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Crystal Structure and Magnetic Behaviour of the New Gadolinium Carboxylates $Gd_2(ClF_2CCOO)_6(hypy)_2$, $Gd_2(F_3CCOO)_6(hypy)_2$, $Gd_2(F_2HCCOO)_6(hypy)_2$ and $Gd_2(Cl_2HCCOO)_6(H_2O)_2(hypy)_2$

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Four complexes with the formulae $Gd_2(ClF_2CCOO)_6(hypy)_2$ (**1**), $Gd_2(F_3CCOO)_6(hypy)_2$ (**2**), $Gd_2(F_2HCCOO)_6(hypy)_2$ (**3**) and $Gd_2(Cl_2HCCOO)_6(H_2O)_2(hypy)_2$ (**4**) have been synthesised and characterised by single-crystal X-ray diffraction methods at room temperature. The title compounds have been obtained by reaction of the corresponding gadolinium carboxylates with 4-hydroxypyridine in a solution of ethanol and water. They crystallise in the triclinic space group $P\bar{1}$ ($Z = 2$) [**1**: $a = 999.8(4)$ pm, $b = 1061.8(5)$ pm, $c = 1283.6(6)$ pm, $\alpha = 91.23(5)°$, $\beta = 111.29(5)°$ and $\gamma = 105.27(5)°$; **2**: $a = 972.4(4)$ pm, $b = 1053.5(5)$ pm, $c = 1252.4(6)$ pm, $\alpha = 94.23(5)°$, $\beta = 110.21(5)°$ and $\gamma = 104.84(5)°$; **3**: $a = 883.3(4)$ pm, $b = 1051.3(4)$ pm, $c = 1284.9(6)$ pm, $\alpha = 100.46(5)°$, $\beta = 109.87(5)°$ and $\gamma = 97.43(5)°$; **4**: $a = 913.7(4)$ pm, $b = 1079.0(5)$ pm, $c = 1137.5(5)$ pm, $\alpha = 93.41(5)°$, $\beta = 109.36(5)°$ and $\gamma = 99.53(5)°$]. The crystal structures consist of dinuclear Gd^{3+}–Gd^{3+} units. The corresponding residuals (all data) for the refined structures are 4.82 % (**1**), 5.93 % (**2**), 5.68 % (**3**) and 4.04 % (**4**). The magnetic behaviour of the compounds was investigated over the temperature range 1.76–300 K. The magnetic data were interpreted by considering exchange interactions within the dimeric units [$J_{ex} = -0.019\ cm^{-1}$ (**1**), $J_{ex} = -0.034\ cm^{-1}$ (**2**), $J_{ex} = -0.064\ cm^{-1}$ (**3**), $J_{ex} = -0.011\ cm^{-1}$ (**4**)].

Introduction

In connection with the investigations of the structural chemistry of polynuclear complexes of lanthanides that are of importance for the study of magnetic interactions,[1–16] we paid attention to the carboxylates $Gd_2(X_kH_mCCOO)_6(H_2O)_n(hypy)_2$ [X = Cl, F; $k = 2, 3$; $m = 0, 1$; $n = 0, 2$; hypy: tautomerised 4-hydroxypyridine = 4-(1*H*)-pyridone]. There are no simple rules to predict the occurrence of ferro- or antiferromagnetic coupling, unlike those of Goodenough and Kanamori for compounds of d elements.[17] In order to eliminate this nescience we determined the magnetic behaviour of the title compounds. The magnetic data were interpreted by considering magnetic exchange coupling in the dinuclear Gd^{3+}–Gd^{3+} units.[17,18]

Results and Discussion

Crystal Structures

The crystal data and details of the refinements for **1**, **2**, **3** and **4** are summarised in Table 1, selected bond lengths can be found in Table 2.

The title compounds crystallise in the triclinic space group $P\bar{1}$ (Z = 2) with **1**: $a = 999.8(4)$ pm, $b = 1061.8(5)$ pm, $c = 1283.6(6)$ pm, $\alpha = 91.23(5)°$, $\beta = 111.29(5)°$ and $\gamma = 105.27(5)°$; **2**: $a = 972.4(4)$ pm, $b = 1053.5(5)$ pm, $c = 1252.4(6)$ pm, $\alpha = 94.23(5)°$, $\beta = 110.21(5)°$ and $\gamma = 104.84(5)°$; **3**: $a = 883.3(4)$ pm, $b = 1051.3(4)$ pm, $c = 1284.9(6)$ pm, $\alpha = 100.46(5)°$, $\beta = 109.87(5)°$ and $\gamma = 97.43(5)°$; **4**: $a = 913.7(4)$ pm, $b = 1079.0(5)$ pm, $c = 1137.5(5)$ pm, $\alpha = 93.41(5)°$, $\beta = 109.36(5)°$ and $\gamma = 99.53(5)°$.

$Gd_2(ClF_2CCOO)_6(hypy)_2$ (1)

The crystal structure is shown in Figure 1. The Gd^{3+} ions are connected (Gd^{3+}–Gd^{3+} distance is 386.6 pm) through two carboxylate groups (μ_2-carboxylato-κ^1O:κ^1O') and two 4-(1*H*)-pyridone molecules (μ_2-pyridone-1:2κ^2O) to form dimers (Figure 2). In addition each Gd^{3+} ion is chelated by two chlorodifluoroacetate ions and one pyridone molecule (Figure 2). The central ion is ninefold coordinated by oxygen atoms originating from the carboxylate groups (Gd^{3+}–O distances are 240.2–268.3 pm) and three pyridone molecules (Gd^{3+}–O distances are 226.4–246.6 pm).

