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Structural Chemistry of Lanthanidedicyclopentadienidehalides. Part 1*. Two Modifications of Gadoliniumdicyclopentadienidebromide, $[Gd(C_5H_5)_2Br]_2$ and $^1_\infty[Gd(C_5H_5)_2Br]$

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Abstract

The crystal structures of two modifications of gadoliniumdicyclopentadienidebromide, $[Gd(C_5H_5)_2Br]_2$ (**I**) and $^1_\infty[Gd(C_5H_5)_2Br]$ (**II**) have been determined from X-ray diffraction data. **I** crystallizes in the $[Sc(C_5H_5)_2Cl]_2$-type structure, space group $P2_1/c$, *with* $a = 14.110(3)$, $b = 16.488(3)$, $c = 13.765(3)$ Å, $\beta = 93.25(2)°$, $V = 3197(2)$ Å^3, and $D_c = 2.289$ g cm^{-3} for $Z = 6$ molecules. **II** crystallizes in space group $P2_1/c$ with $a = 5.946(7)$, $b = 8.447(5)$, $c = 20.239(9)$ Å, $\beta = 90.11(4)°$, $V = 1020(2)$ Å^3, $D_c = 2.392$ g cm^{-3} for $Z = 4$ formula units. The structures have been refined by full matrix least-squares techniques to conventional R factors of 0.034 for 3014 (**I**) and 1964 (**II**) reflections (with $I > 2\sigma(I)$). **I** consists of dimers with two bromine bridges (mean Gd–Br 2.872 Å). **II** has a double chain structure with alternating juxtaposition of gadolinium and bromine atoms (Gd–Br 2.912 Å (once) and 3.133 Å (twice)). The arrangement of the C_5H_5 groups with regard to the metal (η^5 fashion) is nearly identical in **I** and **II** (mean Gd–C 2.63(1) Å (**I**) and 2.62(1) Å (**II**)). Single crystals of **I** and **II** are obtained by sublimation at different temperatures. The formation of both modifications is discussed as to its dependence on the state of the gaseous phase equilibrium $[Gd(C_5H_5)_2Br]_2 \rightleftharpoons 2Gd(C_5H_5)_2Br$. Obviously, **I** crystallizes from gaseous phase dimers while **II** forms from the monomers.

Introduction

In order to ascertain direct and indirect metal–metal interactions in polynuclear complexes, a great deal of magnetochemical investigation has been carried out on d element compounds [1]. The magnetic properties of analogous compounds of the lanthanides, however, have not been established. Yet f element compounds in particular should be suitable for studying superexchange by bridging ligands and its dependence on orbital contributions to the magnetic moment. Compounds of the type $Ln(C_5H_5)_2X$ ($Ln \hat{=}$ lanthanide, $X \hat{=}$ halide) seemed to be relevant to these investigations as they were assumed to consist of binuclear units with halide bridges [2] similar to those found in the crystal structure of $[Sc(C_5H_5)_2Cl]_2$ [3]. The gadolinium compounds were chosen for preparation and crystal structure analysis because of the simple electron configuration $4f^7$ of the paramagnetic centers.

Experimental

Preparation

Due to the high sensitivity of the compounds to air and moisture, all procedures have been carried out under argon which in the last stage was purified by titanium at a temperature of 850 °C. The compound was prepared by stoichiometric reaction of water-free sublimed $GdBr_3$ (purity of the starting material $GdBr_3 \cdot xH_2O$ 99.99%, Johnson-Matthey Company, U.K.) with colourless NaC_5H_5 in benzene following standard methods [4]. Sublimation from the reaction mixture after removing the solvent yielded powders of $Gd(C_5H_5)_2Br$. Single crystals suitable to X-ray structure investigation were obtained in a second step by slow sublimation under controlled thermal conditions. Depending on the temperature during this process, either spherical (~130 °C) or

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*The following parts concerning *inter alia* several new structure types are in preparation: Part 2 ($Dy(C_5H_5)_2Br$, $Er(C_5H_5)_2Br$), Part 3 ($Dy(C_5H_5)_2Cl$), Part 4 ($Er(C_5H_5)_2Cl$), and Part 5 ($Gd(C_5H_5)_2Cl$).

