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Structural Chemistry and Magnetism of Dicyclopentadienidehalides of Lanthanides. Part 6*. Ytterbiumdicyclopentadienidechloride and -bromide, $[Yb(C_5H_5)_2Cl]_2$ and $[Yb(C_5H_5)_2Br]_2$

HEIKO LUEKEN**, JOSEF SCHMITZ, WILLY LAMBERTS, PETER HANNIBAL and KLAUS HANDRICK

Institut für Anorganische Chemie der Technischen Hochschule Aachen, Professor-Pirlet-Str. 1, D-5100 Aachen, F.R.G.

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Abstract

The crystal structures of ytterbiumdicyclopentadienidechloride and -bromide, $[Yb(C_5H_5)_2Cl]_2$ (**I**) and $[Yb(C_5H_5)_2Br]_2$ (**II**), have been determined from X-ray diffraction data. **I** crystallizes in the $[Er(C_5H_5)_2Cl]_2$-type structure, space group $P2_1/c$, with $a = 11.021(4)$, $b = 7.998(2)$, $c = 12.123(4)$ Å, $\beta = 110.37(3)°$, $V = 1002(1)$ Å^3, $D_c = 2.244$ g cm^{-3} and $Z = 2$ dimers. **II** is isotypic to $[Sc(C_5H_5)_2Cl]_2$ (space group $P2_1/c$) with $a = 13.968(3)$, $b = 16.346(5)$, $c = 13.662(3)$ Å, $\beta = 93.78(2)°$, $V = 3112(2)$ Å^3, $D_c = 2.452$ g cm^{-3} and $Z = 6$ dimers. The structures have been refined by full matrix least-squares techniques to conventional R factors of 0.037 for 1556 (**I**) and 0.031 for 1935 (**II**) reflections (with $I > 3\sigma(I)$). Magnetic susceptibility data ($3.7 < T < 295$ K) show temperature dependent magnetic moments which can be explained by ligand field splitting of the Yb^{3+} free ion ground state $^2F_{7/2}$ (idealized symmetry: D_{2d}) and a small negative molecular field parameter.

Introduction

The crystal structures of the complexes $Ln(C_5H_5)_2X$ with Ln = Gd, Dy, Er and X = Cl, Br have been investigated previously. The results are summarized in Table 1. As we are mainly interested in the magnetism of this type of compound, lanthanide ions with an odd number of f electrons are chosen in order to avoid non-magnetic ligand field ground states. We now report on the ytterbium compounds $Yb(C_5H_5)_2Cl$ and $Yb(C_5H_5)_2Br$.

Experimental

Preparation

The compounds $Yb(C_5H_5)_2X$ (X = Cl, Br) were prepared by stoichiometric reactions of water-free sublimed YbX_3 (purity of the starting materials $YbX_3 \cdot xH_2O$: 99.99%, Johnson-Matthey Company, U.K.) with colourless NaC_5H_5 in benzene, following standard methods [5]. All procedures were carried out under purified argon. Single crystals suitable for X-ray structure investigation were obtained by slow sublimation at a temperature of ≈150 °C under low pressure.

Structural Investigation

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

TABLE 1. Survey of Structures of $Ln(C_5H_5)_2X$ Complexes

Lanthanide ion Number of 4f electrons	Gd^{3+} 7	Dy^{3+} 9	Er^{3+} 11	Yb^{3+} 13
Chlorides	tetrameric [1]	polymeric [2]	dimeric [3]	this work
Bromides	dimeric and polymeric [5]	dimeric [4]^a	dimeric [4]^a	

^{a}Inclusive of magnetochemical investigation.

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*For Part 5, see ref. 1.

**Author to whom correspondence should be addressed.

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TABLE 2. Details and Results of Structural and Magnetochemical Investigations

Compound	$[Yb(C_5H_5)_2Cl]_2$	$[Yb(C_5H_5)_2Br]_2$
Crystal structure		
Crystal size (mm)	0.38 × 0.20 × 0.04[a]	0.15 × 0.07 × 0.09
θ range	$0.01° \leq \theta \leq 30°$	$0.01° \leq \theta \leq 24°$
Space group	$P2_1/c$	$P2_1/c$
a (Å)	11.021(4)	13.968(3)
b (Å)	7.998(2)	16.346(5)
c (Å)	12.123(4)	13.662(3)
β (°)	110.37(3)	93.78(2)
V (Å^3)	1002(1)	3112(2)
Z (dimers)	2	6
D_c (g cm^{-3})	2.244	2.452
No. reflections	3553	7980
No. unique reflections	3247	7252
No. reflections in the refinements	1556	1935
Absorption coefficient μ (cm^{-1})	53.1[a]	71.8
R	0.037	0.031
R_w[b]	0.040	0.036
e.s.d.	2.665	6.522
Major peak in final difference Fourier syntheses [e Å^{-3}]	1.0	0.7
Magnetism (150 K < T < 295 K)		
Magnetic moment, expt. (Bohr magnetons)	4.6(1)	
Magnetic moment, theor.	4.54	

