Journal of Alloys and Compounds 408–412 (2006) 618–621

Journal of ALLOYS AND COMPOUNDS

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# Crystal structure and magnetic behavior of the new gadolinium complex compound $[NH_3C_2H_5][Gd(Cl_2HCCOO)_4]$

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Received 30 July 2004; received in revised form 27 September 2004; accepted 15 December 2004
Available online 20 July 2005

## Abstract

Single crystals of $[NH_3C_2H_5][Gd(Cl_2HCCOO)_4]$ have been obtained by reaction of $Gd_2O_3$ with $NH_3C_2H_5Cl$ in an aqueous solution of $Cl_2HCCOOH$. The compound crystallizes in the triclinic space group $P\bar{1}$ (no. 2, $Z = 2$, $a = 813.7(3)$ pm, $b = 1246.9(4)$ pm, $c = 1263.9(4)$ pm, $\alpha = 61.67(4)^\circ$, $\beta = 87.39(4)^\circ$, $\gamma = 84.84(4)^\circ$). The $Gd^{3+}$ ion is eight-fold coordinated by oxygen atoms. The magnetic behavior of the compound was investigated in the temperature range of 1.72–300 K. The magnetic data indicate an intramolecular ferromagnetic interaction within a dimeric unit ($J_{\mathrm{intra}} = +0.029\ \mathrm{cm}^{-1}$) on which an intermolecular antiferromagnetic interaction is imposed ($J_{\mathrm{inter}} = -0.010\ \mathrm{cm}^{-1}$).

*Keywords:* Gadolinium; Dichloroacetate; Crystal structure; Synthesis; Magnetic behavior

## 1. Introduction

There are countless publications on lanthanide carboxylates being of structural interest, but up to now only few $Ln^{3+}$–$Ln^{3+}$ interactions in molecular magnetic materials have been studied such as $[Gd(L_A)]_2{\cdot}2CHCl_3$ ($H_3L_A$ = tris(((2-hydroxybenzyl)amino)ethyl)amine) [1], $[\{Gd(HL_B)(NO_3)\}_2]{\cdot}2MeOH$ ($H_3L_B$ = *N*-salicylidene-2-(bis-(2-hydroxyethyl)amino)ethylamine) [2], $Gd(L_C)_3{\cdot}2H_2O$ ($HL_C$ = trichloroacetic acid) [3], $[Gd(H_2L_D)(HL_D)(L_D){\cdot}H_2O]_n$ ($H_2L_D$ = salicylic acid) [4] and $Gd_2(L_E)_3(H_2O)_6$ ($H_2L_E$ = malonic acid) [5], so there are no simple rules, such as the Goodenough–Kanamori rules for compounds of d-elements to predict the occurrence of ferro- or antiferromagnetic coupling. In order to fill this lack of knowledge, we synthesized the title compound and investigated the magnetic behavior. The magnetic data were interpreted considering magnetic exchange coupling and molecular field approach. For the magnetic investigation, we have deliberately chosen the title compound containing $Gd^{3+}$ ions, as in this case ligand field interactions [6] can be neglected in the calculation of magnetic susceptibilities.

This work tries to relate the bridging modes of the carboxylate groups to the occurrence of ferro-, respectively, antiferromagnetic interactions.

## 2. Experimental section

Single crystals of $[NH_3C_2H_5][Gd(Cl_2HCCOO)_4]$ have been obtained by the reaction of $Gd_2O_3$ (Strem Chemicals, 99.9%) with ethylammonium chloride ($NH_3C_2H_5Cl$; Merck, 98%) in an aqueous solution of dichloroacetic acid ($Cl_2HCCOOH$; Fluka, 98.5%) in a molar ratio of 1:2:8. All starting materials were used without further purification. The transparent and colorless crystals are parallelepiped and air-stable. Anal. calcd.: H: 1.69; C: 16.80; N: 1.96; found: H: 1.72, C: 16.78, N: 1.94.

