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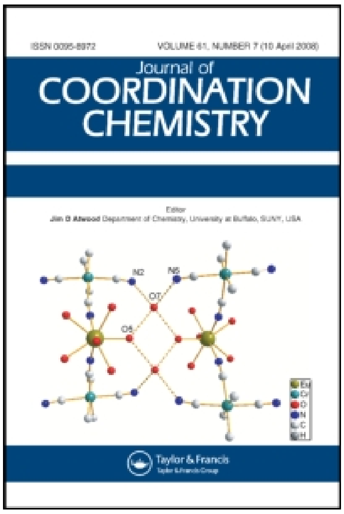

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Thermal, spectroscopic, X-ray powder diffraction, and structural studies on a new Cd(II) mixed-ligand coordination polymer

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Thermal, spectroscopic, X-ray powder diffraction, and structural studies on a new Cd(II) mixed-ligand coordination polymer

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A new coordination polymer derived from Cd(II) with both rigid and flexible spacer ligands *trans*-1,2-bis(4-pyridyl)ethane (bpa) and 4,4′-bipyridine (4, 4′-bipy), $\{[\mathrm{Cd}(\mu\text{-bpa})(4,4'\text{-bipy})_2(\mathrm{H_2O})_2]\cdot(\mathrm{ClO_4})_2\}_n$ has been synthesized and characterized by elemental analysis, IR-, ^{1}H NMR spectroscopy and studied by thermal analyses as well as X-ray crystallography. The single crystal X-ray analysis shows that the complex is a 1-D polymer as a result of bridging 1,3-di(4-pyridyl)propane (bpa). The 1-D chains are further self-assembled into a 3-D network via hydrogen bonding and π–π stacking. In this structure the perchlorates fill the voids. Thermal studies of this polymer show step to step separating of ligands and counter ion at different temperatures.

Keywords: Cadmium(II); 1,2-Bis(4-pyridyl)ethane; 4,4′-Bipyridine; Coordination polymers; Thermal gravimetric analysis

1. Introduction

Coordination polymers, also known as metal-organic coordination networks (MOCNs) or metal-organic frameworks (MOFs), are metal-ligand compounds that extend "infinitely" into one, two or three dimensions (1-D, 2-D or 3-D, respectively) via covalent metal-ligand bonding. Cd(II) with spacer and linker ligands can readily accommodate all kinds of architectures (1-D, 2-D, and 3-D polymers) [1–8]. The ligand must be a bridging organic group at least in one direction [9]. In most of the coordination polymers, N-donor ligands such as 4,4′-bipyridine (4, 4′-bipy) [10–14] or 1,2-bis(4-pyridyl)ethane (bpa) [15–17] are coordinated to a single metal ion. We chose a flexible bipyridine ligand, bpa, and a rigid one 4,4′-bipy, as two organic linkers to construct a new mixed-ligand coordination polymer. We report on the preparation and crystal structure of the first mixed-ligand cadmium(II) complex from the spontaneous

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aggregation of two different bipyridine ligands, 4,4′-bipy and bpa, $\{[Cd(\mu\text{-bpa})(4,4'\text{-bipy})_2(H_2O)_2]\cdot(ClO_4)_2\}_n$ (**1**). This new compound demonstrates the potential of using mixed rigid and flexible ligands to assemble framework structures [18].

2. Experimental

An alcoholic solution of cadmium(II) acetate (0.115 g, 0.50 mmol) and sodium perchlorate (0.061 g, 0.5 mmol) was added dropwise with refluxing to a mixture of 0.50 mmol (0.092 g) of bpa and 0.5 mmol (0.078 g) of 4,4′-bipy. The reaction mixture was stirred for 3 h at 70°C. Single crystals suitable for X-ray analysis were obtained by slow evaporation of this solution at room temperature (m.p. 148°C), were filtered off, washed with acetone, and air dried. Anal. Calcd for $C_{32}H_{32}CdCl_2N_6O_{10}$: C, 45.50; H, 3.79; N, 9.95. Found: C, 45.40; H, 3.50; N, 9.55%. IR (cm^{-1}) selected bonds: 466(m), 631(m), 810(m) 1011(vs), 1083(m), 1226(m), 1411(m), 1596(w), 2930(w), 3049(w) and 3404 (br). ^1H NMR (DMSO; δ): 7.2(d, 1H), 7.7(d, 2H), 8.29(d, 1H), 8.58(d, 2H), 1.8(t, 1H) ppm.

