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Synthesis and Crystal Structure of Two Polydimensional Molecular Architectures from Cobalt(II), Copper(II) Complexes of 2,4-Diamino-6-pyridyl-1,3,5-triazine

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Two new Co(II) and Cu(II) complexes of 2,4-diamino-6-pyridyl-1,3,5-triazine (ptzda) have been synthesized and structurally characterized. Crystal structure studies reveal that Co atom is six-coordinated by four nitrogen atoms from four dicyanamide anions and the other two nitrogen atoms from 2,4-diamino-6-pyridyl-1,3,5-triazine and each cobalt atom are connected by two $[N(CN)_2]^-$ anions to form an infinite double-stranded bridge fashion to give 2D ladder-like motifs. Whereas, Cu atom is five-coordinated by two nitrogen atoms from two dicyanamide anions and the other two nitrogen atoms from 2,4-diamino-6-pyridyl-1,3,5-triazine and each copper atom is connected by one methanol to form an infinite double-stranded bridge fashion to give 1D ladder-like motifs.

Keywords: 1,3,5-Triazines, Polydimentional molecular architectures, X-Ray crystal structure.

INTRODUCTION

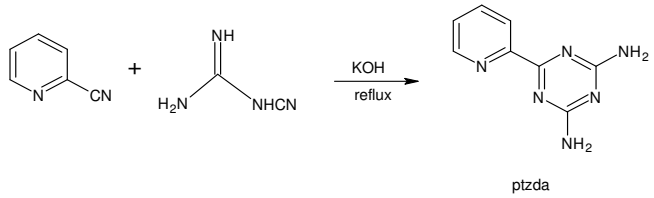
The coordination polymer construction of secondary building units (SBUs) has recently drawn much attention due to their various topologies of structures and fascinating properties, such as porosity, nonlinear optical property and magnetism[1-5]. Since the secondary building units have triangular, square, tetrahedral, or octahedral building-block geometries which can adopt different spatial configurations and maintain their structural integrity throughout the self-assembly process, a variety of multi-dimensional coordination geometries were found in the crystal structure of their complexes, *i.e.*, one dimension (1D), 2D and 3D. At present, interest in rational design and synthesis of polynuclear coordination compounds with predictable functionalities, such as bioactivity[6-10], catalytic ability[11-13] and magnetic interactions[14-19] has increased tremendously. It was reported that 1,3,5-triazole and its derivatives, a type of heterocyclic compound, had a number of biological activity and promising applications in many fields such as pharmacy, pesticide, material, *etc.*[20-22]. 1,3,5-Triazole and its derivatives are also good ligands for transition metal complexes. In this point of view, Co(II) and Cu(II) complexes of 2,4-diamino-6-pyridyl-1,3,5-triazine as the ligand were synthesized and characterized. The complexes were found to have polydimentional molecular architectures.

EXPERIMENTAL

All the chemicals and solvents used for the synthesis were of reagent grade and used without further purification. $Na[N(CN)_2]$ was purchased from Aldrich Company. Elemental analyses (C, H, N) were performed on an Elementar Vario EL III elemental analyzer. X-ray single-crystal diffraction was determined on Bruker APEX II CCD area detector.

Synthesis of 2,4-diamino-6-pyridyl-1,3,5-triazine [ptzda]: The ligand ptzda was prepared by some modification according to the literature[23]. As illustrated in **Scheme-I**, a mixture of one molar proportion of 2-cyanopyridine derivative, l.25 of dicyandiamide, 0.2 of potassium hydroxide and 6.2 of methylcellosolve was refluxed for 4 h. After cooling, the contents of the flask were poured into water and the precipitate was collected by filtration, dried and recrystallized from methylcellosolve. Yield: 92.1 %. Anal. calcd. (%) for $C_8H_{10}N_5$: C,54.53; H, 5.72; N, 9.75. Found (%): C, 54.82; H, 5.28; N, 9.89. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.70 (J = 2.6,H, pyridyl-H); 8.20 (J = 7.7, H, pyridyl-H); 7.91 (J = 7.6, H, pyridyl-H); 7.49 (J = 5.5, H, pyridyl-H); 7.09 (2H, NH_2); 6.87 (2H, NH_2).

