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## A 3D supramolecular network of cobalt(II)(bis(4-pyridyl)ethylene) with terephthalate dianions

Note

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### Abstract

A three dimensional supramolecular network,  $\{[Co(bpee)(H_2O)_4] \cdot (tp) \cdot 2(H_2O)\}_n$  (1) [bpee = trans-1,2-bis(4-pyridyl)ethylene; tp = terephthalate dianion] has been synthesized and characterized by X-ray single crystal structure, magnetic measurement and thermal analysis. The structure determination reveals that the cobalt(II) ions, bridged by bpee and coordinated by four water molecules, give rise to covalently linked 1D polymeric chain. The parallel chains get involved in H-bonding with tp resulting in a 3D architecture. Upon heating 1, which is pink in color, transforms to [Co(bpee)(tp)](1a, blue). The deaquated species (1a) reverts on keeping in humid atmosphere. Low temperature magnetic data indicate weak antiferromagnetic coupling. © 2007 Elsevier B.V. All rights reserved.

Keywords: Cobalt(II); Terephthalate; Crystal structure; Magnetic measurement; Supramolecule

### 1. Introduction

Higher dimensional metal-organic hybrid materials of transition metal ions are of great interest owing to their interesting topologies and potential applications in material science [1]. Commonly used synthetic approaches for such materials are: (a) use of anionic bridging ligands, which can partially/fully counterbalance the charge of the metal centers [2]; (b) combination of anionic as well as neutral spacers, which may enhance the dimensionality of molecular materials [3]; (c) use of only neutral spacers where charges are counterbalanced by non-coordinating anions [4]. Research in this field has been carried out by a number of groups [5] including ours, [6] by using various carboxylates as anionic bridging ligand.

Among the carboxylates, terephthalate dianion (tp) is being recently used as efficient "spacer" for its versatile coordination modes and ability to form large and tightly bound architecture with specific and directional hydrogen bond as well as  $\pi - \pi$  stacking [7]. The combined use of tp with dipyridyl spacers led to novel architectures, namely,  $[Co(4,4'-bipy)(tp)]_n$  [8],  $[Co(bpe)(tp)]_n$  [9], and [Co(bpp)- $(tp)(H_2O)_2]_n$  [7a] (bpp = 1,3-bis(4-pyridyl)propane). Very recently, we have reported an inclined interpenetrated 3D network,  $\{[Co(bpe)(tp)(H_2O)_2] \cdot 2.5(H_2O)\}_n$  (bpe = 1,2bis(4-pyridyl)ethane) [10] showing crystals of low life span. But inclusion of glycol has resulted in [Co(bpe)(tp)- $(H_2O_2)$  (glycol) [10], having higher thermal stability and longer shelf life of crystals since glycol functions as selective H-bonded connector between the opposite walls of the pore inducing contraction of cavity size and higher symmetry of the architecture. We have also reported a 3D supramolecular network,  $\{[Co(dpyo)(tp)(H_2O)_2] \cdot [Co(H_2O)_6] \cdot$  $(tp) \cdot (H_2O)_n [11] (dpyo, 4,4'-dipyridyl N,N'-dioxide) with$ unique H-bonded assembly and rare bridging mode of

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dpyo. The foregoing facts have led us to pursue further on the chemistry of cobalt(II)-terephthalate using a relatively longer and rigid dipyridyl spacer such as *trans*-1,2-bis-(4-pyridyl)ethylene (bpee). In the present contribution, we report on the synthesis, crystal structure, magnetic behavior and thermal analysis of a 3D supramolecular network  $\{[Co(bpee)(H_2O)_4] \cdot (tp) \cdot 2(H_2O)\}_n$  (1).

### 2. Experimental

### 2.1. Materials

High purity (98%) *trans*-1,2-bis(4-pyridyl)ethylene (bpee) was purchased from Aldrich Chemical Company Inc. and used without further purification. All other chemicals were of AR grade.

### 2.2. Physical measurements

Elemental analyses (carbon, hydrogen and nitrogen) were performed using a Perkin–Elmer 240C elemental analyzer. IR spectra were measured using KBr pellets on a Nicolet 520 FTIR spectrometer. Magnetic measurements were carried out on polycrystalline samples in a Quantum Design MPMS XL-5 SQUID magnetometer operating at a magnetic field of 0.1 T between 2 and 300 K. The diamagnetic corrections were evaluated from Pascal's constants. Thermal analysis was done on a Perkin–Elmer Pyris Diamond system.

