

Synthesis, Crystal Structure and Magnetic Behaviour of Dimeric and Polymeric Gadolinium Trifluoroacetate Complexes

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Dedicated to Professor Wolfgang Jeitschko on the occasion of his 70th birthday

The gadolinium(III) trifluoroacetates $((\text{CH}_3)_2\text{NH}_2)[\text{Gd}(\text{CF}_3\text{COO})_4]$ (**1**), $((\text{CH}_3)_3\text{NH})[\text{Gd}(\text{CF}_3\text{COO})_4(\text{H}_2\text{O})]$ (**2**), $\text{Gd}(\text{CF}_3\text{COO})_3(\text{H}_2\text{O})_3$ (**3**) as well as $\text{Gd}_2(\text{CF}_3\text{COO})_6(\text{H}_2\text{O})_2(\text{phen})_3 \cdot \text{C}_2\text{H}_5\text{OH}$ (**4**) (phen = 1,10-phenanthroline) were synthesized and structurally characterized by X-ray crystallography. These compounds crystallize in the space group $P\bar{1}$ (No. 2, $Z = 2$) (**1**, **2** and **4**) and $P2_1/c$ (No. 14, $Z = 4$) (**3**), respectively, with the following lattice constants **1**: $a = 884.9(2)$, $b = 1024.9(2)$, $c = 1173.1(2)$ pm, $\alpha = 105.77(2)$, $\beta = 99.51(2)$, $\gamma = 107.93(2)^\circ$; **2**: $a = 965.1(1)$, $b = 1028.6(1)$, $c = 1271.3(2)$ pm, $\alpha = 111.83(2)$, $\beta = 111.33(2)$, $\gamma = 90.44(2)^\circ$; **3**: $a = 919.6(2)$, $b = 1890.6(4)$, $c = 978.7(2)$ pm, $\beta = 113.94(2)^\circ$; **4**: $a = 1286.7(8)$, $b = 1639.3(8)$, $c = 1712.2(9)$ pm, $\alpha = 62.57(6)$, $\beta = 84.13(5)$, $\gamma = 68.28(5)^\circ$. The compounds consist of Gd^{3+} ions which are bridged by carboxylate groups either to chains (**1** and **2**) or to dimers (**3** and **4**). In addition to the Gd^{3+} dimers, compound (**4**) also contains monomeric Gd^{3+} units. The magnetic behaviour of **2** and **3** was investigated in a temperature range of 1.77 to 300 K. The magnetic data for these compounds indicate weak antiferromagnetic interactions.

Key words: Trifluoroacetates, Gadolinium Carboxylates, Synthesis, Crystal Structure, Magnetic Behaviour

Introduction

In the last decade the interest in the magnetic properties of polynuclear lanthanide compounds has increased [1–13]. For the magnetic investigation compounds containing Gd^{3+} ions often were used, as in this case ligand field interactions can be neglected in the calculation of magnetic susceptibilities [14]. To design such compounds different ligands were used as linkers between the Gd^{3+} ions. Here the carboxylate group was of special interest because of its different linking types to the cation [15]. Most of these compounds show antiferromagnetic interactions [16–27], but for $\text{Gd}(\text{sal})_3(\text{H}_2\text{O})$ ($\text{H}_2\text{sal} = \text{salicylic acid}$) [28], $\text{Gd}_2(\mu_2\text{-OOCFc})_2(\text{OOCFc})_4(\text{MeOH})_2(\text{H}_2\text{O}) \cdot 2\text{MeOH} \cdot 2\text{H}_2\text{O}$ ($\text{Fc} = (\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)$) [29], $\text{Gd}(\text{H}_2\text{sal})(\text{Hsal})(\text{sal}) \cdot \text{H}_2\text{O}$ [30], $\text{Gd}(\text{CH}_3\text{COO})_3(\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}$ [31], $\text{Gd}_2(\text{mal})_3(\text{H}_2\text{O})_6$ ($\text{H}_2\text{mal} = \text{malonic acid}$) [32], and $\text{Gd}_2(\text{H}_2\text{O})_2(\text{DPA})_3$ ($\text{H}_2\text{DPA} = 2,2'$ -diphenic acid) [33] ferromagnetic interactions were found. Recently we reported on intramolecular ferromagnetic interactions within a dimeric unit on

which intermolecular antiferromagnetic interactions are imposed [34,35]. In our research we modify the structural properties of Gd^{3+} compounds containing halogenoacetates in order to get different bridging types and as a consequence of this to get different magnetic interactions between the Gd^{3+} ions [23,25–27,31,34,35]. Up to now only few Gd^{3+} halogenoacetates are structurally known and not all of them were magnetically investigated [36–39].

In this work we describe the crystal structures of four different Gd^{3+} trifluoroacetates. We have synthesized and characterized the compounds $((\text{CH}_3)_2\text{NH}_2)[\text{Gd}(\text{CF}_3\text{COO})_4]$ (**1**), $((\text{CH}_3)_3\text{NH})[\text{Gd}(\text{CF}_3\text{COO})_4(\text{H}_2\text{O})]$ (**2**) and $\text{Gd}_2(\text{CF}_3\text{COO})_6(\text{H}_2\text{O})_2(\text{phen})_3 \cdot \text{C}_2\text{H}_5\text{OH}$ (**4**) and compare their structural properties with those of the “pure” trifluoroacetate $\text{Gd}(\text{CF}_3\text{COO})_3(\text{H}_2\text{O})_3$ (**3**). The crystal structure of **3** was solved by Jingjun *et al.* in 1988 [37] and the results could be confirmed. We also investigated the magnetic behaviour of **2** and **3** in the temperature range of 1.77 to 300 K.