Synthesis of complex 1: $[Co(ptzda)_2(L)]_n$: $CoCl_2{\cdot}6H_2O$ (35.70 mg, 0.15 mmol) was dissolved in 5 mL of methanol and allowed to react with methanolic solution (5 mL) of the ligand ptzda (17.60 mg, 0.1 mmol) in stirring condition. After a few minutes, an aqueous solution (2 mL) of sodium



Scheme-I: Synthesis of ligand 2,4-diamino-6-pyridyl-1,3,5-triazines (ptzda)

dicyanamide (8.90 mg, 0.1 mmol) was added and stirred for 0.5 h. Red single crystals suitable for X-ray analysis were obtained by slow evaporation at room temperature for three weeks. Yield: 62 %. Anal. calcd. (%) for $C_{24}H_{16}N_{24}Co_2$: C, 38.00; H, 2.13; N, 44.32. Found. (%): C, 38.09; H, 2.22; N, 44.21.

Synthesis of complex 2: $[Cu(ptzda)_2(L)]_n$: A 5 mL of methanol solution of $CuCl_2·6H_2O$ (33.70 mg, 0.15 mmol) was mixed with the methanolic solution (5 mL) of the ligand ptzda (17.60 mg, 0.1 mmol) in stirring condition. After a few minutes, an aqueous solution (2 mL) of sodium dicyanamide (8.90 mg, 0.1 mmol) was added and stirred for 0.5 h. Red single crystals suitable for X-ray analysis were obtained by slow evaporation at room temperature for four weeks. Yield: 52 %. Anal. calcd. (%) for $C_{10}H_8N_9OCu$: C, 34.00; H, 2.28; N, 35.69. Found (%): C, 34.19; H, 2.22; N, 36.21.

Crystallographic data collection and structure determination: Intensity data for single crystals of complexes were collected on a BRUKER APEX II CCD detector with graphite-monochromatized MoK_α radiation (λ = 0.071073 nm). For complex **1**, a total of 9383 independent reflections were collected, of which 3416 [$R_{(int)}$ = 0.0423] were considered as observed [$I > 2\sigma(I)$]. For complex **2**, a total of 8408 independent reflections were collected, of which 3110 [$R_{(int)}$ = 0.0393] were considered as observed [$I > 2\sigma(I)$]. The structures were solved by direct method using the program SHELXS-97[24] and subsequent Fourier difference techniques and refined anisotropically by fullmatrix least-squares on F^2 using SHELXL-97[25]. Crystal data and structural refinements of two complexes are shown in Table-1. Crystallographic data of the complexs **1**, **2** have been deposited at the Cambridge Crystallogrphic Data Center, CCDC Nos. 732112 and 732110. Any queries relating to the data can be e-mailed to deposit@ccdc.cam.ac.uk.

RESULTS AND DISCUSSION

For complex **1,** crystal structures reveal that Co atom is six-coordinated by four nitrogen atoms from four dicyanamide anions and the other two nitrogen atoms from ptzda and each coblat atom is connected by two $[N(CN)_2]^-$ anions to form an infinite double-stranded bridge fashion to give 2D ladder-like motifsis (Fig. 1). A neutral, two-dimensional coordination network based on coblat clusters is joined by end-end (EE) $[N(CN)_2]^-$ anions groups. As shown in Fig. 2, the basic unit contains coblat metal centres arranged in linear that are bridged by two end-on (EO) $[N(CN)_2]^-$ anions ligands. In the unit, the Co atom is six-coordination with a distorted octahedral geometry, where two nitrogen atom of 2,4-diamino-6-pyridyl-l,3,5-triazine form the basal plane, while a nitrogen atom of one EE azide bridge occupies the apical position. The basal Co-N bond lengths are in the range of 2.104-2.150 Å which is identical to Cu-$[N(CN)_2]^-$ anions compounds. The N-Co-N bond angles are in the range of 86.39(10)-126.1(2)º (Table-2).