The 4-(1*H*)-pyridone molecules form the extended structure through π–π stacking interactions (Figure 3).[19,20] The shortest orthogonal distance between two aromatic fragments is 325.4 pm.

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Table 1. Crystallographic data for $Gd_2(ClF_2CCOO)_6(hypy)_2$ (**1**), $Gd_2(F_3CCOO)_6(hypy)_2$ (**2**), $Gd_2(F_2HCCOO)_6(hypy)_2$ (**3**) and $Gd_2(Cl_2HCCOO)_6(H_2O)_2(hypy)_2$ (**4**).

Compound	**1**	**2**	**3**	**4**
Crystal system	triclinic	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Lattice constants [pm,°]	a = 999.8(4) b = 1061.8(5) c = 1283.6(6) α = 91.23(5) β = 111.29(5) γ = 105.27(5)	a = 972.4(4) b = 1053.5(5) c = 1252.4(6) α = 94.23(5) β = 110.21(5) γ = 104.84(5)	a = 883.3(4) b = 1051.3(4) c = 1284.9(6) α = 100.46(5) β = 109.87(5) γ = 97.43(5)	a = 913.7(4) b = 1079.0(5) c = 1137.5(5) α = 93.41(5) β = 109.36(5) γ = 99.53(5)
V [pm^3]	$1214.4(9) \times 10^6$	$1145.1(9) \times 10^6$	$1079.7(8) \times 10^6$	$1035.4(8) \times 10^6$
Z	2	2	2	2
ρ (X-ray) [g·cm^3]	2.012	1.991	1.946	2.098
Absorption coefficient μ [mm^{-1}]	3.151	3.013	3.168	4.014
F(000)	706	658	610	626
Crystal dimensions [mm]	$0.333 \times 0.222 \times 0.222$	$0.407 \times 0.333 \times 0.2405$	$0.222 \times 0.992 \times 0.407$	$0.481 \times 0.666 \times 0.148$
Temperature [K]	293(2)			
Wavelength	Mo-K_α (λ = 71.073 pm)			
θ range [°]	$2.29 \le 2\theta \le 26.25$	$2.34 \le 2\theta \le 26.23$	$2.32 \le 2\theta \le 26.24$	$2.41 \le 2\theta \le 26.20$
Index range (h, k, l)	$-12 \le h \le 12$ $-13 \le k \le 13$ $-15 \le l \le 15$	$-11 \le h \le 11$ $-13 \le k \le 13$ $-15 \le l \le 15$	$-10 \le h \le 10$ $-12 \le k \le 12$ $-15 \le l \le 15$	$-11 \le h \le 11$ $-13 \le k \le 13$ $-14 \le l \le 14$
No. of collected reflections	17685	16568	15712	15064
No. of independent reflections	4519	4243	4007	3849
Observed reflections with $F > 2\sigma$	4139	3876	3527	3647
R_{int}	0.0697	0.0912	0.0858	0.0705
Structure refinement	Full-matrix, least-squares			
No. of refined parameters	325	327	298	252
Goodness-of-fit[a]	1.095	1.122	1.078	1.094
Residuals [$I > 2\sigma(I)$][a]	R_1 = 0.0446 wR_2 = 0.1187	R_1 = 0.0559 wR_2 = 0.1445	R_1 = 0.0506 wR_2 = 0.1329	R_1 = 0.0386 wR_2 = 0.1013
Residuals (all data)[a]	R_1 = 0.0482 wR_2 = 0.1241	R_1 = 0.0593 wR_2 = 0.1545	R_1 = 0.0568 wR_2 = 0.1384	R_1 = 0.0404 wR_2 = 0.1045
Largest differential hole and peak [e pm^{-3}]	-1.758×10^{-6}/ 1.431×10^{-6}	-0.551×10^{-6}/ 0.622×10^{-6}	-2.691×10^{-6}/ 1.319×10^{-6}	-2.012×10^{-6}/ 1.684×10^{-6}
CCDC deposition number[27]	604198	604200	604199	604197

[a] Definition given in the literature.[25]

Table 2. Selected interatomic distances [pm] for $Gd_2(ClF_2CCOO)_6(hypy)_2$ (**1**), $Gd_2(F_3CCOO)_6(hypy)_2$ (**2**), $Gd_2(F_2HCCOO)_6(hypy)_2$ (**3**) and $Gd_2(Cl_2HCCOO)_6(H_2O)_2(hypy)_2$ (**4**).

1		**2**		**3**		**4**	
Gd–Gd[a]	386.6(3)	Gd–Gd[a]	387.7(3)	Gd–Gd[a]	388.0(3)	Gd–Gd[b]	405.1(2)
Gd–O(1B)	226.4(4)	Gd–O(1A)	224.8(6)	Gd–O(1A)	228.1(5)	Gd–O(1A)	224.6(4)
Gd–O(1A)	235.7(4)	Gd–O(1B)	234.6(5)	Gd–O(1B)	233.7(5)	Gd–O11	230.4(4)
Gd–O32	240.2(5)	Gd–O31	240.3(5)	Gd–O31	241.1(6)	Gd–O31	237.8(3)
Gd–O31	241.7(5)	Gd–O32	240.8(6)	Gd–O32	242.8(6)	Gd–O22	239.0(4)
Gd–O(1A)[a]	246.6(4)	Gd–O(1B)[a]	247.3(5)	Gd–O22	247.1(7)	Gd–O(1W)	239.3(4)
Gd–O21	248.6(5)	Gd–O22	250.4(6)	Gd–O(1B)[a]	249.6(6)	Gd–O21	239.8(4)
Gd–O12	253.2(6)	Gd–O12	253.4(6)	Gd–O11	257.8(7)	Gd–O32	250.3(4)
Gd–O11	267.4(6)	Gd–O21	266.3(7)	Gd–O12	259.2(8)	Gd–O31[b]	263.8(4)
Gd–O22	268.3(6)	Gd–O11	267.2(7)	Gd–O21	268.0(7)		

