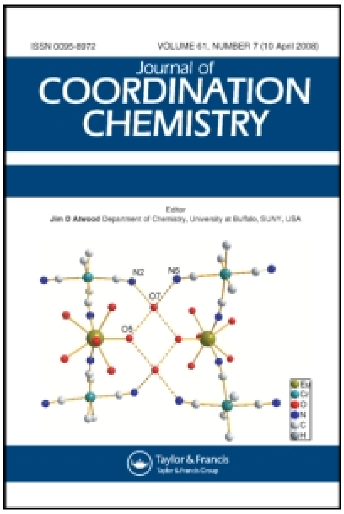

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Preparation, structure and magnetic study of a new linear 1-D Cu(II)-Gd(III) coordination polymer

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To cite this Article Wu, Bin , Zheng, Yunli and Ng, Seik Weng(2008) 'Preparation, structure and magnetic study of a new linear 1-D Cu(II)-Gd(III) coordination polymer', Journal of Coordination Chemistry, 61: 22, 3674 — 3678
To link to this Article: DOI: 10.1080/00958970802108833
URL: http://dx.doi.org/10.1080/00958970802108833

Journal of Coordination Chemistry
Vol. 61, No. 22, 20 November 2008, 3674–3678

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Preparation, structure and magnetic study of a new linear 1-D Cu(II)–Gd(III) coordination polymer

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(*Received 27 January 2008; in final form 13 February 2008*)

A carboxylate-bridged Cu(II)–Gd(III) complex, $[GdCu(CH_2CH(CH_3COO)_4(H_2O)_4]_n(NO_3)_n$, was prepared and characterized. Single crystal X-ray analysis reveals the complex as a carboxylate-bridged 1-D Cu(II)–Gd(III) coordination polymer. The magnetic measurement showed this complex exhibiting weak ferromagnetic behavior.

Keywords: Gadolinium; Copper; Heteronuclear; Crystal structure; Magnetic properties

1. Introduction

Heterometallic 3d and 4f are important to understand the magnetic interaction between 3d and 4f centers, which are potential magnetic materials [1–12]. Many studies focused on discrete Cu(II)–Gd(III) complexes [13–17]. The magnetic interaction between Cu(II) and Gd(III) ions is, in most cases, ferromagnetic in dinuclear complexes. Isolated dinuclear complexes have a great advantage for they only contain the Cu–Gd interaction parameter. On the contrary, although several infinite lanthanide-transition metal complexes containing organic ligands have been obtained, gadolinium(III)-copper(II) polymeric complexes have been poorly explored [18–22]. Carboxylates are excellent ligands for the construction of 3d–4f heteronuclear complexes [23–25]. Herein we described the preparation, crystal structure and magnetic studies of $[GdCu(CH_2CH(CH_3COO)_4(H_2O)_4]_n(NO_3)_n$. To the best of our knowledge, the present case is the first example of a carboxylate-bridged linear 1-D heterometallic Cu(II)–Gd(III) coordination polymer, providing a new model for magnetic investigation.

2. Experimental

$Gd(CH_2CH(CH_3COO)_3$ was synthesized by literature procedure [26]. All other chemicals were of reagent grade obtained from commercial sources and used without further purification.

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ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958970802108833

2.1. *Physical measurements*

Elemental analyses were performed on a Cobra-Erba1110 instrument. IR spectra were recorded on a Nicolet 560 IR spectrophotometer. Magnetic data were measured using a Quantum Design model 6000 magnetometer over the temperature range 2–300 K at 10 kOe applied field. Diamagnetic corrections were made with Pascal's constants for all the constituent atoms.

