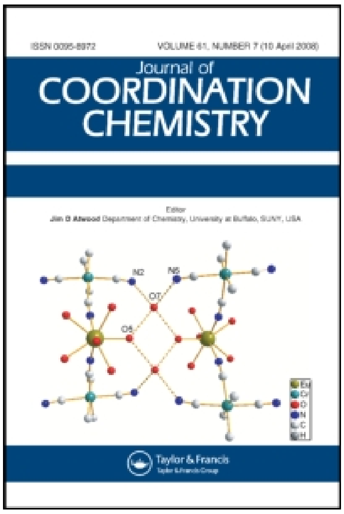

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Synthesis and crystal structure of polymeric 4,4'-bipyridine cadmium(II) sulfate trihydrate

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Synthesis and crystal structure of polymeric 4,4′-bipyridine cadmium(II) sulfate trihydrate

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Polymeric 4,4′-bipyridinecadmium(II) sulfate trihydrate, $[C_{10}H_8CdN_2O_7S]_n$, has been synthesized and characterized by X-ray diffraction and spectroscopic methods. The compound crystallizes in space group $P6_522$, with $a = 11.4465(15)$ Å, $c = 20.7380(18)$ Å. The coordination geometry around cadmium is distorted octahedral with Cd–N2 = 2.311(9), Cd–O1W = 2.278(8) and Cd–O(SO_4) = 2.247(7) Å.

Keywords: Supramolecular chain; Cd(II) sulfate; 4,4′-Bipyridine; X-ray structure; IR spectra

1. Introduction

The design of supramolecular architectures by a combination of coordination and weak intermolecular interactions, such as hydrogen bonding, π–π stacking and electrostatic interactions is of considerable current interest [1–3]. A number of one-, two- and three-dimensional infinite frameworks with diamondoid [4], helix [5], brick wall [6] and ladder motifs [7, 8] have been generated with linear and non-linear organic spacers [9, 10]. 4,4′-Bipyridyl is an excellent synthon in preparing novel structures, owing to its rigidity and ability to form strong hydrogen and coordination bonds via its two nitrogen atoms [11]. Diprotonated 4,4′-bipyridinium cations have been used in the stabilization of molybdenum oxide layers and in isolation of a new anionic lead iodide chain structures [12, 13]. Many supramolecular architectures involving the 4,4′-bipyridinium ion have been reported [14–18]. Here we report the preparation and structural properties of inorganic coordination polymers based on cadmium with 4,4′-bipyridyl.

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2. Experimental

Cadmium sulfate was purchased from Glaxo and 4,4′-bipyridyl from Merck. IR spectra (KBr pellets) were recorded in a Perkin-Elmer Spectrum One FTIR spectrophotometer in the range 4000–400 cm^{-1}.

2.1. *Synthesis*

A hot methanolic solution of 4,4′-bipyridyl and a hot aqueous solution of cadmium sulfate were mixed in a 1 : 1 mol ratio. The resultant solution was warmed on a water bath for half an hour and later on kept at room temperature for crystallization. Colourless crystals were obtained after a few days. Characteristic IR (cm^{-1}) peaks at 1096, 627 and 602 cm^{-1} are attributed to coordinated SO_4^{2-} ion. Aromatic C–C, C–N and O–H stretching vibrations occur at 1601, 1532, 1491, 1415 and 3124 cm^{-1}.

2.2. *Crystal structure determination*

A crystal of dimensions $0.19 \times 0.31 \times 0.34\,\mathrm{mm}^3$ was used for X-ray data collection. All measurements were made on a Bruker AXS Smart diffractometer using graphite-monochromatized Mo-Kα radiation at 293 K using the ω scan technique. The structure was solved by direct methods and refined using SHELXL97 [19]. Refinement involved full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically. Aromatic hydrogen atoms were refined using a riding model. The water hydrogen atoms were not located in difference Fourier maps. All the relevant information concerning data collection and refinement are given in table 1. Selected bond lengths and angles are given in table 2 and hydrogen bonding geometry in table 3.

Table 1. Crystal data and details of the structure determination.

