

# A New One-Dimensional Coordination Polymer [Co(CCl<sub>3</sub>COO)<sub>2</sub>(CH<sub>3</sub>OH)<sub>2</sub>(μ-4,4'-bipy)]<sub>n</sub>: Synthesis and Structural Aspects

Pritha Talukder<sup>a</sup>, Amitabha Datta<sup>a</sup>, Samiran Mitra<sup>a</sup>, and Georgina Rosair<sup>b</sup>

<sup>a</sup> Department of Chemistry, Jadavpur University, Kolkata – 700032, India

<sup>b</sup> Department of Chemistry, Heriot-Watt University, Edinburgh, EH14 4AS, U.K.

Reprint requests to Prof. S. Mitra. Fax: +91-33-24146266. E-mail: smitra\_2002@yahoo.com

Z. Naturforsch. **60b**, 33–36 (2005); received February 10, 2004

A new one-dimensional coordination polymer [Co(CCl<sub>3</sub>COO)<sub>2</sub>(CH<sub>3</sub>OH)<sub>2</sub>(μ-4,4'-bipy)]<sub>n</sub> (**1**), has been synthesised and its crystal structure determined by single-crystal X-ray diffraction. The structure consists of a one-dimensional linear chain of cobalt(II) centres linked by bridging 4,4'-bipyridine units. The Co(II) ion lies at an inversion centre forming an elongated octahedral coordination sphere. There is an intramolecular hydrogen bond [2.02(5) Å] between a trichloroacetate oxygen and a methanolic hydrogen forming a planar six-membered ring.

**Key words:** 1D-Coordination Polymer, 4,4'-Bipyridine, Cobalt(II), Crystal Structure

## Introduction

Coordination polymers are an important class of materials because of their potential applications in catalysis and advanced materials [1]. Recent interest has been focused on the crystal engineering of supramolecular architectures organised by covalent or supramolecular hydrogen-bonding contacts [2–6]. Exo-bidentate ligands, such as pyrazine, 4,4'-bipyridine, 1,2-bis(4-pyridyl)ethane are widely used for the synthesis of polynuclear complexes with extended structures [7–10].

Focusing on 4,4'-bipyridine as a ligand, a number of one-, two- and three-dimensional infinite metal(I, II and III)–4,4'-bipy frameworks have already been generated [9]. Besides this framework, a number of extended structures with diverse topologies have been synthesised, such as interwoven honeycomb [10], interpenetrated diamond lattices [11], railroad-like network [12] and other architectures [13–15]. However, most of the above mentioned frameworks are generated directly by coordination bonds [16–18]. Other metal complexes are further extended into higher dimensional networks by hydrogen-bonding interactions [19]. In this work the principal hydrogen-bonding motif is intramolecular and the framework is extended by coordination of the 4,4'-bipy unit.

Chen *et al.* have been pursuing the synthetic strategies for the preparation of non-interpenetrating open

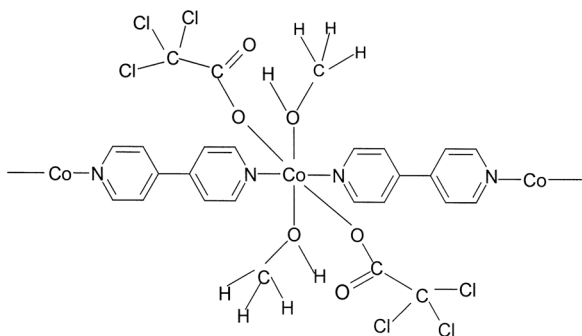
frameworks with variable cavities or channels, in which the rod-like rigid spacers such as 4,4'-bipy, pyrazine and the related species are chosen as building blocks [20–24]. Lu *et al.* have described the synthesis and reactivity of three one-dimensional polymers formed by coordination of 4,4'-bipy to Co(II) ions [25], by using CoSO<sub>4</sub>, CoCl<sub>2</sub> and Co(OAc)<sub>2</sub> as starting materials where the anions are directly coordinated to the metal centres. Wang *et al.* reported a related Co(II) coordinated polymer, [Co(4,4'-bipy)(O<sub>2</sub>CCH<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] where the one-dimensional chains form an interpenetrating, three-dimensional structure *via* interchain hydrogen bonds between acetate and H<sub>2</sub>O [26].

