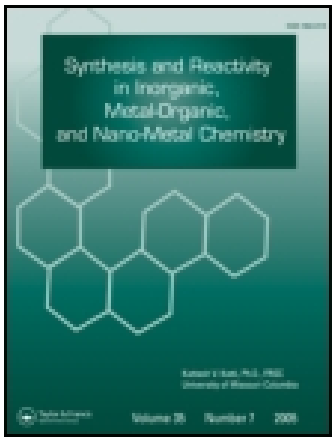

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Synthesis and Crystal Structure of a 3-D Netlike Supramolecular Cobalt Picrate Complex With 2, 6-bis(benzimidazol-2-yl)pyridine

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Synthesis and Crystal Structure of a 3-D Netlike Supramolecular Cobalt Picrate Complex With 2, 6-bis(benzimidazol-2-yl)pyridine

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A novel complex of cobalt picrate with 2, 6-bis(benzimidazol-2-yl)pyridine (L), has been prepared and characterized by elemental analysis, IR spectroscopy, and single-crystal X-ray diffraction. The complex crystallizes in the monoclinic system, space group *c2/c* with $a = 21.8756(6)$ Å, $b = 12.2995(3)$ Å, $c = 27.4827(7)$ Å, $\beta = 95.6060(10)°$, and $Z = 4$. The structure was refined to the final $R_1 = 0.0708$. The complex units are linked by π-π interactions and hydrogen bonds to give infinite two-dimensional (2-D) supramolecular layers, which are further linked by the intermolecular hydrogen bonds to form a three-dimensional (3-D) netlike supramolecule.

Keywords 2, 6-bis(benzimidazol-2-yl)pyridine, crystal structure, cobalt picrate complex, π-π interactions

INTRODUCTION

Tripodal ligands have drawn much attention in recent years, mainly due to their selective coordinating capacity, spheroidal cavities and hard binding sites, therefore stabilizing their complexes, acquiring novel coordination structure and shielding the encapsulated ion from interaction with the surroundings.[1–5] These numerous tripodal ligands have demonstrated their potential use in functional supramolecular chemistry.[6–10] In the present work, an organic ion picrate was chosen as counter anion, which possesses relatively weak coordination activity, the cobalt complex with 2,6-bis(benzimidazol-2-yl)pyridine (L) (Figure 1) was synthesized. The crystal structure indicates that the complex molecule $[CoL_2](Pic)_2(DMF)$ are linked by π-π interactions and intramolecular to give infinite two-dimensional (2-D) supramolecular layers, which are further linked by the intermolecular hydrogen bonds to form a three-dimensional (3-D) netlike supramolecule.

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EXPERIMENTAL

Materials and Physical Measurements

All reagents and solvents were purchased commercially and used without further purification unless otherwise noted. $Co(Pic)_2$ was prepared by the reaction of cobalt carbonate and picric in the hot water. All reagents used were of analytical grade and used without further purification.

IR spectra were recorded on a Nicolet 360 FT-IR instrument using KBr discs in the 4000-400 cm^{-1} region. The crystal structure was determined by a Bruker APEX CCD area-detector diffractometer.

Preparation of the Ligand L

The ligand 2,6-bis(benzimidazol-2-yl)pyridine was prepared by the reaction of pyridine-2,6-dicarboxylic acid and *o*-phenylenediamine in syrupy phosphoric acid (40 mL) at *ca.* 230° for 4 h as described previously,[11] yield 55%, m.p. >250°. IR (cm^{-1}) in KBr pellet: ν(C = N) 1459s; ν(C = C): 1436s; ν(C-N):1274s; ν(N-H) 3083m, 3058m, and ν(O-H) 3180 m.

Synthesis of the Cobalt Picrate Complex

The cobalt picrate complex was prepared by the reaction of $Co(Pic)_2$ and L with 1:1 molar ratio in ethanol as yellow powder. (Found: C: 52.18; H: 2.94; N: 19.78. Anal. Calcd. for $CoL_2(Pic)_2(DMF)$: C, 52.62; H, 3.08; N, 19.68%). IR(cm^{-1}, KBr): ν(C = N): 1614; ν(C = C): 1438; ν(C-N): 1276; ν_{as}(–NO_2): 1554; ν_s(–NO_2): 1341.

