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Synthesis, Crystal Structure, and Magnetic Properties of Binuclear Cobalt(II) Complex with 2-(5-{6-[5-(Pyrazin-2-yl)-1*H*-1,2,4-Triazol-3-yl]-Pyridin-2-yl}-1*H*-1,2,4-Triazol-3-yl)pyrazine[1]

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Abstract—The synthesis and crystal structure of a new Co(II) compound with 2-(5-{6-[5-(pyrazin-2-yl)-1*H*-1,2,4-triazol-3-yl]-pyridin-2-yl}-1*H*-1,2,4-triazol-3-yl)pyrazine (H_2Ptptp) are reported. The new compound $[Co_2(Ptptp)Cl_2(H_2O)_2] \cdot H_2O$ (**I**) has been determined by single-crystal X-ray diffraction (CIF file CCDC no. 1010785) and characterized by elemental analyses and infrared spectrum. The structure **I** consists of two independent Co^{2+} ions, one $Ptptp^{2-}$ anion, two Cl^- anions, two coordinated H_2O molecules and one lattice H_2O molecule. The three-dimensional (3D) supramolecular architecture is formed through the hydrogen bonds among adjacent units. Moreover, magnetic susceptibility measurements indicate that the compound exhibits weak antiferromagnetic coupling interaction.

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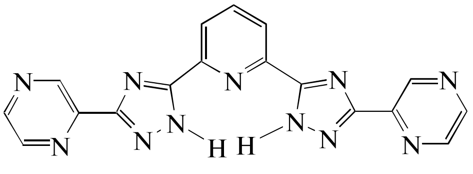
INTRODUCTION

In the past decades, the studies on intriguing structures and potential applications of functional coordination polymers made significant achievements. It improved the development of magnetism, photochemical areas, ion exchange, catalysis and porous materials [1–7].

The 1,2,4-triazole compounds are considered as an interesting heterocycles because of their effective biological importances and applications [8, 9]. Its derivatives constitute an interesting type of ligands, which can be coordinated to a metal atom in different ways, depending on the position and the nature of the substituent [10]. A part of the complexes containing 1,2,4-triazole ligands possess rather peculiar structures and specific magnetic properties [11, 12]. The ligands can adopt multiple coordination modes, such as bidentate, tridentate or tetradentate, to meet the different requirements on the metal centers' coordination [13, 14]. The 1,2,4-triazole and its pyrazine derivatives have many advantages: (i) strong coordination ability; (ii) more coordination points and more patterns; (iii) can be bridging in various ways with metal ions and other bridging ligand; (iv) widely used in the construction of the functional complexes. Heterocyclic H_2Ptptp can rotate around the central C–C bond and adopt different conformations, no matter which conformation it adopts, H_2Ptptp will provide potential tridentate and bidentate binding sites [15].

In this study, a new compound $[Co_2(Ptptp)Cl_2(H_2O)_2 \cdot H_2O$ (**I**) has been prepared by hydrothermal synthesis. 2-(5-{6-[5-(Pyrazin-2-yl)-1*H*-1,2,4-triazol-3-yl]-pyridin-2-yl}-1*H*-1,2,4-triazol-3-yl)pyrazine (H_2Ptptp) was selected as ligand for the synthesis of the new compound. It has been well characterized by elemental analysis, infrared spectroscopy, X-ray single crystal diffraction and variable-temperature magnetic susceptibility.


H_2Ptptp

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EXPERIMENTAL

Materials and physical measurements. H_2Ptptp was purchased from Jinan Camolai Trading Company. Tetrahydrofuran was commercially available from Ainopharm Chemical Reagent Co., Ltd. All starting materials were of analytical grade and were used without further purification.

The IR spectra were recorded as KBr pellets on a Bruker Vectorm 22 spectrometer in the range of 4000 to 400 cm^{-1}. Elemental analyses for C, H, and N were obtained on a Vario EL III elemental analyzer. Variable-temperature magnetic susceptibility measurements (2–300 K) were carried out on a Quantum Design PPMS60000 in a magnetic field of 2000 Oe, and the diamagnetic corrections were evaluated by using Pascal's constants.

Synthesis of I. A mixture of $CoCl_2 \cdot 6H_2O$ (0.0476 g, 0.2 mmol), H_2Ptptp (0.0369 g, 0.1 mmol), 6 mL tetrahydrofuran and 2 mL H_2O was sealed in a 25 mL Teflon-lined autoclave and heated at 160°C for 3 days, and then cooled at a rate of 2°C min^{-1} to room temperature. Black block crystals were obtained. The yield was 40%.

