

SYNTHESIS, CRYSTAL STRUCTURE AND MAGNETIC PROPERTY OF A NEW TWO-DIMENSIONAL $\{Co_3\}$ CLUSTERS COORDINATION POLYMER BASED ON PYRIDINE TETRA-CARBOXYLATE LIGAND

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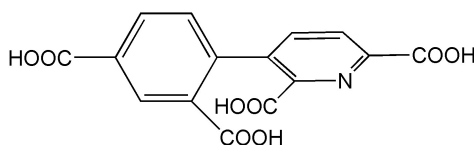
Abstract: A novel 2D $\{Co_3\}$ clusters coordination polymer, $[Co_3(Hdppd)_2(H_2O)_6]_n$ (**1**) based on 3-(2,4-dicarboxylatephenyl)-2,6-pyridinedicarboxylic acid ligand (H_4dppd) has been synthesized and characterized by IR spectra and X-ray single crystal diffraction method. The results show that trinuclear clusters $\{Co_3\}$ are formed in complex **1** which are connected into 2D layer structure by bridging $Hdppd^{3-}$ ligands; neighboring 2D layers are further linked into 3D supramolecular polymers by intermolecular hydrogen bonds. In addition, thermal stability and magnetic property of complex **1** were also studied.

Keywords: *Co(II) complex, crystal structure, magnetic property, N-heterocyclic polycarboxylic acid, thermal stability*

INTRODUCTION

In recent decades, the design and synthesis of multifunctional coordination polymers have attracted extensive attention in material chemistry due to its diverse structure, potential application prospects in luminescence [1] and magnetism [2] and other research fields. Choosing suitable organic ligand is an effective strategy to construct metal complexes with various structural characteristics and potential applications. Among all kinds of ligands, *N*-heterocyclic polycarboxylic acids play an important role in the construction of new complexes because they have rigid aromatic ring and multiple carboxyl coordination modes [3, 4]. Furthermore, additional carboxyl group can form more hydrogen bonds and construct a high-dimensional supramolecule [5].

3-(2,4-Dicarboxyphenyl)-2,6-pyridine dicarboxylic acid (H_4dppd) is a *N*-heterocyclic polycarboxylic acid ligand with one pyridine ring and four carboxylic groups (Scheme 1).



Scheme 1. Structural formula of 3-(2,4-dicarboxyphenyl)-2,6-pyridine dicarboxylic acid (H_4dppd)

The coordination mode and potential applications of metal complexes are also affected by metal centers. We are interested in the synthesis of Co(II) complex because the Co(II) ion can be coordinated by both O- and N-containing ligand in solution and some Co(II) complexes have potential applications as magnetic materials [6, 7].

In this article, we report the synthesis and characterization of a trinuclear Co(II) complex $[Co_3(Hdppd)_2(H_2O)_6]_n$ (**1**) with two-dimensional layered structure, and the two-dimensional layers are connected into a three-dimensional network structure by intermolecular hydrogen bonds. We have published a mononuclear Co(II) complex $(Co(H_2dppc)_2(H_2O)_2)$ based on a similar ligand 3-(2,4-dicarboxylate phenyl)-2-pyridinecarboxylic acid (H_3dppc) [8]. Compared with the reported Co(II) complex, complex **1** is a candidate as magnetic material due to the short Co-Co distance of $\{Co_3\}$ cluster. That is, different number of carboxylate group of the two similar ligands change their coordination modes with Co(II) and influence the magnetic property of the Co(II) complexes. Considering the $\{Co_3\}$ structure character of complex **1**, the thermal stability and magnetic property of the complex are also studied.

MATERIALS AND METHODS

Materials and characterization methods

IR spectrum was measured with a Nicolet FT-IR200 Fourier infrared spectrometer; TG curve was obtained with an Exstar 6000 analyzer from 30 to 900 °C at a heating rate of 10 °C·min⁻¹. The PXRD spectrum was recorded on a Bruker D8 Advance powder diffractometer with Cu-K α ($\lambda = 1.5418$ Å) radiation at room temperature. The crystal

structure was measured using a Bruker SMART APEX II CCD area detector diffractometer (MoK α , λ = 0.71073 Å). Using software Olex2 [9], the structure was solved with the SIR2004 [10] structure solution program using Direct Methods and refined with the ShelXL [11] refinement package using Least Squares minimization. The crystallographic data and structure refinement parameters of complex **1** have been given in Table 1. Variable-temperature magnetic measurement was carried out on a Quantum Design (Madison, WI, USA) SQUID MPMS XL-7 instrument. The magnetic susceptibility was measured from 2 to 300 K under a magnetic field of 2000 Oe.