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TABLE I. Details and Results of Structural Investigations

Modification	I, $[Gd(C_5H_5)_2Br]_2$	II, $^1_\infty[Gd(C_5H_5)_2Br]$
crystal size (mm)	0.25 × 0.20 × 0.15	0.45 × 0.08 × 0.10[a]
θ range	$0.01° \leq \theta \leq 24°$	$0.01° \leq \theta \leq 24°$
Space group	$P2_1/c$	$P2_1/c$
a (Å)	14.110(3)	5.964(7)
b (Å)	16.488(3)	8.447(5)
c (Å)	13.765(3)	20.239(9)
β (°)	93.25(2)	90.11(4)
V (Å^3)	3097(2)	1020(2)
Z	6 (dimers)	4
D_c (g cm^{-3})	2.289	2.392
Number of reflections	9503	3481
Number of unique reflections	8461	3393
Number of reflections in the refinements	3014	1964
Absorption coefficients μ (cm^{-1})	54.7	57.2
R	0.034	0.034
R_w	0.034	0.043
e.s.d.	1.067	1.026

[a] Empirical absorption correction was applied (PSI-scan, programs PSI and EAC, SDP plus [6]).

needle-shaped (~150 °C) crystals were obtained. They belong to two different modifications of $Gd(C_5H_5)_2Br$. For details of this temperature-dependent formation, see 'Discussion'.

Mass Spectroscopy

$Gd(C_5H_5)_2Br$ was characterized by mass-spectroscopy using the double-focusing Varian MAT CH 5 DF mass-spectrometer with electron energies of 70 eV. Mass spectra were consistent with corresponding investigations on the analogous $Yb(C_5H_5)_2Cl$ by Müller [5]. Usually the temperature of the ion source was kept at 170 °C. In order to get more information about the temperature-dependent composition of the gaseous phase, the temperature of the ion source was varied between 150 °C and 250 °C (see 'Discussion').

Structural Investigations

Single crystals of both modifications were sealed in carefully cleaned and well-conditioned thin-walled glass capillaries. Weissenberg photographs (Fe Kα and Mo Kα radiation) 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 (λ = 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 $5° \leq \theta \leq 15°$. 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, absorption coefficient of the two compounds are presented in Table I. The calculations were performed on a VAX 11/730 computer (Digital Equipment Corporation) using the SDP plus program system [6]. Scattering factors for neutral atoms were taken from the International Tables for X-ray Crystallography [7]. 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 [6]).

For a quantitative analysis of the coordination polyhedra of the gadolinium centers in both modifications with respect to their pseudosymmetries, the program PAINLES by Lueken, Elsenhans and Stamm [8] was used. In it the calculations are performed in two steps. First, symmetry-adapted orientations of the real polyhedra in the various point groups of interest are ascertained by fitting procedures using lattice sums of spherical harmonics. Then, the idealized polyhedra are constituted by averaging and optimizing the positional parameters of those ligands which are symmetry-equivalent in the idealized arrangements. The degree of distortion of the real polyhedra compared with the idealized polyhedra is specified by the mean value of relative atom displacements $\overline{\Delta R}$. In order to apply this program to our problem, each C_5H_5 ligand is represented by a pseudoatom located in the ring center of gravity. Results of the calculations are presented below under the heading 'Discussion'.

Structural Results

Modification I, [$Gd(C_5H_5)_2Br]_2$

This modification forms nearly spherical crystals. Its cell parameters (see Table I) resemble those of [$Sc(C_5H_5)_2Cl]_2$ [3] and the two compounds crystallize in the same space group. Therefore, the scandium compound served as a starting model for refinements. The structure refinement using 3014 reflections converged to a final conventional R factor of 0.034 ($R_w = 0.034$, non-Poisson-contribution $w = 1/(\sigma(|F_o|))^2$; estimated standard deviation of an observation of unit weight: 1.067). Major peaks in the final difference Fourier map did not exceed the height of 0.9 e/Å^3. Atomic parameters are given in Table II, bond distances and bond angles in Table III*. The molecular structure is illustrated in Fig. 1.