For $C_{17}H_{15}N_{11}O_3Cl_2Co_2$

anal. calcd., %:	C, 33.46;	H, 2.48;	N, 25.25.
Found, %:	C, 33.47;	H, 2.85;	N, 25.91.

IR for complex **I** (KBr; ν, cm^{-1}): 3386 m, 3063 w, 1615 w, 1568 m, 1517 m, 1434 s, 1285 w, 1149 m, 1033 m, 866 w, 798 w, 670 w.

X-ray crystallography. Diffraction intensities for complex **I** were collected on a Bruker Smart APEX II CCD diffractometer equipped with graphite-monochromated MoK_α radiation ($\lambda = 0.71073$ Å) by using the φ–ω scan technique at room temperature. Absorption corrections were based on symmetry equivalent reflections using the SADABS program. The crystal structure was solved by direct methods with program SHELXL-97 and followed by successive Fourier and difference Fourier syntheses and refined by full-matrix least-squares on F^2 [16]. Non-hydrogen atoms were refined anisotropically. The hydrogen atoms on carbon atoms were generated geometrically. Experimental details of the X-ray analyses are provided in Table 1. The selected bond lengths and bond angles are listed in Table 2.

Supplementary material for structure **I** has been deposited with the Cambridge Crystallographic Data Centre (CCDC no. 1010785; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The crystallographic analysis of **I** presents that each unit consists of two independent Co^{2+} ions, one Ptptp^{2-} anion, two Cl^- anions, two coordinated H_2O molecules and one lattice H_2O molecule. As exhibited in Fig. 1, the coordination geometries of Co(1) and Co(2) in the crystallographically unique unit are slightly different. The Co(1) center is five-coordinated with geometry of distorted trigonal bipyramid by coor-

Table 1. Crystallographic data and experimental details for structure **I**

Parameter	Value
Formula weight	610.16
Crystal system	Monoclinic
Space group	$C2/c$
a, Å	10.5833(18)
b, Å	13.4832(18)
c, Å	15.740(2)
β, deg	95.644(4)
V, Å^3	2235.2(6)
T, K	296(2)
Z	4
ρ_{calcd}, mg m^{-3}	1.813
μ, mm^{-1}	1.771
F(000)	1224
Crystal size, mm	0.30 × 0.27 × 0.24
θ Range, deg	2.45–25.00
Reflections collected/unique	5484/1970
R_{int}	0.0540
R indices ($I > 2\sigma(I)$)	$R_1 = 0.0636$ $wR_2 = 0.1501$
R indices (all data)	$R_1 = 0.1097$ $wR_2 = 0.1771$
GOOF on F^2	1.029
Largest diff. peak and hole, e/Å^3	1.275 and –1.083

Table 2. Selected bond distances (Å) and angles (deg) for **I***

Bond	d, Å	Bond	d, Å
Co(1)–N(1)	2.031(8)	Co(2)–N(4)	2.045(5)
Co(1)–N(2)	2.216(5)	Co(2)–N(5)	2.144(5)
Co(1)–Cl(1)	2.247(3)	Co(2)–O(1w)	2.189(5)
Angle	**ω, deg**	**Angle**	**ω, deg**
N(1)Co(1)N(2)	77.58(15)	Cl(1)$^{\#1}$Co(1)Cl(1)	122.2(3)
N(2)$^{\#1}$Co(1)N(2)	155.2(3)	N(4)Co(2)N(5)	78.1(2)
N(1)Co(1)Cl(1)	118.88(15)	N(5)Co(2)O(1w)	91.5(2)
N(2)Co(1)Cl(1)	95.16(16)	N(4)Co(2)O(1w)	89.0(2)
N(2)Co(1)Cl(1)$^{\#1}$	96.77(15)		

* Symmetry operations: $^{\#1}$ $-x + 1, y, -z + 1/2$.