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

$Gd_2(F_3CCOO)_6(hypy)_2$ (2) and $Gd_2(F_2HCCOO)_6(hypy)_2$ (3)

The crystal structures of **2** (Figure 4) and **3** (Figure 5) comprise dimers [shown in Figure 6 (**2**) and Figure 7 (**3**); Gd^{3+}–Gd^{3+} distance is 387.7 pm for **2** and 388.0 pm for **3**]. The structural characteristics are as described for **1**. The Gd^{3+}–carboxylate O distances for **2** are 240.3–267.2 pm and 241.1–268.0 pm for **3**. The Gd^{3+}–pyridone O distances for **2** are 224.8–247.3 pm and 228.1–249.6 pm for **3**.

The extended structures are also formed by the 4-(1*H*)-pyridone molecules through π–π stacking interactions as in **1**.[19,20] The shortest orthogonal distances between the two aromatic fragments are 331.1 (**2**) and 325.6 pm (**3**).

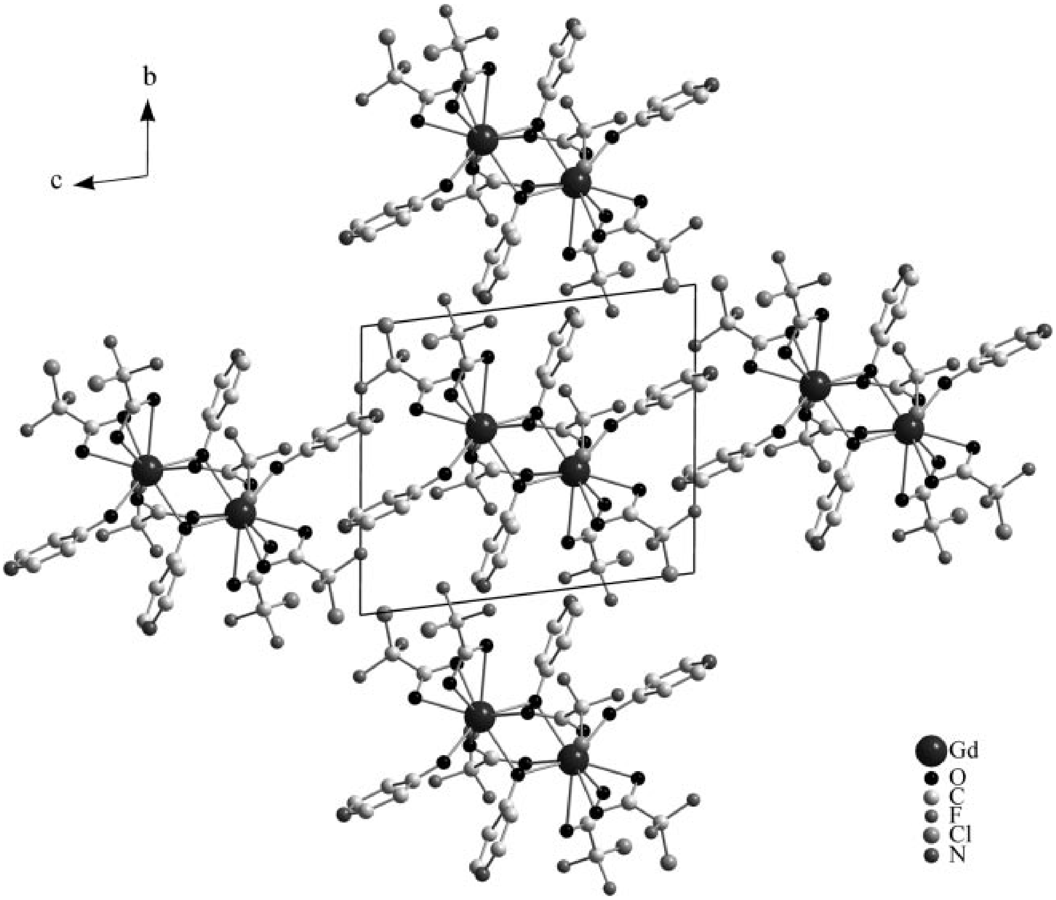

Figure 1. Crystal structure of $Gd_2(ClF_2CCOO)_6(hypy)_2$ (**1**). The triclinic unit cell is given; H atoms are not displayed.

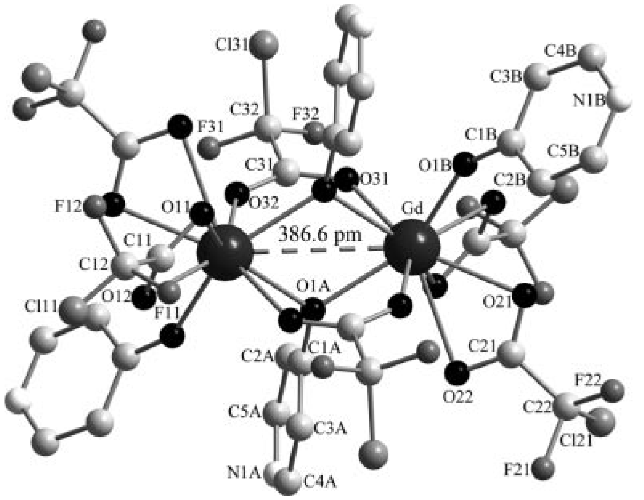

Figure 2. Dimeric unit in $Gd_2(ClF_2CCOO)_6(hypy)_2$ (**1**). The dashed line shows the Gd^{3+}–Gd^{3+} distance; H atoms are not displayed.

