# A Gd–Ag Coordination Polymer with Porous Structure via Hydrothermal Synthesis: $[Gd_2Ag_2(pydc)_4(H_2O)_4]_n$

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A Gd-Ag coordination polymer $[Gd_2Ag_2(pydc)_4(H_2O)_4]_n$ (pydc = pyridine-2,5-dicarboxylate) with lamellar structure was prepared by the hydrothermal reaction of $Gd_2O_3$, $AgNO_3$, $H_2pydc$ and $H_2O$ in a molar ratio of 1 : 4 : 5 : 3100 at 170 °C and characterized by single-crystal X-ray diffraction analysis.

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Studies on the syntheses, structures and properties of lanthanide–transition metal complexes are of intense current interest, because they are important for investigation of the nature of the magnet materials containing rare-earth metals.[1–12] Such studies are essentially focused on 3d–4f systems, especially Cu–Gd complexes.[3–9] Many complexes with discrete structures and several with infinite structures have been synthesized by conventional solution synthetic method.[1–18] Surprisingly, 4d–4f system has been poorly explored. To our best knowledge, only one example of Gd–Ag complex has been reported in literature and it was synthesized by conventional solution reaction of simple silver(I) complex with gadolinium nitrate.[19]

Recently, our group has started the work on the preparation of 4d–4f coordination polymers by rigid ligand with both N and O donor atoms. Based on the coordination behaviors of gadolinium(III) and silver(I), we tried the reaction of gadolinium(III) and silver(I) with sodium pyridine-2,5-dicarboxylate (pydc). Unfortunately, when the reaction was carried out in the conventional solution method, uncharacterized precipitate insoluble in most of common solvents was obtained. Hydrothermal synthesis is a common technique for preparation of transition metal complexes with extended structures such as zeolites[20] and organic–inorganic hybrid material.[21] Through the hydrothermal reaction, many of interesting compounds which is difficult to obtain have been synthesized.[22] Thus, by introducing the hydrothermal synthesis method into the Gd–Ag reaction system and replacing gadolinium(III) with metal oxide as starting material, we obtained a Gd(III)–Ag(I) coordination polymer $[Gd_2Ag_2(pydc)_4(H_2O)_4]_n$ (**1**) with porous structure. Herein, we report its synthesis and crystal structure.

The hydrothermal reaction of $Gd_2O_3$, $AgNO_3$, $H_2pydc$ and $H_2O$ in a molar ratio of 1 : 4 : 5 : 3100 at 170 °C yielded light-yellow crystals suitable for X-ray analysis.[23] IR spectrum of the crystalline product showed the absence of a band in the range 1690–1730 $cm^{-1}$ (C=O vibrations of the $CO_2H$ group). The crystallographic analysis[24] of **1** revealed that its crystal structure is a 2D network consisting of $[Gd_2Ag_2(pydc)_4(H_2O)_4]$ building units, as shown in Figure 1.

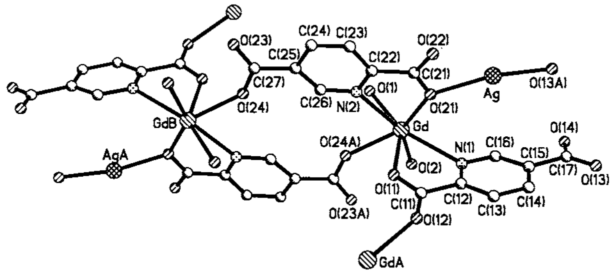
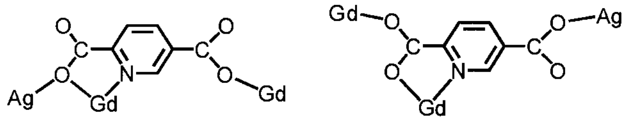


**Figure 1**. Basic unit structure of **1**.

Every Gd(III) is coordinated by two nitrogen and six oxygen atoms, of which four oxygen and two nitrogen atoms come from carboxylate groups of different pydc ligands and two oxygen atom from coordination water molecules. The Gd–N and Gd–O bond lengths range from 2.603 to 2.608 Å and 2.330 to 2.450 Å, respectively. Each silver atom is coordinated by two oxygen atoms from different pydc ligands in a nearly linear fashion of $AgO_2$ with the O–Ag–O angle being 160.6°. The Ag–O bond length is 2.113 Å and Ag–$\mu_2$-O bond length is 2.307 Å. All of pydc ligands act as $\mu_3$-bridge link three metal atoms with two types of coordination modes, which are shown in Scheme 1. Two such basic units are linked together by O(12) atom of carboxylate group of pydc ligand to form a 2D network.



a b

**Scheme 1.** The coordination modes of pydc ligand.

The structure can also be viewed as double Gd(III) chains linked by Ag(I) center via Ag–$O_{pydc}$ bonds. Each Gd(III) connects with one Ag(I) center and three other Gd(III) centers and each Ag connects with two Gd(III) centers through pydc ligands to form 2D structure (Figure 2).