Compound	1	2	3	4
Formula	C ₁₀ H ₈ F ₁₂ GdNO ₈	C ₁₁ H ₁₂ F ₁₂ GdNO ₉	C ₆ H ₆ F ₉ GdO ₉	C ₅₀ H ₃₄ F ₁₈ Gd ₂ N ₆ O ₁₅
MW [g·mol ⁻¹]	655.41	687.45	550.34	1611.29
Crystal colour			colourless	
Crystal size [mm ³]	0.15 · 0.16 · 0.53	0.15 · 0.22 · 0.26	0.26 · 0.33 · 0.67	0.37 · 0.33 · 0.38
Crystal system	triclinic	triclinic	monoclinic	triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$
<i>a</i> [pm]	884.9(2)	965.1(1)	919.6(2)	1286.7(8)
<i>b</i> [pm]	1024.9(2)	1028.6(1)	1890.6(4)	1639.3(8)
<i>c</i> [pm]	1173.1(2)	1271.3(2)	978.7(2)	1712.2(9)
α [°]	105.77(2)	111.83(2)	90	62.57(6)
β [°]	99.51(2)	111.33(2)	113.94(2)	84.13(5)
γ [°]	107.93(2)	90.44(2)	90	68.28(5)
<i>V</i> [10 ⁶ pm ³]	937.4(3)	1076.3(2)	1555.2(5)	2967.8(3)
<i>T</i> [K]			293	
<i>Z</i>	2	2	4	2
<i>D</i> _{calc.} [g·cm ⁻³]	2.322	2.121	2.351	1.803
<i>F</i> (000)	622	658	1036	1564
θ -Range [°]	2.37–28.22	2.16–26.09	2.15–25.96	3.07–31.94
<i>hkl</i> -Ranges	–11 ≤ <i>h</i> ≤ 11 –13 ≤ <i>k</i> ≤ 13 –15 ≤ <i>l</i> ≤ 15	–11 ≤ <i>h</i> ≤ 11 –12 ≤ <i>k</i> ≤ 12 –15 ≤ <i>l</i> ≤ 15	–10 ≤ <i>h</i> ≤ 10 –23 ≤ <i>k</i> ≤ 23 –12 ≤ <i>l</i> ≤ 12	–17 ≤ <i>h</i> ≤ 15 –20 ≤ <i>k</i> ≤ 20 –17 ≤ <i>l</i> ≤ 22
Absorption correction	–	–	numerical	–
μ (Mo-K α) [mm ⁻¹]	3.695	3.227	4.406	2.340
Max./min. transm.	–	–	0.1258 / 0.1915	–
Measured refl.	16348	15413	21911	23683
Independent refl.	4195	3971	2909	12947
Refl. with <i>I</i> > 2 σ (<i>I</i>)	3781	3562	2631	10251
<i>R</i> _{int}	0.0406	0.0659	0.0382	0.0332
Program used	SHELXS-97 [43], SHELXL-97 [44], X-Shape [47] and X-Red [48]			
Refinement method	full-matrix least-squares on <i>F</i> ²			
Refined parameter	291	318	251	826
Residuals	<i>R</i> ₁ = 0.0367 with <i>I</i> > 2 σ (<i>I</i>) ^a <i>wR</i> ₂ = 0.0986	<i>R</i> ₁ = 0.0399 <i>wR</i> ₂ = 0.1036	<i>R</i> ₁ = 0.0307 <i>wR</i> ₂ = 0.0802	<i>R</i> ₁ = 0.0487 <i>wR</i> ₂ = 0.1462
Residuals (all data) ^a	<i>R</i> ₁ = 0.0415 <i>wR</i> ₂ = 0.1076	<i>R</i> ₁ = 0.0463 <i>wR</i> ₂ = 0.1127	<i>R</i> ₁ = 0.0339 <i>wR</i> ₂ = 0.0821	<i>R</i> ₁ = 0.0649 <i>wR</i> ₂ = 0.1851
GooF ^a	1.060	1.083	1.038	1.119
Min./max. res. [10 ⁻⁶ e·pm ⁻³]	–1.038/1.821	–1.164/1.543	–0.759/1.052	–2.040/3.520
CCDC number [49]	285300	285301	280700	295465