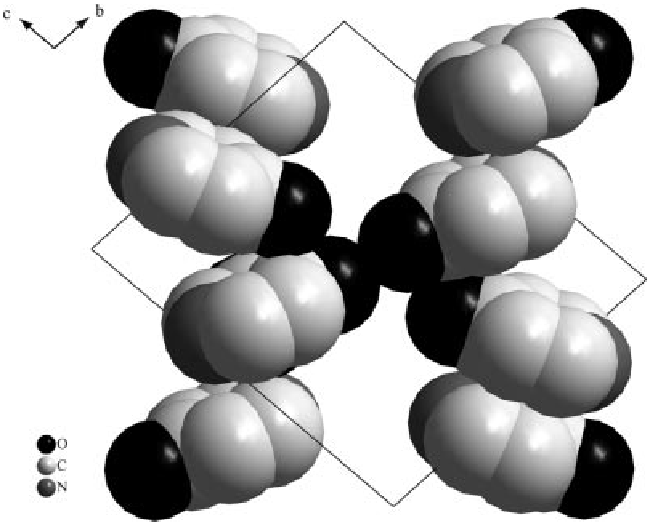

Figure 3. π–π stacking of the 4-(1*H*)-pyridone molecules in $Gd_2(ClF_2CCOO)_6(hypy)_2$ (**1**). The unit cell is given; H atoms are not displayed.

$Gd_2(Cl_2HCCOO)_6(H_2O)_2(hypy)_2$ (4)

The crystal structure of **4** is shown in Figure 8. The structure comprises discrete dimers (Gd^{3+}–Gd^{3+} distance is 405.1 pm) with two kinds of bridging carboxylate groups (μ_2-carboxylato-κ^1O:κ^1O' and μ_2-O';κ^2O,O') along with a chelating dichloroacetate ion, a water and a 4-(1*H*)-pyridone molecule (Figure 9). The Gd^{3+} ion is eightfold coordinated by oxygen atoms originating from five carboxylate

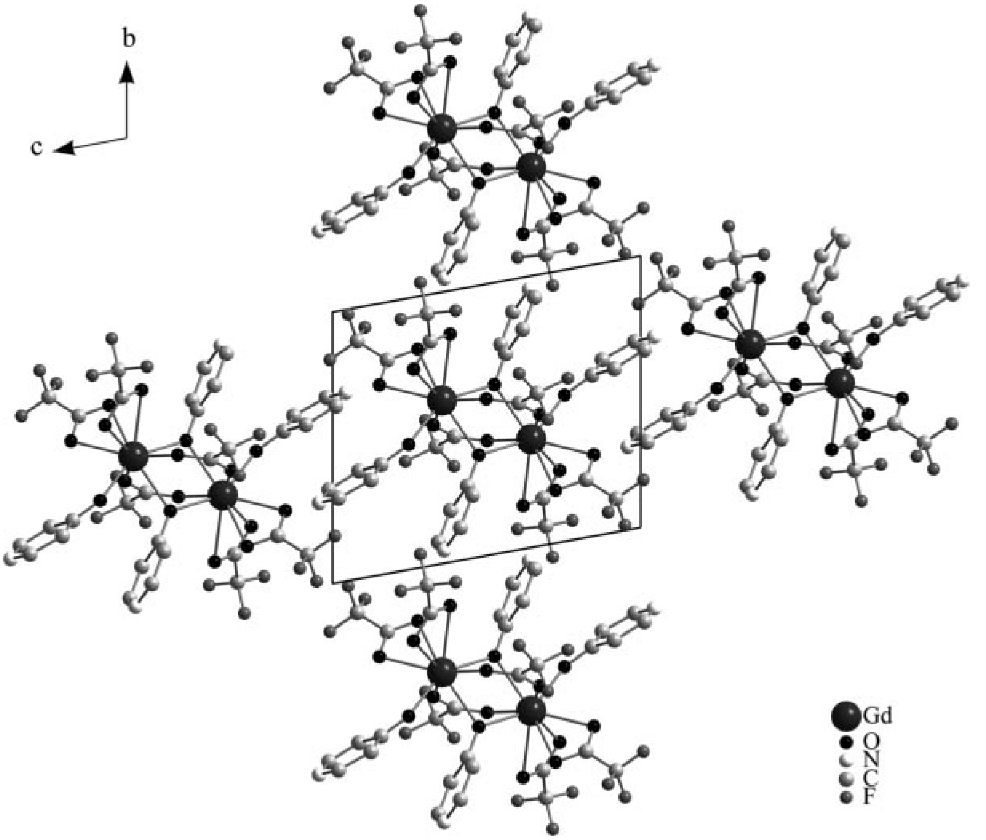

Figure 4. Crystal structure of $Gd_2(F_3CCOO)_6(hypy)_2$ (**2**). The triclinic unit cell is given; H atoms are not displayed.