TABLE II. I, [$Gd(C_5H_5)_2Br]_2$, Atomic Parameters (All Atoms in General Position)

Atom	x	y	z
Gd1	0.05004(4)	0.73148(4)	0.34321(5)
Gd2	0.26068(4)	0.90092(4)	0.44487(4)
Gd3	0.41208(4)	0.40529(4)	0.43785(4)
Br1	0.21369(9)	0.81121(9)	0.27000(9)
Br2	0.09597(9)	0.82501(9)	0.51731(10)
Br3	0.41206(9)	0.57848(7)	0.45043(10)
C1	−0.0430(9)	0.8144(10)	0.2046(11)
C2	−0.0662(9)	0.8510(8)	0.2878(12)
C3	−0.1193(9)	0.7976(8)	0.3396(10)
C4	−0.1320(8)	0.7294(8)	0.2863(11)
C5	−0.0829(9)	0.7403(10)	0.2045(9)
C6	0.0109(11)	0.5745(8)	0.3554(12)
C7	0.0439(12)	0.5956(8)	0.4441(10)
C8	0.1390(11)	0.6112(8)	0.4371(13)
C9	0.1622(10)	0.6033(8)	0.3450(13)
C10	0.0780(12)	0.5811(8)	0.2910(11)
C11	0.3518(9)	0.7842(8)	0.5441(9)
C12	0.4038(9)	0.7962(7)	0.4637(9)
C13	0.4442(8)	0.8715(8)	0.4716(9)
C14	0.4177(8)	0.9087(8)	0.5574(9)
C15	0.3610(8)	0.8521(8)	0.6039(8)
C16	0.1499(11)	1.0223(9)	0.3837(15)
C17	0.1689(13)	1.0347(9)	0.4747(15)
C18	0.2597(14)	1.0566(9)	0.4824(12)
C19	0.2958(11)	1.0507(7)	0.3949(13)
C20	0.2224(12)	1.0289(8)	0.3322(11)
C21	0.3670(10)	0.3453(10)	0.2650(9)
C22	0.3822(11)	0.4275(10)	0.2492(9)
C23	0.4770(10)	0.4379(10)	0.2665(8)
C24	0.5196(12)	0.3667(11)	0.2928(9)
C25	0.4552(14)	0.3123(10)	0.2935(10)
C26	0.2708(9)	0.3096(10)	0.4776(11)
C27	0.3380(9)	0.2974(8)	0.5542(10)
C28	0.3430(9)	0.3668(10)	0.6067(9)
C29	0.2816(10)	0.4191(9)	0.5633(11)
C30	0.2365(10)	0.3825(12)	0.4844(12)
H1	−0.0065	0.8368	0.1552
H2	−0.0478	0.9042	0.3075
H3	−0.1428	0.8079	0.4017
H4	−0.1679	0.6830	0.3022
H5	−0.0771	0.7012	0.1544
H6	−0.0520	0.5567	0.3388
H7	0.0078	0.5995	0.5001
H8	0.1813	0.6250	0.4906
H9	0.2237	0.6115	0.3219
H10	0.0726	0.5728	0.2226
H11	0.3156	0.7372	0.5568
H12	0.4101	0.7593	0.4114
H13	0.4841	0.8955	0.4263
H14	0.4353	0.9611	0.5809
H15	0.3337	0.8595	0.6648
H16	0.0893	1.0056	0.3574
H17	0.1256	1.0327	0.5249
H18	0.2934	1.0718	0.5413
H19	0.3597	1.0609	0.3806
H20	0.2254	1.0216	0.2640
H21	0.3089	0.3161	0.2601
H22	0.3354	0.4664	0.2293
H23	0.5074	0.4890	0.2612
H24	0.5858	0.3611	0.3082
H25	0.4685	0.2572	0.3093
H26	0.2538	0.2697	0.4300
H27	0.3745	0.2500	0.5682
H28	0.3829	0.3775	0.6632
H29	0.2704	0.4736	0.5819
H30	0.1875	0.4035	0.4415

TABLE III. I, [$Gd(C_5H_5)_2Br]_2$, Bond Distances (A) and Angles (°)[a]

Gd1–Gd2	4.257(1)		
Gd3–Gd3*	4.284(1)		
Br1–Br2	3.878(2)		
Br3–Br3*	3.786(2)		
Gd1–Br1	2.888(1)	Br1–Gd1–Br2	84.29(4)
Gd1–Br2	2.892(1)	Br1–Gd2–Br2	85.04(4)
Gd2–Br1	2.871(1)	Gd1–Br1–Gd2	95.34(4)
Gd2–Br2	2.868(1)	Gd1–Br2–Gd2	95.31(4)
Gd3–Br3	2.861(7)	Br3–Gd3–Br3*	82.94(4)
Gd3–Br3*	2.857(1)	Gd3–Br3–Gd3*	97.06(4)

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*See 'Supplemementary Material'.

