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Structural Chemistry of Lanthanide Dicyclopentadienide Halides.
Part 5*. Gadoliniumdicyclopentadienidechloride $[Gd(C_5H_5)_2Cl]_4$**

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Previous investigations have led to new crystal structures in lanthanide (Ln) compounds with the general formula $Ln(C_5H_5)_2Cl$. In the case of dysprosium, a polymeric structure with one-dimensional infinite chains is observed [1], whereas the erbium compound has a dimeric structure [2]. We here report on the oligomeric structure of $Gd(C_5H_5)_2Cl$.

Experimental

Preparation

$Gd(C_5H_5)_2Cl$ was prepared by stoichiometric reaction of anhydrous sublimed $GdCl_3$ (purity of the starting material $GdCl_3 \cdot xH_2O$ 99.99%; Johnson-Matthey Company, U.K.) with colourless NaC_5H_5 in benzene following standard methods [3, 4]. Single crystals were obtained by sublimation at *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 ($\lambda = 0.56087$ 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 $5° < \theta < 15°$. 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 program systems SDP plus [5] and SHELX 76 [6]. Scattering factors for neutral atoms were taken from the International Tables of Crystallography [7]. For full matrix least-squares refinements, reflections with $I > 2\sigma(I)$ were used. Cyclopentadienide rings were refined isotropically as rigid groups (C–C, 1.42 Å [6]) (release of atomic parameters of the individual C atoms had not led to stable arrangements). The positions of the hydrogen atoms were calculated with a C–H bond length of 1.08 Å. In final calculations the H atoms ride on the external bisectors of the C–C–C angles. Atomic parameters are given in Table II, bond distances and bond angles in Table III (see also 'Supplementary Material').

TABLE I. $[Gd(C_5H_5)_2Cl]_4$, Details and Results of Structural Investigation

Crystal size (mm)	0.17 × 0.12 × 0.12
θ range	$0.1 < \theta < 22°$
Space group	*Pbca*
a (Å)	15.230(5)
b (Å)	11.228(5)
c (Å)	23.238(5)
V (Å^3)	3974(2)
Z	4 (tetramers)
D_c (g cm^{-3})	2.159
Number of reflections	6070
Number of unique reflections ($I > 1\sigma(I)$)	2236
Number of reflections in the refinements	1418
Absorption coefficient μ (cm^{-1})	37.2
R	0.065
R_w^{a}	0.078

$^a w = k/(\sigma^2(F_o) + gF_o^2)$ with $k = 1.43$ and $g = 0.001$.

TABLE II. $[Gd(C_5H_5)_2Cl]_4$, Atomic Parameters (all atoms in general position)

Atom	x	y	z
Gd1	0.09173(9)	0.3428(1)	0.53544(7)
Gd2	0.1112(1)	0.3279(2)	0.34843(7)
Cl1	0.1705(6)	0.2201(8)	0.4435(4)
Cl2	0.0277(5)	0.4557(7)	0.4351(4)
C1	−0.024(1)	0.167(2)	0.5218(7)
C2	0.048(1)	0.117(2)	0.5528(7)
C3	0.049(1)	0.171(2)	0.6082(7)
C4	−0.021(1)	0.253(2)	0.6115(7)
C5	−0.067(1)	0.250(2)	0.5581(7)
C6	0.239(2)	0.462(2)	0.5334(9)
C7	0.187(2)	0.524(2)	0.5745(9)
C8	0.178(2)	0.449(2)	0.6234(9)
C9	0.224(2)	0.342(2)	0.6127(9)
C10	0.262(2)	0.350(2)	0.5570(9)
C11	0.213(2)	0.410(3)	0.261(1)
C12	0.172(2)	0.511(3)	0.285(1)
C13	0.206(2)	0.528(3)	0.341(1)
C14	0.269(2)	0.437(3)	0.352(1)
C15	0.273(2)	0.364(3)	0.302(1)

(continued)

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*Part 4: see ref. 2; Part 3: see ref. 1.

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TABLE II. *(continued)*

Atom	*x*	*y*	*z*
C16	0.041(2)	0.116(2)	0.325(1)
C17	−0.032(2)	0.182(2)	0.345(1)
C18	−0.049(2)	0.275(2)	0.305(1)
C19	0.015(2)	0.268(2)	0.261(1)
C20	0.071(2)	0.169(2)	0.273(1)
H1	−0.042(1)	0.144(2)	0.4783(7)
H2	0.093(1)	0.051(2)	0.5370(7)
H3	0.096(1)	0.152(2)	0.6420(7)
H4	−0.038(1)	0.307(2)	0.6481(7)
H5	−0.123(1)	0.303(2)	0.5469(7)
H6	0.258(2)	0.496(2)	0.4916(9)
H7	0.159(2)	0.611(2)	0.5693(9)
H8	0.141(2)	0.470(2)	0.6621(9)
H9	0.230(2)	0.267(2)	0.6417(9)
H10	0.302(2)	0.283(2)	0.5363(9)
H11	0.201(2)	0.374(3)	0.218(1)
H12	0.123(2)	0.566(3)	0.264(1)
H13	0.188(2)	0.597(3)	0.371(1)
H14	0.306(2)	0.425(3)	0.391(1)
H15	0.315(2)	0.287(3)	0.296(1)
H16	0.070(2)	0.040(2)	0.346(1)
H17	−0.070(2)	0.163(2)	0.383(1)
H18	−0.100(2)	0.341(2)	0.308(1)
H19	0.020(2)	0.326(2)	0.224(1)
H20	0.126(2)	0.140(2)	0.247(1)