TABLE-1
CRYSTAL DATA AND STRUCTURE REFINEMENTS FOR COMPLEXES **1** AND **2**

	1	**2**
Empirical formula	$C_{24}H_{16}Co_2N_{24}$	$C_{10}H_8CuN_9O$
Formula weight	758.47	333.79
Temperature (K)	298(2)	298(2)
Wavelength(Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
space group	P2(1)/n	C2/c
A (Å)	7.179(5)	23.205(3)
B (Å)	14.380(10)	9.0844(11)
C (Å)	14.585(10)	12.5312(15)
α	90	90
β	96.288(9)	91.946(2)
γ	90	90.
Volume ($Å^3$)	1496.6(17)	2640.1(5)
Z	2	8
Absorption coefficient (mm^{-1})	1.173	1.669
$F_{(000)}$	764	1344
Crystal size (mm)	0.20 × 0.20 × 0.20	0.21 x 0.16 x 0.10
Theta range for data collection (º)	1.99-27.94	1.76-28.26
Limiting indices	$-9 \Leftarrow h \Leftarrow 7, -17 \Leftarrow k \Leftarrow 18, -11 \Leftarrow l \Leftarrow 19$	$-16 \Leftarrow h \Leftarrow 30, -12 \Leftarrow k \Leftarrow 12, -16 \Leftarrow l \Leftarrow 16$
Reflections collected/unique	9383 / 3416 [$R_{(int)}$ = 0.0423]	8408 / 3110 [$R_{(int)}$ = 0.0393]
Completeness to theta = 27.94	95.00 %	98.10%
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	3416/0/226	3110/0/190
Goodness-of-fit on F^2	1.002	1.051
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0423, wR_2 = 0.0938	R_1 = 0.1158, wR_2 = 0.3593
R indices (all data)	R_1 = 0.0750, wR_2 = 0.1090	R_1 = 0.1536, wR_2 = 0.3813
Largest diff. peak and hole (e $Å^{-3}$)	0.289 ~ -0.370	3.977 ~ -1.223

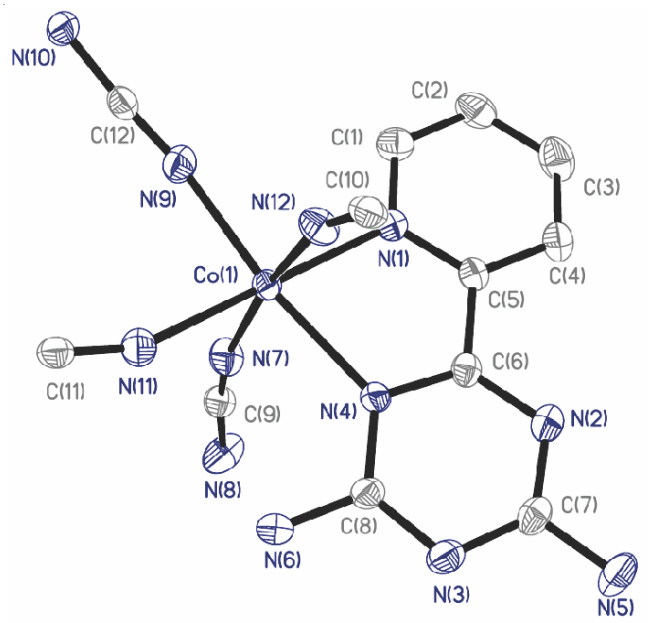
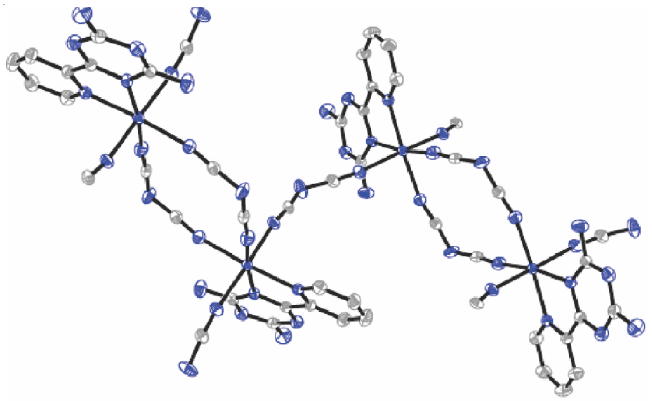
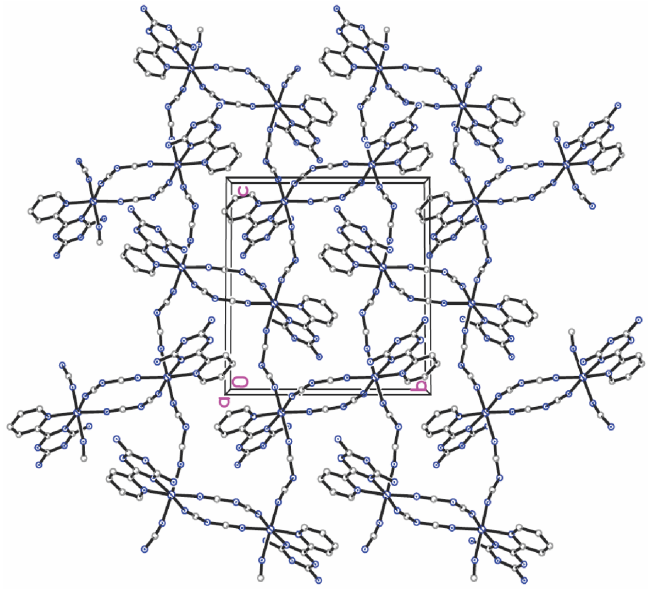


