Crystal Structure and Magnetic Behaviour of the New Gadolinium Complex Compound $Gd_2(ClH_2CCOO)_6(bipy)_2$

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Single crystals of the title compound have been obtained by reaction of $Gd_3(ClH_2CCOO)_9(H_2O)_5$ with 2,2′-bipyridyl (bipy) in a solution of ethanol and water. $Gd_2(ClH_2CCOO)_6(bipy)_2$ crystallises in the triclinic space group $P\bar{1}$ (Z = 2) with a = 959.5(3) pm, b = 980.9(3) pm, c = 1163.9(4) pm, α = 68.67(3) °, β = 84.82(4)° and γ = 82.47(4)°. The crystal structure is built up of discrete molecules of dinuclear Gd^{3+}–Gd^{3+} units. The corresponding residual (all data) for the refined structure is 4.46 %. The magnetic behaviour of the compound was investigated in the temperature range of 1.76–300 K. The magnetic data were interpreted considering exchange interactions within the dimeric unit (J_{ex} = –0.020 cm^{-1}).

Introduction

The research on molecular magnetic materials with lanthanides (Ln) is up to now mostly focused on the interaction of transition metal with lanthanide ions. There are several publications[1–5] concerning magnetic interactions in Ln–Cu, Ln–Ni and Ln–Fe units but only few Ln-Ln interactions in molecular magnetic materials have been studied yet.[6–10] There are no simple rules, such as the ones of Goodenough and Kanamori for compounds of d elements, to predict the occurrence of ferro- or antiferromagnetic coupling.[11] In order to fill this lack of knowledge we synthesised the title compound and determined the magnetic behaviour. The magnetic data were interpreted considering magnetic exchange coupling in the dinuclear Gd^{3+}–Gd^{3+} unit.[11,12]

Results and Discussion

The crystal data and details of the refinements for $Gd_2(ClH_2CCOO)_6(bipy)_2$ are summarised in Table 1, selected bond lengths can be found in Table 2.

The title compound crystallises in the triclinic space group $P\bar{1}$ (Z = 2) with a = 959.5(3) pm, b = 980.9(3) pm, c = 1163.9(4) pm, α = 68.67(3)°, β = 84.82(4)° and γ = 82.47(4)°. The crystal structure is shown in Figure 1 (H atoms are not displayed). The structure is built up by discrete dimers (Gd^{3+}–Gd^{3+}-distance: 399.0 pm) with two kinds of bridging carboxylate groups (μ_2-carboxylato-κ^1O:κ^1O' and μ_2O';κ^2O,O') and besides a chelating monochloroacetate ion (Figure 2).[13] The Gd^{3+} ion is ninefold coordinated by seven oxygen atoms originating from the carboxylate groups (Gd^{3+}–O distances: 236.3 pm to 260.3 pm) and two nitrogen atoms stemming from a 2,2′-bipyridyl molecule (Gd^{3+}–N distances: 255.1 pm and 258.5 pm).

Table 1. Crystallographic data for $Gd_2(ClH_2CCOO)_6(bipy)_2$.

Compound	$Gd_2(ClH_2CCOO)_6(bipy)_2$
Crystal system	triclinic
Space group	$P\bar{1}$
Lattice constants [pm, °]	a = 959.5(3), α = 68.67(3)
	b = 980.9(3), β = 84.82(4)
	c = 1163.9(4), γ = 82.47(4)
V [pm^3]	1010.5(5)·10^6
Z	2
ρ (X-ray) [g/cm^3]	1.952
Absorption coefficient μ [mm^{-1}]	3.713
F(000)	574
Crystal dimensions [mm^3]	0.481 × 0.1184 × 0.592
Temperature [K]	293(2)
Wavelength	Mo-K_α (λ = 71.073 pm)
θ range [°]	2.14 ≤ 2θ ≤ 26.17
Index range (h, k, l)	–11 ≤ h ≤ 11
	–12 ≤ k ≤ 12
	–14 ≤ l ≤ 14
No. of collected reflections	14707
No. of independent reflections	3771
Observed reflections with $F > 2\sigma$	3253
R_{int}	0.1161
Programs used	SHELXS-97[23] and SHELXL-97[24]
Structure refinement	Full-matrix least squares
No. of refined parameters	248
Goodness-of-fit[a]	1.117
Residuals [$I > 2\sigma(I)$][a]	R_1 = 0.0357, wR_2 = 0.0835
Residuals (all data)[a]	R_1 = 0.0446, wR_2 = 0.0933
Largest differential hole and peak [e·pm^{-3}]	–1.198·10^{-6}/1.050·10^{-6}
CCDC deposition number[26]	280805

[a] Definition given in the literature.[24]

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Table 2. Selected interatomic distances [pm] for $Gd_2(ClH_2CCOO)_6(bipy)_2$.