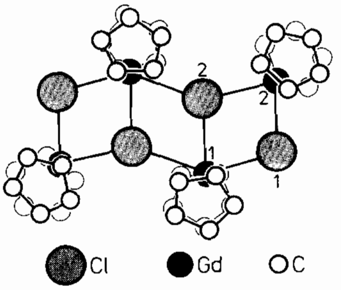

Fig. 1. Molecular structure of $[Gd(C_5H_5)_2Cl]_4$; numbers correspond to the different non-equivalent Gd and Cl atoms.

Results and Discussion

$Gd(C_5H_5)_2Cl$ forms colourless spherical crystals. The structure was solved using Patterson and Fourier techniques. Refinements on the basis of 1418 reflections converged to a final conventional R factor of 0.065 ($R_w = 0.078$, $w = k/(\sigma^2(F_o) + gF_o^2)$ with $k = 1.43$ and $g = 0.001$).

In the structure, tetrameric centrosymmetric units exist (see Fig. 1) which can be considered as fragments of the infinite double chains in $\overset{1}{\infty}[Gd(C_5H_5)_2Br]$ [4]. The Gd atoms in $[Gd(C_5H_5)_2Cl]_4$ are non-equivalent in coordination with respect to the halide ligand. Gd(1) has three Cl neighbours similar to Gd in $\overset{1}{\infty}[Gd(C_5H_5)_2Br]$, whereas Gd(2) is coordinated by two Cl atoms and therefore resembles Gd in $[Gd(C_5H_5)_2Br]_2$ [4]. The geometry of the Gd-$(C_5H_5)_2$ arrangement is nearly identical for both metal centres and very similar to the corresponding groups in the other compounds of this type. Representing each C_5H_5 group by a pseudo atom located at the ring centre of gravity, every metal atom is

TABLE III. $[Gd(C_5H_5)_2Cl]_4$, Bond Distances (A) and Angles (°)[a]

Atoms		Atoms	
Intramolecular		Intermolecular	
Gd1–Gd2	4.359(2)	Gd1–Gd1	7.400(2)
Gd1–Gd1*	4.793(2)	Gd1–Gd2	8.034(2)
Gd1–Gd2*	5.522(2)	Gd2–Gd2	7.028(2)
Gd2–Gd2*	8.719(2)		
Gd1–Cl1	2.811(8)	Cl1–Gd1–Cl2	75.0(2)
Gd1–Cl2	2.827(8)	Gd1–Cl1–Gd2	105.1(3)
Gd1–Cl2*	2.982(8)		
Gd2–Cl1	2.678(9)	Cl1–Gd2–Cl2	77.9(2)
Gd2–Cl2	2.781(8)	Gd1–Cl2–Gd2	102.0(2)
Gd1–C1	2.67(2)	Gd1–C6	2.62(2)
Gd1–C2	2.65(2)	Gd1–C7	2.65(2)
Gd1–C3	2.65(2)	Gd1–C8	2.70(2)
Gd1–C4	2.67(2)	Gd1–C9	2.70(2)
Gd1–C5	2.68(2)	Gd1–C10	2.65(2)
Gd2–C11	2.73(3)	Gd2–C16	2.66(3)
Gd2–C12	2.70(3)	Gd2–C17	2.74(3)
Gd2–C13	2.67(3)	Gd2–C18	2.70(3)
Gd2–C14	2.69(3)	Gd2–C19	2.60(3)
Gd2–C15	2.72(3)	Gd2–C20	2.58(3)

[a] Asterisk = symmetry-related position.

surrounded by five (Gd(1)) or four (Gd(2)) ligands leading in good approximation to C_{2v} symmetry for both metals (in order to achieve this point symmetry the ligands on average have to be displaced by 0.11 and 0.04 Å respectively).

Comparing the $[Gd(C_5H_5)_2Cl]_4$-type structure with the previously investigated dicyclopentadienide-chlorides of dysprosium [1] and erbium [2], it is worth noting that despite the close similarity of the metal radii the type of polynuclear units (binuclear (Er), tetranuclear (Gd) and infinite one-dimensional (Dy) species) and their arrangements in the solid state differ widely. Obviously, a subtle balance of convenient metal coordination and favourable packing of molecular species is responsible for the variety of crystal structures. Moreover, the formation of a distinct crystal structure depends on the species in the gaseous phase during sublimation, *i.e.*, there is a possibility that more than one crystal structure can be found for a given lanthanide compound. This has been proved to be true for $Gd(C_5H_5)_2Br$ [4].

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.

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