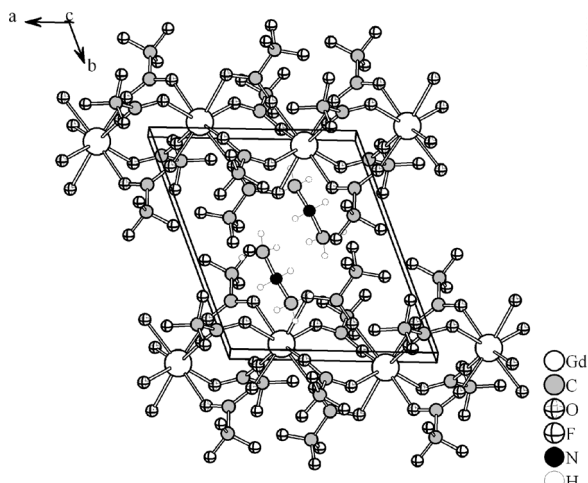
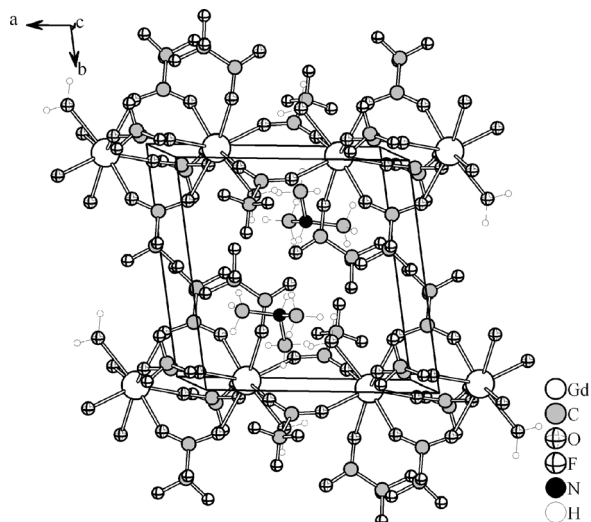
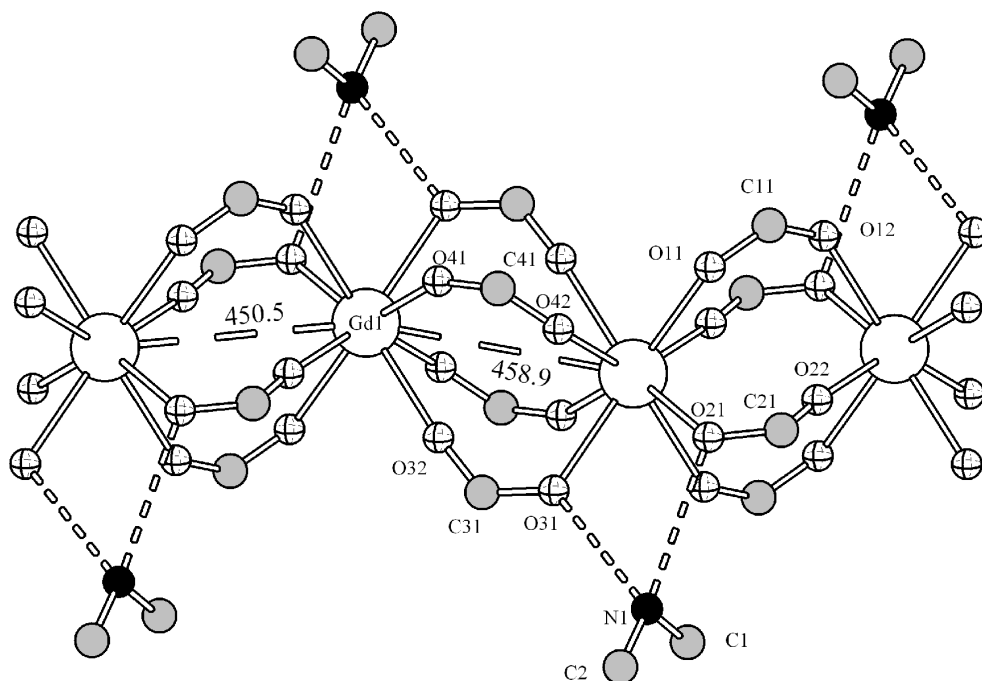
Table 1. Crystallographic data and details for the structure determination of ((CH₃)₂NH₂)-[Gd(CF₃COO)₄] (**1**), ((CH₃)₃NH)[Gd(CF₃COO)₄(H₂O)] (**2**), Gd(CF₃COO)₃(H₂O)₃ (**3**) and Gd₂(CF₃COO)₆(H₂O)₂(phen)₃ · C₂H₅OH (**4**).

^a Definition given in [44].

1		2		3		4	
Gd	–O11 240.1(4)	Gd	–O11 235.7(5)	Gd	–O11 235.1(4)	Gd1	–O11 236.3(4)
	–O12 241.4(4)		–O12 234.4(5)		–O12 ^c 237.6(3)		–O12 242.2(4)
	–O21 248.3(4)		–O21 232.6(4)		–O21 246.4(4)		–O21 239.1(4)
	–O22 236.7(4)		–O22 241.5(5)		–O22 235.2(4)		–O22 238.7(4)
	–O31 246.8(4)		–O31 238.0(5)		–O31 237.6(4)		–O31 234.7(4)
	–O32 236.8(4)		–O32 238.9(4)		–O1W 242.3(4)		–N1A 255.9(5)
	–O41 237.1(4)		–O41 242.8(4)		–O2W 244.0(4)		–N2A 254.4(5)
	–O42 239.0(4)		–O1W 246.8(5)		–O3W 239.6(4)		–O1W 236.7(4)
	–Gd ^a 450.5(2)		–Gd ^a 456.0(5)		–Gd ^d 447.7(9)		–Gd1 ^e 460.0(2)
	–Gd ^b 458.9(2)		–Gd ^b 510.5(5)				
N1	–O21 307.5(3)	N1	–O42 273.6(4)			Gd2	–O41 242.5(4)
	–O31 297.9(4)						–O51 243.7(4)
							–O52 258.4(4)
							–O61 232.8(4)
							–N1B 261.0(5)
							–N2B 259.2(5)
							–N1C 256.2(5)
							–N2C 252.0(5)
							–O2W 239.0(4)