Well-grown crystals were mounted on a STOE imaging plate diffractometer. The data collection was carried out at room temperature. The structure was solved by direct

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doi:10.1016/j.jallcom.2004.12.199

Table 1
Crystallographic data and details for the structure determination of $[NH_3C_2H_5][Gd(Cl_2HCCOO)_4]$

| | |
|---|---|
| Crystal system | Triclinic |
| Space group, $Z$ | $P\bar{1}$ |
| Unit cell dimensions (pm) resp. (°) | $a = 813.7(3)$<br>$b = 1246.9(4)$<br>$c = 1263,9(4)$<br>$\alpha = 61.67(4)^\circ$<br>$\beta = 87.39(4)^\circ$<br>$\gamma = 84.84(4)^\circ$ |
| Cell volume ($pm^3$) | $1124.2(7) \times 10^6$ |
| Density (X-ray) ($g\,cm^{-3}$) | 2.112 |
| Absorption coefficient $\mu$ ($mm^{-1}$) | 3.936 |
| $F$ (0 0 0) | 686 |
| Crystal size ($mm^3$) | $1.11 \times 0.63 \times 0.63$ |
| Temperature (K) | 293 |
| Wavelength | Mo–$K_\alpha$ ($\lambda = 71.073$ pm) |
| Theta range for data collection (°) | 3.01–25.92 |
| Index ranges | $-9 \le h \le 9$<br>$-15 \le k \le 15$<br>$-15 \le l \le 15$ |
| Reflections collected | 15870 |
| Independent reflections | 4061 |
| $R_{int}$ | 0.0600 |
| Programs used | SHELXS-97 [7] und<br>SHELXL-97 [8] |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Refined parameters | 266 |
| GooF[a] | 1.133 |
| Residuals (all data)[a] | $R_1 = 0.0481$<br>$wR_2 = 0.1230$ |
| Extinction coefficient $\varepsilon$ | 0.0304(19) |
| Largest differential hole and peak ($e\,pm^{-3}$) | $-3.656 \times 10^{-6}$<br>$3.584 \times 10^{-6}$ |
| CCDC deposition number [15] | 244493 |

[a] Definitions given in [8].

Table 2
Selected distances (pm) in $[NH_3C_2H_5][Gd(Cl_2HCCOO)_4]$

| | | |
|---|---|---|
| Gd1 | –$O11$ | 238.2(4) |
| | –$O12$[a] | 234.2(4) |
| | –$O21$ | 252.4(4) |
| | –$O22$ | 255.6(4) |
| | –$O22$[b] | 244.3(3) |
| | –$O31$ | 235.5(3) |
| | –$O32$ | 234.2(4) |
| | –$O41$ | 229.2(4) |
| | –Gd1[b] | 418.1(6) |
| | –Gd1[a] | 453.7(7) |
| N1 | $\cdots O42$ | 282.5(5) |
| N1[c] | $\cdots O42$ | 283.2(6) |

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

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

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

methods and were refined with anisotropic displacement parameters based on $F^2$ using SHELXS-97 [7] and SHELXL-97 [8] programs. Data analyses indicate the space group $P\bar{1}$. The final refinement yielded $R_1$ (all data) = 4.81%. Hydrogen atoms were included using a riding model. The crystal data and details of the refinement are summarized in Table 1. The high residual peaks and holes are observed in the vicinity of $Gd^{3+}$, which are normal for complexes containing heavy atoms. Selected bond distances are summarized in Table 2.

Crushed single crystals of $[NH_3C_2H_5][Gd(Cl_2HCCOO)_4]$ were measured with a SQUID magnetometer (MPMS5, Quantum Design) in a temperature range of 1.72–300 K at magnetic fields ($H$) of 0.5 and 1 kOe. 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 [9].