In the present work, we report the synthesis of a new one-dimensional linear chain Co(II) polymer of formula [Co(CCl<sub>3</sub>COO)<sub>2</sub>(CH<sub>3</sub>OH)<sub>2</sub>(μ-4,4'-bipy)]<sub>n</sub> (**1**), which is characterised by elemental analysis, IR and electronic spectra, thermal analysis and room temperature magnetic susceptibility. The crystal structure determination shows that the primary structural motif is a linear chain.

## Results and Discussion

### IR spectrum

The IR spectral bands (KBr pellet) present at 1533, 1414, 1222, 1076 and 827 cm<sup>–1</sup> are the characteristic absorption bands of the 4,4'-bipyridine ligand.



The structural formula drawing of complex **1**.

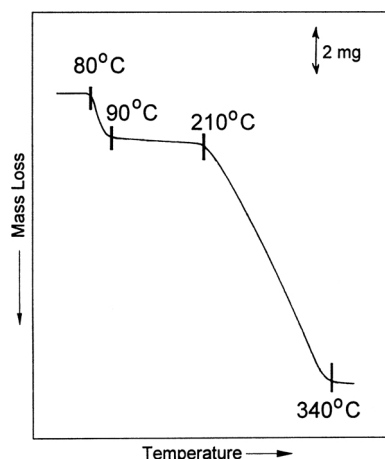


Fig. 1. TGA curve for **1** (—) (weight taken = 15 mg). Heating rate = 10 °C min<sup>-1</sup>.

The bands at 1681 and 1352 cm<sup>-1</sup> correspond to  $\nu_{as}$  (CO<sub>2</sub><sup>-</sup>) and  $\nu_s$  (CO<sub>2</sub><sup>-</sup>), respectively. The  $\Delta\nu$  value of 329 cm<sup>-1</sup> is significantly higher than the value for free CCl<sub>3</sub>CO<sub>2</sub><sup>-</sup>, indicating that the carboxylate group is coordinated with Co(II) in a monodentate orientation. The broad absorption band at 3447 cm<sup>-1</sup> is perhaps attributable to  $\nu(\text{O}-\text{H}\cdots\text{X})$  (where X is an electronegative nitrogen or oxygen atom), indicating the presence of hydrogen bonding in the complex [27].

#### Electronic spectrum

The solid state electronic spectrum of **1** shows three d-d bands at approximately 8500, 14000 and 18200 cm<sup>-1</sup>, which are in the expected range for hexacoordinated Co(II) complexes [28] and can be assigned to the transitions  $^4T_{1g} \rightarrow ^4T_{2g}$  ( $\nu_1$ ),  $^4T_{1g} \rightarrow ^4A_{2g}$  ( $\nu_2$ ) and  $^4T_{1g} \rightarrow ^4T_{1g}$  (P) ( $\nu_3$ ), respectively. These data suggest a polymeric hexacoordinated structure for the cobalt complexes.

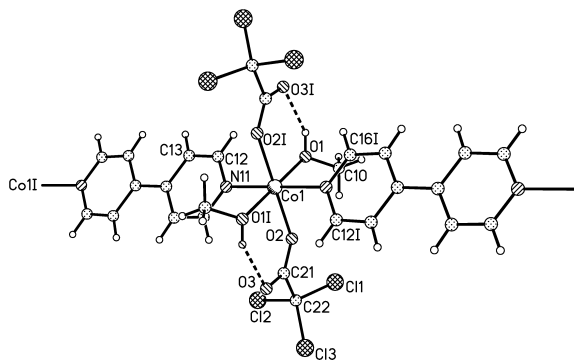


Fig. 2. Molecular structure of **1** showing part of the polymeric chain. Displacement ellipsoids drawn at the 50% probability level.

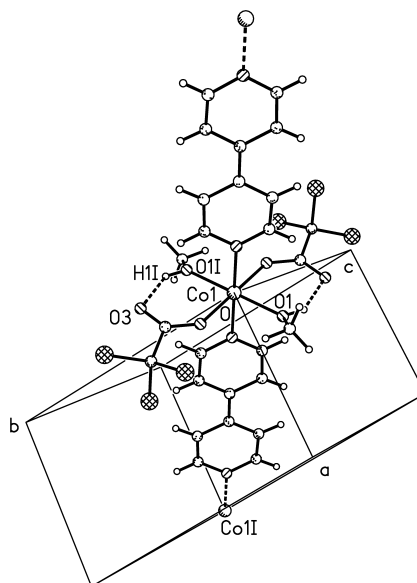


Fig. 3. Unit cell diagram of **1**.

