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**SYNTHESIS AND CRYSTAL STRUCTURE OF TWO  $\{M(4,4'\text{-dpdo})_2[N(\text{CN})_2]_2(\text{H}_2\text{O})_2\}$  COMPLEXES (M = Co(II), Mn(II); 4,4'-dpdo = 4,4'-BIPYRIDYL-N,N'-DIOXIDE)**

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The ligand 4,4'-bipyridyl-N,N'-dioxide (4,4'-dpdo) was used in the synthesis of two complexes,  $\{\text{Co}(4,4'\text{-dpdo})_2[\text{N}(\text{CN})_2]_2(\text{H}_2\text{O})_2\}$  (**1**) and  $\{\text{Mn}(4,4'\text{-dpdo})_2[\text{N}(\text{CN})_2]_2(\text{H}_2\text{O})_2\}$  (**2**). The complexes were found to be isostructural, triclinic, space group *P*-1 with *Z* = 1 and the following unit cell parameters: *a* = 8.158(8) Å, *b* = 8.865(8) Å, *c* = 9.477(9) Å;  $\alpha$  = 70.988(13)°,  $\beta$  = 78.778(13)°,  $\gamma$  = 71.964(10)°; *V* = 612.8(10) Å<sup>3</sup> for **1**; *a* = 8.247(14) Å, *b* = 9.001(16) Å, *c* = 9.707(17) Å;  $\alpha$  = 71.02(2)°,  $\beta$  = 78.63(2)°,  $\gamma$  = 72.62(2)°; *V* = 646(2) Å<sup>3</sup> for **2**. Final *R*-values were 0.075 and 0.083 for **1** and **2**, respectively. In the molecules of the complexes, Co(II) or Mn(II) cation is coordinated by two O-atoms of two 4,4'-dpdo ligands, two terminal N-atoms of two dicyanamides, and two O-atoms of water molecules. The crystals are molecular, with adjacent complex molecules linked through a system of O—H...N and O—H...O hydrogen bonds.

**Key words:** dicyanamide, hydrogen bonding, molecular crystals, crystal structure.

**INTRODUCTION**

Rich topology and related physical properties of polymeric coordination compounds constitute an important subject of contemporary research [1]. Coordination polymers have been extensively reported as exhibiting various combinations of metal cations, dipyriddy-type organic ligands and pseudohalide ligands [2]. In this respect, dicyanamide (dca) has been confirmed to be a remarkably versatile building block for the construction of supramolecular architectures since it may act as a uni-, bi-, tri-topic ligand, or may reveal an unusual  $\mu_4$  coordination mode where one nitrile nitrogen binds to two metal atoms. Nowadays, dicyanamide-bridged polynuclear systems present a fast growing research field due to a large variety of topologies and potentially useful properties that may be obtained from the ligand [3]. Many extended coordination polymers have been reported, for example: 3D structure for  $M^{\text{II}}[\text{N}(\text{CN})_2]_2$  (M = Cu, Co, Ni, Mn, Pb) [4–6], 2D structure for  $[\text{Mn}_4(\text{hmp})_4(\text{Hpdm})_2 \times (\text{dcn})_2](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O} \cdot 2\text{MeCN}$  [7] and  $M(\text{dca})_2(\text{H}_2\text{O}) \cdot \text{phz}$  (M = Co(II), Ni(II)) [8], 1D structure for  $[\text{M}(\text{dca})_2(\text{H}_2\text{O})_2]_n \cdot (\text{hmt})_n$  (M = Mn(II), Co(II)) [2] and  $[\text{Cu}_2(\text{medpt})_2(\text{dca})_2](\text{ClO}_4)_2$  [9], and a dinuclear complex  $[\text{Cu}(\text{bpca})(\text{H}_2\text{O})(\text{dca})_2]$  [10]. Another ligand of this study, 4,4'-bipyridyl-N,N'-dioxide (4,4'-dpdo), may act as a long bridging spacer and may facilitate the formation of large cavities or channels [11]. In addition, as compared to 4,4'-bipy, it has a stronger capability of forming hydrogen bonds that play an important role in the assembly of supramolecular compounds [12]. So far, a variety of 4,4'-dpdo complexes has been reported [11–17]. Herein, we describe the synthesis, IR spectra and crystal structure of Co(II) and Mn(II) complexes with 4,4'-dpdo and dicyanamide ligands.

