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Crystal Structure of a New Coordination Polymer $[LaAg(Pydc)(HPydc)(C_2O_4)_{0.5}(H_2O)_2]_n$ (H_2Pydc = Pyridine-3,5-Dicarboxylic Acid)[1]

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Abstract—A new 3D coordination polymer, $[LaAg(Pydc)(HPydc)(C_2O_4)_{0.5}(H_2O)_2]_n$ (I) (H_2Pydc = pyridine-3,5-dicarboxylic acid), has been hydrothermally synthesized and characterized by elemental analyses and single crystal X-ray diffraction. The X-ray diffraction analysis reveals that I ($C_{15}H_{11}AgLaN_2O_{12}$) crystallizes in triclinic space group $P\bar{1}$ and features an interesting 3D framework constructed by 2D layers via strong Ag–Ag interactions. Unit cell parameters for I ($n = 1$): $a = 7.749(2)$, $b = 8.316(1)$, $c = 14.239(3)$ Å, $\alpha = 97.64(2)°$, $\beta = 100.12(2)°$, $\gamma = 94.37(2)°$, and $Z = 2$.

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INTRODUCTION

The rational design and synthesis of mixed *d–f* metal-organic coordination polymers has attracted much attention [1–8], because such bimetallic arrangements provide new opportunities for potential applications in magnetism [9], catalysis [10], and adsorption [11, 12], as well as their intriguing topologies [13]. A typical strategy used to construct lanthanide-transition metal heterometallic complexes is self-assembly from mixed metal ions and organic ligands containing hybrid donor atoms, such as cyanide [14], carbonyl [15], pyridine-carboxylate ligand [16], and amino acids [17]. The preparation of extended structures with lanthanide-transition metal heterometallic coordination frameworks by selecting the organic ligands and mixed metal ions is still a challenge to chemists, owing to the following factors: (a) the choice of organic ligands; (b) the variable and versatile coordination behavior of 4*f* metal ions; (c) the low stereochemical preference for lanthanide ions; (d) the competitive reactions between lanthanide and transition metals coordinated to the same ligand [18]. So far, a variety of heterometallic complexes have been reported. Among of them, the Ag–Ln heterometallic coordination frameworks are rare [19].

As is well known, the lanthanides have a strong tendency to coordinate to O-donor atoms to form lanthanide-carboxylate coordination polymers [20] and were compared to the Ln^{3+} ions. The soft Ag^+ ion easily bonds to the N-donor atoms [19]. Thus, if a ligand containing both N-donor and O-donor atoms and Ag^+ ion could be introduced to link the lanthanide-carboxylate subunits successfully, the novel 4*d*–4*f* coordination polymers may be obtained though the recognition of the metal ion and their coordinating atoms. On the basis of the recognition action point, we chose oxalic acid and pyridine-3,5-dicarboxylic acid (**H_2Pydc**) as the linkers. In this paper, we report on the syntheses and structures of a 3D La–Ag coordination polymers, $[LaAg(Pydc)(HPydc)(C_2O_4)_{0.5}(H_2O)_2]_n$ (**I**).

EXPERIMENTAL

All reagents and solvents employed were commercially available and used as received without further purification. The C, H, and N microanalyses were carried out with a Perkin Elmer 240 elemental analyzer.

Synthesis I. A mixture of $La(NO_3)_2 \cdot 4H_2O$ (0.5 mmol, 0.154 g), H_2Pydc (0.5 mmol, 0.084 g), $H_2C_2O_4 \cdot 2H_2O$ (0.063 g, 0.5 mmol), NaOH (1 mmol, 0.040 g), and H_2O (10 ml) was mixed in a 23-ml teflon reactor and stirred for 20 min in air. Then it was heated at 160°C for five days followed by cooling to room temperature at a rate of 5 K h^{-1}. Colorless block crystals of I were isolated in 58% yield after being washed with water and dried in air.

For $C_{15}H_{11}AgLaN_2O_{12}$			
anal. calcd, %:	C, 27.38;	H, 1.68;	N, 4.26.
Found, %:	C, 27.31;	H, 1.49;	N, 4.38.