Formula	$[C_{10}H_8CdN_2O_7S]_n$
Formula Weight	540.73
Crystal system	Hexagonal
Space group	$P6_522$
a, c [Å]	11.4465(15), 20.7380(18)
V [Å^3]	2351.8(5)
Z	6
D_c [g cm^{-3}]	2.291
μ(Mo-Kα) [mm^{-3}]	0.07106
$F(000)$	1596
Crystal size [mm^3]	$0.19 \times 0.31 \times 0.34$
Temperature (K)	293
Radiation [Å]	Mo-Kα, 0.71073
θ min, max [°]	2.2, 29.6
Dataset	$-15:5$; $-15:15$; $-27:27$
Tot., uniq. data, R(int)	25685, 1925, 0.036
Observed data [$I > 2\sigma(I)$]	1897
R, wR_2, S	0.0668, 0.1656, 1.28
Flack parameter	0.13(13)
Min. and max. resd. dens. [e Å^{-3}]	−0.76, 0.72

Table 2. Selected bond distances and bond angles (Å, °) for the complex.

Cd1–O1^{i}	2.245 (7)	Cd1–O1	2.247 (7)
Cd1–O1W^{i}	2.277 (8)	Cd1–O1W	2.278 (8)
Cd1–N2	2.311 (9)	Cd1–N1^{ii}	2.350 (13)
N1–C2	1.248 (12)	N1–C2^{i}	1.279 (12)
N1–Cd1^{iii}	2.320 (13)	C2–C3	1.392 (13)
C3–C4	1.336 (10)	C4–C3^{i}	1.303 (10)
C4–C5	1.509 (15)	C5–C6	1.271 (14)
C5–C6^{i}	1.303 (15)	C6–C7	1.404 (18)
C7–N2	1.322 (15)	N2–C7^{i}	1.289 (14)
O1–S1	1.493 (8)	S1–O3	1.313 (14)
S1–O4	1.42 (2)	S1–O4^{iv}	1.44 (2)
S1–O2	1.474 (15)	S1–S1^{iv}	2.319 (9)
O3–O2W^{v}	1.67 (2)	O3–O4	1.79 (3)
O4–O4^{iv}	0.71 (3)	O4–S1^{iv}	1.45 (2)
O2W–O3^{vi}	1.69 (2)	O3W–O3W^{vii}	1.29 (5)
O1^{i}–Cd1–O1	177.7 (4)	O1^{i}–Cd1–O1W^{i}	86.9 (3)
O1–Cd1–O1W^{i}	93.2 (3)	O1^{i}–Cd1–O1W	93.1 (3)
O1–Cd1–O1W	87.0 (3)	O1W^{i}–Cd1–O1W	175.4 (6)
O1^{i}–Cd1–N2	89.57 (18)	O1–Cd1–N2	92.72 (18)
O1W^{i}–Cd1–N2	87.9 (3)	O1W–Cd1–N2	87.5 (3)
O1^{i}–Cd1–N1^{ii}	90.43 (18)	O1–Cd1–N1^{ii}	87.28 (18)
O1W^{i}–Cd1–N1^{ii}	92.1 (3)	O1W–Cd1–N1^{ii}	92.5 (3)
N2–Cd1–N1^{ii}	180.000 (4)	C2–N1–C2^{i}	118.8 (14)
C2–N1–Cd1^{iii}	119.4 (7)	C2^{i}–N1–Cd1^{iii}	121.8 (7)
N1–C2–C3	120.7 (11)	C4–C3–C2	122.0 (9)
C3^{i}–C4–C3	115.7 (12)	C3^{i}–C4–C5	121.0 (6)
C3–C4–C5	123.3 (6)	C6–C5–C6^{i}	115.1 (15)
C6–C5–C4	121.3 (8)	C6^{i}–C5–C4	123.6 (7)
C5–C6–C7	121.5 (13)	N2–C7–C6	124.1 (12)
C7^{i}–N2–C7	113.5 (13)	C7^{i}–N2–Cd1	122.1 (6)
C7–N2–Cd1	124.4 (6)	S1–O1–Cd1	126.6 (4)
O3–S1–O4	81.6 (11)	O3–S1–O4^{iv}	110.1 (9)
O4–S1–O4^{iv}	28.9 (11)	O3–S1–O2	110.4 (11)
O4–S1–O2	117.0 (10)	O4^{iv}–S1–O2	109.2 (11)
O3–S1–O1	104.4 (10)	O4–S1–O1	128.5 (7)
O4^{iv}–S1–O1	114.1 (7)	O2–S1–O1	108.6 (9)
O3–S1–S1^{iv}	101.6 (9)	O4–S1–S1^{iv}	36.4 (8)
O4^{iv}–S1–S1^{iv}	34.9 (7)	O2–S1–S1^{iv}	81.6 (7)
O1–S1–S1^{iv}	146.2 (4)	S1–O3–O2W^{v}	107.2 (12)
S1–O3–O4	51.8 (7)	O2W^{v}–O3–O4	122.7 (15)
O4^{iv}–O4–S	177 (3)	O4^{iv}–O4–S1^{iv}	72 (4)
S1–O4–S1^{iv}	107.9 (9)	O4^{iv}–O4–O3	123 (4)
S1–O4–O3	46.5 (10)	S1^{iv}–O4–O3	126.0 (11)