Gd–Gd[a]	399.0(2)
Gd–O12	236.3(4)
Gd–O32	237.2(4)
Gd–O11	237.7(4)
Gd–O21	243.5(5)
Gd–O22	250.0(4)
Gd–O31	250.2(4)
Gd–O32[a]	260.3(4)
Gd–N(2A)	255.1(5)
Gd–N(1A)	258.5(5)

[a] Symmetry transformation used to generate atoms: $-x + 1, -y + 1, -z + 2$.

The extended structure is formed by π–π stacking of the ligating 2,2′-bipyridyl molecules (Figure 3).[14,15] The shortest orthogonal distance between two aromatic fragments is 345.0 pm.

Former results have shown, that the $\mu_2 O';\kappa^2 O,O'$- is responsible for a ferromagnetic interaction whereas the μ_2-carboxylato-$\kappa^1 O:\kappa^1 O'$-bridging mode leads to an antiferromagnetic interaction.[13,16–20] The title compound with the obtained crystal structure is interesting for magnetic investigations in order to study the influence of the coexistence of both bridging modi.

The presentation of the magnetic data follows the recommendation of S. Hatscher et al.[21] Figure 4 displays the measured effective Bohr magneton number (μ_{eff}) of the $Gd_2(ClH_2CCOO)_6(bipy)_2$ in the temperature range between 1.76 and 300 K ($H^{(ir)}$ = 500 Oe). The curve progression shows an antiferromagnetic behaviour. The measured magnetic susceptibility ($\chi_m^{(ir)}$) is interpreted by Equation (1) given below, where the intramolecular interaction within the dimeric unit is described by the Heisenberg model with a spin Hamiltonian $\hat{H}_{ex} = -2J_{ex}\hat{\boldsymbol{S}}_{Gd1}\cdot\hat{\boldsymbol{S}}_{Gd2}$ ($S_{Gd1} = S_{Gd2} = 7/2$), where N_A is the Avogadro constant, μ_B the Bohr magneton, g the Landé factor, k_B the Boltzmann constant, T the absolute temperature and J_{ex} the magnetic exchange parameter.[12]

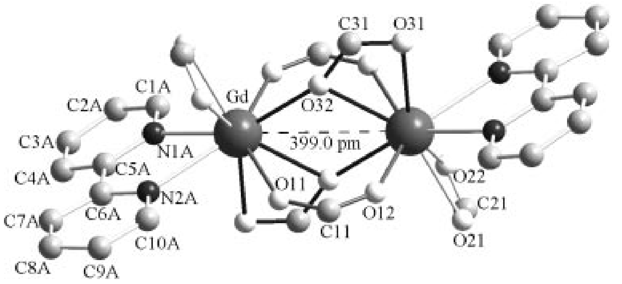

Figure 2. Dimeric unit in $Gd_2(ClH_2CCOO)_6(bipy)_2$; Gd atoms, carboxylate groups and 2,2′-bipyridyl molecules are given. The dashed line shows the Gd^{3+}–Gd^{3+}-distance, dark-grey lines indicate the μ_2-carboxylato-$\kappa^1 O:\kappa^1 O'$- and the black ones the $\mu_2 O';\kappa^2 O,O'$-bridging mode.