Table 1. The crystallographic data and structure refinement parameters of complex **1**

Empirical formula	C ₃₀ H ₂₄ Co ₃ N ₂ O ₂₂
Formula weight	941.32
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, C2/c
Unit cell dimensions	a = 20.5240(16) Å alpha = 90° b = 8.8718(7) Å beta = 110.145(2)° c = 20.5194(16) Å gamma = 90°
Volume	3507.7(5) Å ³
Z, Calculated density	4, 1.779 mg·m ⁻³
Absorption coefficient	1.499 mm ⁻¹
F(000)	1892
Crystal size	0.18 x 0.20 x 0.21 mm
Theta range for data collection	3.05 to 25.09 °
Limiting indices	-24 ≤ h ≤ 22, 0 ≤ k ≤ 10, 0 ≤ l ≤ 24
Reflections collected / unique	3108 / 3108 [R(int) = 0.0000]
Completeness to theta = 25.09	99.4 %
Data / restraints / parameters	3108 / 142 / 291
Goodness-of-fit on F²	1.071
Final R indices [I > 2sigma(I)]	R ₁ = 0.0985, wR ₂ = 0.2158
R indices (all data)	R ₁ = 0.1184, wR ₂ = 0.2228
Largest diff. peak and hole	0.747 and -1.644 e.Å ⁻³

Synthesis procedure

A mixture of 0.1 mmol H₄dppd (0.033 g), 0.2 mmol Co(OAc)₂·4H₂O (0.044 g) and water (6.0 mL) were sealed in a 25 mL teflon-lined stainless steel vessel, reacted at 150 °C for 4320 min (3 days) and cooled to room temperature at a speed of 2 °C·h⁻¹. Purple block crystals of complex **1** were obtained after being filtered, washed with distilled water and dried in air. IR (KBr, cm⁻¹): 3385s, 2360m, 1600vs, 1576vs, 1472w, 1457w, 1400vs, 1367vs, 1260w, 696m.

RESULTS AND DISCUSSION

Crystal structure

The crystal structure of complex **1** is illustrated in Figure 1.

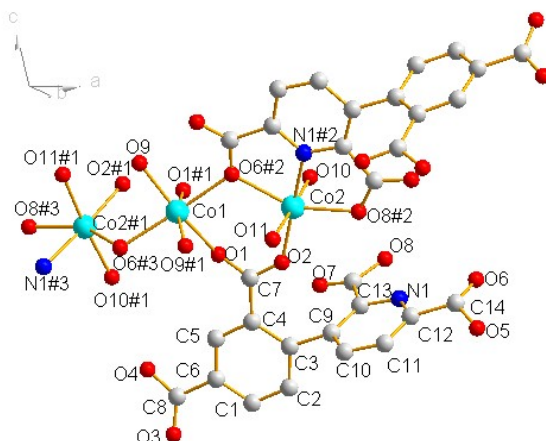


Figure 1. Coordinated environment of the trinuclear Co(II) complex (H atoms are omitted for clarity. #1 $-x, y, 0.5-z$; #2 $0.5-x, -0.5+y, 0.5-z$; #3 $-0.5+x, -0.5+y, z$)

The figure shows that there are two different Co(II) ions (Co1 and Co2) in complex **1**. Co1 features an asymmetric octahedral geometry coordinated by two carboxyl oxygen atoms (O6#2 and O6#3) from pyridine groups and two carboxyl oxygen atoms (O1 and O1#1) from phenyl groups of three different Hdppd³⁻ ligands, as well as two water molecules (O9 and O9#1). Co2 is coordinated by two carboxyl oxygen atoms (O6#2 and O8#2) and one nitrogen atom (N1#2) from pyridine group and one carboxyl oxygen atom (O2) from phenyl group of two different Hdppd³⁻ ligands, as well as two water molecules (O10 and O11) in a distorted octahedral geometry. It's worth noting that the Hdppd³⁻ ligands acting as bridges link three Co(II) ions into a trinuclear cluster {Co₃} (linked by O6#2 and o6#3 atoms) (Figure 1).

