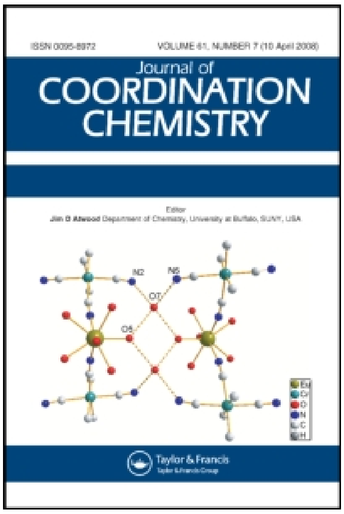

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# One new lanthanide complex with mixed sulfate and oxalate ligands: hydrothermal synthesis, crystal structure, and magnetic properties

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# One new lanthanide complex with mixed sulfate and oxalate ligands: hydrothermal synthesis, crystal structure, and magnetic properties

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A new lanthanide complex $K[Gd(ox)(SO_4)(H_2O)]$ (**1**) with sulfate and oxalate ligands has been synthesized under hydrothermal conditions. The compound crystallizes in the monoclinic space group $P_{21}/c$ with $a = 6.5849(1)$ Å, $b = 8.5660(1)$ Å, $c = 14.7660(2)$ Å, $\beta = 112.470(1)^\circ$, $C_2H_2GdKO_9S$, $M = 398.46$, $Z = 4$, $V = 769.66(2)$ Å$^3$, $F(000) = 740$, $R_1 = 0.0199$ and $\omega R = 0.0514$. The solid-state DC magnetic susceptibility measurements of **1** revealed antiferromagnetic behavior with an $S = 7/2$ ground spin state.

*Keywords*: Hydrothermal synthesis; Lanthanide complex; Zigzag-chain; Ferromagnetic behavior

## 1. Introduction

The design and synthesis of lanthanide complexes have been of great interest due to their intriguing topologies and attractive physical properties [1]. Nd(III), Er(III) and Yb(III) complexes with imidodiphosphinate "Shell" ligands, reported by Zoe and co-workers, showed long-lived near-infrared luminescence [1b]. Multidentate 2-hydroxyisophthalamide complexes of Sm(III), Eu(III), Tb(III), and Dy(III), reported by Raymond and co-workers, are stable lanthanide luminescence agents highly emissive in aqueous solution [1c]. Because of their high spin ground state and large spin–orbit interactions, lanthanide ions have been chosen to construct molecular magnets, some of which behave as single-molecule magnets (SMMs) with high spin ground state and large magnetic anisotropy [2]. The $[ErW_{10}O_{36}]^{9-}$ polyanion and $[(Pc)_2Ln]^-$ doped in diamagnetic $[(Pc)_2Y]^- \cdot TBA^+$ (Ln = Dy, Tb, Ho; Pc = phthalocyaninato; $TBA^+$ = tetrabutylammonium cation) are SMMs or behave as magnets at the single-molecular level [2b–2d]. Small bridging oxalate or sulfate anions, along with lanthanide ions, have been widely used to construct

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multidimensional frameworks [3]. However, lanthanide complexes with mixed oxalate and sulfate ligands are rarely reported [4]. We use oxalate and sulfate salts and gadolinium nitrates to construct molecular magnets and, herein, report the synthesis, crystal structure and magnetic properties of $K[Gd(ox)(SO_4)(H_2O)]$ (**1**, ox = oxalate anion).

## 2. Experimental

### 2.1. *Materials and methods*

All chemicals employed were commercially available and used as received. C, H and S microanalyses were carried out with a Perkin-Elmer 240 elemental analyzer. FT-IR spectra were recorded from KBr pellets in the 4000–400 $cm^{-1}$ range on a Nicolet 5DX spectrometer. Crushed single crystals of $K[Gd(SO_4)(ox)(H_2O)]$ were measured with a SQUID magnetometer (MPMS5, Quantum Design) from 2 to 300 K under 500 Oe magnetic field. The sample was weighed in the lid of a gelatine capsule. To eliminate 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 [5].