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## EXPERIMENTAL

All reagents were of analytical grade quality and were used without further purification. The ligand 4,4'-bipyridyl-N,N'-dioxide (4,4'-dpdo) was synthesized as reported elsewhere [18]. Elemental analyses were carried out on Elementar Carlo EL elemental analyzer. The IR spectra were recorded using KBr disks on a Thermo-Nicolet AVATAR FT-IR 360 spectrophotometer in 4000–400 cm<sup>-1</sup> range.

**Preparation of 1:** 4,4'-dpdo (0.2 mmol, 44.8 mg) and CoCl<sub>2</sub>·6H<sub>2</sub>O (0.2 mmol, 47.58 mg) were dissolved in water (10 ml). An aqueous solution of NaN(CN)<sub>2</sub> (0.4 mmol, 35.6 mg) was added to the reaction mixture dropwise while stirring. Precipitated bulk product was separated by filtration. Red block-shaped crystals suitable for X-ray analysis were obtained after slow evaporation of the mother liquor for two weeks at room temperature. Yield: 68 %. Anal. Calcd. for C<sub>24</sub>H<sub>20</sub>N<sub>10</sub>O<sub>6</sub>Co (%): C 47.55, H 3.1, N 22.8 %. Found (%): C 47.73, H 3.3, N 23.2. IR (KBr disk) (cm<sup>-1</sup>): ν<sub>s</sub> (C≡N) 2163, ν<sub>as</sub> (C≡N) 2283, ν<sub>s</sub> (C—N) 906, ν<sub>as</sub> (C—N) 1361, 3402m, 1675s, 1475m, 1431m, 1362m, 1245m, 1183vs, 1027vs, 838w, 736m.

**Preparation of 2:** Compound **2** was synthesized using a procedure similar to that for **1** except that MnCl<sub>2</sub>·6H<sub>2</sub>O was used instead of CoCl<sub>2</sub>·6H<sub>2</sub>O. Block-shaped crystals for X-ray analysis were obtained after slow evaporation of the liquor for two days at room temperature. Yield: 50 %. Anal. Calcd. for C<sub>24</sub>H<sub>20</sub>N<sub>10</sub>O<sub>6</sub>Mn (%): C 45.0, H 1.9, N 32.8. Found (%): C 44.9, H 2.0, N 33.1. IR (KBr disk) (cm<sup>-1</sup>): ν<sub>s</sub> (C≡N) 2187, ν<sub>as</sub> (C≡N) 2252, ν<sub>s</sub> (C—N) 900, ν<sub>as</sub> (C—N) 1371, 3303m, 1668s, 1474m, 1431m, 1366m, 1247m, 1164vs, 1031vs, 828w, 704m.

Data collections for **1** and **2** were carried out for crystals with dimensions 0.41×0.34×0.22 mm (**1**) and 0.52×0.19×0.11 mm (**2**) on a CCD diffractometer with graphite-monochromated MoK<sub>α</sub> radiation (λ = 0.71073 Å). The crystal structures were solved by direct methods and Fourier synthesis using SHELXS-97 [19] and refined by full-matrix least-square techniques on F<sup>2</sup> using SHELXL-97 [20]. Non-hydrogen atoms were refined anisotropically, while hydrogen atoms were added according to theoretical models. A summary of the crystallographic data and refinement parameters is listed in Table 1. Selected bond distances and bond angles for the two complexes are listed in Table 2 and 3.

Table 1

Crystallographic data for {Co(4,4'-dpdo)<sub>2</sub>[N(CN)<sub>2</sub>]<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>} (**1**) and {Mn(4,4'-dpdo)<sub>2</sub>[N(CN)<sub>2</sub>]<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>} (**2**)