2.3. Synthesis of complex  $\{[Co(bpee)(H_2 \ O)_4] \cdot (tp) \cdot 2(H_2 \ O)\}_n (1)$ 

An aqueous solution (5 mL) of disodium terephthalate (1 mmol, 0.210 g) was added drop wise to an aqueous solution (5 mL) of  $Co(NO_3)_2 \cdot 6H_2O$  (1 mmol, 0.291 g) under stirring condition. To this mixture a methanolic solution (10 mL) of bpee (1 mmol, 0.182 g) was added and stirred for 1 h. It was filtered and the filtrate was kept in a CaCl<sub>2</sub> desiccator. Orange single crystals suitable for X-ray structure determination were obtained after a week. They were separated, washed with ethanol and dried. Yield: 70%. Anal. Calc. for  $C_{20}H_{26}CoN_2O_{10}$  (513.36): C, 46.75; H, 5.06; N, 5.45. Found: C, 46.10; H, 4.96; N, 5.30%. The infrared spectra exhibited the following absorption bands: 3500–2980 (sbr), 1618 (s), 1556 (vs), 1431(w), 1378(vs), 1259(vw), 957(w), 827(w), 758(s), 557(s), 507(w) cm<sup>-1</sup>.

### 2.4. Crystallographic data collection and refinement

Crystal data and details of data collections and refinements for the structure reported are summarized in Table 1. Diffraction data for complex 1 were collected on a Nonius DIP-1030H system using Mo K $\alpha$  radiation. Cell refinement, indexing and scaling of the data sets were carried out using Denzo [12] and Mosflm [13] programs. The structure was solved by direct methods and subsequent Fourier anal-

Table 1	
Crystallographic data and details of structure refinement for complex 1	

	1
Empirical formula	C <sub>20</sub> H <sub>26</sub> CoN <sub>2</sub> O <sub>10</sub>
Formula weight	513.36
Crystal system	triclinic
Space group	$P\overline{1}$
<i>a</i> (Å)	6.752(3)
$b(\mathbf{A})$	6.438(2)
<i>c</i> (Å)	13.604(3)
α (°)	110.65(2)
β(°)	91.69(2)
γ (°)	96.39(2)
$V(\dot{A}^3)$	548.4(3)
Z	1
$D_{\text{calcd}} (\text{g cm}^{-3})$	1.554
$\mu$ Cu K $\alpha$ (mm <sup>-1</sup> )	6.674
F(000)	186
$\theta_{\rm max}$ (°)	64.56
Reflections collected	5335
Unique reflections	1626
R <sub>int</sub>	0.0760
Observed $[I > 2\sigma(I)]$	1603
Parameters	175
Goodness of fit $(F^2)$	1.067
$R_1 [I > 2\sigma(I)]^a$	0.0583
$wR_2^{a}$	0.1568
Residuals (e/Å <sup>3</sup> )	0.537, -0.375

<sup>a</sup>  $R_1(F_o) = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|, \ w R_2(F_o^2) = [\Sigma w (F_o^2 - F_c^2)^2 / \Sigma w (F_o^2)^2]^{1/2}.$ 

yses [14] and refined by the full-matrix least-squares method based on  $F^2$  with all observed reflections [14]. Most of the water hydrogens detected on the  $\Delta$ Fourier map were restrained with a fixed O–H bond distance (0.85 Å). All the calculations were performed using the WinGX System, Ver 1.70.00 [15].

### 3. Results and discussion

# 3.1. Structure description of $\{[Co(bpee)(H_2O)_4] \cdot (tp) \cdot 2(H_2O)\}_n (1)$

The structure determination of the complex 1 reveals Co(H<sub>2</sub>O)<sub>4</sub> units bridged by bpee ligands with the occurrence of 1D coordination polymeric chains running along the crystallographic c direction. An ORTEP drawing with atom numbering scheme of the metal coordination sphere, the dicarboxylate counteranion and the lattice water molecules O3w, is shown in Fig. 1, while a selection of bond lengths and angles is reported in Table 2. The cobalt(II) ion, the bpee ligand, and the terephthalate dianion are located on an inversion center. Besides the two bpee N donors in *trans* position, each cobalt(II) in the chain is coordinated by four water molecules resulting in a CoN2O4 chromophore. The octahedral coordination geometry has bond angles that do not deviate more than 2° from the ideal values. The four water molecules, O1w, O2w and the symmetry related ones, form the equatorial plane around each metal with Co-O1w and Co-O2w distances of 2.101(3) and 2.116(3) Å, respectively, and the Co-N1



Fig. 1. ORTEP diagram (40% thermal ellipsoid) with atom labeling scheme of complex 1, the metal is located on an inversion center [symmetry code (') -x, 2-y, -z].