### 2.2. *Hydrothermal synthesis*

**2.2.1. $K[Gd(SO_4)(ox)(H_2O)]$ (1).** One millimole of $Gd(NO_3)_3 \cdot 6H_2O$, 0.5 mmol $MnSO_4 \cdot 2H_2O$, 0.5 mmol $K_2(C_2O_4)$ and 10 mL deionized water were mixed in a 25 mL Teflon-lined autoclave. After heating for 72 h at 140°C and cooling to room temperature at a rate of 5°C per hour, colorless block crystals could be isolated in ~75% yield and washed with deionized water. Anal. Calcd for $C_2H_2GdKO_9S$ (%): C, 6.03; H, 0.51; S, 8.05. Found: C, 6.02; H, 0.53; S, 8.07. IR(KBr): $\nu_s(H_2O)$ 3453s, $\nu_{as}(ox)$ 1641s, $\nu_s(ox)$ 1410s, $\nu_s(SO_4)$ 1049vs, $\nu_s((SO_4)$ 600 $cm^{-1}$.

### 2.3. *X-ray crystallography*

Diffraction data of **1** were collected at room temperature with a Bruker SMART Apex CCD diffractometer with Mo-K$\alpha$ radiation ($\lambda = 0.71073$ Å) and graphite monochromator using the $\omega$-scan mode. Data reductions and absorption corrections were performed on SAINT and SADABS software, respectively. The structure was solved by direct methods and refined on $F^2$ by full-matrix least squares using SHELXTL [6]. All non-hydrogen atoms were treated anisotropically. Hydrogen atom positions were generated geometrically. Crystallographic data and experimental details for structural analysis are summarized in table 1. Selected bond lengths and angles are listed in table 2. The CCDC reference number is 682051. Copy of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: +44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 1. Crystallographic data for **1**.

| | **1** |
|---|---|
| Formula | $C_2H_2GdKO_9S$ |
| $M$ | 398.46 |
| Crystal system | Monoclinic |
| Space group | $P_{21}/c$ |
| Units cell dimensions (Å, °) | |
| $a$ | 6.5849(1) |
| $b$ | 8.5660(1) |
| $c$ | 14.7660(2) |
| $\alpha$ | 90 |
| $\beta$ | 112.470(1) |
| $\gamma$ | 90 |
| $V$ (Å$^3$) | 769.66(2) |
| $T$ (K) | 298(2) |
| $D_c$ (g cm$^{-3}$) | 3.439 |
| $Z$ | 4 |
| $\mu$(Mo-K$\alpha$) (mm$^{-1}$) | 9.458 |
| Crystal size (mm) | 0.201 × 0.199 × 0.187 |
| $\theta$ range for data collection (°) | 2.81–27.85 |
| Independent reflections ($R_{int}$) | 0.0292 |
| Measured reflections | 1829 |
| $R_1{}^a/wR_2{}^b$ | 0.0199/0.0514 |

$^aR=\sum||F_o|-|F_c||/\sum|F_o|$. $^bwR=[\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Table 2. Selected bond distances (Å) and angles (°) for **1**$^a$.

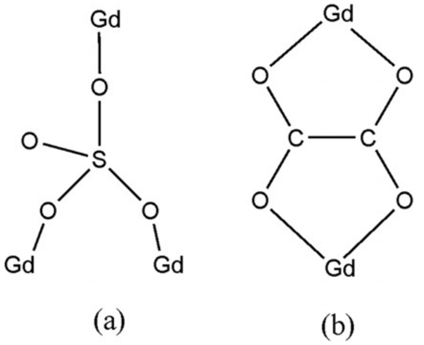
| **1** | | | |
|---|---|---|---|
| Gd(1)–O(4)#1 | 2.332(3) | Gd(1)–O(8)#3 | 2.418(3) |
| Gd(1)–O(1) | 2.350(3) | Gd(1)–O(5) | 2.439(3) |
| Gd(1)–O(3)#2 | 2.355(3) | Gd(1)–O(7)#3 | 2.442(3) |
| Gd(1)–O(1W) | 2.399(3) | Gd(1)–O(6) | 2.454(3) |
| O(4)#1–Gd(1)–O(1) | 75.82(10) | O(4)#1–Gd(1)–O(8)#3 | 86.70(10) |
| O(4)#1–Gd(1)–O(3)#2 | 79.74(10) | O(1)–Gd(1)–O(8)#3 | 78.73(10) |
| O(1)–Gd(1)–O(3)#2 | 133.15(12) | O(3)#2–Gd(1)–O(8)#3 | 138.96(10) |
| O(4)#1–Gd(1)–O(1W) | 96.31(10) | O(1W)–Gd(1)–O(8)#3 | 147.30(9) |
| O(1)–Gd(1)–O(1W) | 70.60(10) | O(4)#1–Gd(1)–O(5) | 146.97(9) |
| O(3)#2–Gd(1)–O(1W) | 73.17(11) | O(1)–Gd(1)–O(5) | 73.90(9) |

Note: $^a$Symmetry codes: #1 $-x+1$, $-y+1$, $-z$; #2 $x-1$, $y$, $z$; #3 $-x+1$, $y+1/2$, $-z+1/2$.