TABLE III. *(continued)*

Next but one gadolinium neighbours			
Gd1–Gd1	6.910(1)		
Gd1–Gd2	6.746(1)		
Gd1–Gd3	7.481(1)		
Gd2–Gd2	7.578(1)		
Gd2–Gd3	6.969(1)		
Gd3–Gd3*	8.579(1)		
Gd1–C1	2.64(1)	Gd1–C6	2.65(1)
Gd1–C2	2.65(1)	Gd1–C7	2.64(1)
Gd1–C3	2.62(1)	Gd1–C8	2.64(1)
Gd1–C4	2.64(1)	Gd1–C9	2.64(1)
Gd1–C5	2.60(1)	Gd1–C10	2.62(1)
Gd2–C11	2.65(1)	Gd2–C16	2.65(1)
Gd2–C12	2.66(1)	Gd2–C17	2.60(2)
Gd2–C13	2.64(1)	Gd2–C18	2.62(1)
Gd2–C14	2.63(1)	Gd2–C19	2.62(1)
Gd2–C15	2.66(1)	Gd2–C20	2.66(1)
Gd3–C21	2.62(1)	Gd3–C26	2.63(1)
Gd3–C22	2.63(1)	Gd3–C27	2.65(1)
Gd3–C23	2.63(1)	Gd3–C28	2.65(1)
Gd3–C24	2.65(1)	Gd3–C29	2.60(1)
Gd3–C25	2.61(2)	Gd3–C30	2.62(1)
C1–C2	1.35(2)	C5–C1–C2	107(1)
C2–C3	1.38(2)	C1–C2–C3	109(1)
C3–C4	1.35(2)	C2–C3–C4	108(1)
C4–C5	1.37(2)	C3–C4–C5	106(1)
C5–C1	1.35(2)	C4–C5–C1	110(1)
C6–C7	1.33(2)	C10–C6–C7	111(1)
C7–C8	1.38(2)	C6–C7–C8	106(1)
C8–C9	1.33(2)	C7–C8–C9	110(1)
C9–C10	1.41(2)	C8–C9–C10	106(1)
C10–C6	1.34(2)	C9–C10–C6	106(1)
C11–C12	1.38(2)	C15–C11–C12	109(1)
C12–C13	1.37(2)	C11–C12–C13	108(1)
C13–C14	1.40(2)	C12–C13–C14	110(1)
C14–C15	1.41(2)	C13–C14–C15	106(1)
C15–C11	1.39(2)	C14–C15–C11	108(1)
C16–C17	1.28(3)	C20–C16–C17	113(2)
C17–C18	1.33(3)	C16–C17–C18	106(2)
C18–C19	1.34(3)	C17–C18–C19	109(2)
C19–C20	1.36(2)	C18–C19–C20	106(2)
C20–C16	1.28(2)	C19–C20–C16	106(2)
C21–C22	1.39(2)	C25–C21–C22	106(1)
C22–C23	1.36(2)	C21–C22–C23	105(1)
C23–C24	1.36(2)	C22–C23–C24	111(1)
C24–C25	1.28(3)	C23–C24–C25	108(2)
C25–C21	1.39(2)	C24–C25–C21	110(2)
C26–C27	1.39(2)	C30–C26–C27	109(1)
C27–C28	1.35(2)	C26–C27–C28	107(1)
C28–C29	1.34(2)	C27–C28–C29	107(1)
C29–C30	1.37(2)	C28–C29–C30	109(1)
C30–C26	1.30(2)	C29–C30–C26	108(1)

[a] Asterisk = symmetry related position.

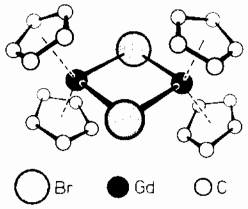

Fig. 1. Molecular structure of a $[Gd(C_5H_5)_2Br]_2$ dimer.

