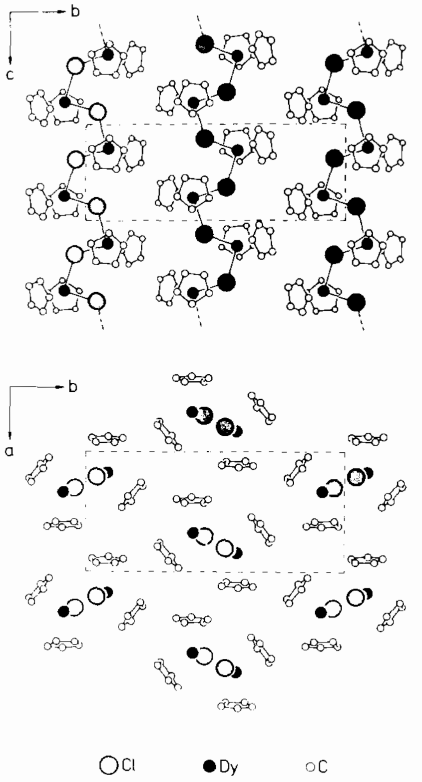

Fig. 1. [100] (top) and [001] (bottom) projections of the unit cell of ${}^{1}_{\infty}[\mathrm{Dy(C_5H_5)_2Cl}]$.

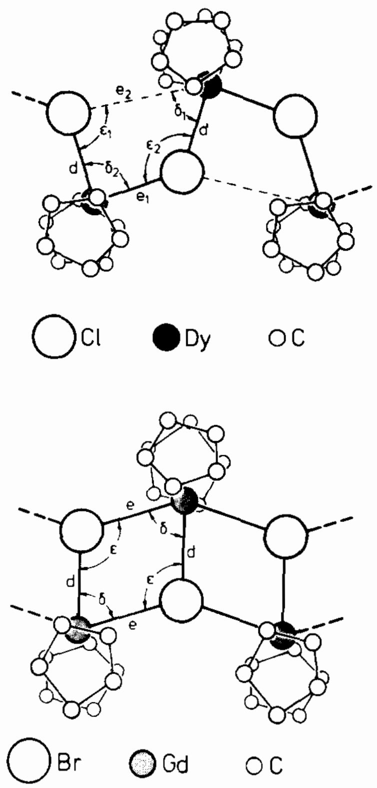

Fig. 2. Sections of the chains in ${}^{1}_{\infty}[\mathrm{Dy(C_5H_5)_2Cl}]$ (top) and ${}^{1}_{\infty}[\mathrm{Gd(C_5H_5)_2Br}]$ (bottom); see also Table IV.

In order to discuss the crystal structure of ${}^{1}_{\infty}[\mathrm{Dy(C_5H_5)_2Cl}]$ in more detail, it is convenient to consider ${}^{1}_{\infty}[\mathrm{Gd(C_5H_5)_2Br}]$ for comparison. In Fig. 2 sections of the two chains are represented from which the arrangement of ligands becomes obvious; further details concerning distances and angles are given in Table IV. With regard to cyclopentadienide, the metal coordinations in the two compounds hardly differ: (i) in both cases the rings are nearly planar and η^5-bonded with mean Ln–C distances of 2.63 and 2.62 Å; (ii) the angle A1–Ln–A2 (A1, A2 = ring centres of gravity of the two coordinated cyclopentadienides) is almost the same (*ca.* 129°); (iii) the shortest non-bonded intramolecular contacts between carbon atoms are nearly equal at 3.36 Å. The two structures, however, differ in coordination of the lanthanide with respect to halide. In the gadolinium compound the metal atoms have two equidistant Br neighbours in the chain direction (Gd–Br = 3.133 Å), whereas in the dysprosium compound the two distances Dy–Cl differ widely (2.68 and 4.17 Å). As a consequence, there are differences in orientation of the ring planes with respect to the chain direction. Due to the symmetric Br–Gd–Br arrangement in ${}^{1}_{\infty}[\mathrm{Gd(C_5H_5)_2Br}]$ the ring planes run along the needle axis; in ${}^{1}_{\infty}[\mathrm{Dy(C_5H_5)_2Cl}]$ the rings form a slight angle with the column axis in order to compensate for the low contribution of the more distant chlorine atom to the coordination sphere of the metal.

TABLE IV. Geometry of the Ln–X Bridge in ${}^{1}_{\infty}[\mathrm{Dy(C_5H_5)_2Cl}]$ and ${}^{1}_{\infty}[\mathrm{Gd(C_5H_5)_2Br}]$ (distances (Å) and angles (°))

	${}^{1}_{\infty}[\mathrm{Dy(C_5H_5)_2Cl}]$		${}^{1}_{\infty}[\mathrm{Gd(C_5H_5)_2Br}]$
Dy–Dy	4.766(1)	Gd–Gd	4.882(1)
d	2.687(2)	d	2.911(1)
e_1	2.678(2)	e	3.133(1)
e_2	4.173(2)		
δ_1	61.42(5)	δ	72.18(2)
δ_2	88.01(6)		
ϵ_1	85.21(4)	ϵ	107.83(3)
ϵ_2	125.35(7)		

The constant $\mathrm{Ln(C_5H_5)_2}$ arrangements in the two compounds lead to remarkable constancy of the lattice parameters $a(\mathrm{Dy})$ = 8.487 Å and $b(\mathrm{Gd})$ = 8.447 Å. This becomes obvious from the orientation of elliptical areas which result from projecting the chain envelopes along (001) and (100) respectively (see lower part of Fig. 1 and ref. 2): the shorter axes of the ellipses which depend nearly exclusively on the metal–cyclopentadienide geometry are orientated mainly in the direction of a(Dy) and b(Gd), respectively, and are therefore responsible for the observed coincidence in length. The long elliptical axes, however, are strongly influenced by the radii of the corresponding halides and by the linkage of the heavy atoms in the chain leading to different lattice parameters b(Dy) = 18.198 Å and c(Gd) = 20.239 Å. As far as linkage within the chains is concerned it is remarkable that despite the smaller radius of chlorine compared to bromine the coordination number of the metal with respect to halide is lower in the chloride. This is reflected more quantitatively by the 'solid angle sum' (SAS, $0 < SAS < 1$) which measures the coordinative crowding of a given centre by its ligands [7]. Applying the model to the dysprosium and gadolinium compound, SAS(Dy) = 0.69 and SAS(Gd) = 0.77 have been obtained. With regard to the 'SAS rule' mean value of 0.73, dysprosium in ${}^{1}_{\infty}[\mathrm{Dy}(\mathrm{C_5H_5})_2\mathrm{Cl}]$ is slightly subcoordinated, whereas gadolinium in ${}^{1}_{\infty}[\mathrm{Gd}(\mathrm{C_5H_5})_2\mathrm{Br}]$ is overcrowded by the same degree. Obviously the ${}^{1}_{\infty}[\mathrm{Gd}(\mathrm{C_5H_5})_2\mathrm{Br}]$-type structure for ${}^{1}_{\infty}[\mathrm{Dy}(\mathrm{C_5H_5})_2\mathrm{Cl}]$ would lead to unfavourable contacts between the cyclopentadienides, in other words the observed low coordination of dysprosium by chlorine is accepted on account of favourable packing of the polymers.

Supplementary Material

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

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