#### Thermal analysis

Complex **1** was heated up to 600 °C in N<sub>2</sub> atmosphere. The TGA curve showed the complex to be stable up to 80 °C (Fig. 1). Beyond this temperature, the complex decomposes and the mass loss occurs in two steps, 80–90 °C and 210–340 °C. In the first step, the mass loss corresponds to the loss of two methanol molecules. The second step is consistent with the loss of one bipyridine molecule and two acetate groups leaving the residue as CoO [25].

#### Magnetic susceptibility

The room temperature magnetic moment was found to be 3.92  $\mu_B$  which is close to the spin only value of Co(II).

Table 1. Crystallographic data for **1**.

Chemical formula	C <sub>16</sub> H <sub>16</sub> Cl <sub>6</sub> CoN <sub>2</sub> O <sub>6</sub>
Formula weight	603.94
Temperature	160(2) K
Wavelength	0.71073 Å
Crystal system	triclinic
Space group	$P = \bar{1}$
Unit cell dimensions	$a = 6.977(2)$ Å, $\alpha = 106.57(2)^\circ$ $b = 9.459(2)$ Å, $\beta = 109.72(3)^\circ$ $c = 9.483(3)$ Å, $\gamma = 91.08(2)^\circ$
Volume	560.1(3) Å <sup>3</sup>
Z	1
Density (calculated)	1.791 Mg [cm <sup>-3</sup> ]
Absorption coefficient	1.519 mm <sup>-1</sup>
$F(000)$	303
Crystal size	0.62 × 0.24 × 0.18 mm <sup>3</sup>
Theta range for data collection	2.26 to 25.00°
Reflections collected	2355
Independent reflections	1924 [ $R_{\text{int}} = 0.0432$ ]
Completeness to $\theta = 25.00^\circ$	97.6%
Max. and min. transmission	0.693 and 0.761
Refinement method	Full-matrix least-squares on $F^2$
Data / restraints / parameters	1924 / 0 / 147
Goodness-of-fit on $F^2$	1.031
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R1 = 0.0439$ , $wR2 = 0.1148$
$R$ indices (all data)	$R1 = 0.0497$ , $wR2 = 0.1193$
Largest diff. peak and hole	0.686 and $-0.550$ e/Å <sup>3</sup>

### X-ray crystal structure

The crystal structure of **1** is a linear chain comprised of bridging 4,4'-bipyridine ligands linking Co(CCl<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>(CH<sub>3</sub>OH)<sub>2</sub> units (Fig. 2). The selected bond lengths and bond angles are given in Table 2. These linear covalently-linked chains are also seen in many related compounds [2, 26, 29]. The Co atom lies on a centre of inversion and is coordinated by two oxygen atoms from two monodentate trichloroacetates; two oxygen atoms from methanol molecules and two nitrogen atoms from *trans* 4,4'-bipyridine ligands, resulting in elongated octahedral geometry around the cobalt centre. Four oxygen atoms occupy the equatorial positions with bond lengths of 2.079(2) and 2.099(2) Å [Co(1)-O(2) and Co(1)-O(1) respectively] and the nitrogen atoms are located in axial positions where the Co(1)-N(11) bond distance is 2.139(3) Å. This distance is slightly shorter, despite being determined at 160 K, than some previously reported Co(II)-N(bipyridine) bond distances, 2.152–2.172 Å [25] and 2.181(6), 2.217(6) Å (room temperature study) [30]. The primary hydrogen bonding motif in **1** is intramolecular, in contrast to Wang's Co(II) polymer [Co(4,4'-bipy)(O<sub>2</sub>CCH<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] [26] where the water ligands extend the hydrogen bonding network into three dimensions. In **1** there is a intramolecular hydro-

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

Co(1)-O(2)	2.079(2)	Co(1)-O(1)	2.099(2)
Co(1)-N(11)	2.139(3)	O(1)-C(10)	1.432(4)
O(2)-C(21)	1.246(4)	O(3)-C(21)	1.231(4)
O(2)-Co(1)-O(11)	89.67(9)	O(2)-Co(1)-O(1)	90.33(9)
O(11)-Co(1)-O(1)	180.00(18)	O(21)-Co(1)-N(11)	91.07(9)
O(2)-Co(1)-N(11)	88.93(9)	O(11)-Co(1)-N(11)	90.55(9)
O(1)-Co(1)-N(11)	89.45(9)		

Symmetry transformations used to generate equivalent atoms: I =  $-x, -y, -z$ .