As a secondary construction unit, the adjacent trinuclear clusters {Co₃} are connected into two-dimensional layer structure by pentadentate Hdppd³⁻ ligand in double-(bridging) and chelated coordination modes, as shown in Figure 2. Due to the presence of additional carboxyl groups, the two-dimensional layers are further expanded into a three-dimensional supramolecular network through intermolecular hydrogen bonds (Figure 3).

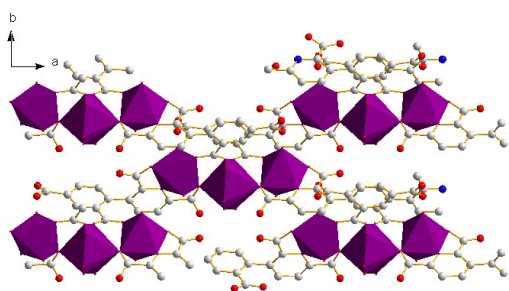


Figure 2. The 2D layer structure of complex **1** formed by {Co₃} clusters

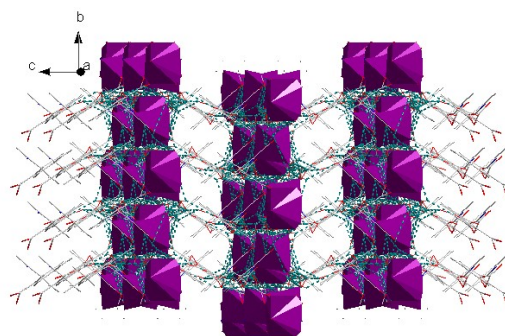


Figure 3. The 3D supramolecular structure of complex **1** linked by H bonds

IR and PXRD spectra

The IR spectrum of the complex was measured in the range of 4000-450 cm^{-1} (Figure 4). A wide absorption band appeared at 3385 cm^{-1} was mainly caused by the stretching vibration of the O-H bond involved in the coordinated carboxyl groups and water. The strong and sharp absorption peak near 1616 cm^{-1} is caused by the stretching vibration of C=O bond, indicating the existence of carboxyl group. The peak at 1567 cm^{-1} is the asymmetric stretching vibration of carboxyl group in the complex, and the peak at 1397 cm^{-1} is the symmetrical stretching vibration of carboxyl group. The purity of the complex was analyzed by X-ray diffraction method, and the simulated and experimental spectra are shown in Figure 5.

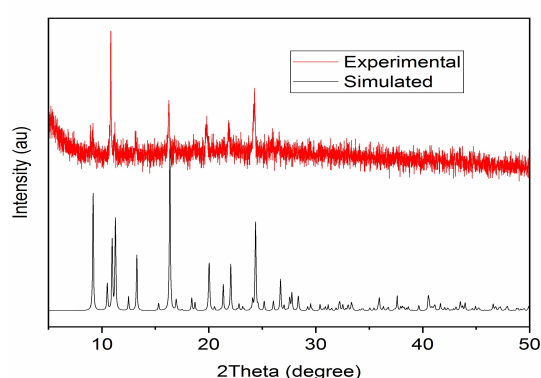
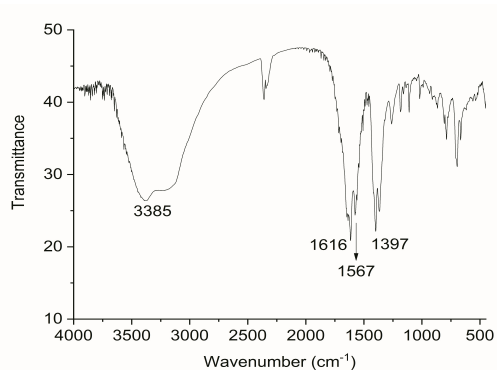


Figure 4. The IR spectra of complex **1** **Figure 5.** The PXRD spectra of complex **1**

Figure 5 indicates that there are obvious peaks at 9.2, 11.2, 13.3, 20.0, 21.9 and 24.2° in the experimental pattern of complex **1**, which are consistent with those in the simulated PXRD patterns, illustrating the high purity of the complex.