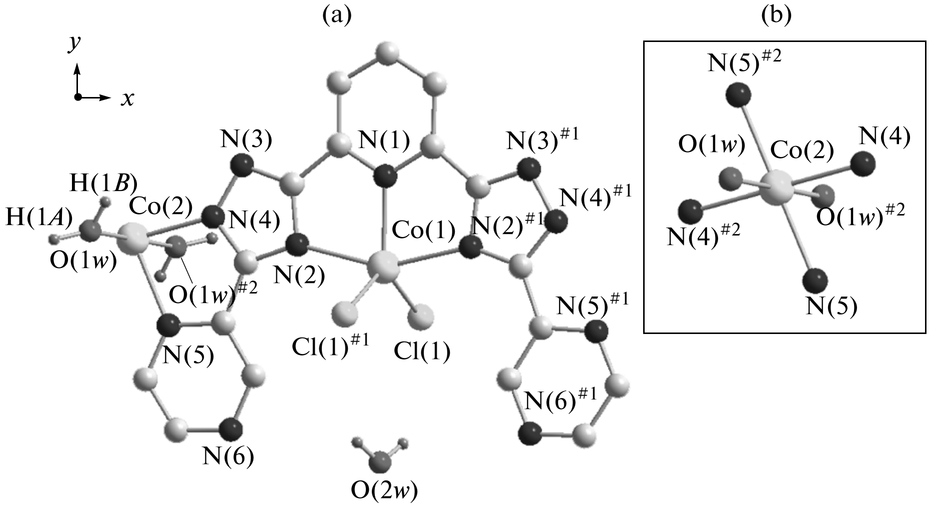

Fig. 1. The dinuclear unit of $[Co_2(Ptptp)Cl_2(H_2O)_2] \cdot H_2O$ (a); view of the coordination environment of the Co(2) in complex **I** (b). Symmetry operations: $^{\#1}$ $-x + 1, y, -z + 1/2$; $^{\#2}$ $-x, -y + 1, -z$.

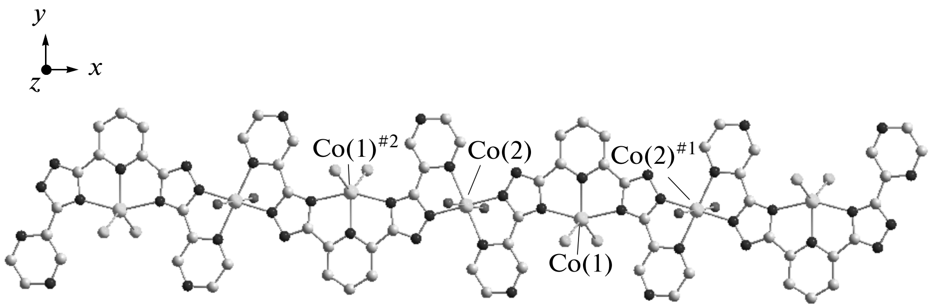

Fig. 2. The 1D chain of **I**.

dination with three N atoms (N(1), N2, N(2)$^{\#1}$ from one $Ptptp^{2-}$ ligand) and two Cl atoms (Cl(1) and Cl(1)$^{\#1}$), while Co(2) center is coordinated by four N atoms (N(4), N(5) from the $Ptptp^{2-}$ ligand and N(4)$^{\#2}$, N(5)$^{\#2}$ from the adjacent binuclear unit) and two O atoms (O(1*w*) and O(1*w*)$^{\#2}$ from the H_2O molecules) but in a slightly distorted octahedral geometry. The Co–N bond lengths range from 2.031 to 2.216 Å, the Co–Cl bond length is 2.247 Å, and the Co–O bond length is 2.189 Å. The angles of N(5)$^{\#2}$Co(2)N(4)$^{\#2}$, N(4)$^{\#2}$Co(2)N(5), N(5)Co(2)N(4), and N(4)Co(2)N(5)$^{\#2}$ added up to 360°, indicating that the Co(2) ion and the four N atoms are on the identical plane.

As show in Fig. 2, the $Ptptp^{2-}$ anion, acting as a connector, links the Co(II) centers to form a one-dimensional (1D) chain. Each $Ptptp^{2-}$ ligand connects one Co(1) and two Co(2) atoms; Co(1) is only coordinated with N atoms from one ligand, while Co(2) is coordinated by N(4), N(5) from one $Ptptp^{2-}$ ligand and N(4)$^{\#2}$, N(5)$^{\#2}$ from the adjacent $Ptptp^{2-}$ ligand, resulting in $[Co_2(Ptptp)]_n$ 1D belts with the Co(1)···Co(2), Co(1)···Co(1)$^{\#2}$ and Co(2)···Co(2)$^{\#1}$ distances of 6.3004(8), 12.6008(16), and 12.5523(16) Å, respectively. The distances between Co···Co also tell us the Co(II) centers are not in an absolutely straight line.

The 1D chains are connected through the intermolecular hydrogen bonds between the coordinated water molecules and lattice water molecules (2.925 Å for O(1*w*)···O(2*w*)$^{\#3}$). There are just one type H-bond in this complex. The angle of O(1*w*)–H(1*B*)···O(2*w*)$^{\#3}$ is 154.086°. Every oxygen atom of the lattice water molecules is all in part connecting adjacent two units of $[Co_2(Ptptp)Cl_2(H_2O)_2]$. Thus, 3D supramolecular structure of this compound is formed (Fig. 3).