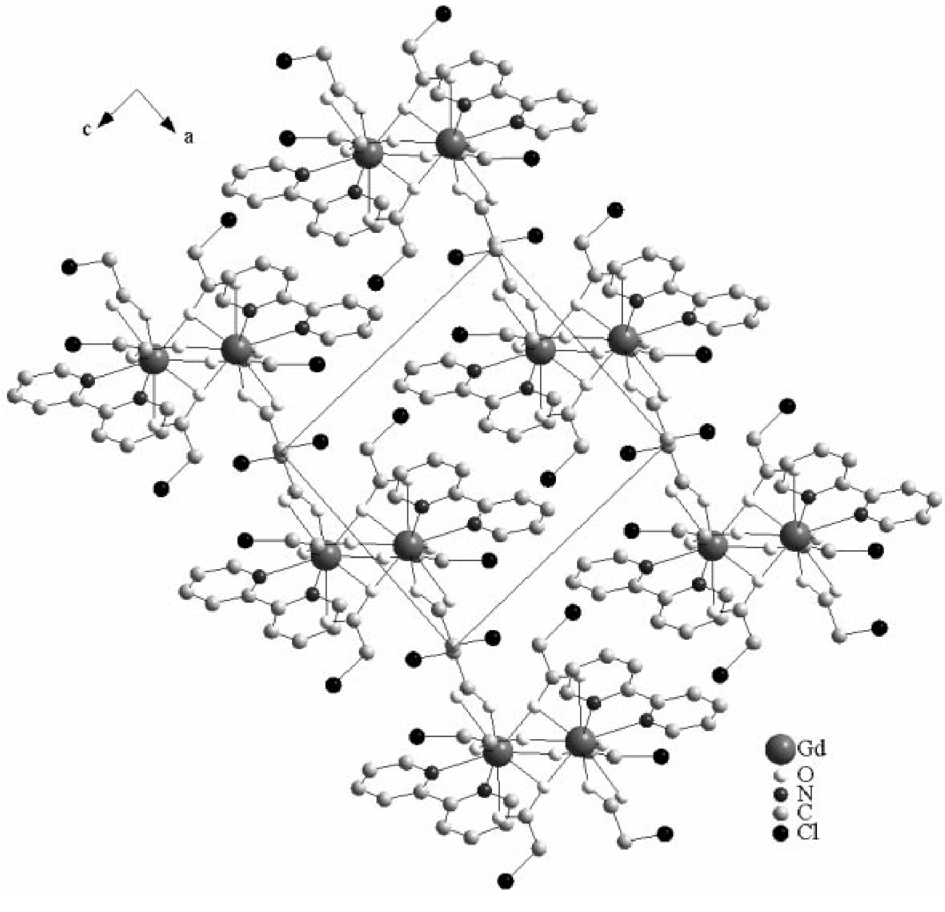

Figure 1. Crystal structure of $Gd_2(ClH_2CCOO)_6(bipy)_2$. The triclinic unit cell is given; H atoms are not displayed.

$$\chi_{\mathrm{m}}^{(\mathrm{ir})} = \frac{N_{\mathrm{A}}\mu_{\mathrm{B}}^{2}g^{2}}{k_{\mathrm{B}}T} \cdot \frac{e^{2x}+5e^{6x}+14e^{12x}+30e^{20x}+55e^{30x}+91e^{42x}+140e^{56x}}{1+3e^{2x}+5e^{6x}+7e^{12x}+9e^{20x}+11e^{30x}+13e^{42x}+15e^{56x}}$$

$$\text{with } x = J_{\mathrm{ex}}/k_{\mathrm{B}}T \qquad (1)$$

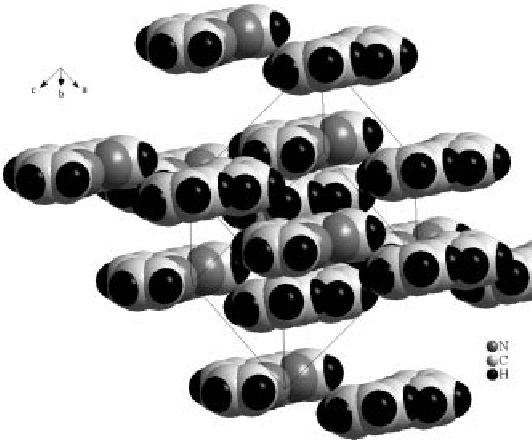

Figure 3. π–π Stacking of the 2,2′-bipyridyl molecules in $Gd_2(ClH_2CCOO)_6(bipy)_2$. The unit cell is given.

The fitting procedure leads to J_{ex} = –0.020 cm^{-1}, with g = 2.00. The accordance of the measured and calculated μ_{eff} values is shown in Figure 4.

The value of J_{ex} for the title compound is comparable with the ones of other carboxylates containing Gd^{3+} (cf. Table 3). The coexistence of the $\mu_2O';\kappa^2O,O'$- and the μ_2-carboxylato-$\kappa^1O{:}\kappa^1O$-bridging mode in $Gd_2(ClH_2CCOO)_6$(bipy)$_2$ leads to a negative exchange parameter, meaning a dominating antiferromagnetic interaction, as found in (**2**).[20]

Experimental Section

Transparent, colourless, air-stable, single crystals of $Gd_2(ClH_2CCOO)_6(bipy)_2$ have been obtained by reaction of $Gd_3(ClH_2CCOO)_9(H_2O)_5$ with 2,2′-bipyridyl (Fluka, ≥ 98.0%%) (molar ratio 2:1) in a solution of ethanol and water (1:1). The starting compound $Gd_3(H_2ClCCOO)_9(H_2O)_5$ was prepared as given in the literature.[22]

Well grown single crystals were mounted on a STOE imaging plate diffractometer. The data collection was carried out at room temperature. The structure was solved by Patterson methods and were refined with anisotropic displacement parameters based on F^2 using SHELXS-97[23] and SHELXL-97[24] programs. Data analysis indicate the space group $P\bar{1}$. The final refinement yielded R_1 (all data) = 4.46%. Hydrogen atoms were included using a riding model. The crystal data and details of the refinement are summarised in Table 1 and selected bond lengths can be found in Table 2. Elemental analysis (Vario EL, Elementar Analysesysteme GmbH, Hanau, Germany) for $C_{16}H_{20}Cl_3GdN_2O_6$ (593.91): calcd. C 32.36, H 2.38, N 4.72; found C 32.29, H 2.47, N 4.69.