Thermal properties

In order to study the thermal stability of the complex, TG experiment was carried out and the result is shown in Figure 6.

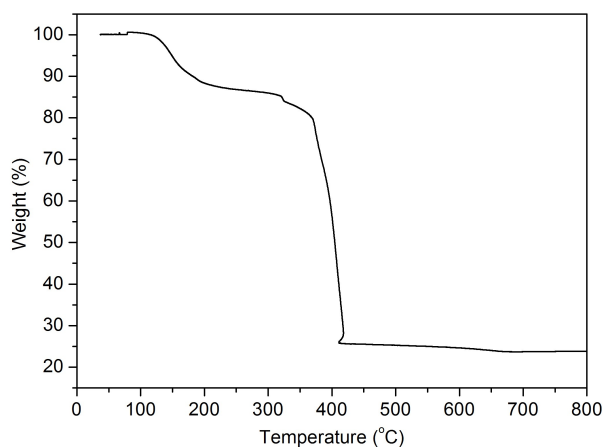


Figure 6. TG curves of the complex

The figure shows that the complex is stable from room temperature to 100 °C. The complex shows an obvious weight loss (11.7 %) from 100 to 198.2 °C which is attributed to the loss of six coordinated water molecules (calcd. 11.5 %). There is a sharp weight loss from 317 to 418 °C indicating the decomposition of organic ligand. The residue may be CoO who account for 23.8 % (calcd. 23.9 %).

Magnetic property

The magnetic property of the complex is studied and the curve is shown in Figure 7.

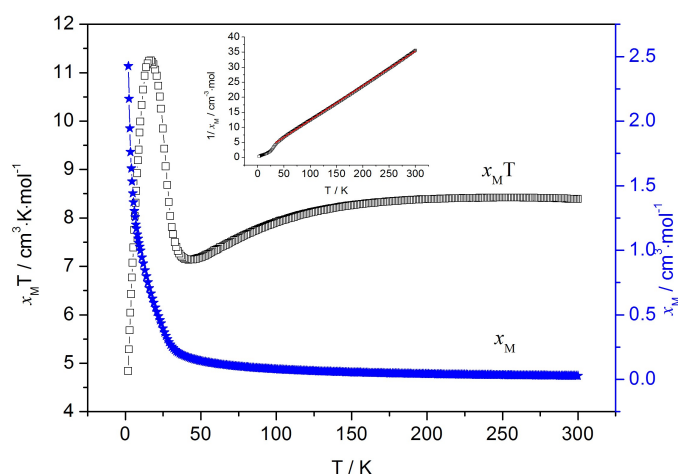


Figure 7. Magnetic curves of the complex

The figure shows that the magnetic susceptibility (χ_M) gradually reduced with the increase of temperature, especially in the temperature range of 0-33 K. The $\chi_M T$ of complex 1 at room temperature is $8.38 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$. The value is obviously larger than that expected for three uncoupled Co(II) ions ($5.61 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$), which may be caused by the strong orbital contribution [12]. Upon cooling, the $\chi_M T$ curve shows a plateau from 300-160 K and then decreases slowly until 40 K, indicating the weak antiferromagnetic coupling trend at higher temperature range. Below 38 K, the $\chi_M T$ curve rises sharply, shows a large value of $11.2 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ at 17 K, and decreases steeply down to $4.83 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ at 2 K. The $\chi_M T$ curve indicates the magnetic phase transition at lower temperature range [13].

The magnetic susceptibility curve in the temperature range of 40-300 K conforms to Curie-Weiss law ($1/\chi_M = (T-\theta) / C$) with Weiss constant $\theta = -8.85 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$, $C = 0.114 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ and $R = 3.68 \times 10^{-4}$. The negative θ value and the decrease of $\chi_M T$ with increasing temperature indicate the weak antiferromagnetic interactions of the complex during higher temperature range [14].

CONCLUSION

We have synthesized and characterized a Co(II) coordination polymer containing $\{\text{Co}_3\}$ clusters. Deprotonated Hdppd³⁻ ligands connect neighboring $\{\text{Co}_3\}$ clusters to form 2D layer structure, which are further linked into 3D supramolecular structure by hydrogen

bonds. The variable temperature magnetic experiment indicates that there are weak antiferromagnetic interactions between the bridging trinuclear Co(II) ions of {Co₃} cluster.

