

Synthesis, Crystal Structure and Magnetic Properties of 1D Coordination Polymer $\{[\text{Co}(\text{cpna})(\text{H}_2\text{biim})]\cdot\text{H}_2\text{O}\}_n$

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A coordination polymer, namely $\{[\text{Co}(\text{cpna})(\text{H}_2\text{biim})]\cdot\text{H}_2\text{O}\}_n$ (**1**) has been constructed hydrothermally using H_2cpna [H_2cpna = 5-(2'-carboxylphenyl)nicotic acid], H_2biim (H_2biim = 2,2'-biimidazole) and $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$. The compound crystallizes in the triclinic system, space group P-1 with $a = 7.8002$ (5) Å, $b = 10.5401$ (13) Å, $c = 12.6954$ (10) Å, $\alpha = 66.519$ (10), $\beta = 74.768$ (6), $\gamma = 84.428$ (7)°, $V = 923.66$ (15) Å³, $D_c = 1.626$ g cm⁻³, $Z = 2$, $R = 0.0456$ and $wR = 0.1032$ ($I > 2\sigma(I)$). The cpna^{2-} ligands bridge the adjacent Co(II) ions to form a 1D double-chain, which is further assembled into a 3D supramolecular framework by N-H...O hydrogen bonding and π - π stacking interactions. Magnetic susceptibility measurement indicates $\{[\text{Co}(\text{cpna})(\text{H}_2\text{biim})]\cdot\text{H}_2\text{O}\}_n$ shows a weak antiferromagnetic coupling between the Co(II) ions. CCDC: 952137.

Keywords: Coordination polymer, Cobalt(II) compound, Magnetic properties.

INTRODUCTION

Recently, supramolecular chemistry has become an exciting research field owing to the creation of various intriguing structural topologies as well as their potential applications in the area of catalysis, gas storage, separation, magnetism and luminescence¹⁻⁵. The self-assembly of a supramolecular coordination polymer is the result of a combination of various forces, including not only strong interactions (for example metal-ligand coordination bonds) but also weaker interactions such as hydrogen bonds and π - π stacking interactions⁶⁻⁸. According to previous studies, organic ligands play a crucial role in directing the final structures and properties⁴⁻⁸. Many multicarboxylate or heterocyclic carboxylic acids have been used for this purpose⁴⁻¹⁰. In order to extend our research in this field, we have selected 5-(2'-carboxylphenyl) nicotic acid (H_2cpna) as a functional building block on account of the following considerations: (a) H_2cpna possesses two carboxyl groups that may be completely or partially deprotonated, depending on the pH; (b) it is a flexible ligand allowing the rotation of the C-C single bond between pyridyl and phenyl rings^{11,12}.

We herein report the synthesis, crystal structure, magnetic properties of Co(II) compound with cpna^{2-} ligand.

EXPERIMENTAL

All chemicals and solvents were of A.R. grade and used without further purification. Carbon, hydrogen and nitrogen

were determined using an Elementar Vario EL elemental analyzer. IR spectra were recorded using KBr pellets and a Bruker EQUINOX 55 spectrometer. Thermogravimetric analysis (TG) data were collected on a LINSEIS STA PT1600 thermal analyzer with a heating rate of 10 °C min⁻¹. Powder X-ray diffraction patterns (PXRD) were determined with a Rigaku-Dmax 2400 diffractometer using $\text{CuK}\alpha$ radiation. Magnetic susceptibility data were collected in the 2-300 K temperature range with a Quantum Design SQUID Magnetometer MPMS XL-7 with a field of 0.1 T. A correction was made for the diamagnetic contribution prior to data analysis.