[a] Empirical absorption correction was applied (PSI-scan, programs PSI and EAC, SDP plus [6]). [b] $w = 1/(\sigma|F_o|)^2$.

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 2. 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 of Crystallography [7]. For full matrix least-squares refinements, reflections with $I > 3\sigma(I)$ were used. The positions of 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]).

Magnetic Susceptibility Measurements

Variable temperature (3.7–295 K) magnetic susceptibility measurements on powdered samples (weighed portions 2–4 mg) were carried out on a Faraday balance with $HgCo(SCN)_4$ as standard at low magnetic fields (0.07–0.25 T [8]). Susceptibilities were corrected for the diamagnetism of the molecular system (-190×10^{-11} m^3 mol^{-1}/Ln atom [9], SI units).

Structural Results

[Yb(C$_5$H$_5$)$_2$Cl]$_2$

$[Yb(C_5H_5)_2Cl]_2$ forms orange–red coloured lamella-like crystals. The cell parameters resemble those of $[Er(C_5H_5)_2Cl]_2$ [3] and the two compounds crystallize in the same space group. Therefore the erbium compound served as a starting model for refinements. Specific details concerning the structural refinements (conventional R factor, R_w, weighting scheme, e.s.d., major peaks in final difference Fourier synthesis) are presented in Table 2. Atomic parameters are given in Table 3, bond distances and bond angles in Table 4. See also 'Supplementary Material'. Structural refinements confirm the $[Er(C_5H_5)_2Cl]_2$-type structure.

[Yb(C$_5$H$_5$)$_2$Br]$_2$

The dark red crystals of $[Yb(C_5H_5)_2Br]_2$ are column-shaped. As the cell parameters resemble those of $[Er(C_5H_5)_2Br]_2$ [4] ($[Sc(C_5H_5)_2Cl]_2$-type structure [10]) and the two compounds crystallize in the same space group, the crystal structure of the erbium compound served as a starting model. In Table 2 some details concerning the structure refinement are represented. Atomic parameters are given in Table 5, bond distances and bond angles in Table 6. See also

TABLE 3. $[Yb(C_5H_5)_2Cl]_2$, Atomic Parameters (all atoms in general positions)

Atom	x	y	z
Yb	0.19228(5)	0.01902(6)	0.05747(4)
Cl	−0.0062(3)	0.1532(4)	0.0991(3)
C1	0.402(2)	−0.104(2)	0.205(1)
C2	0.331(1)	−0.049(2)	0.272(1)
C3	0.223(1)	−0.144(2)	0.251(1)
C4	0.223(2)	−0.262(2)	0.170(1)
C5	0.340(2)	−0.233(2)	0.142(1)
C6	0.199(2)	0.161(2)	−0.132(1)
C7	0.320(1)	0.107(2)	−0.074(1)
C8	0.371(2)	0.193(2)	0.023(1)
C9	0.285(2)	0.306(2)	0.029(1)
C10	0.171(1)	0.285(2)	−0.069(1)
H1	0.482	−0.058	0.207
H2	0.353	0.043	0.324
H3	0.160	−0.131	0.287
H4	0.160	−0.347	0.138
H5	0.366	−0.294	0.087
H6	0.141	0.118	−0.205
H7	0.363	0.020	−0.100
H8	0.455	0.177	0.080
H9	0.298	0.387	0.089
H10	0.092	0.345	−0.087

TABLE 4. $[Yb(C_5H_5)_2Cl]_2$, Bond Distances (Å) and Angles (°)[a]

