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Inorganic Chemistry Communications 8 (2005) 178–181
INORGANIC CHEMISTRY COMMUNICATIONS
www.elsevier.com/locate/inoche

$\{[GdAg_2(dtpa)(H_2O)] \cdot 3H_2O\}_n$: the first 2D Gd–Ag coordination polymer with Ag–Ag interaction

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Received 15 June 2004; accepted 1 December 2004

Abstract

A novel 4d–4f coordination polymer $\{[GdAg_2(dtpa)(H_2O)] \cdot 3H_2O\}_n$ (**1**) (dtpa = diethylenetriamine pentaacetate) was synthesized and characterized by magnetic and EPR studies. Its one-dimensional Gd–Ag ladder-like chains built upon tetranuclear rings are further connected by Ag–O bonds and Ag–Ag interactions to form a lamellar 2D packing.

Keywords: Gadolinium; Silver; Crystal structure; Two-dimensional layer; Ag–Ag interaction

In recent years chemists pay intense interest on lanthanide–transition metal complexes, considering that the high coordination number of Ln(III) may render the structural flexibility and increase the thermal dynamic stability. Various types of lanthanide–transition metal complexes have been reported for their intriguing network topologies and potential in microelectronics, nonlinear optics, luminescent materials, and so on [1]. In the previous reports [2], we described the preparation and properties of 3d–4f zeolite-type coordination polymers with nanotubular structures. However, the published infinite lanthanide(III)–transition metal compounds are essentially focused on 3d–4f systems [2–7], polymeric compounds of 4d–4f system are still limited.

With a view to the lagging of studies on 4d–4f systems, we explored such area more recently. In respect that diethylenetriamine pentaacetate (dtpa) forms stable metal chelates with a variety of metal ions, and especially, Gd(III) complexes with dtpa is a strong paramagnetic compound in magnetic resonance of imaging (MRI) [8], we utilize dtpa to construct coordination polymers with Gd(III) and Ag(I). Only two examples of Gd–Ag polymers have been reported previously: $Ag[Gd(dipic)_2(H_2O)_3] \cdot 3H_2O$ (1D chain structure) and $[Gd_2Ag_2(pydc)_4(H_2O)_4]_n$ (2D network) (dipic = pyridine-2,6-dicarboxylate; pydc = pyridine-2,5-dicarboxylate) [9], in both of which there are no Ag–Ag interactions and the nearest Ag···Ag distance is 3.59 Å. By introducing the hydrothermal synthetic method, we obtained a 2D complex with Ag–Ag interactions, $\{[GdAg_2(dtpa)(H_2O)] \cdot 3H_2O\}_n$ (**1**) [10]. To our best knowledge, **1** is the first 2D Gd–Ag polymer with Ag–Ag interactions (Ag–Ag distance, 2.9983(19) Å).

The single-crystal X-ray analysis of **1** reveals that dtpa behaves as an octadentate ligand towards Gd^{3+} with three nitrogen atoms (N1, N2, N3) and five carboxylate oxygen atoms (O2, O3, O6, O8, O9) (Fig. 1). The average Gd–N (2.680 Å) and Gd–O (2.407 Å) bond lengths are comparable to those Gd–dtpa complexes [11]. The coordination sphere of Gd^{3+} is completed by the oxygen atom (Gd1–O11, 2.562(6) Å) of coordinated

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doi:10.1016/j.inoche.2004.12.004