Table 2. Selected interatomic distances *d* /pm for ((CH₃)₂NH₂)-[Gd(CF₃COO)₄] (**1**), ((CH₃)₃NH)[Gd(CF₃COO)₄(H₂O)] (**2**), Gd(CF₃COO)₃(H₂O)₃ (**3**) and Gd₂(CF₃COO)₆(H₂O)₂(phen)₃ · C₂H₅OH (**4**).

^a –*x* + 1, –*y*, –*z* + 1; ^b –*x*, –*y*, –*z* + 1; ^c –*x* + 1, –*y* + 1, –*z* + 2; ^d –*x*, –*y*, –*z*; ^e –*x* + 1, –*y* + 1, –*z* + 1.

Fig. 1. Crystal structure of **1**. The unit cell is shown.Fig. 3. Crystal structure of **2**. The unit cell is shown.Fig. 2. Polymeric chains of **1**; only Gd atoms, carboxylate groups and dimethylammonium cations are displayed. Hydrogen bonds are shown by dotted lines.

Results and Discussion

Crystal structures

Crystal data and details of the refinements for **1**, **2**, **3** and **4** are summarized in Table 1, selected bond distances can be found in Table 2.

$((\text{CH}_3)_2\text{NH}_2)[\text{Gd}(\text{CF}_3\text{COO})_4]$ (**1**) crystallizes in the triclinic space group $P\bar{1}$ (No. 2, $Z = 2$). The crystal structure is shown in Fig. 1. The Gd^{3+} ion is surrounded by eight oxygen atoms originating from eight carboxylate groups with Gd–O distances between 236.7(4) and 248.3(4) pm. The characteristic structural units are polymeric ${}^1_2[\text{Gd}(\text{CF}_3\text{COO})_4]$ chains, running

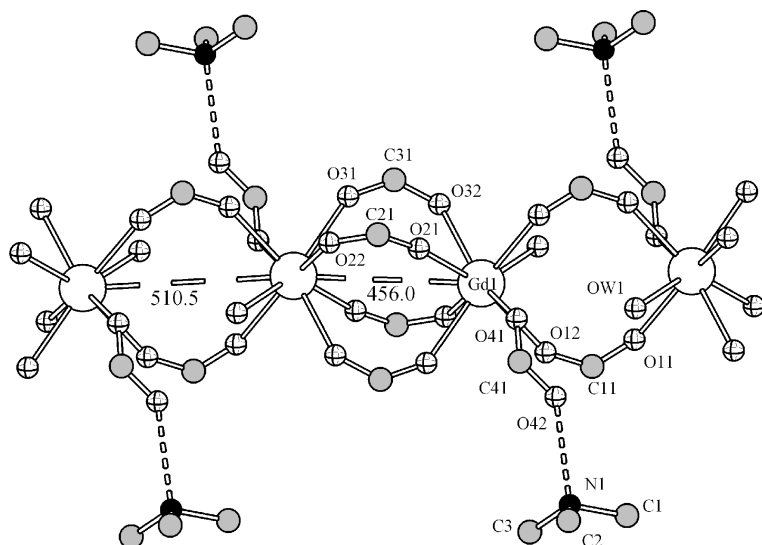


Fig. 4. Polymeric chains of **2**; only Gd atoms, carboxylate groups and dimethylammonium cations are displayed. Hydrogen bonds are shown by dotted lines.

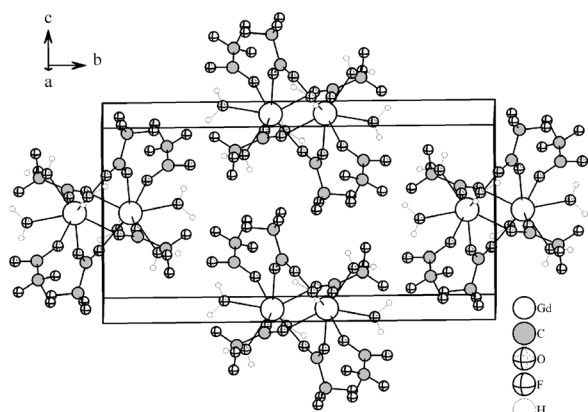


Fig. 5. Crystal structure of **3**. The unit cell is shown.

along [100] (*cf.* Fig. 1 and 2) with bidentate bridging carboxylate groups (μ_2 -carboxylato- $\kappa^1O : \kappa^1O'$). For each Gd-Gd bridge four carboxylate groups are required. Because of the similar bridging between the Gd^{3+} ions there are two comparable Gd-Gd distances (450.5(2) and 458.9(2) pm). The dimethylammonium cation is bonded *via* hydrogen bonds to two oxygen atoms of carboxylate groups. The O-N distances are 297.9(4) and 307.5(3) pm.