## 3. Results and discussion

The structure of $[NH_3C_2H_5][Gd(Cl_2HCCOO)_4]$ is shown in Fig. 1. The $Gd^{3+}$ ion is eight-fold coordinated by oxygen atoms with Gd–O distances between 229.2 and 255.6 pm. The characteristic structural units are polymeric chains $[Gd(Cl_2HCCOO)_4]_\infty$, running along (1 0 0) with two kinds of bridging modes for the carboxylate groups. One of them is a $\mu_2 O';\kappa^2 O,O'$-, the other is a $\mu_2$-carboxylato-$\kappa^1 O{:}\kappa^1 O'$ mode. Because of the different bridging types, there are two different $Gd^{3+}$–$Gd^{3+}$ distances (418.1 and 453.7 pm). Thus the chain may be thought to consist of dimeric $Gd^{3+}$–$Gd^{3+}$ units. There is another non-bridging carboxylate group, which is linked via hydrogen bonding to the ethylammonium cation (cf. Table 2). As we reported earlier [10], the $\mu_2 O';\kappa^2 O,O'$ mode might give rise to ferromagnetic, the $\mu_2$-carboxylato-$\kappa^1 O{:}\kappa^1 O'$ mode, however, to antiferromagnetic coupling.

Fig. 2 shows the measured effective Bohr magneton number ($\mu_{eff}$) for $[NH_3C_2H_5][Gd(Cl_2HCCOO)_4]$ in the temperature range between 1.72 and 150 K ($H = 0.5$ kOe). With the decrease of the temperature, $\mu_{eff}$ increases slowly reaching a maximum value of 7.99 at 3 K and then decreases, which indicates the presence of weak intramolecular ferromagnetic coupling in the dimeric $Gd^{3+}$–$Gd^{3+}$ unit on which a weak intermolecular antiferromagnetic interaction is imposed. The magnetic behavior is interpreted by the equation given below, where the intramolecular interaction within the dimeric unit is described by the Heisenberg model with a spin Hamiltonian $\hat{H} = -2J_{\text{intra}}\hat{S}_{\text{Gd1}} \cdot \hat{S}_{\text{Gd2}}$ ($S_{\text{Gd1}} = S_{\text{Gd2}} = 7/2$), and the intermolecular interaction between the dimeric units by the