We investigated the variable temperature magnetic susceptibilities of this compound, which were measured on the field of 2000 Oe in the temperature range of 2.0–300 K as shown in Fig. 4. The $\chi_M T$ values at 300 K is 2.57 $cm^3 mol^{-1}$ K, which is higher than the expected spin-only value for isolated Co^{2+} ion (1.86 cm^3 K mol^{-1},

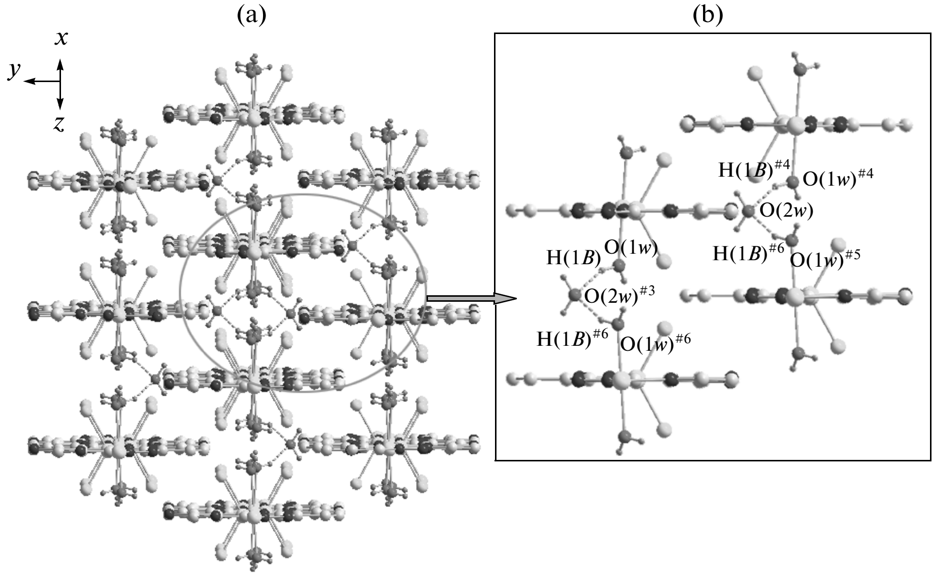

Fig. 3. Schematic representation of 3D framework of $[Co_2(Ptptp)Cl_2(H_2O)_2] \cdot H_2O$. Symmetry operations: $^{\#3}\, x - 1/2, y + 1/2, z$; $^{\#4}\, x + 1/2, y - 1/2, z$; $^{\#5}\, -x + 1/2, y - 1/2, -z + 1/2$; $^{\#6}\, -x, y, -z + 1/2$.

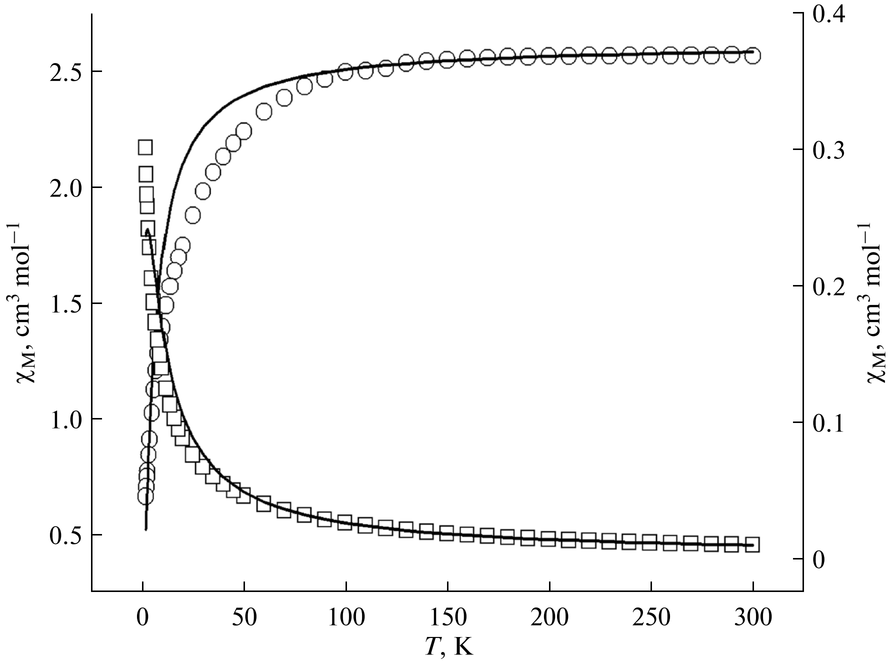

Fig. 4. Plots of $\chi_M T$ (□) and χ_M (○) versus T for **I**. The solid line denotes the theoretical curve with the best-fit parameters.