TABLE IV. **II**, $^1_\infty[Gd(C_5H_5)_2Br]$, Atomic Parameters (All Atoms in General Position)

Atom	*x*	*y*	*z*
Gd	0.25004(6)	0.92357(4)	0.90986(2)
Br	0.74990(10)	0.96697(10)	0.95377(3)
C1	0.0868(21)	0.6494(12)	0.8744(6)
C2	0.2952(27)	0.6525(14)	0.8520(6)
C3	0.4313(17)	0.6440(14)	0.8969(12)
C4	0.3216(28)	0.6349(12)	0.9540(6)
C5	0.1017(22)	0.6389(12)	0.9382(6)
C6	0.4093(21)	0.1630(14)	0.8391(5)
C7	0.2131(32)	0.2070(15)	0.8556(6)
C8	0.0752(17)	0.1275(19)	0.8262(6)
C9	0.1674(36)	0.0132(19)	0.7901(6)
C10	0.3964(24)	0.0434(15)	0.7997(5)
H1	−0.0472	0.6550	0.8490
H2	0.3352	0.6596	0.8067
H3	0.5897	0.6445	0.8923
H4	0.3855	0.6264	0.9969
H5	−0.0190	0.6345	0.9687
H6	0.5438	0.2119	0.8538
H7	0.1773	0.2890	0.8859
H8	−0.0824	0.1429	0.8279
H9	0.1010	−0.0687	0.7645
H10	0.5187	−0.0115	0.7812

Modification II, $^1_\infty[Gd(C_5H_5)_2Br]$

The crystals of this modification are needle-shaped. Space group, cell parameters, etc. are given in Table I. The crystal structure was solved using Patterson and difference Fourier techniques which led to the locations of all non-hydrogen atoms. Refinements analogous to those described for **I** converged to a final conventional *R* factor of 0.034 using 1964 reflections ($R_w = 0.043$, non-Poisson-contribution $w = 1/(\sigma(|F_o|))^2$; estimated standard deviation of an observation of unit weight: 1.026). Major peaks in the final difference Fourier map did not exceed 1.2 e/Å^3. Atomic parameters are given in Table IV, bond distances and bond angles in Table V*. Whereas in **I** isolated dimers were observed, infinite double-chains along the crystallographic *a*-axis (which is identical with the long needle axis)

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*See 'Supplementary Material'.

TABLE V. **II**, $^1_\infty[Gd(C_5H_5)_2Br]$, Bond Distances (Å) and Angles (°)

Gd–Gd	4.882(1)		
Br–Br	3.565(1)		
Gd–Br	2.911(1)	Br–Gd–Br	72.18(2)
Gd–Br	3.133(1)	Gd–Br–Gd	107.83(3)
Next but one gadolinium neighbour			
Gd–Gd	5.964(1)		
Gd–C1	2.61(1)	Gd–C6	2.65(1)
Gd–C2	2.59(1)	Gd–C7	2.64(1)
Gd–C3	2.61(1)	Gd–C8	2.63(1)
Gd–C4	2.63(1)	Gd–C9	2.59(1)
Gd–C5	2.63(1)	Gd–C10	2.60(1)
C1–C2	1.32(2)	C5–C1–C2	106(1)
C2–C3	1.22(2)	C1–C2–C3	112(1)
C3–C4	1.33(2)	C2–C3–C4	109(1)
C4–C5	1.35(2)	C3–C4–C5	106(1)
C5–C1	1.30(2)	C4–C5–C1	108(1)
C6–C7	1.27(2)	C10–C6–C7	109(1)
C7–C8	1.22(2)	C6–C7–C8	109(1)
C8–C9	1.33(2)	C7–C8–C9	113(1)
C9–C10	1.39(2)	C8–C9–C10	101(1)
C10–C6	1.29(2)	C9–C10–C6	107(1)