The crystal structure of $((CH_3)_3NH)[Gd(CF_3COO)_4(H_2O)]$ (**2**) is shown in Fig. 3. **2** crystallizes in the triclinic space group $P\bar{1}$ (No. 2, $Z = 2$). The Gd^{3+} ions are coordinated eightfold by seven carboxylate O atoms (Gd-O distances between 232.6(4) and 242.8(4) pm) and one water molecule (Gd-O distance 246.8(5) pm). The Gd^{3+} cations are bridged al-

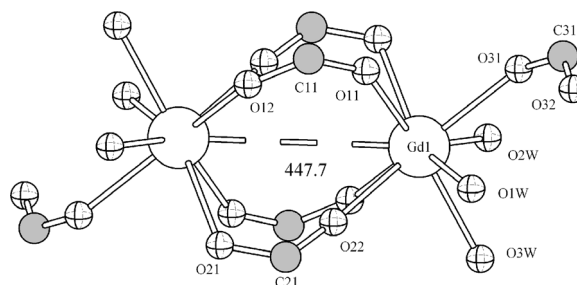


Fig. 6. Dimeric unit of **3**.

ternately by two and by four carboxylate groups in a bidentate fashion (μ_2 -carboxylato- $\kappa^1O : \kappa^1O'$) to chains (*cf.* Fig. 4). One carboxylate group is coordinated monodentately. As there are two rather different Gd-Gd distances (456.0(5) and 510.5(5) pm) the characteristic unit can be described as a chain of dimers. The trimethylammonium cation is bonded *via* a hydrogen bond to the non-coordinated oxygen atom of the monodentate carboxylate group (O-N distance 273.6(4) pm).

The crystal structure of $Gd(CF_3COO)_3(H_2O)_3$ (**3**) is shown in Fig. 5. The structure is built up of $Gd_2(CF_3COO)_6(H_2O)_6$ units (*cf.* Fig. 6). The Gd^{3+} ions are coordinated eightfold by oxygen atoms originating from five carboxylate groups (Gd-O distances: 235.1(4)–246.4(4) pm) and three water molecules (Gd-O distances: 239.6(4)–244.0(4) pm). The Gd^{3+} ions are connected to dimers by four of the six carboxylate groups in a μ_2 -carboxylato- $\kappa^1O : \kappa^1O'$ -bridging mode (Gd-Gd distance: 447.7(9) pm).

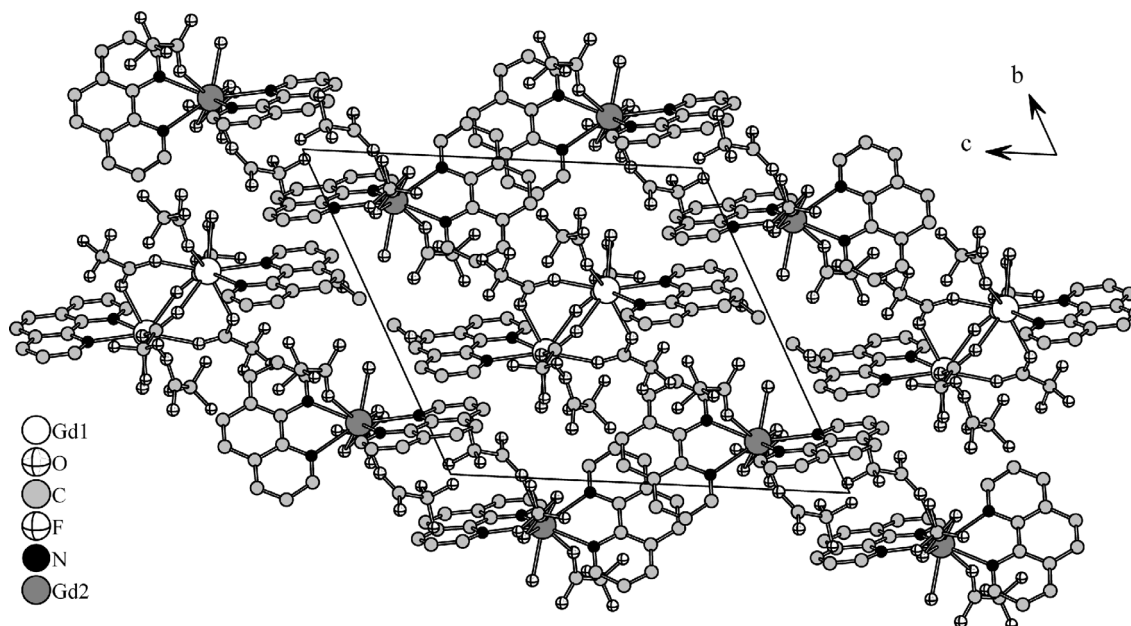


Fig. 7. Crystal structure of **4**. H atoms are not displayed. The unit cell is shown.

The other carboxylate groups are connected monodentately. Compound **3** is isomorphous with $\text{Ln}(\text{CF}_3\text{COO})_3(\text{H}_2\text{O})_3$ ($\text{Ln} = \text{Pr} - \text{Lu}$) [40].