Symmetry codes are (i): $x-y, -y, 1-z$; (ii): $x-1, y, z$; (iii): $1+x, y, z$; (iv): $x, x-y-1, 5/6-z$; (v): $-x+y, -x, 1/3+z$; (vi): $-y, x-y, z-1/3$; (vii): $-y, -x, 7/6-z$.

Table 3. Hydrogen bonding geometries (Å, °) for the complex.

D–H···A	D–H	H···A	D···A	D–H···A
C3–H3···O10^{i}	0.931	2.494	3.128(19)	125.62
C3–H3···O12^{i}	0.931	2.460	3.34(3)	158.79
C4–H4···O2W^{ii}	0.954	2.548	3.50(3)	178.49
C7–H7···O2W^{ii}	0.932	2.446	3.36(3)	166.06
C8–H8···O3W^{iii}	0.953	2.519	3.25(4)	133.40
C8–H8···O10^{i}	0.953	2.581	3.23(2)	125.26

Symmetry codes are (i): $-x, -x+y, 1/3-z$; (ii): $-1+x, -1+y, z$; (iii): $1-y, 1-x, 1/6-z$.

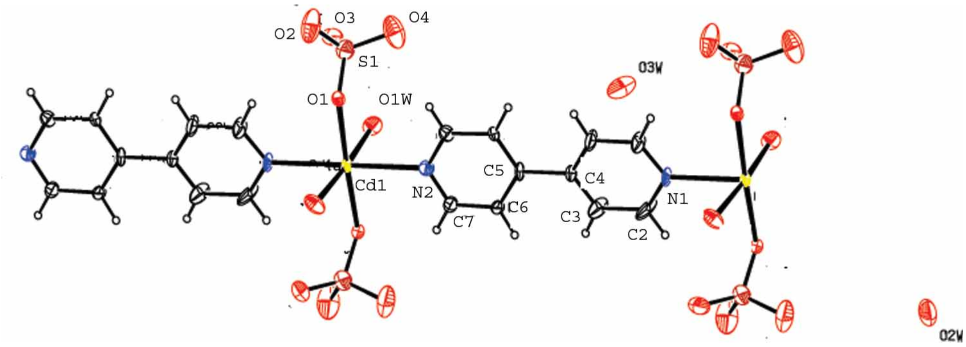

Figure 1. An ORTEP view of the complex showing the atom numbering scheme.