Fig. 1. A view of the molecule structure of **1** with the atomic labeling scheme



(A)



(B)

Fig. 2. A and B view showing the weak pairing of **1** molecules within the unit cell

TABLE-2
BOND LENGTHS [Å] AND ANGLES [°] FOR COMPLEX **1**

Co(1)-N(7)	2.104(3)	N(7)-Co(1)-N(9)	95.18(12)
N(1)-C(5)	1.343(4)	C(5)-N(1)-C(1)	118.2(3)
N(5)-H(5A)	0.8600	C(11) -N(10)-C(12)	118.4(3)
N(6)-C(8)	1.327(4)	N(1)-C(1)-C(2)	122.3(3)
N(6)-H(6A)	0.8600	C(3)-C(2)-C(1)	118.6(3)
N(7)-C(9)	1.135(4)	N(7)-C(9)-N(8)	172.2(4)

As for complex **2**, Cu atom is five-coordinated by two nitrogen atoms from two dicyanamide anions and the other two nitrogen atoms from ptzda and each copper atom is connected by one methanol to form an infinite double-stranded bridge fashion to give 1D ladder-like motifs (Fig. 3). The clusters act as rod-shaped SBUs and are joined into a 1D network by the EE azide groups in the bc plane (Fig. 4). Each rod-shaped unit is directly connected to four neighboring rods through four EE azide bridges. In the solid state, the 1D network extend to three-dimension architecture by two hydrogen bonds of N7- H7A···N4 (symmetry: -x + 1, -y + 1, -z + 1), N(6)-H(6B)···O(1) (Tables 3 and 4).

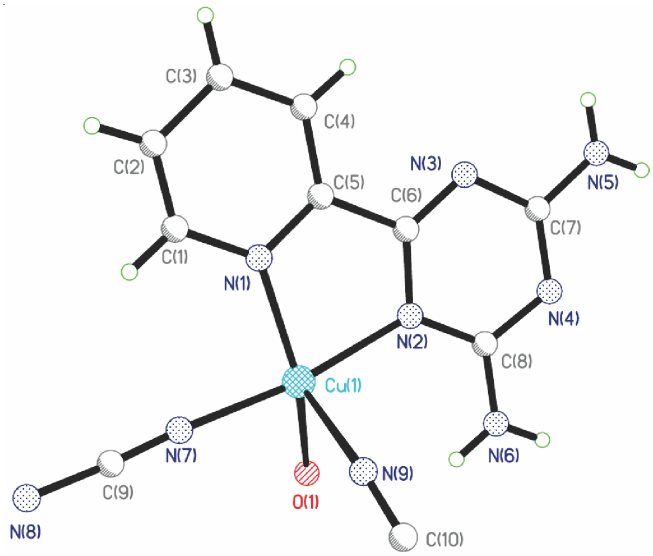


Fig. 3. A view of the molecule structure of **2** with the atomic labeling scheme