2.1. *Crystallography*

Crystallographic measurements for this complex were made at 298(2) K using a Bruker APEX area-detector diffractometer. The intensity data were collected within the range $2.08 \leq \theta \leq 29.00°$ using graphite monochromated Mo-Kα radiation. The structure was solved by direct methods and refined by full-matrix least-squares on F^2. Structure solution and refinement was accomplished using SIR97, SHELXL-97, and WinGX [19]. All H atoms were positioned geometrically and allowed to ride on their parent atoms. The molecular structure plots were prepared by using ORTEPIII and Mercury programs [20].

Crystal data and structure refinement are given in table 1. Selected bond lengths, angles, anisotropic thermal parameters, observed and calculated structure factors, full lists of bond distances, bond angles and torsion angles are given in the Supplementary material.

3. Results and discussion

Crystals formulated as $\{[Cd(\mu\text{-bpa})(4,4'\text{-bipy})_2(H_2O)_2]\cdot(ClO_4)_2\}_n$ (**1**) were obtained from reaction between cadmium(II) acetate and sodium perchlorate with mixture of bpa/4,4′-bipy. IR spectrum display characteristic absorption bands for bpa, 4,4′-bipy, perchlorate, and H_2O. Relatively weak absorption bands at 3049 cm^{-1} are due to C–H modes involving the aromatic ring hydrogens. The C–H modes involving the aliphatic hydrogens of bpe and bpp are at 2930 cm^{-1}. Absorption bands with variable intensity in the frequency range 1400–1580 cm^{-1} correspond to ring vibrations of bpa and 4,4′-bipy. The characteristic bands of perchlorate appear at 1083 cm^{-1}. The broad absorption band at 3404 cm^{-1} is assigned to $\nu(H_2O)$, from

Table 1. Crystal data and structure refinement for **1**.

Empirical formula	$C_{32}H_{32}CdCl_2N_6O_{10}$
Formula weight	843.94
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$C2/c$
Unit cell dimensions (Å, °)	
a	22.1677(8)
b	15.7980(6)
c	12.4330(5)
α	90
β	123.294
γ	90
Volume (Å^3)	3639.4(2)
Z	4
Density (Calcd) (Mg m^{-3})	1.540
Absorption coefficient (mm^{-1})	0.810
$F(000)$	1712
Crystal size (mm^3)	$0.45 \times 0.18 \times 0.14$
θ range for data collection (°)	2.08–29.00
Index ranges	$-30 \leq h \leq 30$, $-21 \leq k \leq 21$, $-16 \leq l \leq 16$
Reflections collected	21,665
Independent reflections	4808 [$R(\text{int}) = 0.0223$]
Observed reflections [$I > 2\sigma(I)$]	3826
Completeness to $\theta = 29.00°$	99.1%
Absorption correction	Semi-empirical from equivalents
Max and min transmission	0.895 and 0.739
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4808/16/234
Goodness-of-fit on F^2	1.011
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0416$, $wR_2 = 0.1115$
R indices (all data)	$R_1 = 0.0522$, $wR_2 = 0.1219$
Largest different peak and hole (e Å^{-3})	0.969 and −0.643

ν(O–H···X) hydrogen bonds. The ^{1}H NMR spectrum of DMSO solution of this compound displays two different py groups at 7.2 and 8.29 ppm of the bpa and at 7.70 and 8.58 ppm of the 4,4′-bipy. The spectrum shows a band at 1.8 ppm assigned to $-CH_2-CH_2-$ of bpa. The X-ray powder diffraction (XRPD) pattern of the synthesized material is in good agreement with the simulated diffractogram from the single crystal data of this polymer (Supplementary material), indicating a single phase product under the reaction condition employed.