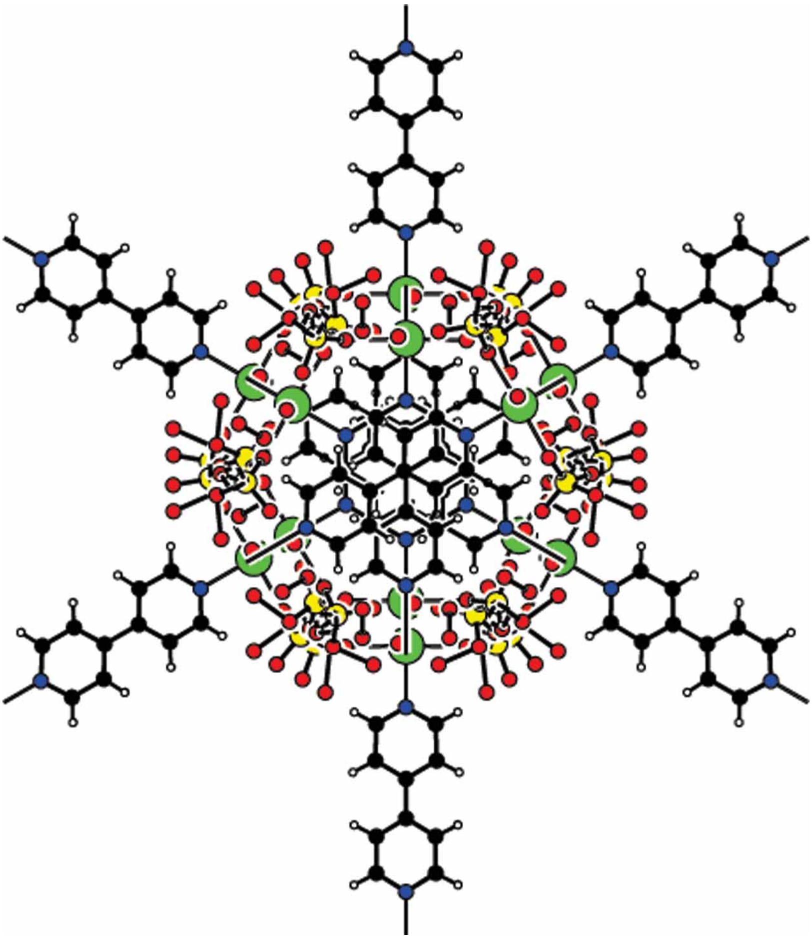

Figure 2. The structure looking down the *c* direction showing the hexagonal motif.

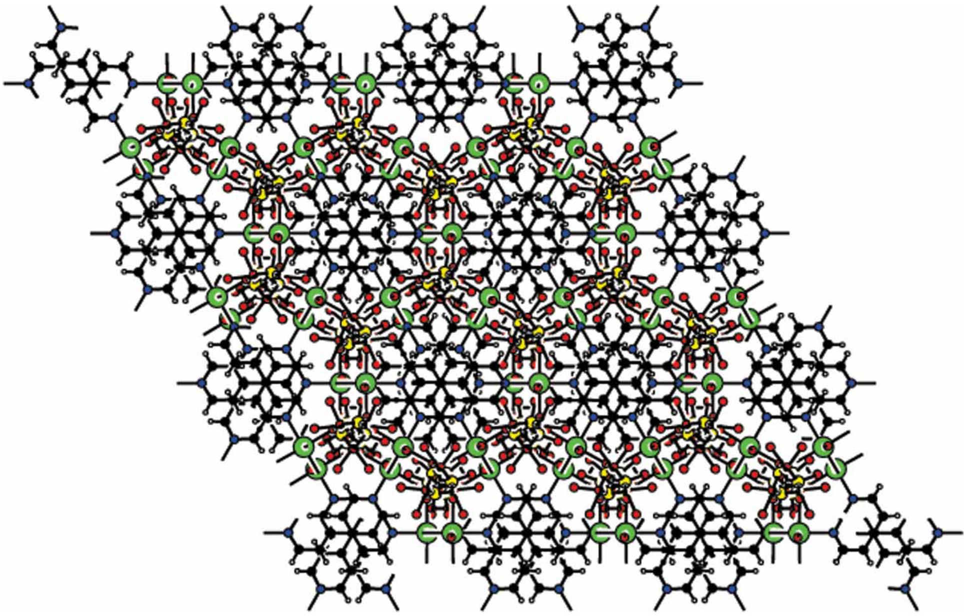

Figure 3. The overall packing arrangement of the complex looking down the *c* direction.