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REFERENCES

1. Badiane, A.M., Freslon, S., Daiguebonne, C., Suffren, Y., Bernot, K., Calvez, G., Costuas, K., Camara, M., Guillou, O.: Lanthanide-based coordination polymers with a 4,5-dichlorophthalate ligand exhibiting highly tunable luminescence: toward luminescent bar codes, *Inorganic Chemistry*, **2018**, 57 (6), 3399-3410;
2. Li, S., Lu, L., Zhu, M., Feng, S., Su, F., Zhao, X.: Exploring the syntheses, structures, topologies, luminescence sensing and magnetism of Zn (II) and Mn (II) coordination polymers based on a semirigid tricarboxylate ligand, *CrystEngComm*, **2018**, 20 (36), 5442-5456;
3. Feng, Y.-F., Tang, Q., Luo, K.-L., Wu, J.-Q., Zhang, Z., Liang, Y.-N., Liang, F.-P.: Controllable assembly of Cu (ii) coordination compounds based on a flexible zwitterionic benzimidazole–dicarboxylate ligand: synthesis, structural diversity, reversible SCSC transformation and magnetic properties, *CrystEngComm*, **2017**, 19 (36), 5442-5459;
4. Feng, X., Feng, Y.-Q., Liu, L., Wang, L.-Y., Song, H.-L., Ng, S.-W.: A series of Zn-4f heterometallic coordination polymers and a zinc complex containing a flexible mixed donor dicarboxylate ligand, *Dalton Transactions*, **2013**, 42 (21), 7741-7754;
5. Etaiw, S.E.D.H., El-bendary, M.M.: Hydrogen bonded 3D-network of silver and 2, 6-pyridinedicarboxylic acid complex: Structure and applications, *Journal of Molecular Structure*, **2018**, 1173, 7-16;
6. Valigura, D., Rajnák, C., Moncol, J., Titiš, J., Boča, R.: A mononuclear Co (II) complex formed from pyridinedimethanol with manifold slow relaxation channels, *Dalton Transactions*, **2017**, 46 (33), 10950-10956;
7. Li, J., Han, Y., Cao, F., Wei, R.M., Zhang, Y.Q., Song, Y.: Two field-induced slow magnetic relaxation processes in a mononuclear Co(II) complex with a distorted octahedral geometry, *Dalton Transactions*, **2016**, 45 (22), 9279-9284;
8. Liu, X., Du, L., Zhang, W., Li, R., Feng, F., Feng, X.: Syntheses, structures and hirshfeld surface analyses of two 3D supramolecules based on nitrogen-heterocyclic tricarboxylate ligand, *Journal of Molecular Structure*, **2019**, 1194, 138-143;
9. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J., Howard, J.A.K., Puschmann, H.: OLEX2: a complete structure solution, refinement and analysis program, *Journal of Applied Crystallography*, **2009**, 42, 339-341;
10. Sheldrick, G.M.: SHELXT – Integrated space-group and crystal-structure determination, *Acta Crystallographica Section A: Foundations and Advances*, **2015**, 71, 3-8;
11. Sheldrick, G.M.: Crystal structure refinement with SHELXL, *Acta Crystallographica Section C: Structural Chemistry*, **2015**, 71, 3-8;
12. Wang, X.-F., Zhang, Y.-B., Xue, W., Qi, X.-L., Chen, X.-M.: Two temperature-induced isomers of metal-carboxylate frameworks based on different linear trinuclear Co₃(RCOO)₈ clusters exhibiting different magnetic behaviours, *CrystEngComm*, **2010**, 12 (11), 3834-3839;

13. Huang, W.-J., Hsu, C.-J., Tsai, S.-K., He, H.-Y., Ding, J.-J., Hsu, T.-W., Yang, C.-C., Chen, J.-D.: Homo- and heterometallic coordination networks based on linear trinuclear Co(II) units: syntheses, structures and magnetic properties, *RSC Advances*, **2015**, 5 (30), 23374-23382;
14. Han, M.-L., Wu, H.-X., Zhao, K.-Y., Zhang, Z.-Q.: Two new metal-organic frameworks based on 5-bromoisophthalic acid and 1,3-bis(4-pyridyl)propane: hydrothermal syntheses, structures, and magnetic properties, *Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry*, **2012**, 42 (4), 590-595.