Structure X-ray determination. Crystallographic data of **I** were collected at room temperature with a Bruker P4 diffractometer with MoK_α radiation (λ = 0.71073 Å) and a graphite monochromator using the ω scan mode. The structure was solved by direct methods

[1] The article is published in the original.

Table 1. Crystallographic parameters and a summary of data collection and refinement for complex **I**

Parameter	Value
Empirical formula	$C_{15}H_{11}AgLaN_2O_{12}$
Formula weight	658.04
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions:	
a, Å	7.749(2)
b, Å	8.316(1)
c, Å	14.239(3)
α, deg	97.64(2)
β, deg	100.12(2)
γ, deg	94.37(2)
V, Å^3	890.6(3)
Z	4
ρ_{calcd}, g cm^{-3}	2.454
μ, mm^{-1}	3.541
F(000)	630
Crystal size, mm	0.37 × 0.32 × 0.26
θ, range for data collection, deg	2.12–27.50
Reflections collected	4872
Independent reflections (R_{int})	3964 (0.0228)
Max and min transmission	0.4642 and 0.3549
T, K	293(2)
Goodness-of-fit on F^2	1.000
Parameters	280
Final R indices ($I > 2\sigma(I)$)*	$R_1 = 0.0291$ $wR_2 = 0.0729$
R indices (all data)	$R_1 = 0.0386$ $wR_2 = 0.0854$
Largest diff. peak and hole, e Å^{-3}	1.103, –1.142

* $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR_2 = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$.

Table 2. Selected bond distances and angles for **I***

Bond	d, Å	Angle	ω, deg
La(1)–O(3)	2.472(3)	O(3)La(1)O(5)	141.49(12)
La(1)–O(5)	2.499(3)	O(3)La(1)O(2*w*)	147.84(11)
La(1)–O2*w*	2.588(3)	N(2)$^{\#4}$Ag(1)N(1)	164.84(15)
La(1)–O(7)$^{\#1}$	2.428(3)	N(1)Ag(1)Ag(1)$^{\#5}$	90.53(11)
Ag(1)–N(1)	2.161(4)	O(3)La(1)O(1*w*)	70.76(12)
Ag(1)–Ag(1)$^{\#5}$	3.143(1)	O(5)La(1)O(10)$^{\#3}$	82.31(11)
La(1)–O(9)	2.544(3)	N(2)$^{\#4}$Ag(1)Ag(1)$^{\#5}$	103.86(10)
La(1)–O1*w*	2.519(3)		
La(1)–O(6)$^{\#2}$	2.490(3)		
La(1)–O(10)$^{\#3}$	2.516(3)		
Ag(1)–N(2)$^{\#4}$	2.154(4)		

* Symmetry transformations used to generate equivalent atoms: $^{\#1}$ $-x-1, -y+1, -z+2$; $^{\#2}$ $-x-1, -y, -z+2$; $^{\#3}$ $-x, -y+1, -z+2$; $^{\#4}$ $x+1, y, z-1$; $^{\#5}$ $-x+1, -y, -z+1$.

and refined on F^2 by full-matrix least squares using SHELXTL [21]. All non-hydrogen atoms were treated anisotropically. Positions of hydrogen atoms 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 atomic coordinates and other parameters of structure **I** have been deposited with the Cambridge Crystallographic Data Center (no. 694522); deposit@ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

X-ray structural analysis shows that **I** crystallizes in triclinic space group $P\bar{1}$ with an asymmetric unit of the unit cell consisting of one La center, one Ag center, one Pydc ligand, one HPydc ligand, a half C_2O_4 ligand, and two aqua ligands (Fig. 1). Each La is surrounded by eight oxygen atoms from three Pydc ligands, one HPydc ligand, one oxalate ligands, and two water molecules. The coordination geometry around the La(III) center can be described as a dicapped-octahedral geometry with the La–O bond lengths (from 2.428(3) to 2.588(3) Å), and the OLaO bond angles (from 72.4(1)° to 145.6(1)°) are in the normal range [22]. As far as the Ag^+ ion in the coordination framework is concerned, it exhibits a two-coordinate linear coordination geometry, being coordinated by two N atoms from two Pydc ligand (Ag–N(1), 2.161(4), Ag–N(2*A*) ($x+1, y, z-1$) 2.154(4) Å). Crystallographically unique HPydc and