Parameter	<b>1</b> *	<b>2</b>
Empirical formula	C <sub>24</sub> H <sub>20</sub> CoN <sub>10</sub> O <sub>6</sub>	C <sub>24</sub> H <sub>20</sub> MnN <sub>10</sub> O <sub>6</sub>
Formula weight	603.43	599.44
Crystal system	Triclinic	Triclinic
Space group	<i>P</i> -1	<i>P</i> -1
<i>a</i> , <i>b</i> , <i>c</i> , Å	8.158(8), 8.865(8), 9.477(9)	8.247(14), 9.001(16), 9.707(17)
α, β, γ, deg.	70.988(13), 78.778(13), 71.964(10)	71.02(2), 78.63(2), 72.62(2)
<i>V</i> , Å <sup>3</sup>	612.8(10)	646(2)
<i>Z</i>	1	1
μ, mm <sup>-1</sup>	0.765	0.572
<i>D</i> <sub>c</sub> , g/cm <sup>3</sup>	1.635	1.540
θ range, deg.	2.29 to 25.02	2.23 to 25.02
Crystal size, mm	0.41 × 0.34 × 0.22	0.52 × 0.19 × 0.11
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]: <i>R</i> 1, <i>wR</i> 2	0.075, 0.168	0.083, 0.188
GOOF	1.002	0.964
Max peak / hole, e/Å	0.588 / -0.622	0.427 / -0.625
CCDC deposition no.	607585	607586

\* Low temperature data were published in [23].

Table 2

Selected bond distances (Å) and angles (deg.) in the studied compounds  $\{M(4,4'\text{-dpdo})_2[\text{N}(\text{CN})_2]_2(\text{H}_2\text{O})_2\}$  (**1**, M = Co; **2**, M = Mn)

Bond	1	2	Angle	1	2
M(1)—O(1)	2.097(4)	2.237(4)	O(1)—M(1)—O(3) <sup>a</sup>	92.46(16)	93.42(19)
M(1)—O(3)	2.139(4)	2.263(4)	O(1)—M(1)—N(3) <sup>a</sup>	92.09(15)	89.43(14)
M(1)—N(3)	2.084(4)	2.204(5)	O(3)—M(1)—N(3) <sup>a</sup>	87.45(16)	87.35(15)
N(1)—O(1)	1.326(4)	1.346(5)	M(1)—O(1)—N(1)	119.6(2)	121.5(2)
N(2)—O(2)	1.309(5)	1.317(5)	M(1)—N(3)—C(11)	172.0(4)	172.7(4)
C(3)—C(8)	1.471(6)	1.503(6)	N(3)—C(11)—N(4)	171.9(6)	170.2(5)
N(3)—C(11)	1.151(6)	1.120(6)	C(11)—N(4)—C(12)	124.0(5)	123.2(4)
C(11)—N(4)	1.287(7)	1.332(6)	N(4)—C(12)—N(5)	172.7(6)	171.3(6)
N(4)—C(12)	1.316(7)	1.328(6)			
C(12)—N(5)	1.139(6)	1.165(6)			

<sup>a</sup> Symmetry code for this atom in compound **2**:  $2-x, -y, 2-z$ .

Table 3

The geometry of hydrogen bonds D—H...A (distances, Å and angles, deg.) in **1**

Bond D—H...A	D—H	H...A	DHA	D...A
O3—H9...N5'	0.898	2.101	154.28	2.936
O3—H10...O2''	0.898	1.838	163.95	2.712

Symmetry codes: (')  $-x+1, -y+1, -z$ ; (")  $x-1, y+1, z-1$ .

Full crystallographic data for the two structures reported in this paper have been deposited at the Cambridge Crystallographic Data Centre, CCDC nos. 607585 (**1**) and 607586 (**2**). Copies of the data can be obtained free of charge on application to CCDC ([www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk); [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

#### DESCRIPTION OF THE CRYSTAL STRUCTURES

The complexes **1** and **2** are isostructural. The crystal structures reveal molecular complex units described by the formula  $\{M(4,4'\text{-dpdo})_2[\text{N}(\text{CN})_2]_2(\text{H}_2\text{O})_2\}$ , where M = Co(II) (**1**) or Mn(II) (**2**). The metal cation is coordinated by six donor atoms in a distorted octahedral geometry: by two terminal N-atoms of two dicyanamides, two O-atoms of two 4,4'-dpdo ligands, and two O-atoms of water molecules.