## 3. Results and discussion

### 3.1. *Hydrothermal synthesis*

The sulfate oxalate lanthanide complex, K[Gd(ox)($SO_4$)($H_2O$)] (**1**), was synthesized by treating Gd(III) nitrates with potassium oxalates and manganese sulfates in water solution at 140°C. The formation of **1** was supported by elemental analysis. The ox and $SO_4^{2-}$ anions exhibited the coordination modes as shown in scheme 1, as tetradentate and tridentate ligands, respectively.



Scheme 1. The coordination models of the sulfate (a) and the oxalate (b) ligands in **1**.

### 3.2. *Crystal structure*

**3.2.1. K[Gd(ox)($SO_4$)($H_2O$)] (1).** The crystal structure of **1** is shown in figure 1. The asymmetric unit [figure 1a] was composed of one Gd(III), one-coordinated water, one-coordinated sulfate, one-coordinated ox and one potassium ion. The central Gd(III) is eight-coordinate fulfilled by three $SO_4^{2-}$–O, four ox–O and one aqua–O atoms. The average bond distance of Gd–O is 2.399 Å.

Due to their differing coordination modes, ox and sulfate anions play different roles in constructing the structure. As shown in figure 1(b) and (c), the adjacent Gd(III) cations and the tetradentate ox bridges give rise to a $\{[\mathrm{Gd(ox)}]^+\}_n$ zigzag chain ($\mathrm{Gd}\cdots\mathrm{Gd} = 6.184$ Å), while an inorganic ladder $\{[\mathrm{Gd(SO_4)}]^+\}_n$ is constructed by Gd(III) cations and the tridentate sulfate bridges. Because of the coexistence of ox and sulfate bridges, **1** exhibits a more complicated 3-D brick-wall framework [figure 1d] than other complexes only containing one of the two bridges. In the 3-D brick-wall framework, the adjacent $\{[\mathrm{Gd(ox)}]^+\}_n$ zigzag chains are connected by sulfates to form 'bricks' with dimension of 6.18 × 11.18 Å, and each 'brick' contains four $[\mathrm{Gd(ox)}]^+$ and two $[\mathrm{Gd(SO_4)}]^+$ ions.

### 3.3. *Magnetic property*

The solid-state dc magnetic susceptibility measurements for **1** are recorded for polycrystalline sample at an applied magnetic field of 500 Oe over the temperature range 2–300 K, shown as plots of $\chi_M$T and $1/\chi_M$ *versus* T in figure 2. The room temperature $\chi_M$T value is 7.90 $\mathrm{cm^3\,K\,mol^{-1}}$/formula unit, close to the spin-only value (calculated 7.88 $\mathrm{cm^3\,K\,mol^{-1}}$) of one Gd atom with $S_{\mathrm{Gd}} = 7/2$ (assuming $g = 2.0$). As the temperature is lowered, the $\chi_M$T value decreases from 7.90 $\mathrm{cm^3\,K\,mol^{-1}}$ (300 K) to 7.78 $\mathrm{cm^3\,K\,mol^{-1}}$ (54 K), and then increased abruptly to 8.64 $\mathrm{cm^3\,K\,mol^{-1}}$ at 2 K. The rapid increase of $\chi_M$T at low temperature may be due to increase of the correlation length within adjacent $S_{\mathrm{Gd}} = 7/2$ spins along opposite directions [7]. The presence of the minimum value of $\chi_M$T reveals an overall antiferromagnetic interaction between the adjacent Gd(III) cations. The $1/\chi_M$ data obey the Curie–Weiss Law, $\chi = C/(T - \theta)$, with Curie constant $C = 7.873$ $\mathrm{cm^3\,K\,mol^{-1}}$ and Weiss constant $\theta = -0.20$ K, supporting the presence of weak antiferromagnetic coupling between the paramagnetic cations.