Crystal Structure Determination

Red crystal suitable for X-ray diffraction was obtained by slow evaporation of the ethanol solution of the Co complex. Single-crystal X-ray diffraction study of the title complex was performed on a Bruker SMART CCD diffractometer equipped with a graphite crystal monochromator situated in the incident beam for data collection. Single crystal with dimensions of $0.48 \times 0.44 \times 0.40$ mm^3 was chosen for X-ray diffraction studies. The determination of unit cell parameters and data collections were performed with Mo *K*a radiation ($\lambda = 0.71073$ Å) at 294(2) K on a Bruker SMART diffractometer. The structure was solved by direct method using SHELXS program of

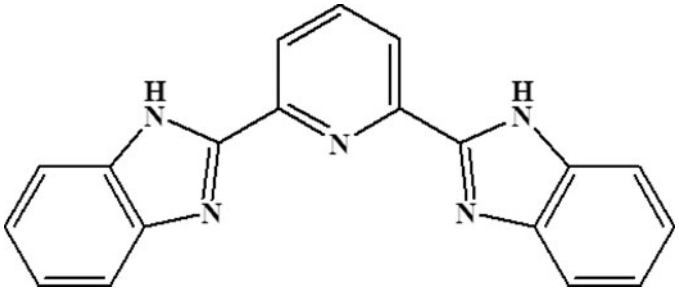

FIG. 1. The chemical structure of the ligand L.

the SHELXL-97 package and refined with SHELXL.[12] Cobalt centers were located from the *E*-map and other non-hydrogen atoms were located in successive difference Fourier syntheses. The final refinement was performed by full matrix least-squares method with anisotropic thermal parameters for non-hydrogen atoms on F^2. The hydrogen atoms were added geometrically and not refined. The final $R = 0.0708$ and $wR = 0.1831$ ($w = 1/[\sigma^2(F_o^2) + (0.1131P)^2 + 3.1714P]$, where $P = (F_o^2 + 2F_c^2)/3$), $S = 1.053$, $(\Delta\rho)_{max} = 0.601$, $(\Delta\rho)_{min} = -0.253$ e/Å^3, and $(\Delta/\sigma)_{max} = 0.000$.

RESULTS AND DISCIUSSION

A summary of crystallographic data and details of the structure refinements are listed in Table 1. The selected bond lengths and bond angles are given in Table 2.

As shown in Figure 2, in the complex $[CoL_2](Pic)_2(DMF)$, Co(II) atom is coordinated with six nitrogen atoms from two tridentates ligand L to form a distorted octahedron (Figure 3). Two picrate groups act as the counter anions, and one DMF molecule locates at the outer coordination sphere. All atoms of the same ligand L are almost in a plane, and the dihedral angle between two planes formed by the two ligands is 85.64°.

A 3D netlike supramolecule was further formed through the hydrogen bonds and π-π interactions. The π-π interactions between the picrate group and one benzene ring of the benzimidazole rings [the centroid (C1, C2, C3, C4, C5, and C6) to the centroid (C19, C20, C21, C22, C23, and C24) distances are 3.732 Å (symmetry code: –1/2 + *x*, 1/2 + *y*, *z*)] form a one-dimensional (1-D) supramolecule chains.[13,14] The chains are linked by hydrogen bonds [C(10–H(10)···O, C(14)–H(14)···O, N(7)–H(7)···O], thus generating a two-dimensional (2-D) supramolecular layer as shown in Figure 4.[15] The layers are linked by intermolecular hydrogen bond C(9)—H(9)···O(5) to form a three-dimensional (3-D) netlike supermolecule as shown in Figure 5. In addition, there is an intermolecular hydrogen bond N(8)—H(8A)···O(8) between the tridentates ligand L and the DMF molecular in the complex. Hydrogen bonding parameters of the complex are given in Table 3.

TABLE 1
Crystal and experimental data

Empirical formula	$C_{56}H_{44}N_{18}O_{24}Co$
Formula weight	1412.02
Temperature	294(2)
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, *c*2/*c*
Unit cell dimensions	$a = 21.8756(6)$ Å $b = 12.2995(3)$ Å $\beta = 95.6060°(10)$ $c = 27.4827(7)$ Å
Volume	7359.1(3) Å^3
Z	4
*D*x	1.274 Mg·m^{-3}
Absorption coefficient	0.316 mm^{-1}
F(000)	2900
Crystal size	0.48 × 0.44 × 0.40 mm
Theta range for data collection	1.87–25.60°
Limiting indices	$-26 \le h \le 15$, $-14 \le k \le 14$, $-33 \le l \le 33$
Reflections collected/unique	19606/6897
Data/restraints/parameters	6897/0/450
Goodness-of-fit on F^2	1.053
Final *R* indices [*I*>2sigma(*I*)]	$R_1 = 0.0708$, $wR_2 = 0.1831$
Largest diff. peak and hole	0.601 and –0.253 e·Å^{-3}
Refinement method	Full-matrix least-squares on F^2

Measurement: Bruker SMART CCD; Programs system: SHELXTL-97; Structure determination: SHELXS-97.