A labeled ORTEP plot of the structure of compound **1** is shown in Fig. 1. The Co(II) cation is coordinated in the equatorial plane by two N-atoms of two symmetry-related  $[\text{N}(\text{CN})_2]^-$  ligands (with Co(1)—N(3) distance of 2.084(4) Å) and two O-atoms of two 4,4'-dpdo ligands (Co(1)—O(1) distance of 2.097(4) Å), and axially with two O-atoms of two water molecules (Co(1)—O(3) distance of

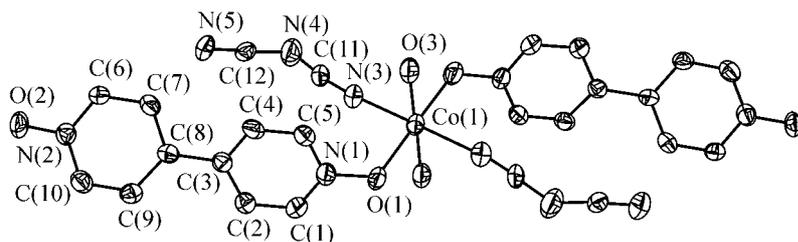
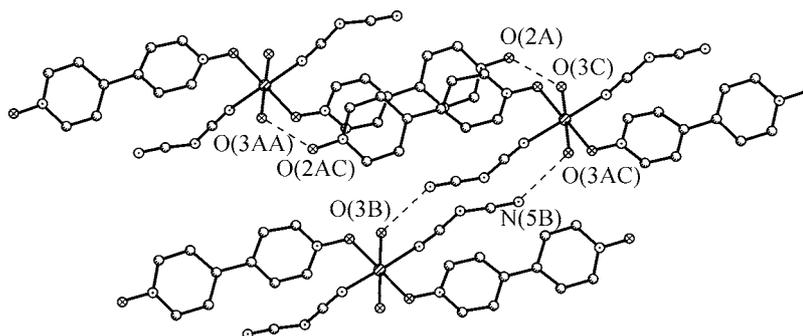


Fig. 1. Molecular structure of  $\{\text{Co}(4,4'\text{-dpdo})_2[\text{N}(\text{CN})_2]_2(\text{H}_2\text{O})_2\}$

Fig. 2. Fragment of crystal packing in **1** (down the *a* axis) showing a chain (two upper molecules) and two types of H-bonds (broken lines)



2.139(4) Å). Nonlinear coordination of the  $[N(CN)_2]^-$  ligands to the Co(II) cation is apparent, with Co(1)—N(3)—C(11) angle of 172.0°. The N—O distance in the 4,4'-dpdo ligand of 1.309(5) Å for the non-coordinated end of the ligand is shorter than 1.326(4) Å for the coordinated end. Although compound **1** is a mononuclear cobalt complex, adjacent mononuclear units are linked through O—H...N and O—H...O hydrogen bonds (see Table 3) to form H-bonded chains. The O(3) atom from the coordinated water molecule takes part in two hydrogen bonds, to N-atom of dicyanamide belonging to a molecule from adjacent chain and to O-atom of 4,4'-dpdo of a neighboring molecule of the same chain (Fig. 2), with the O...N and O...O distances of 2.936 and 2.712 Å, respectively.

The structure **2** is very similar, with the corresponding coordination bonds being longer (see Table 2). In particular, the distances M(1)—N(3), M(1)—O(1) and M(1)—O(3) are 2.204(5), 2.237(4) and 2.263(4) Å, respectively, for Mn, while 2.084(4), 2.097(4) and 2.139(4) Å, respectively, for Co.

## DISCUSSION

In our previous studies, we synthesized several coordination polymers with flexible ligand dicyanamide, e.g.  $[Cu(tpzt)(bpcam)][N(CN)_2] \cdot 7H_2O$  [21],  $\{Co(NITmPy)_2[N(CN)_2]_2\}_n$  [22]. In  $[Cu(tpzt)(bpcam)][N(CN)_2] \cdot 7H_2O$ , dicyanamide is included as a solvated molecule in the crystal structure that is it does not interact chemically with another component. In complex  $\{Co(NITmPy)_2[N(CN)_2]_2\}_n$ , dicyanamide acts as a bridging ligand. Moreover, in this paper, the molecule plays the role of terminal ligand. In addition to the mentioned complexes, the flexible ligand, which can adopt various conformations, may induce the formation of coordination polymers with novel topologies. The various structures of the complexes indicate that the resulting supramolecular topologies are highly influenced by counterions and synthesis conditions.

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