Table 2 Selected bond distances (Å) and angles (°) in complex 1

Co–O(1w)	2.101(3)	O(1w)-Co-O(2w)	89.81(11)
Co-O(2w)	2.116(3)	O(1w)-Co-O(2w')	90.19(11)
Co-N(1)	2.119(3)	O(1w)-Co-N(1)	89.23(11)
		O(1w)-Co-N(1')	90.77(11)
O(1w')-Co-O(1w)	180.0	O(2w)-Co-N(1)	92.35(11)
O(2w)-Co-O(2w')	180.0	O(2w)-Co-N(1')	87.65(11)
N(1)-Co-N(1')	180.0		

Symmetry code (') -x, 2-y, -z.



Fig. 2. Perspective view of crystal packing of 1 [dotted lines indicate H-bonds].

distance (2.119(3) Å) shows a comparable value. The bpee presents coplanar atoms and separates the cobalt atoms along the chain by 13.604(3) Å (axis c), while the shortest

Table 3 H-bond distances (Å) and angles (°) in complex 1

inter-chain metal-metal distance is 6.438 Å. In the terephthalate dianion the carboxylate groups form a dihedral angle of  $11.3(3)^{\circ}$  with the phenvl ring. The dicarboxylates are located among the coordination polymers giving rise to a 3D structure through an ordered H-bonded scheme with the water molecules (Fig. 2). It is worthy to note that the lattice water O3w is involved in a quadruple hydrogen bonded module, that is, double donor (towards O3 and O4) and acceptor (from Olw and O2w) H-bonding (Fig. 2, Table 3). The structure has the same stoichiometry, but a different crystal packing, of the complexes [ $\{M(4,4'-bipy)\}$ - $(H_2O)_4$   $(C_5O_5)$   $(H_2O)_2$   $[n]_n$  (M = Mn, Fe, Co) [16]. In the latter derivatives the croconate dianions, engaged in a H-bonding scheme, are sandwiched between bipy rings of adjacent chains (distance of about 3.4 Å) and take part in  $\pi$ - $\pi$  interactions. On the other hand, in the present complex no such interaction is detected (Figs. 2 and 3). The (shorter) distance between the centroids of bpee rings and terephthalate dianion is 4.802(3) Å and the dihedral angle formed by their mean planes is 34.57°. Thus, the crystal packing is driven only by the H-bonding scheme involving the water molecules.

#### 3.2. Magnetic properties

The  $\chi_M T$  versus T plot for 1 ( $\chi_M$  is the molar magnetic susceptibility for one Co<sup>II</sup> ion) is shown in Fig. 4.  $\chi_M T$  value, which is 3.62 cm<sup>3</sup> mol<sup>-1</sup> K at 300 K, continuously decreases and becomes 2.1 cm<sup>3</sup> mol<sup>-1</sup> K at 2 K.

Based on the reasoning already reported by us [7a] with regard to the calculation of an estimated J value, we have used the two-exponential Rueff expression [17,18],  $\chi_{\rm M}T = A\exp(-E_1/kT) + B\exp(-E_2/kT)$  [where A + Bequals the Curie constant ( $\approx 2.8-3.4$  cm<sup>3</sup> mol<sup>-1</sup> K for octahedral cobalt(II) ions), and  $E_1$ ,  $E_2$  represent the "activation energies" corresponding to the spin orbit coupling and the antiferromagnetic exchange interaction], which is suitable for any temperature greater than the possible  $T_{\rm c}$  [17,18]. The best fit values obtained with this procedure are:  $A + B = 3.52 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ , in good agreement with those given in the literature for the Curie constant ( $C \approx 2.8$ -.4 cm<sup>3</sup> mol<sup>-1</sup> K) [17,18];  $E_1/k = 40.1$  K, that is, of the same magnitude to those reported by Rueff et al. for several one- and two-dimensional cobalt(II) complexes [18]. As the value found for the antiferromagnetic exchange interaction is very weak ( $E_2/k = 0.28$  K), corresponding to J =-0.56 K (= $-0.81 \text{ cm}^{-1}$ ), according to the Ising chain

D_H	d(D_H)	d(H A)	/DHA	$d(\mathbf{D} = \mathbf{A})$	Δ	Symmetry code
	u(D 11)			u(D1)		Symmetry code
Olw-H11	0.89	1.813	170.12	2.693	O3	[-x+1, -y+1, -z]
O1w-H12	0.89	1.923	170.76	2.807	O3w	
O2w-H21	0.88	1.898	171.77	2.771	O4	[x, y + 1, z]
O2w-H22	0.87	1.922	173.59	2.785	O3w	[-x+1, -y+2, -z]
O3w-H31	0.89	1.954	164.39	2.820	O4	
O3w-H32	0.89	1.893	169.48	2.774	O3	[x, y + 1, z]



Fig. 3. View of crystal packing down *a*-axis showing the H-bonding scheme between terephthalate dianion and water molecules (of the –  $Co(H_2O)_4$ -bpee– polymers only water molecules shown; larger sphere represents the lattice water molecule O3w).