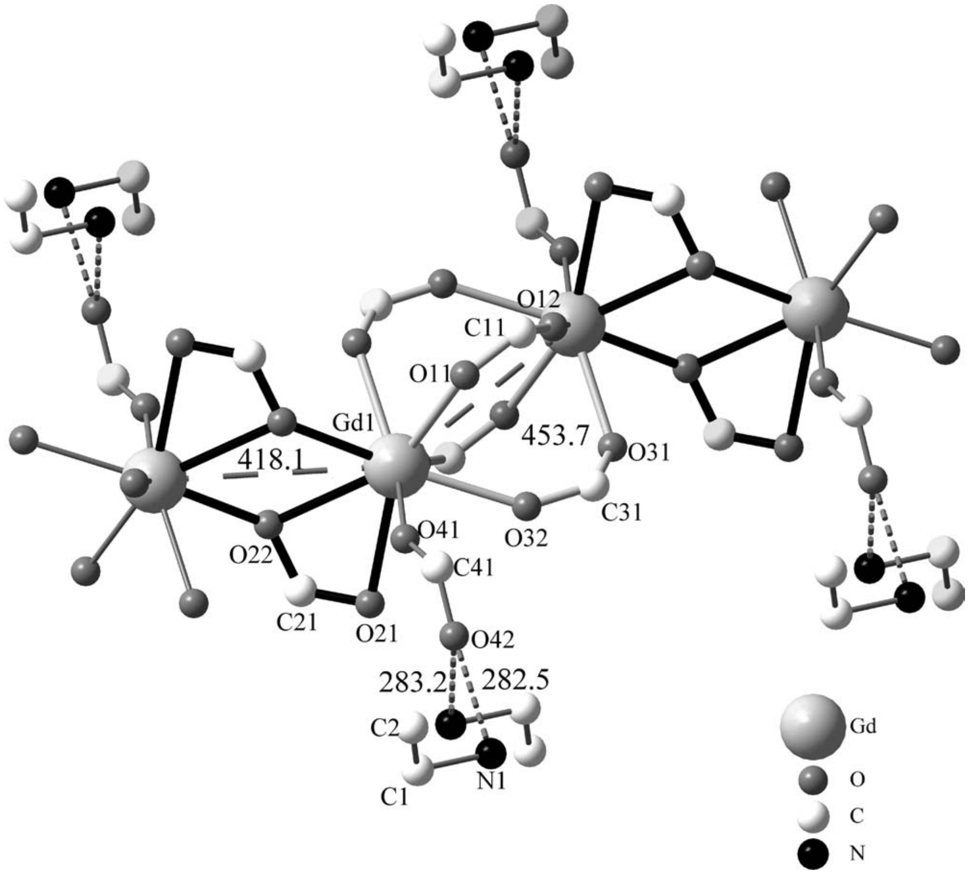

Fig. 1. Molecular structure of $[NH_3C_2H_5][Gd(Cl_2HCCOO)_4]$, only Gd atoms, the carboxylate groups and the ethylammonium cations are displayed. Hydrogen bonds are shown by dotted lines (including distances in pm). The dashed lines show the $Gd^{3+}$–$Gd^{3+}$ distances, bold-faced ones indicate the $\mu_2 O';\kappa^2 O,O'$-, weak ones the $\mu_2$-carboxylato-$\kappa^1 O{:}\kappa^1 O'$ bridging mode.

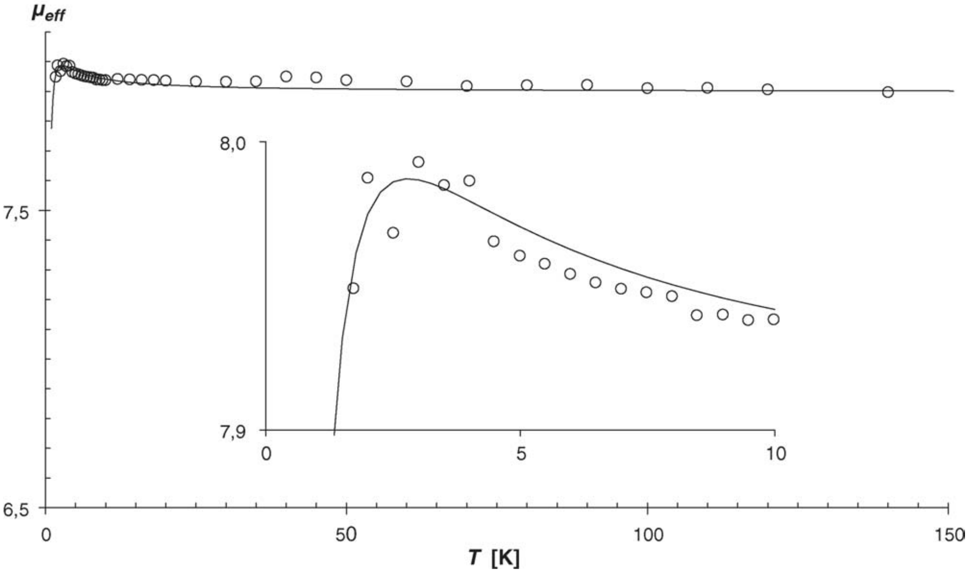

Fig. 2. Comparison of measured (○, $H = 0.5$ kOe) and calculated (—) effective Bohr magneton numbers for $[NH_3C_2H_5][Gd(Cl_2HCCOO)_4]$.