TABLE 2
Selected bond distances (Å) and angles (°)

Co(1)-N(1)	2.074 (3)	Co(1)-N(2)	2.128 (3)	Co(1)-N(3)	2.151 (3)
Co(1)-N(1–2)	2.074 (3)	Co(1)-N(2–2)	2.128 (3)	Co(1)-N(3–2)	2.151 (3)
N(1)-Co(1)-N(1–2)	175.66 (17)	N(2)-Co(1)-N(2–2)	94.07 (17)	N(1–2)-Co(1)-N(3)	100.44 (12)
N(1)-Co(1)-N(2)	76.22 (12)	N(2)-Co(1)-N(1–2)	106.85 (12)	N(2–2)-Co(1)-N(3)	94.94 (12)
N(1)-Co(1)-N(2–2)	106.85 (12)	N(2)-Co(1)-N(3)	152.58 (12)	N(1–2)-Co(1)-N(2–2)	76.22 (12)
N(1)-Co(1)-N(3)	76.39 (12)	N(2)-Co(1)-N(3–2)	94.9 4(12)	N(1–2)-Co(1)-N(3–2)	76.39 (12)
N(1)-Co(1)-N(3–2)	100.44 (12)	N(3)-Co(1)-N(3–2)	88.81 (18)	N(2–2)-Co(1)-N(3–2)	152.58 (12)

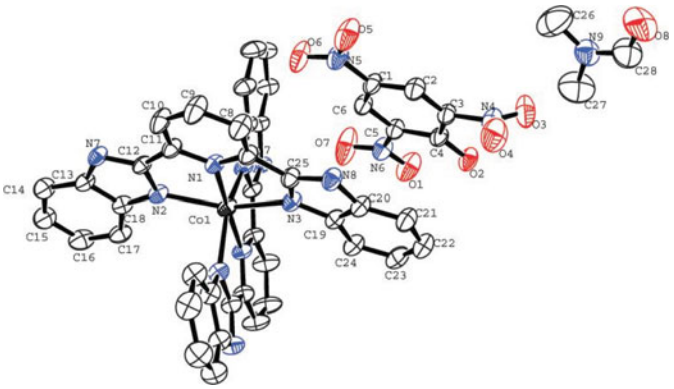

FIG. 2. ORTEP diagram (30% probability ellipsoids) showing the molecular structure of the Co complex (Color figure available online).

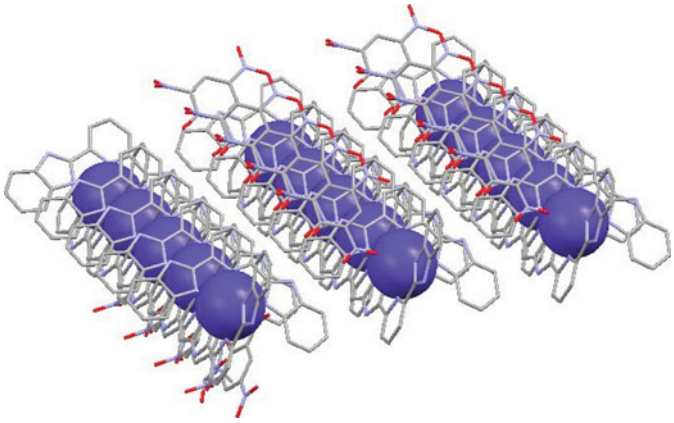

FIG. 4. 2-D supramolecular layers generated by hydrogen bonds and π-π interactions in the title complex (Color figure available online).