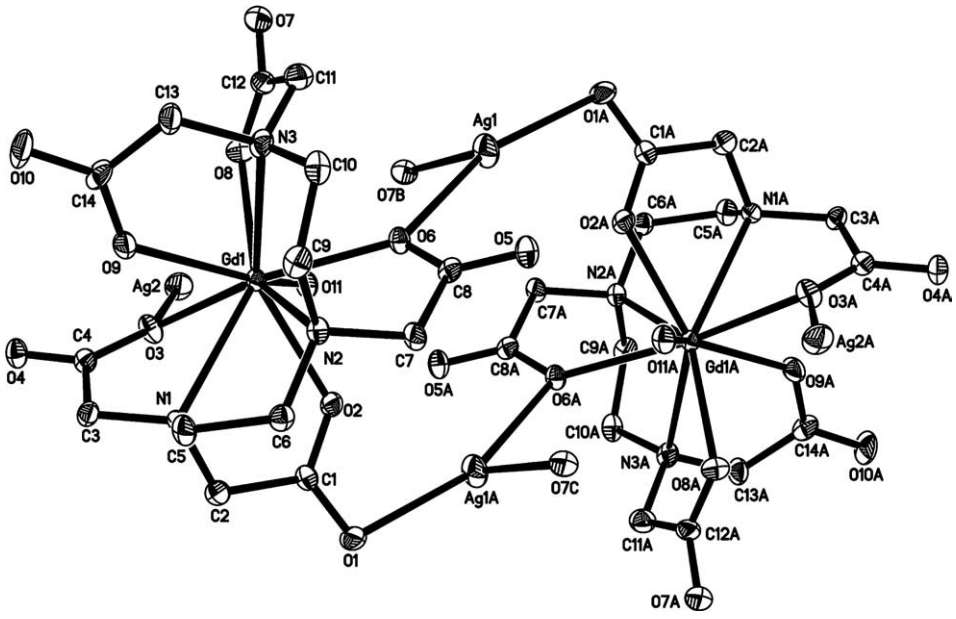

Fig. 1. The tetranuclear heterometallic ring in $\{[GdAg_2(dtpa)(H_2O)] \cdot 3H_2O\}_n$ (**1**). The lattice water molecules and hydrogen atoms have been cancelled for clarity.

water molecule, designing a polyhedron close to a tricapped trigonal prism with N1, N3 and O11 as the capping atoms [10,11]. A dihedral angle of 5.6° is observed between the prism bases defined by O2, O6, N2 and O3, O8, O9. The Ag1 and Ag1A link two Gd^{3+} ions via Ag–O(Ag1–O6 = 2.456(5), Ag1–O1A = 2.433(6) Å) bonds forming a tetranuclear heterometallic ring. The Gd1···Gd1A distance is 7.859 Å, and the Ag1···Ag1A distance is 5.399 Å.

The coordination geometry around Ag1 and Ag1A is T-shape like triangle with the Ag(I) ion deviating from the plane by 0.2616 Å. The bond angle of O6–Ag1–O1A is 159.29°. The Ag1–O7B and Ag1A–O7C bonds connect neighboring tetranuclear heterometallic rings into one-dimensional structure (Fig. 2).

The two crystallographically independent silver ions have a different coordination scheme. Ag1 (Ag1A) shows a trigonal geometry, while Ag2A ion is four-coordinated by three carboxylate oxygen atoms (Ag–O (av.) 2.384(6) Å) and one Ag(I) ion (Ag–Ag 2.9983(19) Å), which develop the 1D chain into 2D network (Fig. 3). The Ag–Ag distance of 2.9983(19) Å, which is similar to the Ag–Ag distance of 2.977(1) Å in the three-dimensional $[Ag(4,4'\text{-bpy})](NO_3)$ polymer (bpy = bipyridine) [12–15], is well below the sum of the van der Waals radii for two silver atoms (3.44 Å) and very close to the Ag–Ag separation in silver metal (2.89 Å) accounting for the significant Ag–Ag interactions.

The 2D layers are further linked by the hydrogen bonds among the uncoordinated oxygen atoms of dtpa ligands and hydrogen atoms of dtpa from adjacent layers to form a three-dimensional porous network.

The magnetic susceptibilities are measured in the temperature range of 5–300 K. The μ_{eff} value of Gd^{3+} at 300 K of 7.89 μ_B is close to the theoretical value of 7.94 μ_B for free Gd^{3+}. With the temperature decreasing to 50

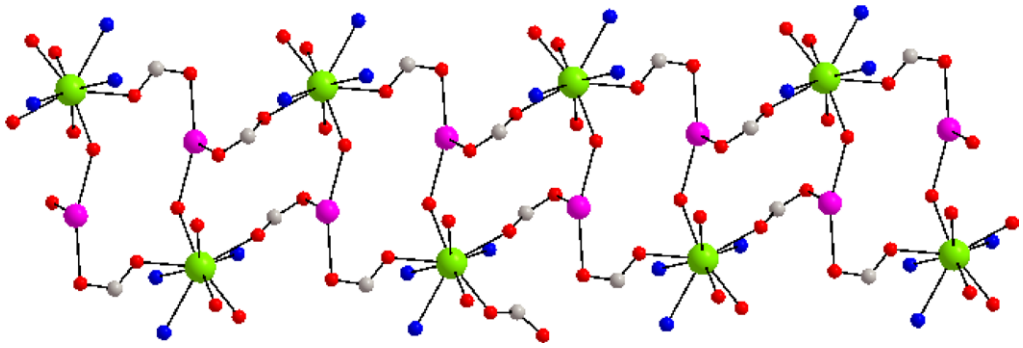

Fig. 2. One-dimensional structure bridged through carboxylic groups in **1**: Gd, green; Ag, purple; N, blue; C, gray; O, red. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)