2.2. *Synthesis*

$GdL_3 \cdot H_2O$ (1 mmol, 430 mg, $HL = CH_2C(CH_3)COOH$) and $Gd(NO_3)_3 \cdot 6H_2O$ (6 mmol, 2600 mg) were added to water (20 mL). A solution of $Cu(NO_3)_2$ (2 mL, 1 M) was added to give a clear blue solution. After filtration, the filtrate was allowed to stand at room temperature and blue single crystals suitable for X-ray work were obtained after several weeks. Elemental analysis for $C_{16}H_{28}CuGdNO_{15}$: calculated C, 27.64; H, 4.06; N, 2.01%. Found: C, 27.52; H, 4.19; N, 2.08%. IR (KBr, cm^{-1}): ν_{as}(COO) 1576, ν_s(COO) 1424, ν(C=C) 1642.

2.3. *X-ray crystallographic studies*

Crystallographic data were collected using a Rigaku R-AXIS RAPID area detector diffractometer. Absorption corrections were applied using multi-scan. The structure was solved by direct methods and refined for all data using SHELXL 97 [27]. Crystal data: $C_{16}H_{28}CuGdNO_{15}$, $M = 695.18$, monoclinic, space group $P2_1/m$, $a = 7.556(3)$ Å, $b = 18.165(5)$ Å, $c = 9.643(3)$ Å, $\beta = 96.45(2)^\circ$, $V = 1315.2(7)$ Å^3, $Z = 2$, $\mu = 3.374\ mm^{-1}$, 20693 reflections measured, 3103 unique ($R_{int} = 0.027$) which were used in all calculations. The final wR (F^2) was 0.052 (all data). The crystal structure consists of polycationic chains in which the dianionc tetraacrylatocuprate unit functions as a bridge to connect the tetraaquagadolium units. Both units are disordered, the tetracrylatocuprate disordered in the acrylate groups and the tetragadolium disordered in two of the four water molecules.

3. Results and discussion

3.1. *Crystal structure*

The structure of the complex, shown in figure 1 with selected atomic numbering schemes, consists of polycationic chains and nitrate anions. The chain is made by the carboxylate-bridged alternating Cu(II)–Gd(III) fragments. The Cu^{2+} ions are four-coordinate with four oxygen atoms of four carboxylate ligands. The Gd^{3+} ions are eight-coordinate with four oxygens of four water molecules and four oxygens of four carboxylate ligands. The geometry of copper is a square plane and gadolinium is a square antiprism. The angles Gd–Cu–Gd and Cu–Gd–Cu have the same value in each compound (177.88°), so the chain runs along the structure in a nearly perfect line. Each gadolinium has two different intramolecular distances with each of the two neighboring copper ions (3.765 and 3.792 Å), so the chain could be considered as an