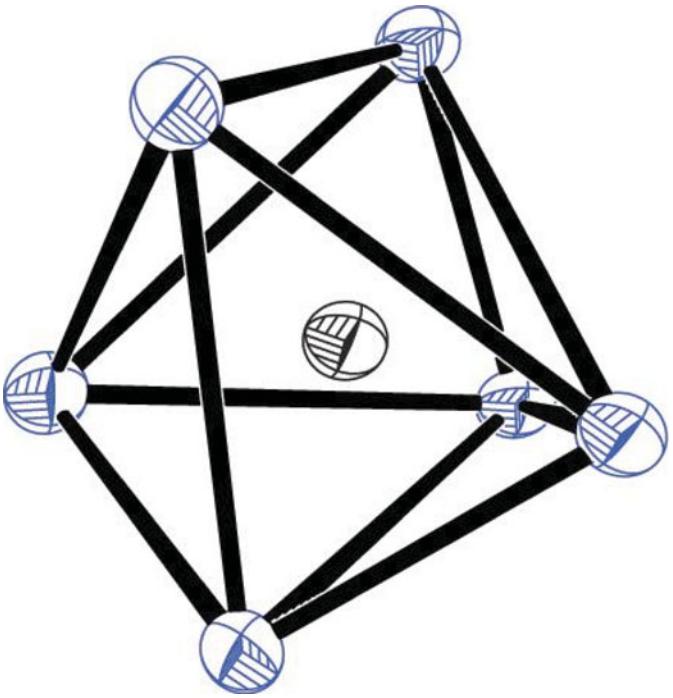

FIG. 3. Coordination polyhedron of Co ion (Color figure available online).

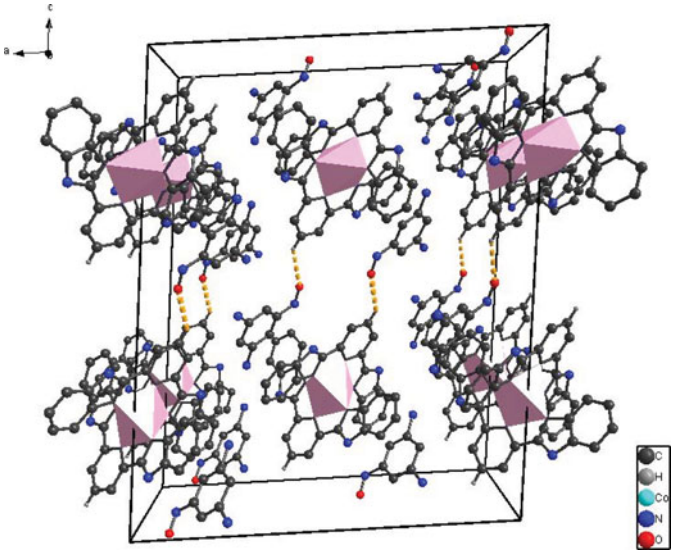

FIG. 5. 3-D supramolecular network generated by intermolecular hydrogen bonds (hydrogen bonds are indicated by the yellow dashed lines) (Color figure available online).

TABLE 3
Hydrogen-bonds in crystal packing (Å, °)

D—H···A	*d*(D—H)/nm	*d*(H. . .A)/nm	*d*(D. . .A)/nm	∠DHA/(°)	Symmetry
N(8)—H(8A)···O(8)	0.86	1.84	2.6984	174	–x, 2 – y, –z
C(9)—H(9)···O(5)	0.93	2.56	3.3041	138	1/2 – x, 3/2 – y, –z
N(7)—H(7)···O(1)	0.86	2.60	3.1547	123	
N(7)—H(7)···O(2)	0.86	1.97	2.7929	161	
C(10)—H(10)···O(2)	0.93	2.26	3.1161	153	
C(10)—H(10)···O(3)	0.93	2.55	3.1761	125	
C(14)—H(14)···O(1)	0.93	2.48	3.1278	127	

SUPPLEMENTARY MATERIALS

The X-ray crystallographic file for Table 1, in CIF format, has been deposited with the Cambridge Crystallographic Data Center, CCDC No. 899095. Copy of this information may be obtained free of charge from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge, CB2 1EZ, UK (e-mail: deposit@ccdc.cam.ac.uk)