Table 3. Hydrogen bonds for **1** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1)...O(3I)	0.84(5)	2.02(5)	2.723(3)	141(4)
C(13)-H(13)...O(3II)	0.95	2.55	3.504(4)	178.6
C(15)-H(15)...O(3III)	0.95	2.41	3.357(4)	171.6

Symmetry transformations used to generate equivalent atoms: I:  $-x, -y, -z$ ; II:  $x+1, y, z+1$ ; III:  $-x, -y+1, -z$ .

gen bond [2.02(5) Å] between O(3) of a trichloroacetate molecule and a methanolic hydrogen H(1) giving a planar six-membered ring (Table 3).

In each unit cell, the Co-bipy-Co chains lie along the body diagonal of the unit cell, in the (111) direction. The aromatic rings in the bipy ligands are coplanar. The molecules pack as layers of bipy ligands with the acetate and methanol ligands lying in between the layers. These layers are undulating, the chains within these layers are connected by longer hydrogen bonds bifurcated at O(3) to bipy hydrogen atoms H(13), but these are weaker C-H...O links (Table 3). There are no direct bipy-bipy interactions between these chains. Within the polymeric chains the Co...Co distance is 11.392 Å.

## Experimental Section

### Materials

All chemicals and solvents used for the synthesis were of reagent grade. 4,4'-Bipyridine (Aldrich) was obtained commercially and used as received. Cobalt(II) trichloroacetate was prepared by the neutralisation reaction of cobalt(II) carbonate and trichloroacetic acid.

### Physical techniques

Elemental analyses were carried out using a Perkin-Elmer 2400 II elemental analyser. The infrared spectrum was recorded on a Perkin-Elmer 883 infrared spectrophotometer. The electronic spectrum was measured on a Hitachi U-3400 (UV/VIS/NIR.) spectrometer in methanol. Thermal investigation was carried out on a Shimadzu TGA-50 thermal analyser under a dynamic nitrogen environment. The room temperature magnetic susceptibility was measured with a model

155 PAR vibrating sample magnetometer fitted with a Waker Scientific 175FBAL magnet.

*Synthesis of  $[Co(CCl_3COO)_2(CH_3OH)_2(\mu-4,4'-bipy)]_n$  (**1**)*

A solution of 4,4'-bipyridine (0.156 g, 1 mmol) in methanol (10 ml) was added slowly to a solution of cobalt(II) trichloroacetate (0.383 g, 1 mmol) in the same solvent (20 ml), over a period of 5 min with constant stirring. The reaction mixture was allowed to evaporate slowly at room temperature. Light pink crystals of the title compound suitable for X-ray analysis were obtained one week later. Analysis for  $C_{16}H_{16}Cl_6CoN_2O_6$  ( $M_w$ : 603.94) calcd. C 31.79, H 2.64, N 4.53; found C 31.64, H 2.58, N 4.51.

*X-ray crystal structure determination*

A pink crystal of **1** was mounted on a glass fibre on a Bruker AXS P4 diffractometer and cooled to 160 K by an Oxford Cryosystems Cryostream. No significant crystal decay was found. Data were corrected for absorption by

$\psi$  scans. The structure was solved by direct and different Fourier methods, and refined by full-matrix least-squares on  $F^2$ . All non-hydrogen atoms were refined with anisotropic displacement parameters. Crystallographic computing was performed using SHELXTL [30] programs. Further details are given in Table 1.

*Supplementary data*

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC reference number 223878. Copies of the information may be obtained free of charge from The Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

*Acknowledgements*

We thank CSIR and UGC (New Delhi, India) for financial assistance and wish to acknowledge the use of EPSRC's Chemical Database at Daresbury.