Synthesis: A mixture of $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$ (0.071 g, 0.3 mmol), H_2cpna (0.073 g, 0.3 mmol), H_2biim (0.040 g, 0.3 mmol), NaOH (0.012 g, 0.3 mmol) and H_2O (10 mL) was stirred at room temperature for 15 min and then sealed in a 25 mL Teflon-lined stainless steel vessel and heated at 160 °C for 3 days, followed by cooling to room temperature at a rate of 10 °C h⁻¹. Pink block-shaped crystals of $\{[\text{Co}(\text{cpna})(\text{H}_2\text{biim})]\cdot\text{H}_2\text{O}\}_n$ were isolated manually and washed with distilled water. Yield: 75 % (based on Co). Anal. calcd. for $\text{C}_{19}\text{H}_{15}\text{N}_5\text{O}_5\text{Co}$ (%): C 50.46, H 3.34, N 15.48; found: C 51.31, H 3.05, N 15.37. IR (KBr, ν_{max} , cm⁻¹): 3453 m, 1617 s, 1567 s, 1430 s, 1389 s, 1320 m, 1130 m, 781 m, 762 m, 700 m. The compound is insoluble in water and common organic solvents, such as methanol, ethanol, acetone and DMF.

Structure determinations: Single-crystal data of **1** were collected at 293 (2) K on a Bruker Smart Apex 1000 CCD

diffractometer with MoK α radiation ($\lambda = 0.71073 \text{ \AA}$). A summary of the crystallography data and structure refinement is given in Table-1 and selected bond lengths and angles of the compound **1** are listed in Table-2. The structure was solved using direct methods, which yielded the positions of all non-hydrogen atoms. These were refined first isotropically and then anisotropically. All the hydrogen atoms were placed in calculated positions with fixed isotropic thermal parameters and included in structure factor calculations in the final stage of full-matrix least-squares refinement. All calculations were performed using the SHELXTL-97 system¹³.

TABLE-1
CRYSTAL DATA FOR COMPOUND **1**

Compound	1
Chemical formula	C ₁₉ H ₁₅ N ₅ O ₅ Co
Molecular weight	452.29
Crystal system	Triclinic
Space group	P-1
a/ \AA	7.8002 (5)
b/ \AA	10.5401 (13)
c/ \AA	12.6954 (10)
α ($^\circ$)	66.519 (10)
β ($^\circ$)	74.768 (6)
γ ($^\circ$)	84.428 (7)
V/nm ³	0.92366(15)
Z	2
F (000)	462
Crystal size/mm	0.25 \times 0.25 \times 0.18
θ range for data collection	3.13-25.05
Limiting indices	-9 \leq h \leq 7, -12 \leq k \leq 12, -15 \leq l \leq 14
Reflections collected/unique (R _{int})	5537 / 3266 (0.0355)
D _c /(Mg cm ⁻³)	1.626
μ /mm ⁻¹	0.974
Data/restraints/parameters	3266 / 0 / 274
Goodness-of-fit on F ²	1.087
Final R indices [I \geq 2 σ (I)] R ₁ , ω R ₂	0.0456, 0.1032
R indices (all data) R ₁ , ω R ₂	0.0577, 0.1138
Largest diff. peak and hole/(e \AA^{-3})	0.560 and -0.418

RESULTS AND DISCUSSION

Description of the structure: As shown in Fig. 1, the asymmetric unit of compound **1** contains one crystallographically unique Co(II) atom, one cpna²⁻ ligand, one chelating H₂biim moiety and one lattice water molecule. The Co(II) ion is six-coordinated by two N atoms of the H₂biim ligand, three carboxylate O and one N atoms from three different cpna²⁻ moieties, resulting in a distorted octahedral geometry. The Co-O and Co-N bonds span the range of 2.021(2) - 2.286(2) and 2.107(3) - 2.172(3) \AA , which are in good agreement with those distances observed in some other Co(II) compounds^{4,8,11}.