TABLE-3
BOND LENGTHS [Å] AND ANGLES [°] FOR COMPLEX **2**

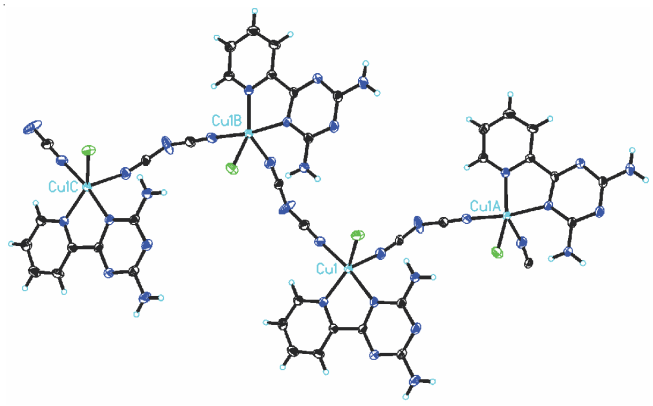
Cu(1)-N(7)	1.982(5)	N(7)-Cu(1)-N(1)	89.87(17)
Cu(1)-Cl	2.3449(14)	N(7)-Cu(1)-Cl	89.98(15)
N(1)-C(1)	1.340(6)	C(1)-N(1)-C(5)	118.1(4)
N(6)-H(6A)	0.8600	C(1)-N(1)-Cu(1)	127.1(3)
C(3)-C(4)	1.377(9)	C(6)-N(2)-C(8)	114.0(4)
C(10)-N(8)#1	1.305(7)	C(7)-N(5)-H(5A)	120.0

#1 x,-y, z+1/2 #2 x, -y, z-1/2.

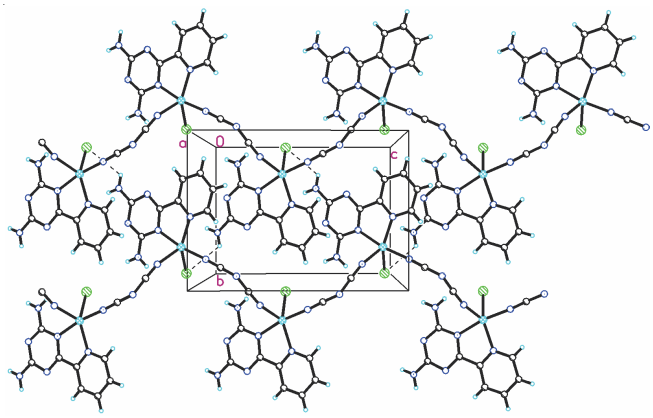
TABLE-4
HYDROGEN BONDS COMPLEX **2** [Å AND °]

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
N(7)-H(7A)···N(4)#3	0.86	2.20	3.052(12)	173.9
N(6)-H(6B)···O(1)	0.86	2.54	3.221(9)	136.7

Symmetry transformations used to generate equivalent atoms: #1 x, -y, z + 1/2 #2 x, -y, z-1/2 #3 -x+1, -y+1, -z+1.



(A)



(B)

Fig. 4. A and B view showing the weak pairing of **2** molecules within the unit cell

Conclusion

The Co(II) and Cu(II) complexes of 2,4-diamino-6-pyridyl-1,3,5-triazine were synthesized by the chemical reaction of $MCl_2 \cdot 6H_2O$ (M = Co or Cu) with 2,4-diamino-6-pyridyl-l,3,5-triazine and sodium dicyanamide in methanol. The complexes exhibit polydimentional molecular architectures in which the dicyanamide anion acts as the bridged ligand, featuring special formations probably endowed with some application.

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