Yb–Yb*	3.9875(7)		
Cl–Cl*	3.468(5)		
Yb–Cl	2.639(3)	Yb–Cl–Yb*	98.0(1)
Yb–Cl*	2.645(3)	Cl–Yb–Cl*	82.0(1)
Next but one metal–metal distance			
Yb–Yb	7.1016(7)		
Yb–C1	2.58(1)	Yb–C6	2.58(2)
Yb–C2	2.57(1)	Yb–C7	2.57(2)
Yb–C3	2.61(2)	Yb–C8	2.56(2)
Yb–C4	2.59(1)	Yb–C9	2.58(1)
Yb–C5	2.57(2)	Yb–C10	2.58(2)
C1–C2	1.38(2)	C5–C1–C2	108(1)
C2–C3	1.36(2)	C1–C2–C3	111(1)
C3–C4	1.37(2)	C2–C3–C4	107(1)
C4–C5	1.45(2)	C3–C4–C5	106(1)
C5–C1	1.33(2)	C4–C5–C1	108(2)
C6–C7	1.36(2)	C10–C6–C7	108(1)
C7–C8	1.32(2)	C6–C7–C8	109(2)
C8–C9	1.33(2)	C7–C8–C9	108(1)
C9–C10	1.40(2)	C8–C9–C10	108(1)
C(10)–C6	1.34(2)	C9–C10–C6	105(1)

[a] Asterisk = symmetry related position.

TABLE 5. $[Yb(C_5H_5)_2Br]_2$, Atomic Parameters (all atoms in general positions)

Atom	x	y	z
Yb1	0.04806(7)	0.73248(6)	0.34738(8)
Yb2	0.25679(7)	0.90134(6)	0.44355(7)
Yb3	0.41187(7)	0.40778(7)	0.43725(7)
Br1	0.2078(2)	0.8111(2)	0.2731(2)
Br2	0.0939(2)	0.8279(2)	0.5158(2)
Br3	0.5859(2)	0.4218(2)	0.5478(2)
C1	−0.043(2)	0.811(2)	0.210(2)
C2	−0.063(2)	0.849(2)	0.292(2)
C3	−0.118(2)	0.799(2)	0.347(2)
C4	−0.129(2)	0.730(2)	0.296(2)
C5	−0.090(2)	0.735(2)	0.211(2)
C6	0.012(2)	0.582(1)	0.374(2)
C7	0.050(3)	0.604(2)	0.453(2)
C8	0.140(2)	0.615(2)	0.452(3)
C9	0.155(2)	0.611(2)	0.352(2)
C10	0.073(2)	0.585(2)	0.302(2)
C11	0.343(2)	0.783(1)	0.538(2)
C12	0.395(2)	0.802(2)	0.462(2)
C13	0.437(2)	0.877(2)	0.468(2)
C14	0.409(2)	0.907(2)	0.556(1)
C15	0.357(2)	0.855(1)	0.601(2)
C16	0.145(2)	1.013(2)	0.382(3)
C17	0.167(3)	1.034(2)	0.477(3)
C18	0.256(2)	1.056(1)	0.479(2)
C19	0.296(2)	1.046(2)	0.386(2)
C20	0.217(3)	1.023(2)	0.327(2)
C21	0.366(2)	0.348(3)	0.268(2)
C22	0.388(3)	0.431(2)	0.250(2)
C23	0.486(2)	0.436(2)	0.274(2)
C24	0.522(2)	0.362(2)	0.304(2)
C25	0.449(2)	0.312(2)	0.298(2)
C26	0.279(2)	0.315(2)	0.480(2)
C27	0.342(2)	0.303(2)	0.553(2)
C28	0.346(2)	0.376(2)	0.601(2)
C29	0.278(2)	0.424(2)	0.560(2)
C30	0.244(2)	0.384(2)	0.481(2)
H1	−0.004	0.820	0.161
H2	−0.043	0.903	0.308
H3	−0.142	0.811	0.409
H4	−0.160	0.683	0.319
H5	−0.094	0.695	0.160
H6	−0.053	0.566	0.362
H7	0.015	0.609	0.511
H8	0.187	0.626	0.504
H9	0.213	0.622	0.322
H10	0.061	0.573	0.234
H11	0.306	0.735	0.549
H12	0.401	0.766	0.408
H13	0.477	0.902	0.424
H14	0.425	0.960	0.581
H15	0.333	0.863	0.664
H16	0.085	0.993	0.357
H17	0.124	1.032	0.528
H18	0.289	1.077	0.536
H19	0.361	1.053	0.373

(continued)