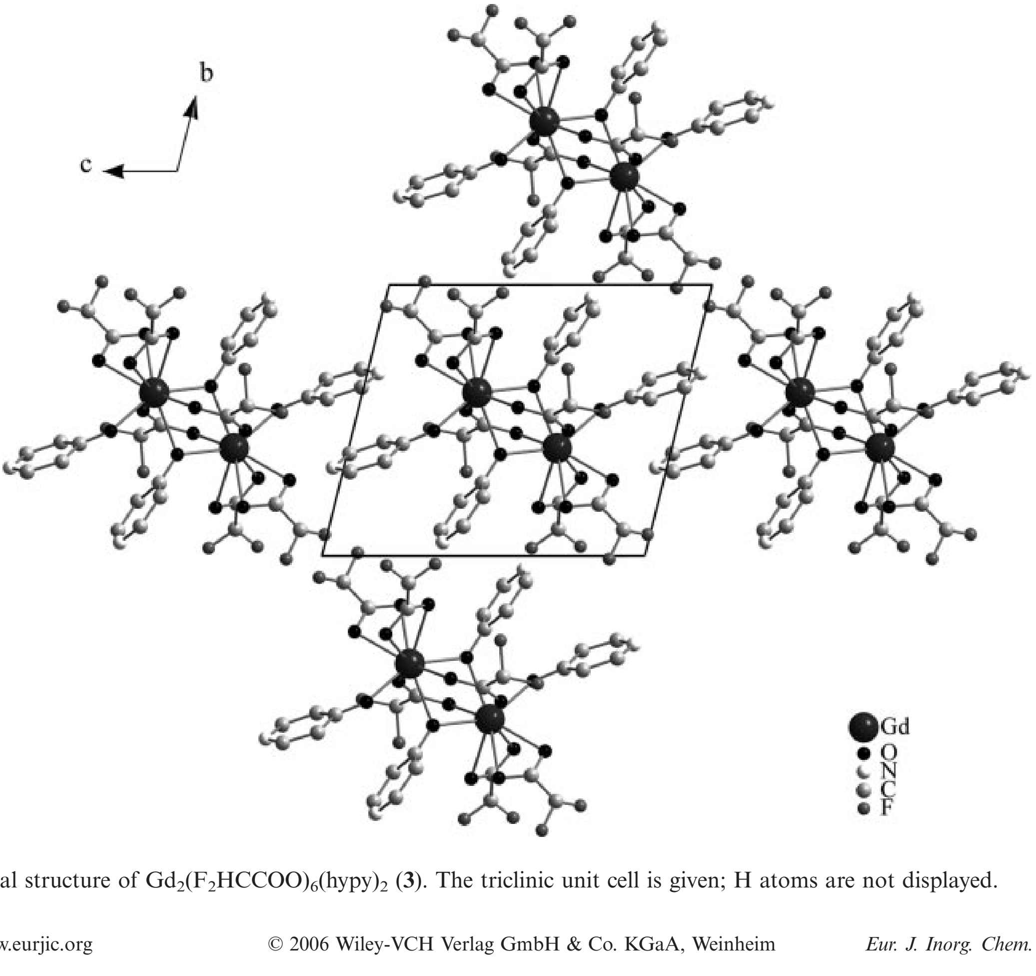

Figure 5. Crystal structure of $Gd_2(F_2HCCOO)_6(hypy)_2$ (**3**). The triclinic unit cell is given; H atoms are not displayed.

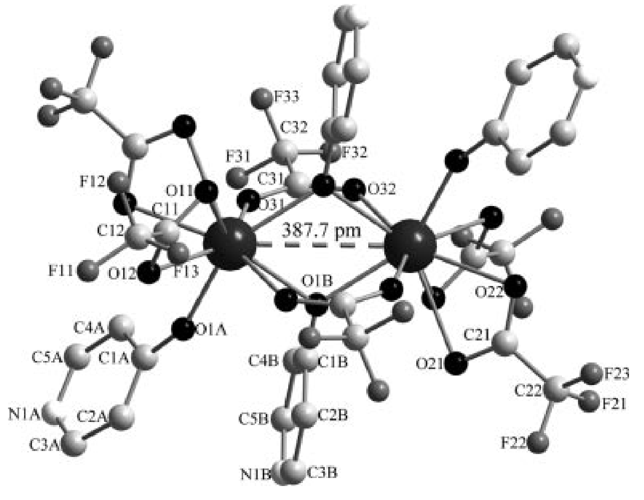

Figure 6. Dimeric unit in $Gd_2(F_3CCOO)_6(hypy)_2$ (**2**). The dashed line shows the Gd^{3+}–Gd^{3+} distance; H atoms are not displayed.

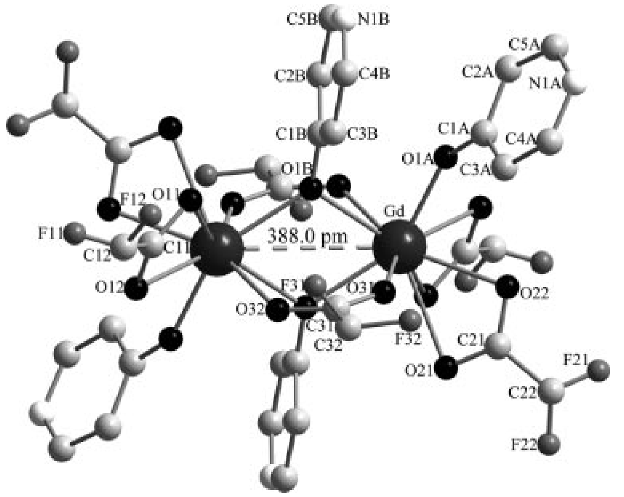

Figure 7. Dimeric unit in $Gd_2(F_2HCCOO)_6(hypy)_2$ (**3**). The dashed line shows the Gd^{3+}–Gd^{3+} distance; H atoms are not displayed.