Table 3
Comparison of $J$ (cm$^{-1}$), bridging mode and $Gd^{3+}$–$Gd^{3+}$ distance (pm) for $[NH_3C_2H_5][Gd(Cl_2HCCOO)_4]$ (**1**), $Gd(H_3CCOO)_3(H_2O)_2\cdot 2H_2O$ (**2**), $Gd(F_2HCCOO)_3(H_2O)_2\cdot H_2O$ (**3**), $Gd(ClF_2CCOO)_3(H_2O)_3$ (**4**) and $[NH_3CH_3][Gd(Cl_2HCCOO)_4]$ (**5**)

| Compound | $J$ | Bridging mode | $Gd^{3+}$–$Gd^{3+}$ distance | Ref. |
|---|---|---|---|---|
| (**1**) | +0.029 | $\mu_2 O';\kappa^2 O,O'$ | 418.1 | This work |
| (**2**) | +0.025 | $\mu_2 O';\kappa^2 O,O'$ | 420.6 | [10,12] |
| (**5**) | +0.023 | $\mu_2 O';\kappa^2 O,O'$ | 418.4 | [14] |
| (**1**) | −0.010 | $\mu_2$–carboxylato–$\kappa^1 O:\kappa^1 O'$ | 453.7 | This work |
| (**3**) | −0.012 | $\mu_2$–carboxylato–$\kappa^1 O:\kappa^1 O'$ | 445.6 | [10] |
| (**4**) | −0.006 | $\mu_2$–carboxylato–$\kappa^1 O:\kappa^1 O'$ | 447.6 | [13] |
| (**5**) | −0.007 | $\mu_2$–carboxylato–$\kappa^1 O:\kappa^1 O'$ | 451.6 | [14] |

simple molecular field approximation [11]:

$$\chi_{\text{mol}}^{-1} = \left( \frac{N_{\text{A}}\mu_{\text{B}}^2 g^2}{k_{\text{B}}T} \; \frac{e^{2x} + 5e^{6x} + 14e^{12x} + 30e^{20x} + 55e^{30x} + 91e^{42x} + 140e^{56x}}{1 + 3e^{2x} + 5e^{6x} + 7e^{12x} + 9e^{20x} + 11e^{42x} + 15e^{56x}} \right)^{-1} - \lambda$$

where $x = J_{\text{intra}}/k_{\text{B}}T$, $N_{\text{A}}$ is the Avogadro constant, $\mu_{\text{B}}$ the Bohr magneton, $g$ the Landé-factor, $k_{\text{B}}$ the Boltzmann constant, $T$ the absolute temperature, $J_{\text{intra}}$ the intramolecular exchange constant and $\lambda$ the molecular field parameter, which is given by:

$$\lambda = \frac{2zJ_{\text{inter}}}{N_{\text{A}}\mu_{\text{B}}^2 g^2},$$

with $z = 2$ (number of neighbors) and $J_{\text{inter}}$ the intermolecular exchange constant.

The fitting procedure leads to $J_{\text{intra}} = +0.029\,\text{cm}^{-1}$, $J_{\text{inter}} = -0.010\,\text{cm}^{-1}$, with $g = 1.99$ ($R = 1.72 \times 10^{-6}$; $R = \Sigma[(\chi_{\text{mol}})_{\text{obs}} - (\chi_{\text{mol}})_{\text{cal}}]^2/\Sigma[(\chi_{\text{mol}})_{\text{obs}}]^2$). The calculated $\mu_{\text{eff}}$ values are shown in Fig. 2.

The values of $J_{\text{intra}}$ and $J_{\text{inter}}$ and the $Gd^{3+}$–$Gd^{3+}$ distances in the title compound are comparable with the ones for $Gd(H_3CCOO)_3(H_2O)_2\cdot 2H_2O$, $Gd(F_2HCCOO)_3(H_2O)_2\cdot H_2O$, $Gd(ClF_2CCOO)_3(H_2O)_3$ and $[NH_3CH_3][Gd(Cl_2HCCOO)_4]$ [10,12–14] (Table 3). Also, there a ferromagnetic interaction is found for the $\mu_2 O';\kappa^2 O,O'$-, and an antiferromagnetic one for the $\mu_2$-carboxylato-$\kappa^1 O:\kappa^1 O'$ bridging mode.

We are planning to prepare carboxylates with $Gd^{3+}$ entities of higher nuclearity than dimers. The results of this paper will help to interpret the magnetic behavior of such compounds.

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[15] CCDC 244493 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).