3. Results and discussion

In the crystal structure, the Cd atom is coordinated to water molecules, sulfate anions and 4,4′-bipyridyl ligands to form a distorted octahedral environment. Cd centers are bridged by 4,4′-bipyridine ligands, resulting in the formation of infinite linear bipy-Cd-bipy chains as shown in figure 1. The Cd, N1, N2, C4 and C5 atoms occupy special positions. Oxygen atoms from water molecules and sulfate anions occupy the equatorial plane of the octahedron and N atoms of 4,4′-bipyridyl the axial positions [Cd–N2 = 2.311(9), Cd–O1W = 2.278(8), Cd–O(SO_4) = 2.247(7) Å]. These values are close to others reported in the literature [20]. Infinite [bipy-Cd-bipy]$_n$ chains extend along the *b* axis and are linked by sulfate anion and water molecules to form a three dimensional framework with a hexagonal motif along the 6_5 screw axis as shown in figure 2. The chains form layers parallel to the *ab* plane and stack along the *c* axis. Adjacent layers are rotated by 60° to produced hexagonal cavities occupied by 4,4′-bipyridyl as shown in figure 3. Further, this structure is stabilized by weak C–H $\cdots$ O hydrogen bonds (table 3).

Supplementary data

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC No. 235899). Copies of this information can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/Cif, by emailing data_request@ccdc.cam.ac.uk, or by the contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 IEZ, UK; Fax: +44 1223 336033.

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References

[1] V.G. Albano, M.C. Aragoni, M. Area, C. Castellari, F. Demartin, F.A. Devillanova, F. Isaia, V. Lippolis, L. Loddo, G. Verani. *J. Chem. Soc., Chem. Comm.*, **11**, 1170 (2002).

[2] M.M. Chowdhry, D.M.P. Mingos, A.J.P. White, D.J. Williams. *J. Chem. Soc., Chem. Comm.*, **8**, 899 (1996).

[3] J.A. Schlueter, R.J. Funk, U. Geiser. *Acta Cryst.*, **C61**, m304 (2005).

[4] S.S.M. Chung, W.S. Li, M. Schrodor. *J. Chem. Soc., Chem. Comm.*, **11**, 1005 (1997).

[5] L. Carlueei, G. Ciani, D.W. Gudenberg, D.M. Proscrpio. *Inorg. Chem.*, **36**, 3812 (1997).

[6] M. Fujita, Y.J. Kwon, O. Sasaki, K. Yamaguchi, K. Ogura. *J. Am. Chem. Soc.*, **117**, 7287 (1995).

[7] H.J. Choi, M.P. Suh. *J. Am. Chem. Soc.*, **120**, 10622 (1998).

[8] T.L. Hennigar, D.C. MacQuarrie, P. Losier, R.D. Rogers, M.J. Zaworotko. *Angew. Chem. Int. Ed. Engl.*, **36**, 972 (1997).

[9] M. Fujita, Y.J. Kowon, S. Washiza, K. Ogura. *J. Am. Chem. Soc.*, **116**, 1151 (1994).

[10] G.R. Desiraju. *Crystal Engineering. The Design of Organic Solids*, Elsevier, Amsterdam (1989).

[11] A.J. Lough, P.S. Wheatley, G. Ferguson, C. Glidwell. *Acta Cryst.*, **B56**, 261 (2000).

[12] P.J. Zapf, R.C. Haushatter, J. Zubieta. *J. Chem. Soc., Chem. Comm.*, **7**, 697 (1997).

[13] O.M. Yaghi, H. Li. *J. Am. Chem. Soc.*, **7**, 10401 (1995).

[14] M. Kondo, T. Yoshitomi, K. Seki, H. Matsuzaka, S. Kitagawa. *Angew. Chem.*, **109**, 1844 (1977).

[15] A.J. Blake, S.J. Hill, P. Hubberstey, W.-S. Li. *J. Chem. Soc., Dalton Trans.*, **6**, 913 (1997).

[16] N. Masciocchi, P. Cairati, L. Carlucci, G. Mezza, G. Ciani, A. Sironi. *J. Chem. Soc., Dalton Trans.*, **13**, 2739 (1996).

[17] P.T. Muthiah, M. Hemamalini, G. Bocelli, A. Cantoni. *Acta Cryst.*, **E59**, o2015 (2003).

[18] M. Hemamalini, P.T. Muthiah, G. Bocelli, A. Cantoni. *Acta Cryst.*, **C60**, o284 (2004).

[19] G.M. Sheldrick. *SHELXS 97 and SHELXL97*, University of Göttingen, Germany (1997).

[20] S.D. Huang, R.-G. Xiong, J. Han, B.R. Weiner. *Inorg. Chim. Acta*, **294**, 95 (1999).