The crystal structure of $\text{Gd}_2(\text{CF}_3\text{COO})_6(\text{H}_2\text{O})_2(\text{phen})_3 \cdot \text{C}_2\text{H}_5\text{OH}$ (**4**) is shown in Fig. 7. It is built up of dimeric and monomeric units (*cf.* Fig. 8). The Gd^{3+} ions of the dimeric unit are coordinated eightfold by six oxygen atoms originating from five carboxylate groups and one water molecule (Gd-O distances: 234.7(4)–242.2(4) pm) and by two nitrogen atoms stemming from a 1,10-phenanthroline molecule (Gd-N distances: 254.4(5) and 255.9(5) pm). The Gd^{3+} ions are connected into dimers by four of the six carboxylate groups in a μ_2 -carboxylato- $\kappa^1\text{O} : \kappa^1\text{O}'$ -bridging mode (Gd-Gd distance: 460.0(2) pm). The other carboxylate groups are connected monodentately. The Gd^{3+} ion of the monomeric unit is coordinated ninefold by five oxygen atoms originating from four carboxylate groups and one water molecule (Gd-O distances: 232.8(4)–258.4(4) pm) and by four nitrogen atoms stemming from two 1,10-phenanthroline molecules (Gd-N distances: 252.0(5)–261.0(5) pm).

In all these compounds the Gd^{3+} ions are connected *via* bidentate bridged carboxylate groups to dimers and chains, respectively. The Gd-Gd distances lie between 447.7(9) and 510.5(5) pm. The rather large distance of 510.5 pm is caused by the smaller number of the bridging carboxylate groups.

Magnetic behaviour

The short Gd-Gd distances within the compounds **2** and **3** are of interest for the study of magnetic interactions. We previously reported the magnetic behaviour of similar compounds like $\text{Gd}(\text{CClF}_2\text{COO})_3(\text{H}_2\text{O})_3$ [25], $\text{Gd}(\text{CHF}_2\text{COO})_3(\text{H}_2\text{O})_2 \cdot \text{H}_2\text{O}$ [23] and $(\text{NH}_3\text{CH}_3)[\text{Gd}(\text{CHCl}_2\text{COO})_4]$ [35]. In these compounds the Gd^{3+} ions are bridged by carboxylate groups also to dimers and chains in a μ_2 -carboxylato- $\kappa^1\text{O} : \kappa^1\text{O}'$ -bridging mode. The Gd-Gd distances are similar to the ones of **2** and **3**.

Magnetic susceptibility data for **2** and **3** were measured in the temperature range of 1.77 to 300 K at magnetic fields ($H^{(\text{ir})}$) of 500 and 1000 Oe for **2** and 300 and 1000 Oe for **3**, respectively. The measured susceptibility values are field independent.

Figs. 9 and 10 show the measured effective Bohr magneton number (μ_{eff} [41]) for **2** (Fig. 9) and **3** (Fig. 10). In both cases the r. t. values of μ_{eff} are close to the expected value for the Gd^{3+} ion ($\mu_{\text{eff}} \approx 7.9$). With the decrease of temperature, μ_{eff} decreases slowly. At 2 K the μ_{eff} values are about 7.5 and 7.65, respectively. This is a typical behaviour for weak antiferromagnetic interactions. A more detailed analysis shows that the molar magnetic susceptibility can be expressed by eq. (1) with $x = J_{\text{ex}}/k_{\text{B}}T$, derived from the spin Hamiltonian $\hat{H}_{\text{ex}} = -2J_{\text{ex}}\hat{S}_{\text{Gd1}} \cdot$