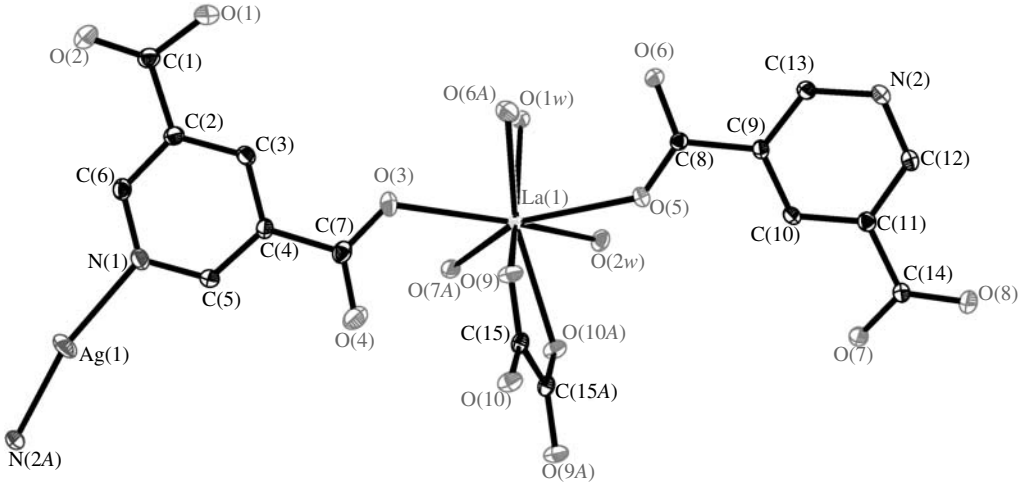


Fig. 1. ORTEP drawing of the asymmetric unit of **I**. All H atoms are omitted for clarity.

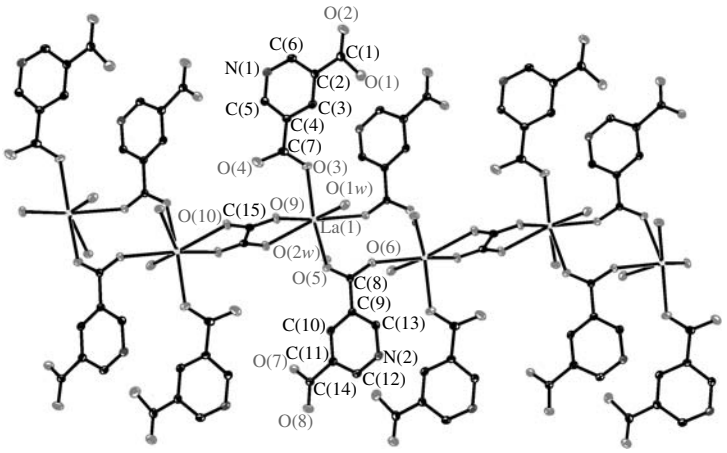
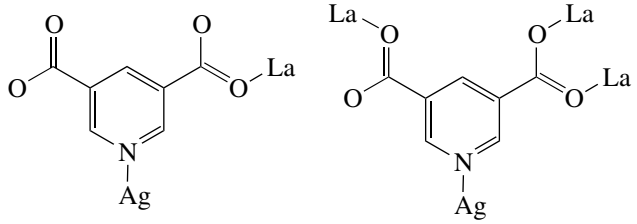


Fig. 2. View of the individual 1D lanthanide-carboxylate chain in **I**. All H atoms are omitted for clarity.