REFERENCES

1. Ding, D.G.; Zhang, X. A novel copper diphosphonate complex Cu(aedp) with two-dimensional framework structure. *Synth. React. Inorg. Met.-Org. Nano-Met. Chem.* **2012**, *42*, 1087–1090.
2. Li, G.B.; Liu, J.M.; Cai, Y.P.; Su, C.Y. Structural diversity of a series of Mn(II), Cd(II), and Co(II) complexes with pyridine donor diimide ligands. *Cryst. Growth Des.* **2011**, *11*, 2763–2772.
3. Zhang, Q.Z.; Xu, X.J.; Lu, H.D.; Tian, C.G.; Yang, B.H. Synthesis and structure of a 1D copper(II) complex $[Cu(Hbtc)(PyBIm)_2]_n$ (H_3btc = 1,3,5-benzenetricarboxylic acid, PyBIm = 2-(4-pyridyl)benzimidazole). *Synth. React. Inorg. Met.-Org. Nano-Met. Chem.* **2013**, *43*, 135–139.
4. Kovalenko, E.A.; Naumov, D.Yu; Fedin, V.P.; Müller, A. Synthesis and crystal structure of $[Na_2(\mu\text{-}H_2O)(H_2O)CB[5]]Cl_2{\cdot}6H_2O$, $[Na_3(\mu\text{-}H_2O)_4(H_2O)_4(CNPy@CB[6])]Cl_3{\cdot}8H_2O$, and $[Rb_2(\mu\text{-}H_2O)_2(CNPy@CB[6])]Cl{\cdot}8H_2O$. *Russ. J. Coord. Chem.* **2012**, *38*, 153–158.
5. Wu, H.L.; Bai, Y.; Yuan, J.K.; Wang, H.; Pan, G.L.; Kong, J. Synthesis, crystal structures, and DNA-binding properties of a ternary cadmium(II) complex with tripod ligand Tris(2-benzimidazylmethyl)amine and cinnamate. *Synth. React. Inorg. Met.-Org. Nano-Met. Chem.* **2013**, *43*, 237–242.
6. Li, S.J.; Zhu, D.Y.; Ran, C.L.; Li, W.J.; Xu, Y.; Song, M.P. Syntheses, structures of two coordination polymers based on bipyridyl and carboxyl groups. *Synth. React. Inorg. Met.-Org. Nano-Met. Chem.* **2012**, *42*, 1078–1082.
7. Shi, S.M.; Gu, Y.Q.; Chen, Z.F.; Liu, Y.C.; Liang, H. One-dimensional chain copper(II) and nickel(II) coordination polymers with N-salicylideneglycine Schiff base ligand. *Synth. React. Inorg. Met.-Org. Nano-Met. Chem.* **2012**, *42*, 1262–1266.
8. Hamann, C.S.; Zelewsky, A.V.; Barbieri, A.; Barigelletti, F.; Muller, G.; Riehl, J.P.; Neels, A. Diastereoselective formation of chiral tris-cyclometalated iridium (III) complexes: characterization and photophysical properties. *J. Am. Chem. Soc.* **2004**, *126*, 9339–9348.
9. Liu, Y.; Pan, M.; Li, K.; Yan, C.; Shen, Y.; Zhao, C.Y.; Wang, W.; Su, C.Y. Metal-directed assembly of hexameric ring, dimeric ring and 1D chain from a branched tripodal ligand. *Cryst. Growth Des.* **2011**, *11*, 4876–4884.
10. Zhu, A.X.; Zhang, J.P.; Lin, Y.Y.; Chen, X.M. Pentanuclear and heptanuclear helicates by self-assembly of d^{10} metal ions and a rigid aromatic bis-bidentate chelator. *Inorg. Chem.* **2008**, *47*, 7389–7395.
11. Yan, Z.Z.; Xu, Z.H.; Dai, G.L.; Liang, H.D.; Zhao, S.L. Synthesis, crystal structure, and DNA-binding of a 3-D netlike supramolecular manganese picrate complex with 2,6-bis(benzimidazol-2-yl)pyridine. *J. Coord.* **2010**, *63*, 1097–1106.
12. Sheldrick, G.M. *SHELXS-97, A Program for X-ray Crystal Structure Solution, and SHELXL-97, A Program for X-ray Structure Refinement*; University of Göttingen, Germany, **1997**.
13. Janiak, C. A critical account on π-π stacking in metal complexes with aromatic nitrogen-containing ligands. *J. Chem. Soc., Dalton Trans.* **2000**, *21*, 3885–3896.
14. Li, J.M.; Zhao, Y.L.; Jiang, Y.M. Synthesis and crystal structure of a 1-D Copper(II) Coordination Polymer with N-(2-pyridylmethylidene)taurine. *Synth. React. Inorg. Met.-Org. Nano-Met. Chem.* **2010**, *40*, 715–718.
15. Desiraju, G.R. The C−H···O hydrogen bond: structural implications and supramolecular design. *Acc. Chem. Res.* **1996**, *29*, 441–449.