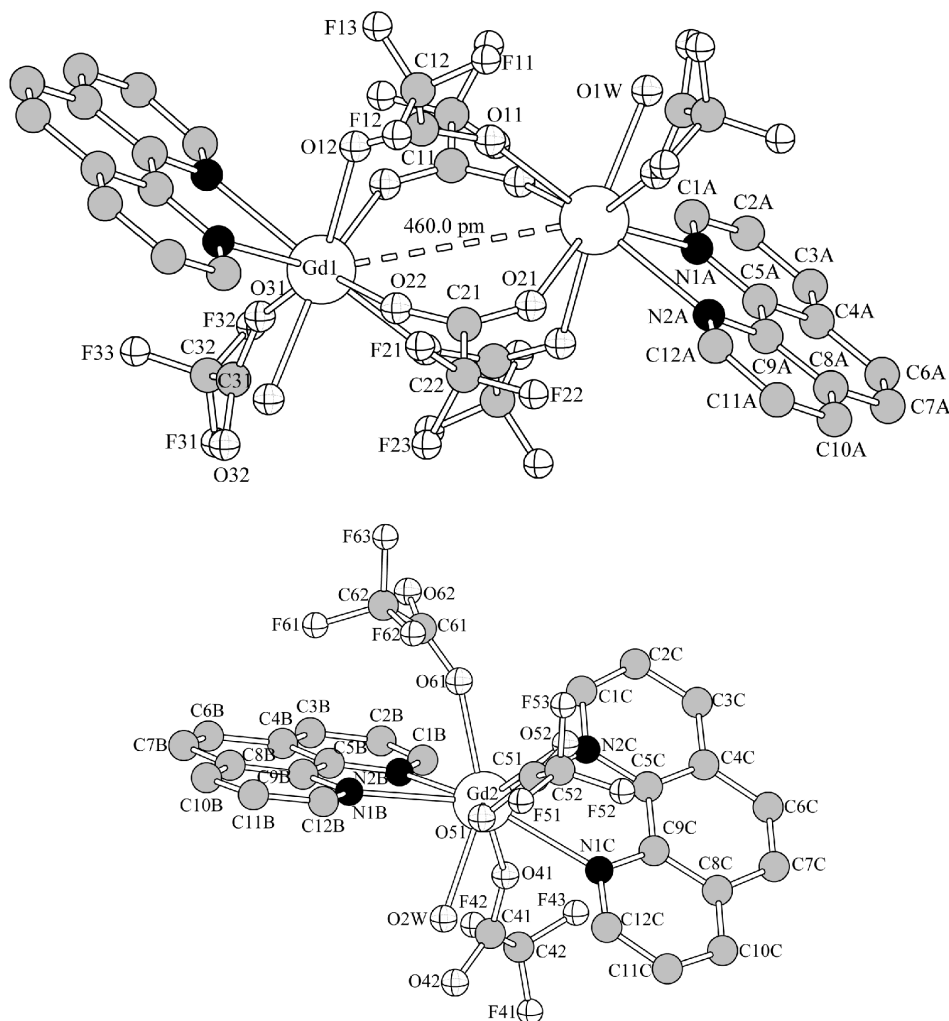


Fig. 8. Dimeric (above) and monomeric (below) unit of **4**.

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

\hat{S}_{Gd2} ($S_{\text{Gd1}} = S_{\text{Gd2}} = 7/2$) [42], 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. The fitting procedure for **2** leads to $J_{\text{ex}} = -0.0099 \text{ cm}^{-1}$, with $g = 1.98$ ($R = 8.82 \cdot 10^{-5}$; $R = \Sigma[(\mu_{\text{eff}})_{\text{obs}} - (\mu_{\text{eff}})_{\text{calc}}]^2 / \Sigma[(\mu_{\text{eff}})_{\text{obs}}]^2$), and for **3** to $J_{\text{ex}} = -0.0073 \text{ cm}^{-1}$, with $g = 1.99$ ($R = 9.18 \cdot 10^{-7}$). The values of J_{ex} and the Gd-Gd distances d in **2** and **3** are comparable with the ones for similar compounds (Table 3), where an antiferromagnetic interaction was also found for the μ_2 -carboxylato- $\kappa^1 O : \kappa^1 O'$ -bridging

Table 3. Magnetic exchange parameter $J_{\text{ex}} / \text{cm}^{-1}$ and Gd-Gd distance d / pm for Gd^{3+} carboxylates with bidentate bridging modes (* this work).

Compound	J_{ex}	d	ref.
$\text{Gd}(\text{CHF}_2\text{COO})_3(\text{H}_2\text{O})_2 \cdot \text{H}_2\text{O}$	-0.0125	445.6(2)	[23]
$[\text{NH}_3\text{C}_2\text{H}_5][\text{Gd}(\text{HCCl}_2\text{COO})_4]$	-0.010	453.7(7)	[34]
$(\text{CH}_3)_3\text{NH}[\text{Gd}(\text{CF}_3\text{COO})_4(\text{H}_2\text{O})]$ (2)	-0.0099	456.0(5)	*
$\text{Gd}(\text{CF}_3\text{COO})_3(\text{H}_2\text{O})_3$ (3)	-0.0073	447.7(9)	*
$[\text{NH}_3\text{CH}_3][\text{Gd}(\text{HCCl}_2\text{COO})_4]$	-0.007	451.6(7)	[35]
$\text{Gd}(\text{CClF}_2\text{COO})_3(\text{H}_2\text{O})_3$	-0.006	447.6(2)	[25]

mode. Further studies on gadolinium compounds may give insight into the exchange coupling mechanism.

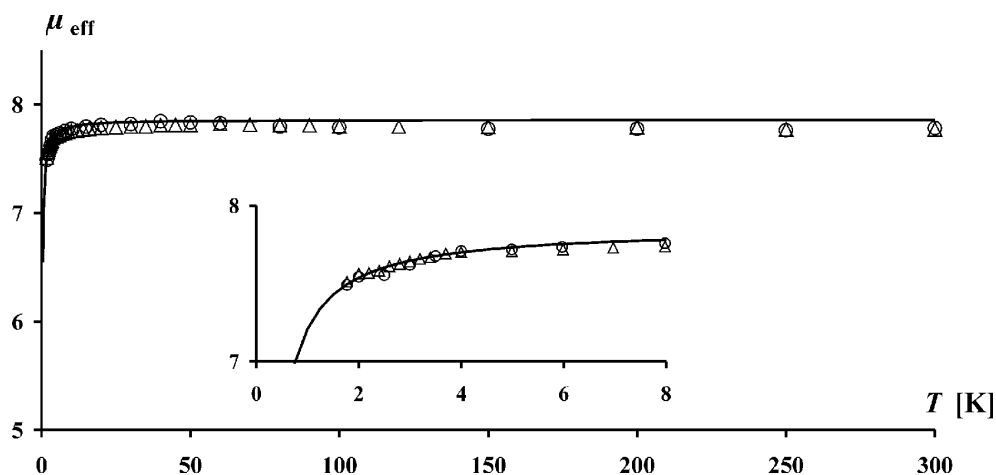


Fig. 9. Comparison of measured (Δ , $H^{(ir)}$: 500 Oe; \circ , $H^{(ir)}$: 1000 Oe) and calculated (—) effective Bohr magneton numbers for **2**.