TABLE-2
SELECTED BOND DISTANCES (\AA) AND BOND ANGLES ($^\circ$) FOR COMPOUND **1**

Co(1)-O(1)I	0.2286(2) (2)	Co(1)-O(2)I	0.2152(2)	Co(1)-O(3)II	0.2021(2)
Co(1)-N(1)	0.2107(3)	Co(1)-N(2)	0.2172(3)	Co(1)-N(4)	0.2166(3)
O(3)II-Co(1)-N(1)	94.84(11)	O(3)II-Co(1)-O(2)I	105.89(10)	N(1)-Co(1)-O(2)I	94.37(10)
O(3)II-Co(1)-N(4)	87.48(10)	N(1)-Co(1)-N(4)	93.92(10)	O(2)I-Co(1)-N(4)	163.59(10)
O(3)II-Co(1)-N(2)	160.88(10)	N(1)-Co(1)-N(2)	97.77(11)	O(2)I-Co(1)-N(2)	87.46(10)
N(4)-Co(1)-N(2)	77.40(11)	O(3)II-Co(1)-O(1)I	89.82(10)	N(1)-Co(1)-O(1)I	153.43(10)
O(2)I-Co(1)-O(1)I	59.29(8)	N(4)-Co(1)-O(1)I	112.43(9)	N(2)-Co(1)-O(1)I	85.30(10)

Symmetry transformations used to generate equivalent atoms: I: x+1, y, z; II: -x+1, -y+2, -z+1.

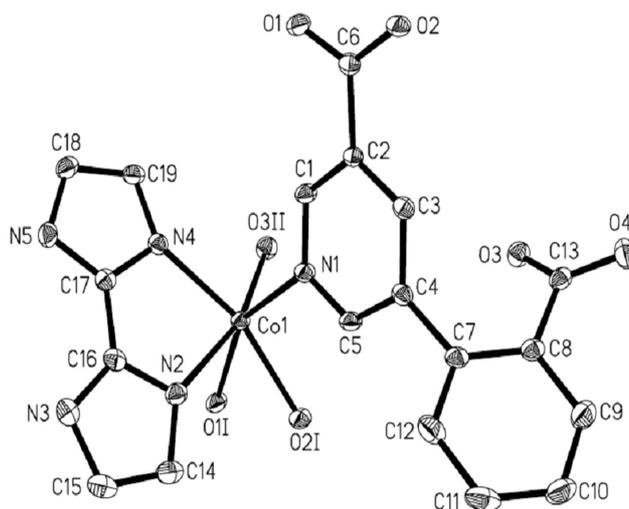


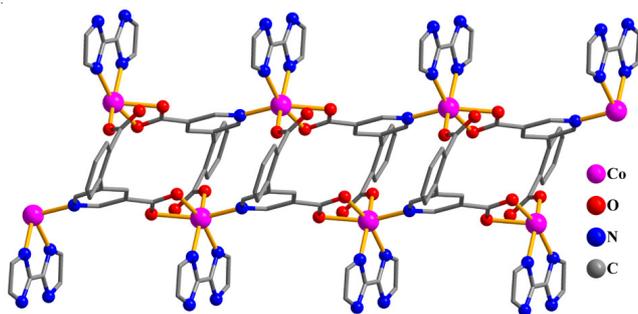
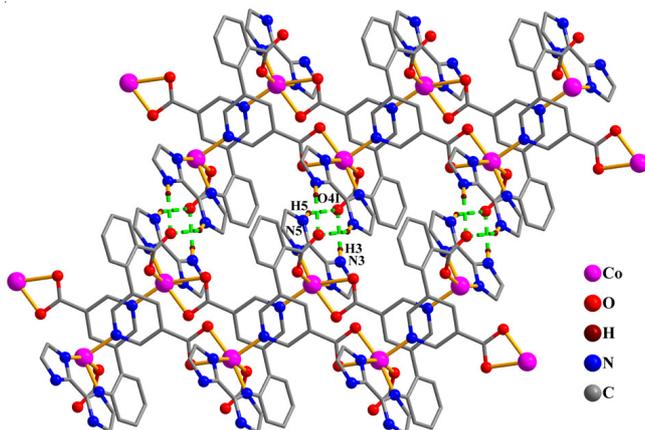
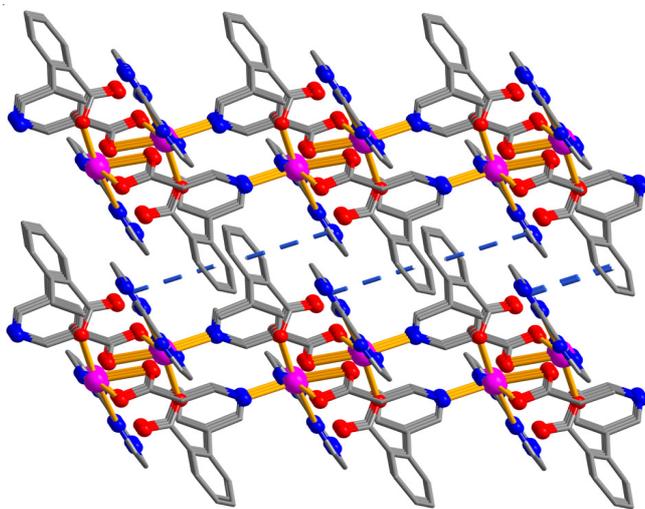
Fig. 1. Drawing of the asymmetric unit of compound **1** (H atoms and lattice water molecule were omitted for clarity, symmetry codes: I: x + 1, y, z; II: -x + 1, -y + 2, -z + 1)