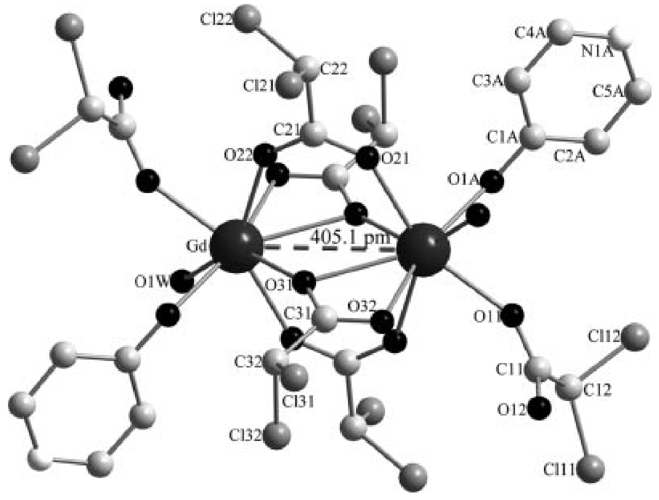

Figure 9. Dimeric unit in $Gd_2(Cl_2HCCOO)_6(H_2O)_2(hypy)_2$ (**4**). The dashed line shows the Gd^{3+}–Gd^{3+} distance; H atoms are not displayed.

groups, one water and one pyridone molecule (Gd^{3+}–O distances are 224.6–263.8 pm).

Former results have shown that the μ_2-O';κ^2O,O' mode is responsible for a ferromagnetic interaction, whereas the μ_2-carboxylato-κ^1O:κ^1O' bridging mode leads to an antiferromagnetic interaction.[21,10–16] The obtained crystal structures of the compounds **1-3** are of interest for magnetic investigations in order to study the influence of the bridging pyridone oxygen atom and of the μ_2-carboxylato-κ^1O:κ^1O' bridging mode of the carboxylate group. Compound **4** is interesting for magnetic investigations in order to study the influence of the coexistence of the μ_2-O';κ^2O,O'- and the μ_2-carboxylato-κ^1O:κ^1O' bridging modes.

Magnetic Behaviour

The presentation of the magnetic data follows the recommendation of Hatscher et al.[22] Figures 10, 11, 12 and 13

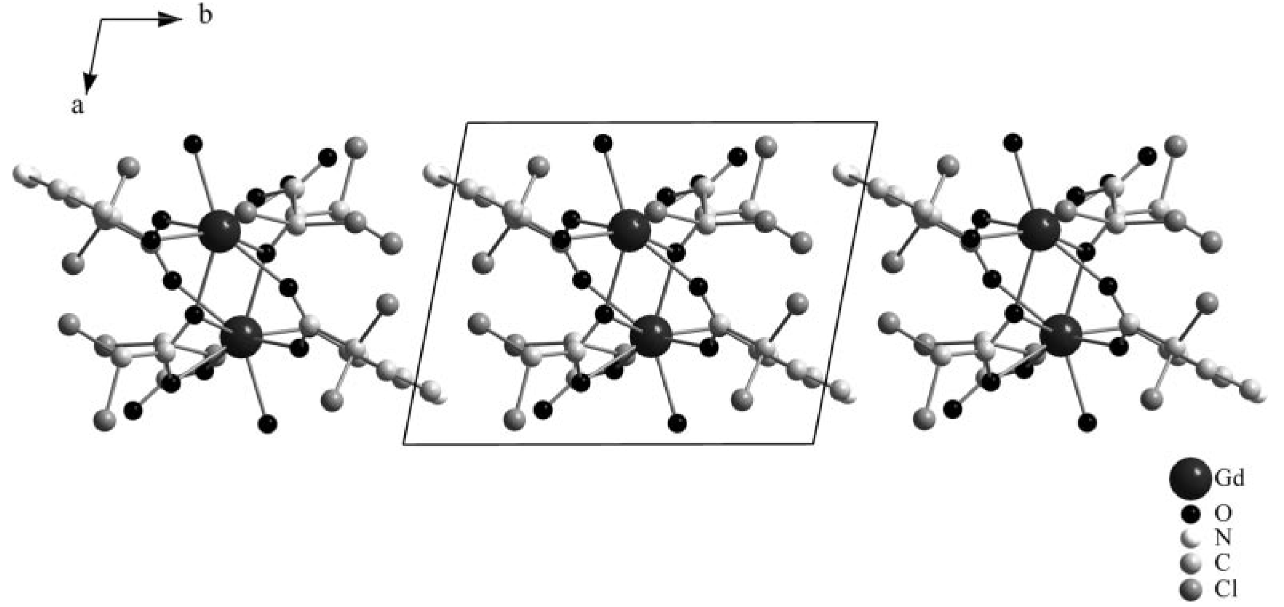

Figure 8. Crystal structure of $Gd_2(Cl_2HCCOO)_6(H_2O)_2(hypy)_2$ (**4**). The triclinic unit cell is given; H atoms are not displayed.

display the measured effective Bohr magneton numbers (μ_{eff}) of **1**–**4** in the temperature range 1.76–300 K ($H^{(\mathrm{ir})}$ = 500 and 1000 Oe). The curve progression shows antiferromagnetic behaviour in each case. The measured magnetic susceptibility ($\chi_{\mathrm{m}}{}^{(\mathrm{ir})}$) 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 $\hat{H}_{\mathrm{ex}} = -2J_{\mathrm{ex}}\hat{\boldsymbol{S}}_{\mathrm{Gd1}}\cdot\hat{\boldsymbol{S}}_{\mathrm{Gd2}}$ ($S_{\mathrm{Gd1}} = S_{\mathrm{Gd2}}$ = 7/2):[18]

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

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

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 excoohange parameter.