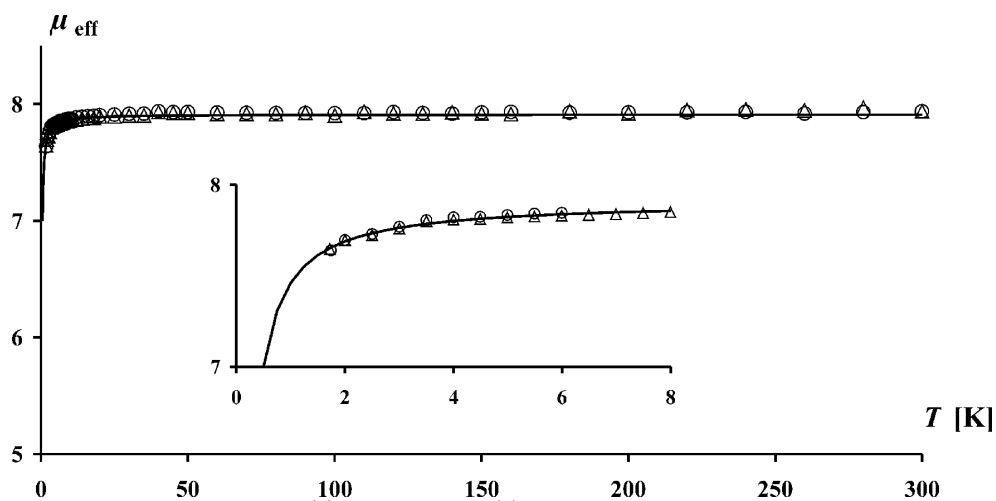


Fig. 10. Comparison of measured (Δ , $H^{(ir)}$: 300 Oe; \circ , $H^{(ir)}$: 1000 Oe) and calculated (—) effective Bohr magneton numbers for **3**.

Experimental Section

General

All reagents were commercially available and used without purification (Gd_2O_3 : Strem Chemicals, 99.9%; trifluoroacetic acid, dimethylammonium chloride, trimethylammonium chloride: Fluka, 98%; 1,10-phenanthroline: Aldrich, 99%; ethanol: Sigma-Aldrich, 99.8%). The homogeneity of all samples was investigated using X-ray powder diffraction.

Preparation of **1**

Compound **1** was prepared by the reaction of 0.58 g Gd_2O_3 (3.2 mmol Gd) and 1.37 g (12.01 mmol) trifluoroacetic acid in 10 ml H_2O at about 50 °C in a glass container. After

the oxide was dissolved, the solution was allowed to cool to r. t. and 0.24 g (2.94 mmol) dimethylammonium chloride was added. After a few weeks colourless crystals had formed. The crystals are suitable for X-ray single crystal structure analysis.

Preparation of **2**

Compound **2** was prepared by the reaction of 0.54 g Gd_2O_3 (2.98 mmol Gd) and 1.35 g (11.84 mmol) trifluoroacetic acid in 10 ml H_2O at about 50 °C in a glass container. After the oxide was dissolved, the solution was allowed to cool to r. t. and 0.29 g (3.03 mmol) trimethylammonium chloride was added. After few weeks colourless crystals had formed.

Preparation of 3

1.09 g (3 mmol Gd) Gd₂O₃ was suspended in water (10 ml) and 1.14 g (10 mmol) trifluoroacetic acid was added. In the solution colourless crystals formed after several days.

Preparation of 4

Compound **4** was prepared by reaction of 0.55 g of **3** (1 mmol Gd) and 0.36 g (1 mmol) 1,10-phenanthroline in a solution of ethanol and water (1:1). After a few days transparent, colourless, air stable crystals were obtained.

X-ray crystallographic studies

The intensities for all compounds were measured on a STOE imaging plate diffractometer. The data collection was carried out at r. t. The structures were solved by direct methods and were refined with anisotropic displacement parameters based on F^2 using SHELXS-97 [43] and SHELXL-97

[44] programs. The hydrogen atoms (compounds **1**, **2** and **4**) were positioned with idealized geometry and refined with isotropic displacement parameters. The crystal data and details of the refinement are summarized in Table 1.

Magnetic measurement

Crushed single crystals of **2** and **3** were measured with a SQUID magnetometer (MPMS5, Quantum Design) in a temperature range of 1.77 to 300 K at magnetic fields ($H^{(ir)}$) of 0.5 and 1 kOe (**2**) and 0.3 and 1 kOe (**3**), respectively. No field dependence was observed. The sample was weighed into the lid of a gelatin capsule. To evade orientation effects during the measurement, the bottom of the gelatin capsule was pressed on the sample to fix it. A second lid closed the capsule. Then the container was sewn in a plastic straw. The raw magnetic data were corrected for diamagnetism of the sample carrier and the sample, using the increments of Haberditzl [45]. The presentation of the magnetic data follows the recommendation of Hatscher *et al.* [46].

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