As illustrated in Fig. 2, the cpna²⁻ ligands bridge the adjacent Co(II) ions to form a 1D double-chain along the b axis. The cpna²⁻ ligand adopts a μ_3 -coordination mode, in which two deprotonated carboxylate groups show the μ_1 - η^1 : η^1 bidentate and μ^1 - η^1 : η^0 monodentate modes. The dihedral angle of the pyridyl and phenyl rings in the cpna²⁻ is 59.66°. Interestingly, the chain can be viewed as a series of alternating grids containing a 16-membered ring (Co₂N₂C₁₀O₂) and a 18-membered ring (Co₂O₂C₁₄), respectively. Within the (Co₂N₂C₁₀O₂) ring, the distance between the two Co(II) atoms is 6.424 \AA , while in the (Co₂O₂C₁₄) ring, the Co...Co distance is 6.959 \AA . Adjacent chains are connected to a 2D sheet through interchain N-H...O hydrogen bonding interactions (Fig. 3 and Table-3). The sheets are further assembled into a 3D supramolecular framework via π - π stacking interactions between adjacent phenyl plane of the cpna²⁻ ligand and imidazole plane of the H₂biim moiety with the centroid-centroid separation of 3.792 \AA (Fig. 4).

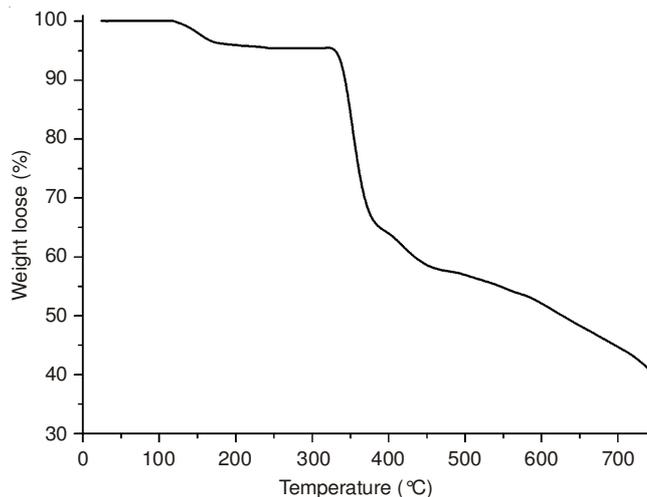
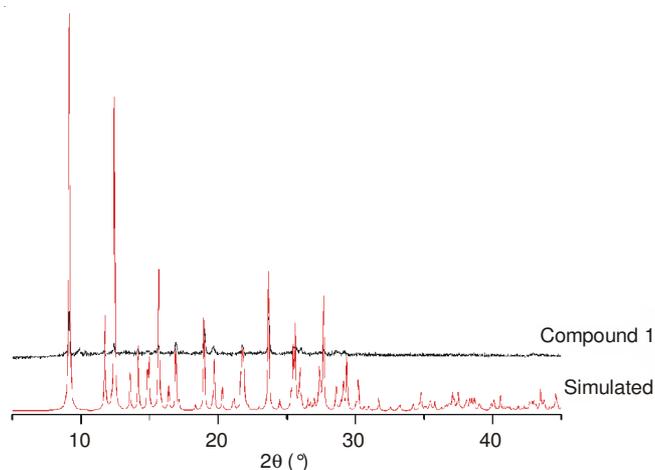
TABLE-3
HYDROGEN BOND LENGTHS (\AA)
AND ANGLES ($^\circ$) OF COMPLEX **1**