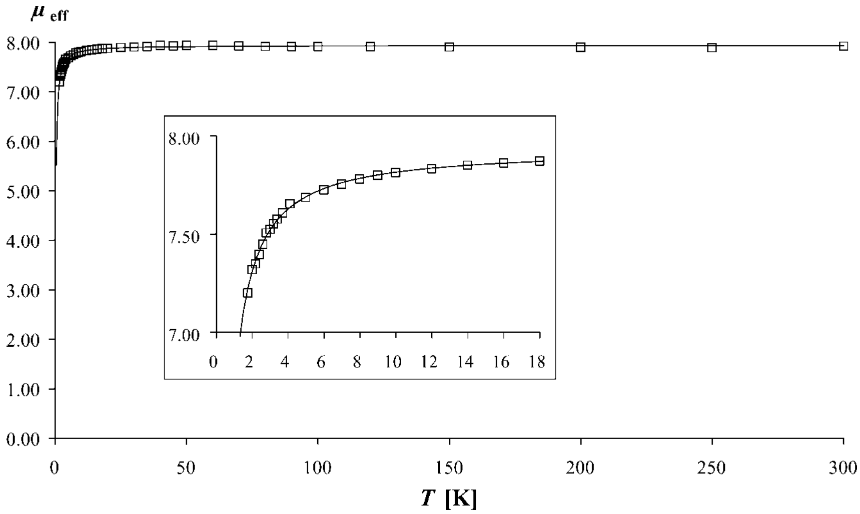

Figure 4. Comparison of measured (□, $H^{(ir)}$ = 0.5 kOe) and calculated (−) effective Bohr magneton numbers for $Gd_2(ClH_2CCOO)_6(bipy)_2$.

Table 3. Comparison of J_{ex} [cm^{-1}], bridging mode and Gd^{3+}–Gd^{3+}-distance (pm) for $Gd_2(ClH_2CCOO)_6(bipy)_2$ (**1**) $Gd(CF_2HCOO)_3(phen)$ (**2**), $[NH_3C_2H_5][Gd(Cl_2HCCOO)_4]$ (**3**), $[NH_3CH_3][Gd(Cl_2HCCOO)_4]$ (**4**), $Gd(H_3CCOO)_3(H_2O)_2{\cdot}2H_2O$ (**5**) and $Gd(F_2HCCOO)_3(H_2O)_2{\cdot}H_2O$ (**6**).

Compound	J_{ex}	Bridging mode	Gd^{3+}–Gd^{3+} distance	Ref.
1	–0.020	$\mu_2O';\kappa^2O,O'$ and μ_2-carboxylato-$\kappa^1O{:}\kappa^1O'$	399.0	this work
2	–0.016	$\mu_2O';\kappa^2O,O'$ and μ_2-carboxylato-$\kappa^1O{:}\kappa^1O'$	403.4	[20]
3	+0.029	$\mu_2O';\kappa^2O,O'$	418.1	[19]
4	+0.023	$\mu_2O';\kappa^2O,O'$	418.4	[18]
5	+0.025	$\mu_2O';\kappa^2O,O'$	420.6	[16]
6	–0.012	μ_2-carboxylato-$\kappa^1O{:}\kappa^1O'$	445.6	[13]
4	–0.007	μ_2-carboxylato-$\kappa^1O{:}\kappa^1O'$	451.6	[18]

Pulverised single crystals of the title compound were measured with a SQUID magnetometer (MPMS5, Quantum Design) in a temperature range of 1.76 to 300 K at magnetic fields ($H^{(ir)}$) of 500 and 1000 Oe. No field dependence of the magnetic data was observed. The sample was weighed into the lid of a gelantine capsule. To avoid orientation effects during the measurement, another gelantine capsule was pressed on the sample to fix it. Subsequently the container was sewn in a plastic straw. Using the increments of Haberditzl, the raw magnetic data were corrected for diamagnetism of the sample carrier and the sample.[25]

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[26] CCDC-280805 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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