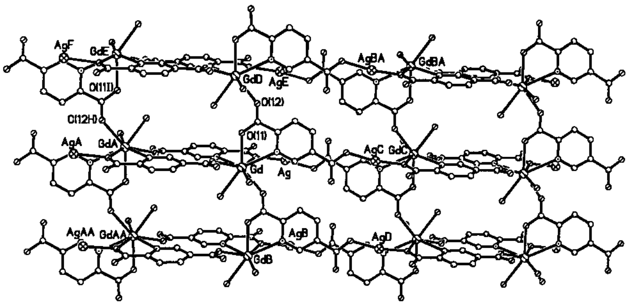


**Figure 2.** 2D layer with macroporus structure in **1**.

From Figure 2, one can see that four gadolinium atoms were linked by pydc ligands forming a rectangular cavity with size of 6.3 × 7.9 Å. Symmetry operations generate a 2D network. The 2D layers are further linked by the hydrogen bond interactions among the uncoordinated oxygen atoms of pydc ligands and the coordinated water molecules from adjacent layers to form a three-dimension (3D) network (Figure 3). The hydrogen bond distances of $O_1 \cdots O_{22}$ and $O_2 \cdots O_{14}$ are 2.719 and 2.612 Å, respectively.

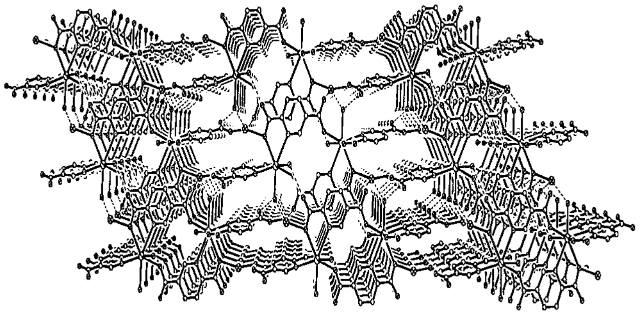


**Figure 3**. 3D Packing structure of **1** through hydrogen bond interactions.

To our best knowledge, this structure represents the second example of Gd–Ag coordination polymers and the first example of Gd–Ag coordination polymer with 2D network. The other example known to us of Gd–Ag coordination polymer is Goodgame's $[Ag\{Gd(dipic)_2(H_2O)_3\}]\cdot 3H_2O$ (dipc = 2,6-pyridinedicarboxylate) mentioned above, which possesses a chain structure.[19] The different structures between ours and Goodgame's may result from either different synthetic methods, i.e., hydrothermal reaction and conventional solution method, or different ligands uesed.

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23 Synthesis of $[Gd_2Ag_2(pydc)_4(H_2O)_4]_n$(**1**): Heating a mixture of $Gd_2O_3$ (0.090 g, 0.25 mmol), $AgNO_3$(0.170 g, 1.0 mmol), pyridine-2,5-dicarboxylic acid (0.210 g, 1.25 mmol), and $H_2O$ (14 mL) in a 25 mL stainless-steel reactor with Teflon liner at 170 °C for 72 h. Light-yellow crystals of **1** were collected by slowly decreasing temperature to ca. 25 °C in the yield of 40%. IR (KBr, $cm^{-1}$): 3404(br, vs), 1614(vs), 1479(m), 1387(s), 1358(s), 1282(m), 1032(m), 760(s), 523(s).

24 Crystallographic data: Crystal dimensions 0.20 × 0.09 × 0.09 mm, Formula: $C_{14}H_{10}AgGdN_2O_{10}$, Fw 631.36, triclinic, *P-1*, $a$ = 6.289(2), $b$ = 8.193(3), $c$ = 16.560(6) Å, $\alpha$ = 76.04(3), $\beta$ = 86.20(4), $\gamma$ = 73.13(3)°, $V$ = 792.4(5) $Å^3$, $Z$ = 1, $R(wR)$ = 0.0590 (0.1402) for 2781 independent reflections with $F \geq 2.0\ \sigma(Fo)$. The intensity data were collected on a Siemens Smart CCD diffractometer with graphite-monochromated Mo K$\alpha$ ($\lambda$ = 0.71073 Å) radiation at room-temperature. The structures were solved by directed methods and the positions of H atoms were generated geometrically (C–H bond fixed at 0.96 Å), assigned isotropic thermal parameters, and allowed to ride on their parent carbon atoms before the final cycle of refinement. All of the calculations were performed by using the SHELXTL-93 program package on a Legand computer. Detail crystallographic data of **1** have been deposited at the Cambridge Crystallographic Data Center (CCDC-143099).