TABLE 5. *(continued)*

Atom	*x*	*y*	*z*
H20	0.219	1.016	0.259
H21	0.306	0.321	0.261
H22	0.345	0.473	0.227
H23	0.522	0.486	0.271
H24	0.587	0.352	0.323
H25	0.458	0.256	0.315
H26	0.269	0.273	0.433
H27	0.379	0.257	0.575
H28	0.388	0.395	0.654
H29	0.257	0.477	0.578
H30	0.195	0.401	0.435

TABLE 6. $[Yb(C_5H_5)_2Br]_2$, Bond Distances (Å) and Angles (°)[a]

Yb1–Yb2	4.164(1)		
Yb3–Yb3*	4.187(1)		
Br1–Br2	3.782(3)		
Br3–Br3*	3.686(3)		
Yb1–Br1	2.821(3)	Br1–Yb1–Br2	84.22(8)
Yb1–Br2	2.818(3)	Br1–Yb2–Br2	84.73(8)
Yb2–Br1	2.803(3)	Yb1–Br1–Yb2	95.53(8)
Yb2–Br2	2.809(3)	Yb1–Br2–Yb2	94.45(8)
Yb3–Br3	2.786(3)	Br3–Yb3–Br3*	82.73(7)
Yb3–Br3*	2.793(3)	Yb3–Br3–Yb3*	97.27(8)
Next but one metal–metal distances			
Yb1–Yb1	6.855(2)	Yb2–Yb2	7.588(1)
Yb1–Yb2	6.771(1)	Yb2–Yb3	6.971(2)
Yb1–Yb3	7.394(1)		
		Yb3–Yb3	8.559(1)
Yb1–C1	2.54(3)	Yb1–C6	2.53(2)
Yb1–C2	2.55(2)	Yb1–C7	2.54(3)
Yb1–C3	2.56(3)	Yb1–C8	2.67(3)
Yb1–C4	2.52(2)	Yb1–C9	2.49(3)
Yb1–C5	2.59(2)	Yb1–C10	2.52(3)
Yb2–C11	2.58(3)	Yb2–C16	2.51(3)
Yb2–C12	2.53(3)	Yb2–C17	2.56(3)
Yb2–C13	2.55(2)	Yb2–C18	2.58(3)
Yb2–C14	2.54(3)	Yb2–C19	2.56(3)
Yb2–C15	2.59(2)	Yb2–C20	2.58(3)
Yb3–C21	2.55(3)	Yb3–C26	2.49(3)
Yb3–C22	2.58(2)	Yb3–C27	2.56(3)
Yb3–C23	2.56(2)	Yb3–C28	2.52(3)
Yb3–C24	2.57(3)	Yb3–C29	2.61(3)
Yb3–C25	2.54(3)	Yb3–C30	2.49(3)
C1–C2	1.33(4)	C5–C1–C2	107(2)
C2–C3	1.38(4)	C1–C2–C3	109(2)
C3–C4	1.32(4)	C2–C3–C4	106(2)
C4–C5	1.32(4)	C3–C4–C5	112(3)
C5–C1	1.40(4)	C4–C5–C1	106(3)

(continued)

TABLE 6. *(continued)*

C6–C7	1.22(4)	C10–C6–C7	113(3)
C7–C8	1.27(5)	C6–C7–C8	113(3)
C8–C9	1.40(5)	C7–C8–C9	102(3)
C9–C10	1.36(4)	C8–C9–C10	109(3)
C10–C6	1.34(4)	C9–C10–C6	101(3)
C11–C12	1.33(4)	C15–C11–C12	102(2)
C12–C13	1.36(4)	C11–C12–C13	114(3)
C13–C14	1.38(4)	C12–C13–C14	103(2)
C14–C15	1.29(4)	C13–C14–C15	112(3)
C15–C11	1.47(3)	C14–C15–C11	108(2)
C16–C17	1.36(5)	C20–C16–C17	113(3)
C17–C18	1.31(5)	C16–C17–C18	104(3)
C18–C19	1.42(5)	C17–C18–C19	112(3)
C19–C20	1.36(4)	C18–C19–C20	102(3)
C20–C16	1.30(5)	C19–C20–C16	109(3)
C21–C22	1.41(6)	C25–C21–C22	106(3)
C22–C23	1.39(5)	C21–C22–C23	104(3)
C23–C24	1.36(5)	C22–C23–C24	111(3)
C24–C25	1.30(5)	C23–C24–C25	106(3)
C25–C21	1.35(5)	C24–C25–C21	113(3)
C26–C27	1.29(4)	C30–C26–C27	113(3)
C27–C28	1.36(4)	C26–C27–C28	104(3)
C28–C29	1.32(4)	C27–C28–C29	108(3)
C29–C30	1.32(5)	C28–C29–C30	105(3)
C30–C26	1.22(5)	C29–C30–C26	110(3)

[a] Asterisk = symmetry related position.