D-H...A	D-H	H...A	D...A	\angle DHA
O(5)-H(2W)...O(1)II	0.085	0.223	0.3014	153.9
N(3)-H(3)...O(4)I	0.086	0.209	0.2841	145.5
N(5)-H(5)...O(4)I	0.086	0.207	0.2834	148.1

Symmetry code: I: x + 1, y, z - 1; II: x, y - 1, z

Fig. 2. View of the 1D double chain structure of complex **1** along b axisFig. 3. 2D structure formed by N-H...O hydrogen bond interactions in the adjacent chains in **1** (green dashed lines present the N-H...O hydrogen bond interactions, symmetry code: I: $x + 1, y, z - 1$)Fig. 4. 3D supramolecular framework formed by π - π stacking interactions in the neighbouring sheets in **1** (blue dashed lines present the π - π stacking interactions)

TG analysis and powder XRD results: To study the stability of compound **1**, its thermal behavior was investigated under nitrogen atmosphere by TGA. As shown in Fig. 5, compound **1** loses its one lattice water molecule (exptl, 3.85 %; calcd., 3.98 %) in the 105-180 °C range, followed by the decomposition at 325 °C. Powder X-ray diffraction experiment was carried out for compound **1**. The pattern for the as-synthesized bulk material closely matches the simulated one from the single-crystal structure analysis, thus confirming the purity of bulk sample (Fig. 6).

Fig. 5. TG plot of compound **1**Fig. 6. Powder XRD pattern of compound **1** at room temperature

Magnetic properties: Variable-temperature magnetic susceptibility measurement was performed on powder samples of compound **1** in the 2-300 K temperature range (Fig. 7). As shown in Fig. 7, the $\chi_M T$ value at room temperature is $3.19 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$, which is larger than that ($1.87 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$) expected for one magnetically isolated high-spin Co(II) ion with the $S = 3/2$, revealing a significant orbital contribution as also found in other high spin Co compounds^{14,15}. The monotonic decrease of $\chi_M T$ upon cooling the temperature is indicative of the dominant antiferromagnetic interaction. In the 150-300 K temperature range, the magnetic susceptibility obeys the Curie-Weiss law, $\chi_M = C_M / (T - \theta)$, with $\theta = -11 \text{ K}$ and $C_M = 3.27 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$. The negative θ value indicates the presence of the dominant antiferromagnetic interactions between the adjacent Co(II) centers. We tried to fit the magnetic data of **1** using the following expression¹⁶ for a 1D Co(II) chain: $\chi_{\text{chain}} = (\text{Ng}^2\beta^2/kT)[2 + 0.0194x + 0.777x^2] \times [3 + 4.346x + 3.232x^2 + 5.834x^3]^{-1}$, $x = |J|/kT$. By using this rough model, the susceptibilities of **1** above 100 K were simulated, leading to $J = -5.52 \text{ cm}^{-1}$, $g = 2.35$ and the agreement factor $R = 3.89 \times 10^{-5}$ ($R = \sum(\chi_{\text{obs}} T - \chi_{\text{calc}} T)^2 / \sum(\chi_{\text{obs}} T)^2$). A rather low J parameter indicates that an extremely weak antiferromagnetic exchange coupling exists between the adjacent Co(II) centers, which is in agreement with a negative θ value.