The fitting procedure leads to J_{ex} = –0.019 cm^{-1} (**1**), J_{ex} = –0.034 cm^{-1} (**2**), J_{ex} = –0.064 cm^{-1} (**3**) and J_{ex} = –0.011 cm^{-1} (**4**), with g = 2.00. The agreement between the measured and calculated μ_{eff} values [μ_{eff} = 2.8279-$(T\chi_{\mathrm{m}}{}^{(\mathrm{ir})})^{1/2}$] are shown in Figures 10–13.

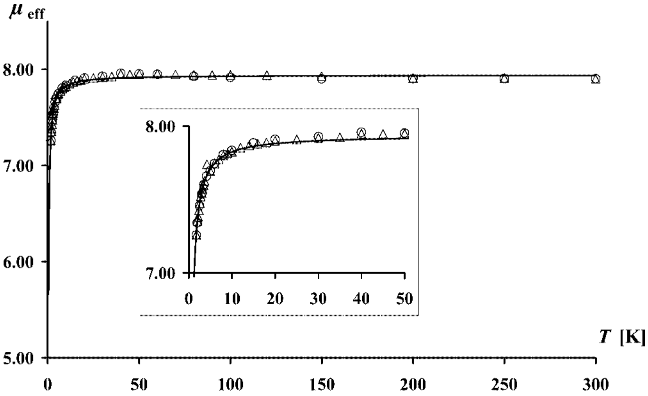

Figure 10. Comparison of measured (Δ, $H^{(\mathrm{ir})}$ = 0.5 kOe; ○, $H^{(\mathrm{ir})}$ = 1.0 kOe) and calculated (–) effective Bohr magneton numbers for $\mathrm{Gd_2(ClF_2CCOO)_6(hypy)_2}$ (**1**).

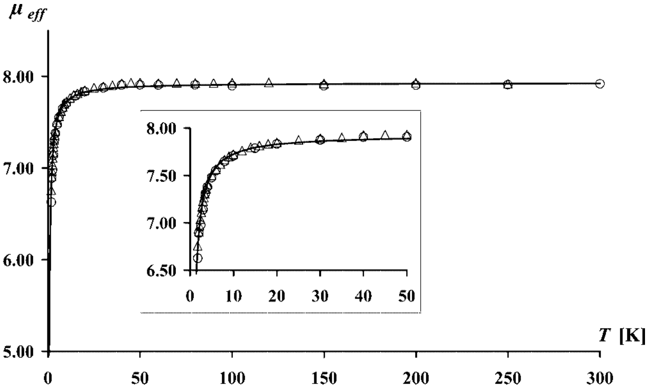

Figure 11. Comparison of measured (Δ, $H^{(\mathrm{ir})}$ = 0.5 kOe; ○, $H^{(\mathrm{ir})}$ = 1.0 kOe) and calculated (–) effective Bohr magneton numbers for $\mathrm{Gd_2(F_3CCOO)_6(hypy)_2}$ (**2**).

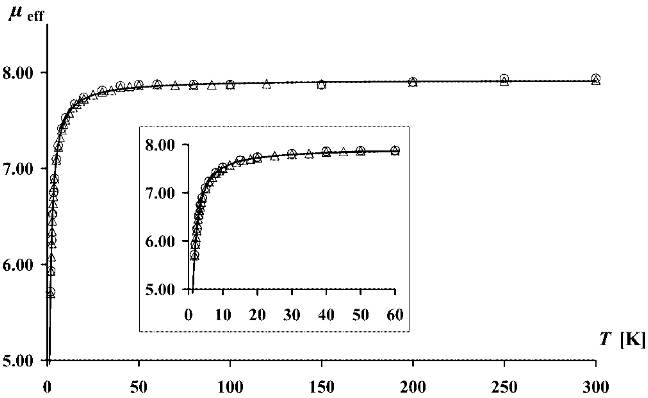

Figure 12. Comparison of measured (Δ, $H^{(\mathrm{ir})}$ = 0.5 kOe; ○, $H^{(\mathrm{ir})}$ = 1.0 kOe) and calculated (–) effective Bohr magneton numbers for $\mathrm{Gd_2(F_2HCCOO)_6(hypy)_2}$ (**3**).

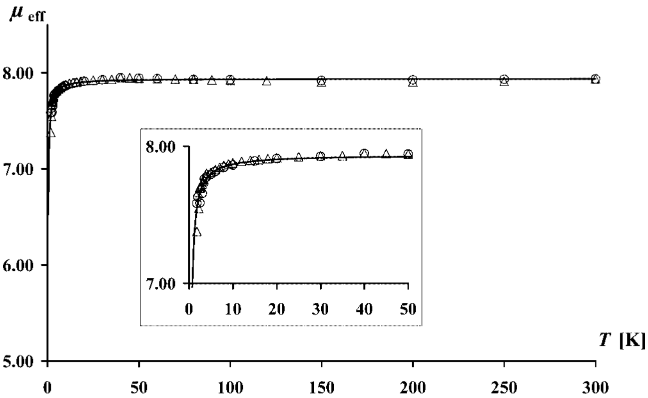

Figure 13. Comparison of measured (Δ, $H^{(\mathrm{ir})}$ = 0.5 kOe; ○, $H^{(\mathrm{ir})}$ = 1.0 kOe) and calculated (–) effective Bohr magneton numbers for $\mathrm{Gd_2(Cl_2HCCOO)_6(H_2O)_2(hypy)_2}$ (**4**).