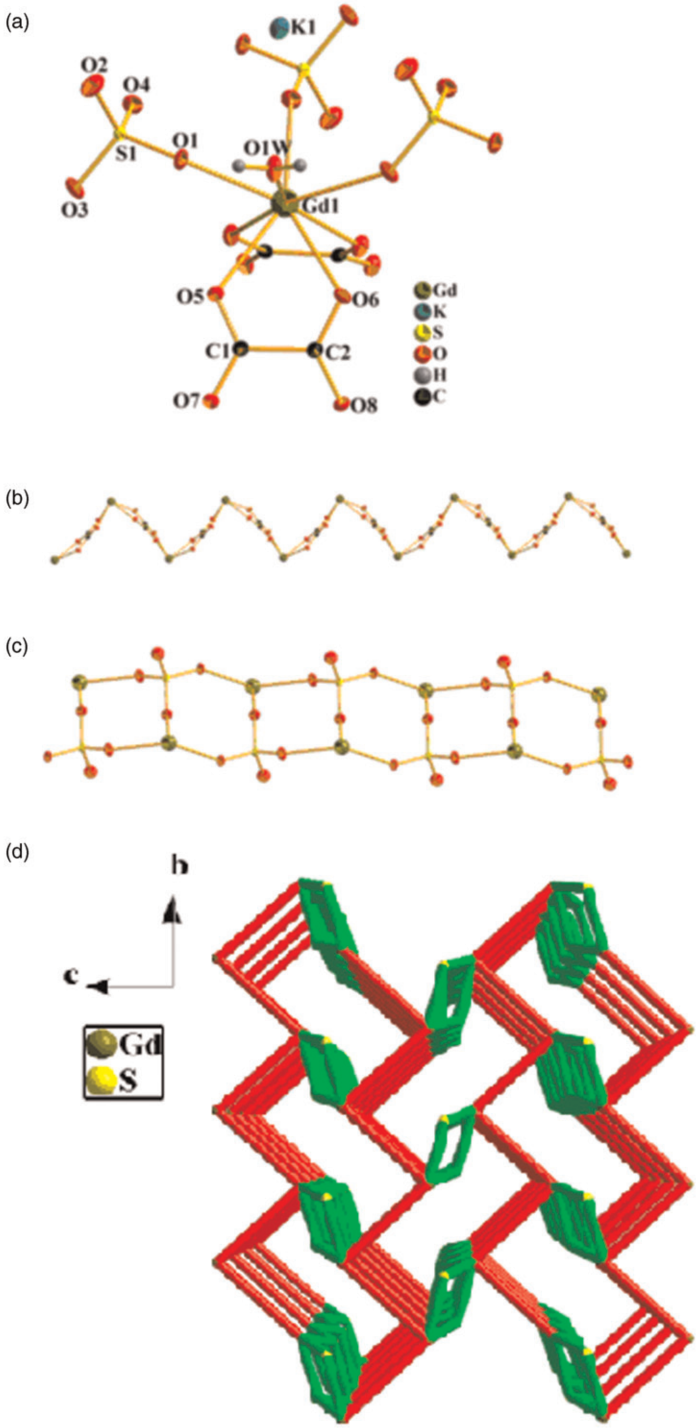


Figure 1. (a) ORTEP view of the asymmetric unit of **1** with 50% probability displacement ellipsoids. (b) The $\{[Gd(ox)]^{+}\}_n$ zigzag-chain based on oxalate bridges. (c) The $\{[Gd(SO_4)]^{+}\}_n$ ladder based on sulfate bridges. (d) View of the 3D brick-wall framework for **1**. Red rods represent the ox connections; green rods represent the sulfate connections.