- [1] C. Janiak, Dalton Trans. 2781 (2003); Y. Pei, O. Khan, J. Sletten, J. P. Renard, R. Georges, J. C. Gianduzzo, J. Curely, X. Qiang, Inorg. Chem. **27**, 47 (1988).
- [2] S. L. James, Chem. Soc. Revs. **32**, 276 (2003); D. Braga, F. Grepioni, G. R. Desiraju, Chem. Rev. **98**, 1375 (1998).
- [3] J. C. M. Rivas, L. Brammer, New J. Chem. **22**, 1315 (1998).
- [4] M. Fujita, Y. J. Kwon, S. Washizu, K. Ogura, J. Am. Chem. Soc. **116**, 1151 (1994).
- [5] C. J. Kepert, D. Hessek, P. D. Beer, M. J. Rosseinsky, Angew. Chem. Int. Ed. **37**, 3158 (1998).
- [6] C. B. Aakeroy, A. M. Beatty, D. S. Leinen, Angew. Chem. Int. Ed. **38**, 1815 (1999).
- [7] M. J. Zaworotko, J. Chem. Soc., Chem. Commun. **1** (2001).
- [8] S. R. Batten, R. Robson, Angew. Chem. Int. Ed. **37**, 1460 (1998).
- [9] A. J. Blake, N. R. Champness, P. Hubberstey, W.-S. Li, M. A. Withersby, M. Schroder, Coord. Chem. Rev. **183**, 117 (1999).
- [10] L. R. MacGillivray, S. Subramanian, M. J. Zaworotko, J. Chem. Soc., Chem. Commun. 1325 (1994).
- [11] G. J. E. Davidson, S. J. Leob, Angew. Chem. Int. Ed. **42**, 74 (2003).
- [12] O. M. Yaghi, H. Li, T. L. Groy, Inorg. Chem. **36**, 4292 (1997).
- [13] O. M. Yaghi, H. Li, J. Am. Chem. Soc. **118**, 295 (1996).
- [14] F. Robinson, M. J. Zaworotko, J. Chem. Soc., Chem. Commun. 2413 (1995).
- [15] L. Carlucci, G. Ciani, D. M. Proserpio, A. Sironi, J. Chem. Soc., Chem. Commun. 2755 (1994).
- [16] A. J. Blake, S. J. Hill, P. Hubberstey, W. S. Li, J. Chem. Soc., Dalton Trans. 913 (1997).
- [17] L. Carlucci, G. Ciani, D. M. Proserpio, A. Sironi, J. Chem. Soc. Dalton Trans. 1801 (1997).
- [18] G. De Munno, D. Armentano, T. Poerio, M. Julve, J. A. Real, Dalton Trans. 1813 (1999).
- [19] G. R. Lewis, A. G. Orpen, J. Chem. Soc., Chem. Commun. 1873 (1998). A. Beatty, Coord. Chem. Rev. **246**, 131 (2003).
- [20] X.-M. Chen, M.-L. Tong, Y.-J. Luo, Z.-N. Chen, Aust. J. Chem. **49**, 835 (1996).
- [21] M.-L. Tong, X.-M. Chen, X.-L. Yu, T. C. W. Mak, J. Chem. Soc., Dalton Trans. 5 (1998).
- [22] M.-L. Tong, B.-H. Ye, J.-W. Cai, X.-M. Chen, S. W. Ng, Inorg. Chem. **37**, 2645 (1998).
- [23] M.-L. Tong, X.-M. Chen, B.-H. Ye, S. W. Ng, Inorg. Chem. **37**, 5278 (1998).
- [24] M.-L. Tong, S.-L. Zheng, X.-M. Chen, J. Chem. Soc., Chem. Commun. 561 (1999).
- [25] J. Lu, C. Yu, T. Niu, T. Paliwala, G. Crisci, F. Somosa, A. J. Jacobson, Inorg. Chem. **37**, 4637 (1998).
- [26] Y.-S. Zhang, G. D. Enright, S. R. Breeze, S. N. Wang, New J. Chem. **23**, 625 (1999).
- [27] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, 3rd edn., Wiley, New York (1978).
- [28] A. B. P. Lever, Inorganic Electronic Spectroscopy, 2nd. edn. Elsevier, Amsterdam (1984).
- [29] B.-Q. Ma, S. Gao, T. Yi, G.-X. Xu, Polyhedron **20**, 1255 (2001).
- [30] G. M. Sheldrick, Structure determination and refinement programs, SHELXTL Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA (1999).