$S = 3/2$), indicating an orbital contribution to the spin-orbital coupling of the Co^{2+} ions [17]. As the temperature is lowered, the $\chi_M T$ value decreases continuously and falls rapidly in the lower temperature region, which is 0.517 cm^3 K mol^{-1} at 2 K. This behavior suggests the occurrence of antiferromagnetic interactions between adjacent Co^{2+} ions.

According to the structural data, the systems could be treated as magnetically isolated 1D chain. The compound contain Co(II) chain interlinked by the H_2Ptptp ligands. A 1D chain model has been utilized to simulate the experimental magnetic behavior for the purpose of understand quantitatively the magnitude of magnetic interaction. Then the interaction (J) can be expressed by the spin Hamiltonian $H = -J\sum S_iS_{i+1}$. In the classical-spin approximation, the following expression (Eq. 1) of magnetic susceptibility was deduced by Fisher [17].

$$\chi_{\text{chain}} = \frac{Ng^2\beta^2S(S+1)}{3kT}\left(\frac{1+\mu}{1-\mu}\right), \quad (1)$$

where μ is the Langevin function $\mu = \coth[JS(S + 1)/kT] - kT/[JS(S + 1)]$, with $S = 3/2$. The best fit gives the parameters $J = -1.18$ cm^{-1}, $g = 2.34$ and $F = 3.78 \times 10^{-3}$. The investigation on magnetic properties reveal that there is a weak antiferromagnetic behavior, which mainly arises from the antiferromagnetic coupling interaction in the 1D chains through H_2Ptptp bridges.

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REFERENCES

1. Middlemiss, D.S., Lawton, L.M., Morrison, C.A., and Wilson, C.C., *Chem. Phys. Lett.*, 2008, vol. 459, p. 119.
2. Patrick, B.O., Stevens, C.L., Storr, A., and Thompson, R.C., *Polyhedron*, 2005, vol. 24, p. 2242.
3. Li, L., Chen, S., Zhou, R.M., et al., *Spectrochim. Acta*, *A*, 2014, vol. 120, p. 401.
4. Li, G.L., Yin, W.D., Liu, G.Z., et al., *Inorg. Chem. Commun.*, 2014, vol. 43, p. 165.
5. Ranjbar, Z.R. and Morsali, A., *Inorg. Chim. Acta*, 2012, vol. 382, p. 171.
6. Li, C.P., Guo, J., and Du, M., *Inorg. Chem. Commun.*, 2013, vol. 38, p. 70.
7. Bohnsack, A.M., Ibarra, I.A., Bakhmutov, V.I., et al., *J. Am. Chem. Soc.*, 2013, vol. 135, p. 16038.
8. Bayrak, H., Demirbas, A., Karaoglu, S.A., and Demirbas, N., *Eur. J. Med. Chem.*, 2009, vol. 44, p. 1057.
9. Bagihalli, G.B., Avaji, P.G., Patil, S.A., and Badami, P.S., *Eur. J. Med. Chem.*, 2008, vol. 43, p. 2639.
10. Zhao, Q.H., Li, H.F., Chen, Z.D., and Fang, R.B., *Inorg. Chim. Acta*, 2002, vol. 336, p. 142.
11. Cheng, L., Wang, J.Q., and Gou, S.H., *Inorg. Chem. Commun.*, 2011, vol. 14, p. 261.
12. Gao, J.Y., Wang, N., Xiong, X.H., et al., *Inorg. Chem. Commun.*, 2013, vol. 37, p. 197.
13. Lysenko, A.B., Govor, E.V., Krautscheid, H., and Domasevitch, K.V., *Daltron Trans.*, 2006, p. 3772.
14. Senchyk, G.A., Lysenko, A.B., Krautscheid, H., et al., *Acta Crystallogr.*, *C*, 2008, vol. 64, p. m246.
15. Jia, Y.Y., Li, H.J., Zhao, B., et al., *Eur. J. Inorg. Chem.*, 2013, vol. 2013, p. 438.
16. Sheldrick, G.M., *Acta Crystallogr., A*, 2008, vol. 64, p. 112.
17. Fisher, M.E., *Am. J. Phys.*, 1964, vol. 32, p. 343.