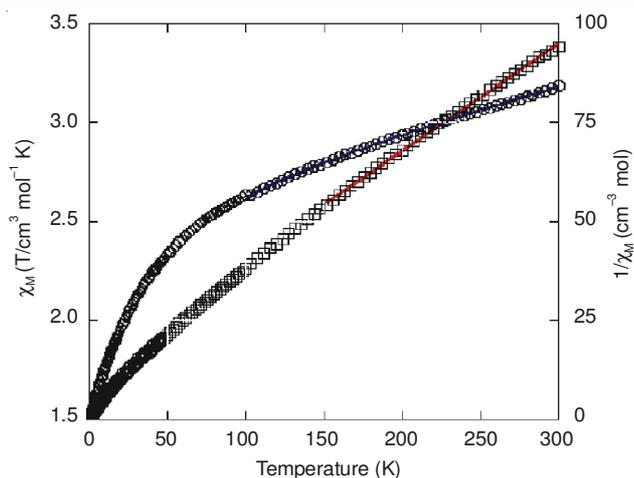


Fig. 7. Temperature dependence of $\chi_M T$ (O) and $1/\chi_M(\theta)$ vs. T for compound **1**. The blue lines represent the best fit to the equations in the text. The red lines show the Curie-Weiss fitting.

Conclusion

In conclusion, we have successfully synthesized and characterized the 1D cobalt coordination polymer ($\{[\text{Co}(\text{cpna})(\text{H}_2\text{biim})]\cdot\text{H}_2\text{O}\}_n$ (**1**)). Magnetic susceptibility measurement indicates that compound **1** shows a weak antiferromagnetic coupling between the Co(II) ions.

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REFERENCES

1. X.D. Zheng and T.B. Lu, *CrystEngComm.*, **12**, 324 (2010).
2. J.R. Li, R.J. Kuppler and H.C. Zhou, *Chem. Soc. Rev.*, **38**, 1477 (2009).
3. Q. Chen, W. Xue, J.B. Lin, R.B. Lin, M.H. Zeng and X.M. Chen, *Dalton Trans.*, **41**, 4199 (2012).
4. Y. Lu, W. Zhao, Y. Liu, B. Liu, X. Feng, J. Tan, X. Li and X. Yang, *J. Solid State Chem.*, **192**, 144 (2012).
5. Y.X. Hu, W.W. Zhang, L.F. Wang and J.F. Bai, *Chinese J. Inorg. Chem.*, **29**, 1471 (2013).
6. J.Z. Gu, D.Y. Lv, Z.Q. Gao, J.Z. Liu and W. Dou, *Transition Met. Chem.*, **36**, 53 (2011).
7. J.Z. Gu, D.Y. Lv, Z.Q. Gao, J.Z. Liu, W. Dou and Y. Tang, *J. Solid State Chem.*, **184**, 675 (2011).
8. S.-Q. Zang, Y.-J. Fan, J.-B. Li, H.-W. Hou and T.C.W. Mak, *Cryst. Growth Des.*, **11**, 3395 (2011).
9. W.G. Lu, J.Z. Gu, L. Jiang, M.Y. Tan and T.B. Lu, *Cryst. Growth Des.*, **8**, 192 (2008).
10. P.K. Yadav, N. Kumari, P. Pachfule, R. Banerjee and L. Mishra, *Cryst. Growth Des.*, **12**, 5311 (2012).
11. J.Z. Gu, Z.Q. Gao and Y. Tang, *Cryst. Growth Des.*, **12**, 3312 (2012).
12. J.Z. Gu, J. Wu, D.Y. Lv, Y. Tang, K.Y. Zhu and J.C. Wu, *Dalton Trans.*, **42**, 4822 (2013).
13. G.M. Sheldrick, SHELXL NT Version 5.1, Program for Solution and Refinement of Crystal Structures, University of Göttingen, Germany (1997).
14. M. Kurmoo, *Chem. Soc. Rev.*, **38**, 1353 (2009).
15. Z. Chen, Y. Li, C. Jiang, F.P. Liang and Y. Song, *Dalton Trans.*, **5290** (2009).
16. O. Kahn, *Molecular Magnetism*; VCH Publishers Inc., New York, p. 258 (1993).