Fig. 4.  $\chi_M T$  versus T plot for complex 1. The solid line represents the bestfit. Inset: Plot of the reduced magnetization  $(M/N\beta)$  versus H at 2 K for complex 1.

approximation,  $\chi_M T \propto \exp(J/2kT)$ . The small J value is compatible with the long bridging ligand. The reduced magnetization curve,  $M/N\beta$ , at 2 K tends to 2.5  $N\beta$  at 5 T (Fig. 4, inset), which is in perfect agreement with the values reported [17].

### 3.3. Thermal study

Complex 1 (pink) upon heating loses two lattice water and four coordinated water molecules in one step (70– 120 °C) yielding a blue species, 1a (solid state electronic spectra: 19250, 17960, 13990–15460, and 8825 cm<sup>-1</sup>;  $\mu_{eff}$ , 4.80 BM at 300 K), which is stable up to 200 °C. Species 1a reverts on exposure to humid (RH ~80%) atmosphere. The sharp deaquation does not allow to generate {[Co(bpee]-(H<sub>2</sub>O)<sub>4</sub>](tp)}<sub>n</sub> as intermediate species in the solid state. Crystal structure is in favor of such type of deaquation as coordinated as well as lattice water molecules are involved in H-bonding with encapsulated tp. The IR spectra of 1 and 1a show a slight shift in v(COO) band supporting de-encapsulation of tp after release of water molecules to maintain the tetrahedral geometry of cobalt(II).

### 4. Conclusion

In this investigation we report another contribution to the study of cobalt(II)-terephthalate coordination polymers using N,N'-donor ligands. The structure determination reveals that tp does not get involved in coordination remains as lattice moiety in between the and  $-[Co(H_2O)_4 bpee]_n$  chains. But extensive hydrogen bonding among the coordinated/lattice water molecules and lattice tp enhances the dimensionality to 3D. A comparison of available Co(II)-terephthalate structures (Table 4) reveals that the topology and the dimensionality of the network not only depend on the associated coligands but also on the number of coordinated water molecules. It is apparent that the augmentation of coordinated water molecules induces a decrease in dimensionality from 3D to 2D and ultimately to 1D. Moreover, the long ligands, i.e., rigid 4,4'-bipy/flexible bpp/bpe favor the interpenetration. Although it is difficult to rationalize these results, the relatively longer rigid bpee used in the present system seems to

Table 4

Cobalt-terephthalate networks in combination with dipyridyl spacers

Complex	Description	Reference
$[Co(4,4'-bipy)(tp)]_n$	Two fold interpenetrated 3D coordination polymer formed by tp and 4,4'-bipy	[8]
$[Co(bpe)(tp)]_n$ (bpe = 1,2-bis(4- pyridyl)ethane)	Two fold interpenetrated 3D net of cuboidal building blocks formed by tp and bpe	[9]
$\{ [Co(bpe)(tp)(H_2O)_2] \cdot 2.5(H_2O) \}_n$	Inclined interpenetrated 2D sheets of tp and bpe having (4,4) topology. Water molecules	[10]
	fill the channels in the interlocked 3D structure	
$\{ [Co(bpe)(tp)(H_2O)_2] \cdot (glycol) \}_n$	Inclined interpenetrated 2D sheets of tp and bpe having (4,4) topology. Glycol molecules	[10]
	fill the channels in the interlocked 3D structure	
$[Co(bpp)(tp)(H_2O)_2]_n$ (bpp = 1,3-bis(4- pyridyl)propane)	Parallel interpenetrated 2D layers of tp and bpp having (4,4) topology leading to a 3D supramolecular network through H-bonding interactions	[7a]
$\{ [Co(dpyo)(tp)(H_2O)_2] \cdot [Co(H_2O)_6] $	1D coordination polymer (built up by Co(II) ions doubly bridged tp and dpyo oxygen). A	[11]
$(\mathbf{tp}) \cdot (\mathbf{H}_2\mathbf{O})\}_n$	3D supramolecular network originated through H-bonds with $[Co(H_2O)_6]^{2+}$ , lattice tp and water molecules	
$\{ [Co(bpee)(H_2O)_4] \cdot (tp) \cdot 2(H_2O) \}_n$	1D polymeric chain -[Co(H <sub>2</sub> O) <sub>4</sub> -bpee] A 3D supramolecular network is achieved by	this work
(bpee = trans-1, 2-bis(4-pyridyl)ethylene)	H-bond interactions of lattice tp and water molecules	

impede tp to enter in the coordination network and fix it through encapsulation.

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### Appendix A. Supplementary data

CCDC 634486 contains the supplementary crystallographic data. The data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2007.07.037.

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