Pydc ligands exhibit different coordination modes, as shown below:



That is, one coordinates one Ag^+ ion and one La^{3+} ion, the other bonds to one Ag^+ ion and three La^{3+} ions. The oxalate ligand adopts chelating and bridging coordination modes. On the basis of these connection modes, the La^{3+} ions are first linked by two HPydc and two Pydc ligands via *syn-syn* coordination modes to form a binuclear $[La_2(HPydc)_2(Pydc)_2]$ subunit. Furthermore, the adjacent binuclear $[La_2(HPydc)_2(Pydc)_2]$ were connected by oxalate ligands to form a 1D linear chain with the Eu···Eu separation of 5.411(2) and 6.518(3) Å (Fig. 2). Interestingly, the N atoms of the adjacent 1D linear chains were furthermore linked by Ag^+ ions via N–Ag–N to form a wavelike 2D layer (Fig. 3). The adjacent 2D layers were furthermore linked via strong Ag–Ag interactions to form a 3D framework (Fig. 4). The Ag–Ag distance of 3.143(1) Å, which is similar to the Ag–Ag distance of 3.245(1) Å in the 3D $[Ag_4(Mim)_4(C_6H_6)]_n$ coordination polymer (HMim = 2-methylimidazole) [23] and 3.309(6) Å in the hexanuclear 4*d*–4*f* heterometallic complexes, $[Sm_2Ag_4(Ina)_8(H_2O)_{10}][NO_3]_2 \cdot 4H_2O$ (HIna = isonicotinic acid) [7], is well below the sum of the van der Waals radii of two Ag atoms (3.44 Å) [24].

In conclusion, a 3D La(II) coordination polymer $[LaAg(Pydc)(HPydc)(C_2O_4)_{0.5}(H_2O)_2]_n$ has been successfully synthesized in which La(II) centers are eight-coordinated with oxygen atoms from HPydc, Pydc and C_2O_4 groups. The HPydc and Pydc ligands adopt biden-

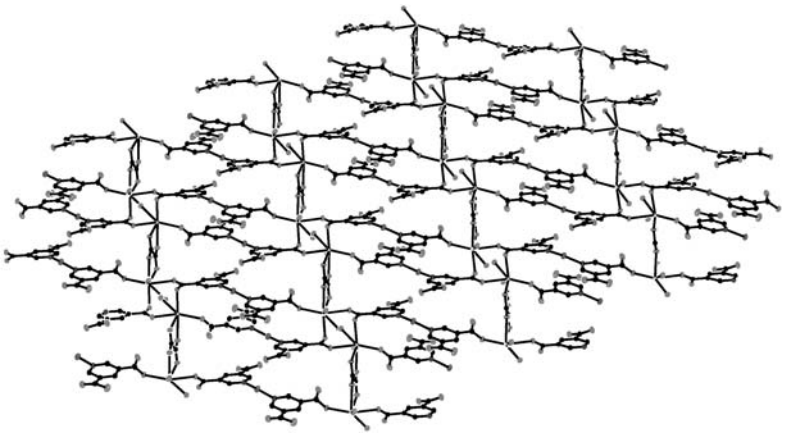


Fig. 3. The 2D layer constructed by linear La-carboxylate chains and Ag^+ ions.

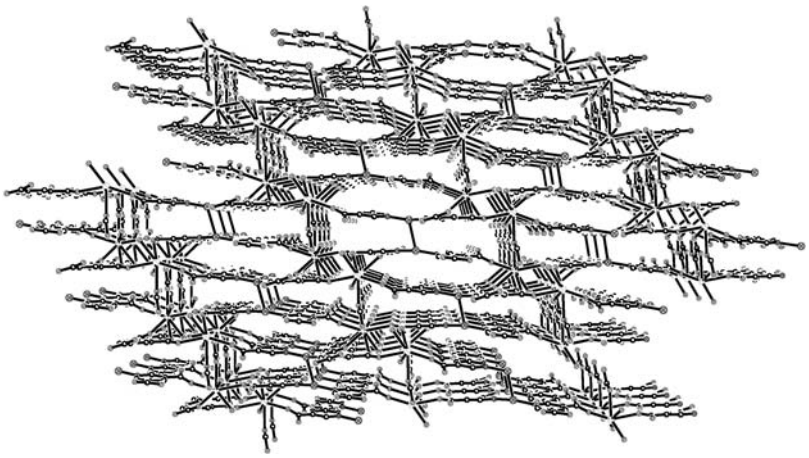


Fig. 4. The 3D framework of **I** viewed along the *y* axis.

tate and tetradentate coordination modes, respectively. An interesting 3D framework is formed via 2D layer and Ag–Ag interactions.

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