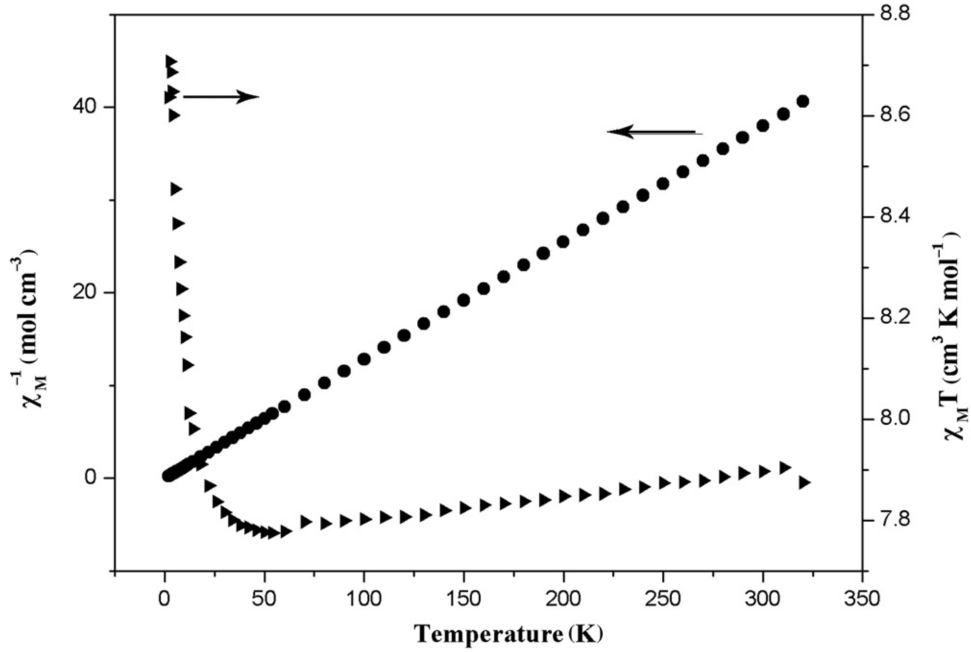


Figure 2. Plots of $\chi_M T$ and $\chi_M{}^{-1}$ *vs. T* of **1**.

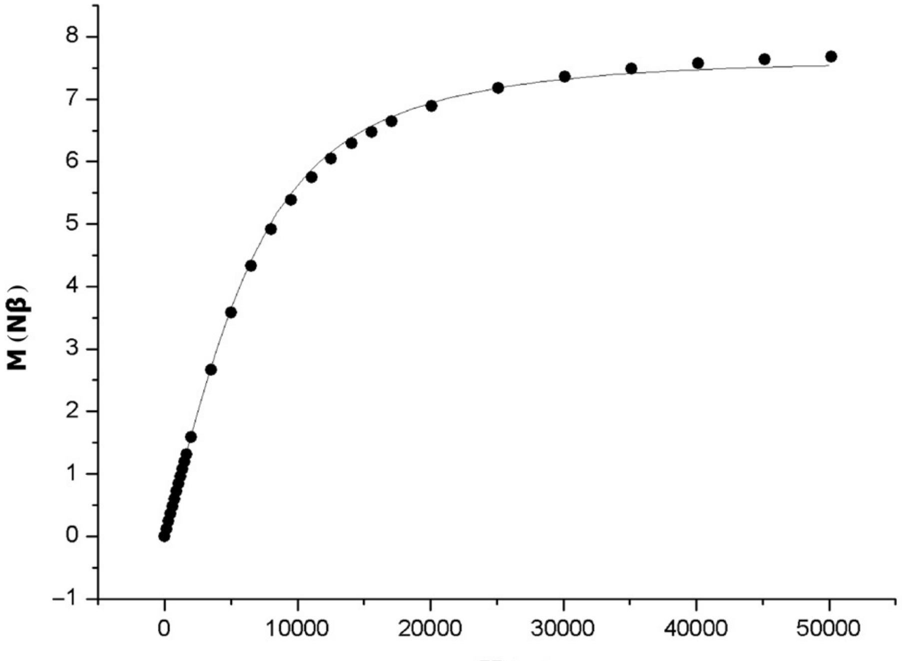


Figure 3. Field dependence of the magnetization for **1**. The solid dots represent the experimental data and the solid line represents the calculated results based on Brillouin Function with $g = 2.14$, $S = 7/2$ and $T = 2K$.

The magnetization process of **1** was performed at 2 K in the range of 0–50000 Oe. As shown in figure 3, the saturation magnetization could be reached under 50000 Oe and the magnetization at 50000 Oe is 7.68 N$\beta$, which is close to the calculated value 7.54 N$\beta$ based on Brillouin Function with $g = 2.14$, $S = 7/2$.

## 4. Conclusions

A new lanthanide complex K[Gd(ox)($SO_4$)($H_2O$)] has been synthesized under hydrothermal conditions. Crystallography reveals eight-coordinate Gd(III) and a 3-D brick-wall framework based on tetradentate ox and tridentate sulfate bridges. The solid-state dc magnetic susceptibility measurements revealed overall weak antiferromagnetic interactions between adjacent paramagnetic lanthanide cations through ox and/or sulfate bridges and field dependent magnetization experiments showed $S = 7/2$ ground spin state with $g = 2.14$.

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