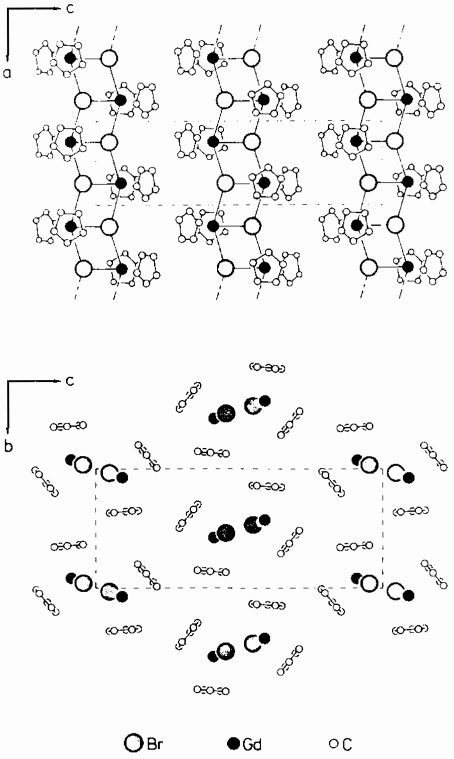

Fig. 2. (010) (top) and (100) (bottom) projections of the unit cell of $^1_\infty[Gd(C_5H_5)_2Br]$.

exist in **II**. The linkage within the double-chains is effected by gadolinium and bromine atoms. The coordination of the metal centers by halide increases from 2 (in **I**) to 3 (in **II**). The geometry of the double-chains and their packing are illustrated in two projections of the crystal structure along *b* and *a* axes (see Fig. 2). Within the double-chains the heavy atom arrangement is planar.

Inspecting the cell parameters of **II**, it is remarkable that the monoclinic angle $\beta = 90.11(4)°$ is very close to a right angle; *i.e.*, the unit cell has nearly orthorhombic metric. Refinements of **II** on the basis of an orthorhombic model in the space group *Pnma* (derived from systematic absences) lead to higher values for R, R_w and estimated standard deviation (e.s.d.) (*Pnma*: $R = 0.039$; $R_w = 0.055$, e.s.d. = 1.281; $P2_1/c$: $R = 0.034$, $Rw = 0.043$, e.s.d. = 1.026) and different C–C distances (*Pnma*: 1.24–1.49 Å; $P2_1/c$: 1.22–1.39 Å) compared to the corresponding values in **I**. The higher difference in C–C distances is caused by a vertical mirror through the C_5H_5 rings. Low-temperature X-ray structure investigations might lead to more unequivocal results due to the decrease of thermal motion. Such experiments will shortly be carried out.

Discussion

As described above ('Structural Results'), $Gd(C_5H_5)_2Br$ is found to crystallize in two modifications, *i.e.*, either as isolated dimers (**I**) or as infinite one-dimensional polymers (**II**). **II** results from sublimation at a higher temperature than that which is needed for **I**. We assume that this fact is connected with the temperature dependence of the gaseous phase equilibrium:

$$[Gd(C_5H_5)_2Br]_2 \rightleftharpoons 2Gd(C_5H_5)_2Br$$

With a low sublimation temperature the gaseous phase contains almost exclusively $[Gd(C_5H_5)_2Br]_2$ and condenses to **I**. A higher sublimation temperature shifts the balance to monomeric $Gd(C_5H_5)_2Br$; subsequent crystallization yields **II**. The temperature dependence of the gaseous phase equilibrium is confirmed by mass spectra of the compound recorded at various ion source temperatures. Raising the temperature from 150 to 240 °C causes an increase of the monomer peak ($Gd(C_5H_5)_2Br^+$, $m/e = 369$ u/e) from less than 1% (related to the highest peak of the spectrum ($Gd(C_5H_5)_2^+$, $m/e = 288$ u/e)) to 5.7%.

At the same time the relative intensity of the dimer peak ($Gd_2(C_5H_5)_4Br_2^+$, $m/e = 736$ u/e) decreases from 13.0% to 7.0% (see ref. 5). Routine mass spectra at 170 °C of both crystalline modifications do not differ from those of powder samples obtained from the first sublimation process (see 'Experimental'). In the spectra up to 1500 u/e there was no sign of higher gaseous phase oligomers, which could possibly originate from broken-up $^1_\infty[Gd(C_5H_5)_2Br]$-chains.