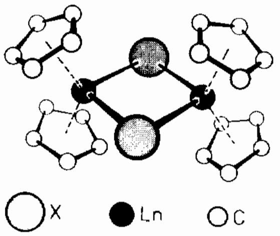

Fig. 1. Molecular structure of $[Ln(C_5H_5)_2X]_2$ (Ln = Yb; X = Cl, Br).

'Supplementary Material'. Structural refinements confirm the $[Sc(C_5H_5)_2Cl]_2$-type structure.

The molecular structure of the dimeric units existing in $[Yb(C_5H_5)_2Cl]_2$ and $[Yb(C_5H_5)_2Br]_2$ is illustrated in Fig. 1. The two crystal structures differ in the packing of the dimers (for details, see ref. 3).

Magnetochemical Investigations

The $1/\chi_{mol}$ *versus* T and the μ *versus* T diagrams of Figs. 2 and 3 respectively show the results of the susceptibility measurements and fitting procedures concerning $[Yb(C_5H_5)_2Cl]_2$. The compound has Curie–Weiss behaviour above ≈150 K with a magnetic moment close to the Yb^{3+} free ion value (see Table 2). At temperatures below 150 K deviations

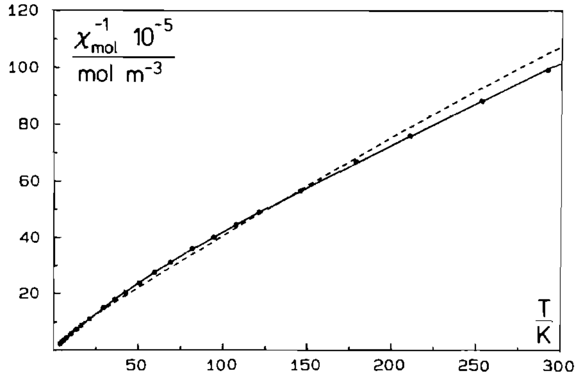

Fig. 2. $[Yb(C_5H_5)_2Cl]_2$; $1/\chi_{\text{mol}}$ *vs.* T diagram (SI units): ●●● experimental data; ---- best fit to the cubic model; —— best fit to the tetragonal model.

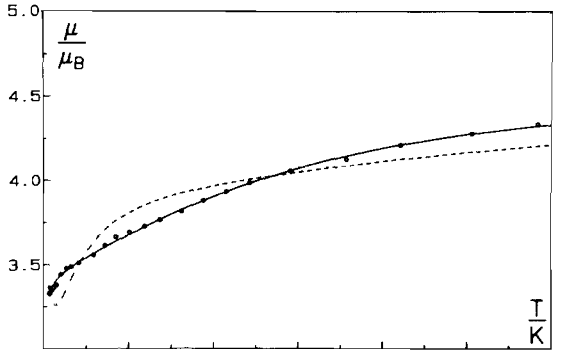

Fig. 3. $[Yb(C_5H_5)_2Cl]_2$; μ *vs.* T diagram; ●●● experimental data; ---- best fit to the cubic model; —— best fit to the tetragonal model.

from the Curie–Weiss straight line occur which may be mainly caused by ligand field effects. There is no indication that down to the lowest available temperature (3.7 K) the susceptibility reaches a maximum. This, however, was the case with $[Dy(C_5H_5)_2Br]_2$ [4] and probably caused by antiferromagnetically coupled lanthanide ions within the dimer. The magnetic susceptibility data of $[Yb(C_5H_5)_2Br]_2$ correspond to those of $[Yb(C_5H_5)_2Cl]_2$, *i.e.* no characteristic feature down to 3.7 K is observed.