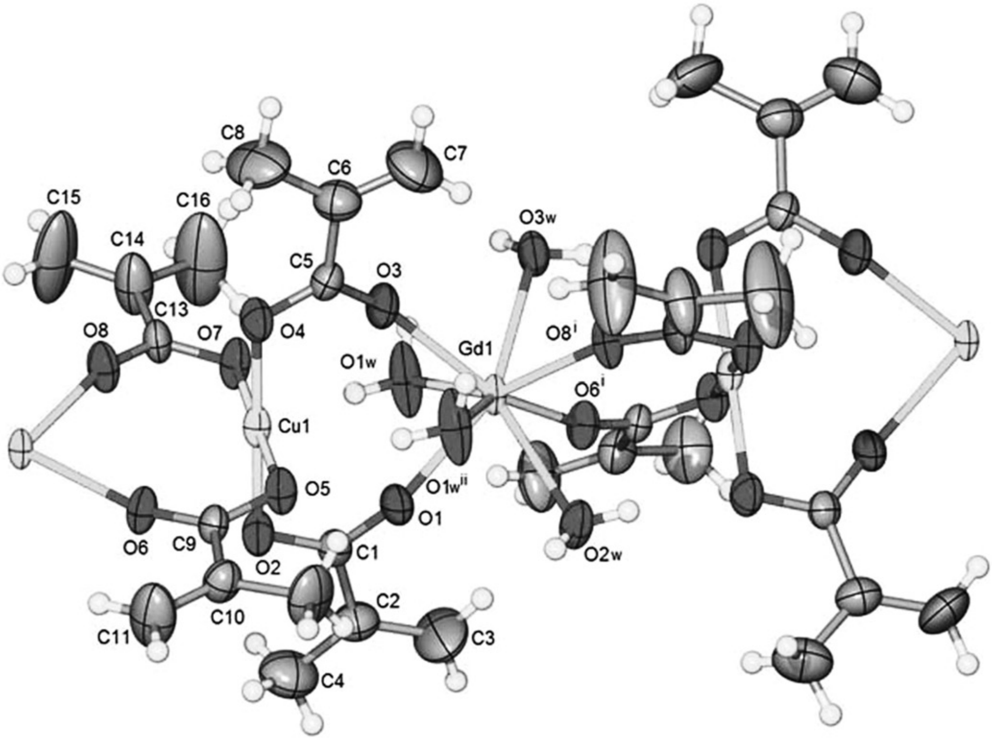

Figure 1. ORTEP view of the Gd–Cu polycationic chain with 50% thermal probability ellipsoids and selected atom labelling scheme; for the sake of clarity, the anions have been omitted.

alternating chain. Between the chains, there are nitrate groups. The chains are linked together through hydrogen bonding by nitrate groups.

3.2. *Magnetic properties*

The temperature dependences of the magnetic susceptibilities were examined in the temperature range 2–300 K in an applied field of 10 kOe. Diamagnetic corrections for the sample and sample holder were applied to the data. The plot of $\chi_m T$ and $1/\chi_m$ *versus* T is presented in figure 2. The experimental value at room temperature ($8.13\,\mathrm{cm^3\,K\,mol^{-1}}$) is close to the value calculated for one Cu(II) ($S=1/2$) and one Gd(III) ($S=7/2$) noninteracting ions of $8.25\,\mathrm{cm^3\,K\,mol^{-1}}$. On lowering the temperature, the $\chi_m T$ increases gradually to reach a maximum value, $8.54\,\mathrm{cm^3\,K\,mol^{-1}}$, at 6 K and then decreases abruptly. The increase at higher temperature indicates ferromagnetic interaction between Cu(II) and one Gd(III) ions. The abrupt decrease in the lower temperature region can be ascribed to weak intermolecular antiferromagnetic interaction. The plot of $1/\chi_m$ *versus* T follows the Curie-Weiss law on the whole with the Weiss constant $\theta = 0.31$ K. The observed behaviors indicate that weak ferromagnetic interactions take place between adjacent paramagnetic centers. The magnetic behavior is similar to those of discrete gadolinium-copper complexes [3, 24, 28].

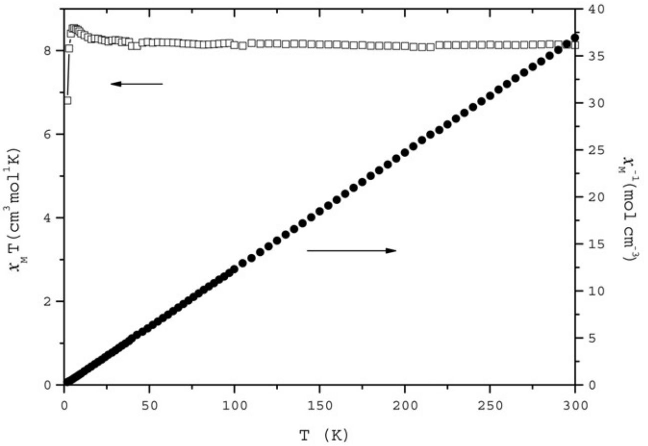

Figure 2. Plots of $\chi_m T$ and $1/\chi_m$ *vs*. *T* for complex.

Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 622503. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ UK (Fax: +44 1223 336033; Email: deposit@ccdc.cam.ac.uk).

Acknowledgement

This work was supported by the Natural Science Foundation of Zhejiang Province (M203105).

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