The two modifications differ in density (see Table I). The higher density of **II** could be caused by higher coordinative crowding of the metal atom in **II** compared to the coordination of gadolinium in **I**. With regard to cyclopentadienide, the metal center coordinations in the two modifications hardly differ:

(i) In both cases the rings are nearly planar and η^5-bonded, with Gd–C distances ranging from 2.60 to 2.66 Å (mean 2.63 Å) in **I** and from 2.59 to 2.65 Å (mean 2.62 Å) in **II**.

(ii) The angle A_1–Gd–A_2 (A_1, A_2 $\hat{=}$ ring centers of gravity of the two coordinated cyclopentadienides) in **II** (128.5°) is within the range of the three corresponding angles in **I** (128.5–131.0 Å).

(iii) The shortest nonbonded intramolecular contacts between carbon atoms in **I** and **II** are nearly equal at 3.36(2) Å (for comparison, the shortest intermolecular carbon distances are 3.70(2) Å in both cases). Hence any differences in coordination between **I** and **II** essentially follow differences in the bromine arrangements. In order to gain a quantitative approach to the problem, the cone packing model [9] has been used. Based on crystal structure data (metal-to-ligand distances, ligand extension) the so-called 'solid angle sum' (*SAS*) ($0 \leqslant SAS \leqslant 1$) can be calculated, which measures the coordinative crowding of a given center by its ligands. Evaluation of numerous organolanthanide(III) structures by Fischer and Li [10] led to an average *SAS* of 0.73 with deviations of ±0.05 ('*SAS* rule'). This mean value seems to indicate favourable coordinative saturation for lanthanide(III) centers in organometallics. Applying the model to **I** and **II**, $SAS(\mathbf{I}) = 0.68$ and $SAS(\mathbf{II}) = 0.77$ have been obtained. With regard to the '*SAS* rule' mean value, the metal centers in **I** are slightly subcoordinated whereas those in **II** are overcrowded by the same degree. The different *SAS* values parallel the differences in density.

A more detailed description of the geometry of the molecules and the environment of the gadolinium atoms can be gained from idealization procedures carried out with the computer program 'PAINLES' [8]. Representing each C_5H_5 group by a pseudo atom located at the ring center of gravity, every metal atom is surrounded by four (**I**) or five (**II**) ligands. In the first set of calculations, the average displacement $\overline{\Delta R}$ has been determined in order to achieve point symmetry D_{2h} for each of the two types of dimers in **I**. The molecule in general position is idealized to D_{2h} by displacing the ligands to an average of 0.03 Å, whereas each ligand of the centrosymmetric dimer has to be displaced by an average of 0.06 Å. These results show that the deviation from D_{2h} is very small in both cases and that geometrical differences between the two types of dimers are nearly negligible. The latter has already been mentioned in the discussion of the $[Sc(C_5H_5)_2Cl]_2$ structure [3]. Following from D_{2h} pseudosymmetry of the dimers, it has been ascertained in a second set of calculations that the three gadolinium atoms in **I** have nearly C_{2v} symmetry with respect to their four ligands. Here the mean displacements are $\overline{\Delta R_1} = 0.01$ Å (Gd1), $\overline{\Delta R_2} = 0.03$ Å (Gd2) and $\overline{\Delta R_3} = 0.06$ Å (Gd3). An idealization to T_d, however, is rather unprofitable. The corresponding $\overline{\Delta R}$ values are nearly 0.60 Å and more than ten times larger than in the case of an idealization to C_{2v}. The main reason for this is that the real metal–ligand distances (Gd–$A_{1,2}$, Gd–Br) differ widely. In **II**, the five-ligand coordination polyhedron of the gadolinium atom can also easily be idealized to C_{2v} symmetry ($\overline{\Delta R} = 0.05$).

Conclusions

(i) The results show that in case of $Gd(C_5H_5)_2Br$ the occurrence of different crystal structures is closely related to the variability of Gd–Br arrangements. In order to evaluate the factors controlling structures of this type of organolanthanides, the knowledge of the corresponding chloride structures will be useful for comparison.

(ii) In addition to structural investigations, the magnetism of **I** and **II** is of interest because changing the units from binuclear species to infinite chains can be expected to affect exchange interactions between the metal centers. Magnetochemical investigations down to low temperature are in progress.

Supplementary Material

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

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