Ligand Field Model

In order to confirm the predominant influence of ligand fields on the magnetic behaviour of $[Yb(C_5H_5)_2Cl]_2$, fits to the experimental data have been carried out on the basis of simple models. In a first approach we have tried to interpret the susceptibility data in terms of a cubic (tetrahedral) ligand field model by applying the Hamiltonian

$$\mathcal{H}_{\text{LF}} = B_4^0(\hat{O}_4^0 + 5\hat{O}_4^4) + B_6^0(\hat{O}_6^0 - 21\hat{O}_6^4)$$

on the manifold of the angular momentum $J = 7/2$ where $\hat{O}_k^q$ are operator equivalents and coefficients B_k^q are crystal field intensity parameters [11]. The lanthanide centres have the low pseudosymmetry C_{2v}, and a tetrahedral arrangement of the ligands in this type of compound constitutes a drastic approximation. This model, however, could delineate the ligand field effects in the case of the corresponding dysprosium and erbium dimers [4] and is therefore used here as a starting model. The perturbing influence of the cubic crystal field leads to a splitting of the eightfold degenerate $^2F_{7/2}$ ground term into two doublets (Γ_6, Γ_7) and a quartet (Γ_8). Susceptibility can be calculated from the Van Vleck equation [12]

$$\chi_{\text{LF}} = -\frac{\mu_0 N}{H}\frac{\Sigma_i(\delta E_i/\delta H)\exp\{-E_i/(kT)\}}{\Sigma_i \exp\{-E_i/(kT)\}}$$

where μ_0 is the vacuum permeability, N is Avogadro's number, and $-(\delta E_i/\delta H) = \mu_i$ the magnetic moment of the ith level in the direction of the applied field H.

In addition to ligand field effects the magnetic behaviour of the lanthanide can be influenced by exchange interactions through the intervening halide ions. Using the molecular field model the magnetic susceptibility can be given by

$$1/\chi = 1/\chi_{\text{LF}} - \lambda$$

where λ is the molecular field parameter.

The best fit on the basis of the cubic model (with the parameters $B_4^0 \approx 0.37\ \text{cm}^{-1}$, $B_6^0 \approx -0.014\ \text{cm}^{-1}$, $\lambda \approx 10^5\ \text{mol m}^{-3}$) is represented by broken lines in Figs. 2 and 3. From the μ *versus* T diagram it is obvious that the fit is poor, although the same model leads to satisfactory results in the case of the erbium and dysprosium compound. The reason for this diverse behaviour might be that with Yb^{3+} ($J = 7/2$) the composition of the symmetry adapted ligand field states is independent of the parameters B_4^0 and B_6^0, leading to a susceptibility formula which responds less flexibly to inadequacy of the model than in the case of Er^{3+} and Dy^{3+} ($J = 15/2$) where the coefficients of the corresponding $|M_J\rangle$ linear combinations depend on B_4^0 and B_6^0.

With an extended ligand field model of tetragonal symmetry (D_{2d}) using the operator

$$\mathcal{H}_{\text{LF}} = B_2^0\hat{O}_2^0 + B_4^0\hat{O}_4^0 + B_4^4\hat{O}_4^4 + B_6^0\hat{O}_6^0 + B_6^4\hat{O}_6^4$$

satisfactory agreement between measured and calculated data is achieved (see solid line in Figs. 2 and 3). The determination of the parameters B_k^q, however, is not unequivocal. There are series of parameter combinations leading to a similar accuracy in the fits, among them the set where the ratios B_4^4/B_4^0 and B_6^4/B_6^0 take on the cubic field quantities (5 and −21 respectively). In this case, which is represented in the diagrams, the remaining parameters have the following values: $B_2^0 \approx -10\ \text{cm}^{-1}$, $B_4^0 \approx 0.093\ \text{cm}^{-1}$, $B_6^0 \approx -0.0073\ \text{cm}^{-1}$ and $\lambda \approx -0.15 \times 10^5\ \text{mol m}^{-3}$. A further discussion of this result appears meaningless because of the aforementioned ambiguity. One aspect, however, should be mentioned: although small in magnitude, the molecular field parameter λ significantly improves the accuracy of the fit, especially in the low temperature region. Transformed to the θ scale of Curie–Weiss behaviour, λ corresponds to $\theta \approx -0.5$ K, which value is similar to those obtained in the case of the erbium and dysprosium compound [4].

Model calculations, based on a combined Heisenberg/molecular field model for the description of exchange interactions within lanthanide dimers [13], are consistent with the observed low temperature magnetic behaviour of the dysprosium, erbium and ytterbium compounds. Assuming an antiferromagnetic coupling of equal strength, the temperature where the susceptibility reaches its maximum strongly depends on the total spin S of the respective lanthanide ion and should be highest in the dysprosium complex ($S_{\mathrm{Dy}} = 5/2$) and distinctly lower in the other compounds ($S_{\mathrm{Er}} = 3/2, S_{\mathrm{Yb}} = 1/2$).

Supplementary Material

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

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