The values of J_{ex} for the title compounds are comparable with those of other carboxylates containing Gd^{3+}. The coexistence of the μ$_2$-pyridone-1:2κ^2*O*- or μ$_2$-*O′*;κ^2*O*,*O′* bridging mode and the μ$_2$-carboxylato-κ^1*O*:κ^1*O′* bridging mode in **1**–**4** leads to a negative exchange parameter (Table 3). Thus, only in the case where the carboxylate group exclusively bridges the Gd^{3+} ions in a μ$_2$-*O′*;κ^2*O*,*O′* bridging mode is a ferromagnetic interaction observed.

Experimental Section

Transparent, colourless, air stable single crystals of **1**–**4** have been obtained by reaction of the corresponding gadolinium carboxylate with 4-hydroxypyridine (Fluka, ≥95.0%) [molar ratio 2:1 for **1**, **2** and **4**; 1:2 for **3**] in a solution of ethanol (Sigma–Aldrich, 99.8%) and water (1:1). The starting compounds $\mathrm{Gd(ClF_2CCOO)_3(H_2O)_3}$, $\mathrm{Gd(CF_3COO)_3(H_2O)_3}$, $\mathrm{Gd(HF_2CCOO)_3(H_2O)_2{\cdot}H_2O}$ and $\mathrm{Gd_3(H_2ClCCOO)_9(H_2O)_5}$ were prepared as given in the literature.[11,16,21,23]

Well-grown single crystals were mounted on a STOE imaging plate diffractometer. The data collection was carried out at room temperature. The structures were solved by Patterson methods and

Table 3. Comparison of J_{ex} [cm^{-1}], bridging mode and Gd^{3+}–Gd^{3+} distance [pm] for $Gd_2(ClF_2CCOO)_6(hypy)_2$ (**1**), $Gd_2(F_3CCOO)_6(hypy)_2$ (**2**), $Gd_2(F_2HCCOO)_6(hypy)_2$ (**3**), $Gd_2(Cl_2HCCOO)_6(H_2O)_2(hypy)_2$ (**4**), $Gd_2(ClH_2CCOO)_6(bipy)_2$ (**A**), $Gd(CF_2HCOO)_3(phen)$ (**B**), $Gd(F_2HCCOO)_3(H_2O)_2{\cdot}H_2O$ (**C**), $[NH_3CH_3][Gd(Cl_2HCCOO)_4]$ (**D**), $[NH_3C_2H_5][Gd(Cl_2HCCOO)_4]$ (**E**) and $Gd(H_3CCOO)_3(H_2O)_2{\cdot}2H_2O$ (**F**).

Compound	J_{ex}	Bridging mode	Gd^{3+}–Gd^{3+} Distance	Reference
3	–0.064	μ_2-pyridone-1:2κ^2O and μ_2-carboxylato-κ^1O:κ^1O'	388.0	this work
2	–0.034	μ_2-pyridone-1:2κ^2O and μ_2-carboxylato-κ^1O:κ^1O'	387.7	this work
A	–0.020	μ_2-O';κ^2O,O' and μ_2-carboxylato-κ^1O:κ^1O'	399.0	[15]
1	–0.019	μ_2-pyridone-1:2κ^2O and μ_2-carboxylato-κ^1O:κ^1O'	386.6	this work
B	–0.016	μ_2-O';κ^2O,O' and μ_2-carboxylato-κ^1O:κ^1O'	403.4	[14]
4	–0.011	μ_2-O';κ^2O,O' and μ_2-carboxylato-κ^1O:κ^1O'	405.1	this work
C	–0.012	μ_2-carboxylato-κ^1O:κ^1O'	445.6	[21]
D	–0.007	μ_2-carboxylato-κ^1O:κ^1O'	451.6	[12]
E	0.029	μ_2-O';κ^2O,O'	418.1	[13]
F	0.025	μ_2-O';κ^2O,O'	420.6	[10]
D	0.023	μ_2-O';κ^2O,O'	418.4	[12]

were refined with anisotropic displacement parameters based on F^2 by using the SHELXS-97[24] and SHELXL-97[25] programs. Each data analysis indicated the $P\bar{1}$ space group. The final refinement yielded R_1 (all data) = 4.82% (**1**), R_1 (all data) = 5.93% (**2**), R_1 (all data) = 5.68% (**3**) and R_1 (all data) = 4.04% (**4**). Hydrogen atoms were always included by using a riding model. The crystal data and details of the refinements are summarised in Table 1. Selected bond lengths can be found in Table 2.

Elemental analysis (Vario EL, Elementar Analysesysteme GmbH, Hanau, Germany) for **1** $C_{16}H_{10}Cl_3F_6GdN_2O_8$ (735.86): calcd. C 26.12, H 1.37, N 3.81; found C 26.03, H 1.41, N 3.78. For **2** $C_{16}H_{10}F_9GdN_2O_8$ (686.50): calcd. C 27.99, H 1.47, N 4.08; found C 28.01, H 1.49, N 4.00. For **3** $C_{16}H_{13}F_6GdN_2O_8$ (632.53): calcd. C 30.38, H 2.07, N 4.43; found C 30.36, H 2.10, N 4.41. For **4** $C_{11}H_{10}Cl_6GdNO_8$ (654.17): calcd. C 20.20, H 1.54, N 2.14; found C 20.26, H 1.59, N 2.14.

Pulverised single crystals of the title compounds were measured with a SQUID magnetometer (MPMS5, Quantum Design) over the temperature range 1.76–300 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 gelatine capsule. To avoid orientation effects during the measurement, another gelatine capsule was pressed on the sample to fix it. Subsequently, the container was sewn in a plastic straw. The raw magnetic data were corrected for diamagnetism of the sample carrier and the sample by using the increments of Haberditzl.[26]

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[27] CCDC 604198 (**1**), -604200 (**2**), -604199 (**3**) and -604197 (**4**) contain 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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