Determination of the structure of **1** by X-ray crystallography showed that the complex in solid state consists of monomeric units (figure 1). The cadmiums are bonded by two nitrogens of bpa, two nitrogens of 4,4′-bipy, and two oxygens of water, six-coordinate with N_4O_2 donors octahedral around Cd (figure 1). Two 4,4′-bipy ligands and two waters are in the *trans* positions (figure 1). The aromatic rings of coordinated bpa are coplanar because the dihedral angle between the two py rings within this bpa ligand is 180° (figure 1). Perchlorate molecule is not coordinated to cadmium. Dimers are held together via O–H···N_{bipy} and O–H···$O_{\text{perchlorate}}$ hydrogen bonds between the coordinated water with the nitrogens of the 4,4′-bipy ligands with a O–H···N_{bipy} distance of 2.02(2) Å and with two O–H···$O_{\text{perchlorate}}$ distances of 2.11 and 2.14 Å. The 1-D structure of this polymer is shown in figure 2. There are face-to-face π–π stacking interactions

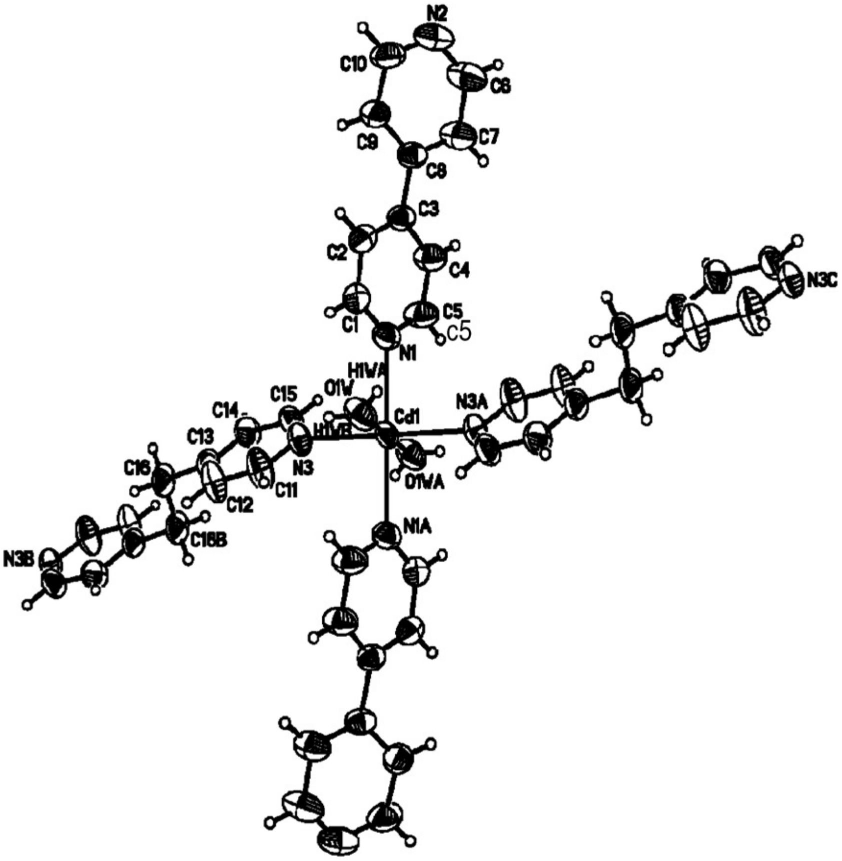

Figure 1. Molecular view of $\{[Cd(\mu\text{-bpa})(4,4'\text{-bipy})_2(H_2O)_2]\cdot(ClO_4)_2\}_n$ (**1**).

between aromatic rings of 4,4′-bipy ligands of the neighboring chains [21–28]. The centroid–centroid distance of py groups is 3.992 Å and the angle between the ring normal and the centroid vectors is 57.42°. This 1-D coordination polymer further extends into 3-D networks via hydrogen bondings and π–π stacking interactions (figure 2).

The thermal decomposition behavior was investigated in nitrogen from ambient temperature to 700°C (Supplementary material). Two water molecules are lost by 204°C. The experimental mass loss of 5% is consistent with the calculated value of 4.27% for the elimination of two molecules of H_2O. The weight loss of 37% from 204°C to 278°C is equivalent to the loss of the two coordinated 4,4′-bipy molecules [Anal Calcd 36.99%] with two exothermic effects at 244.7 and 313.4°C. At higher temperatures, the decomposition of the residue occurs with two exothermic events at 419 and 461°C. This final process is accompanied by the decomposition of bpa and perchlorate, ultimately giving a solid that appears to be CdO [observed: 15.23%, Anal Calcd 15%].

In summary, a 1-D cadmium(II) polymer based on a rigid and a flexible ligand, $\{[Cd(\mu\text{-bpa})(4,4'\text{-bipy})_2(H_2O)_2]\cdot(ClO_4)_2\}_n$ (**1**), has been prepared. This 1-D coordination polymer further extends into 3-D networks via hydrogen bonding. Further

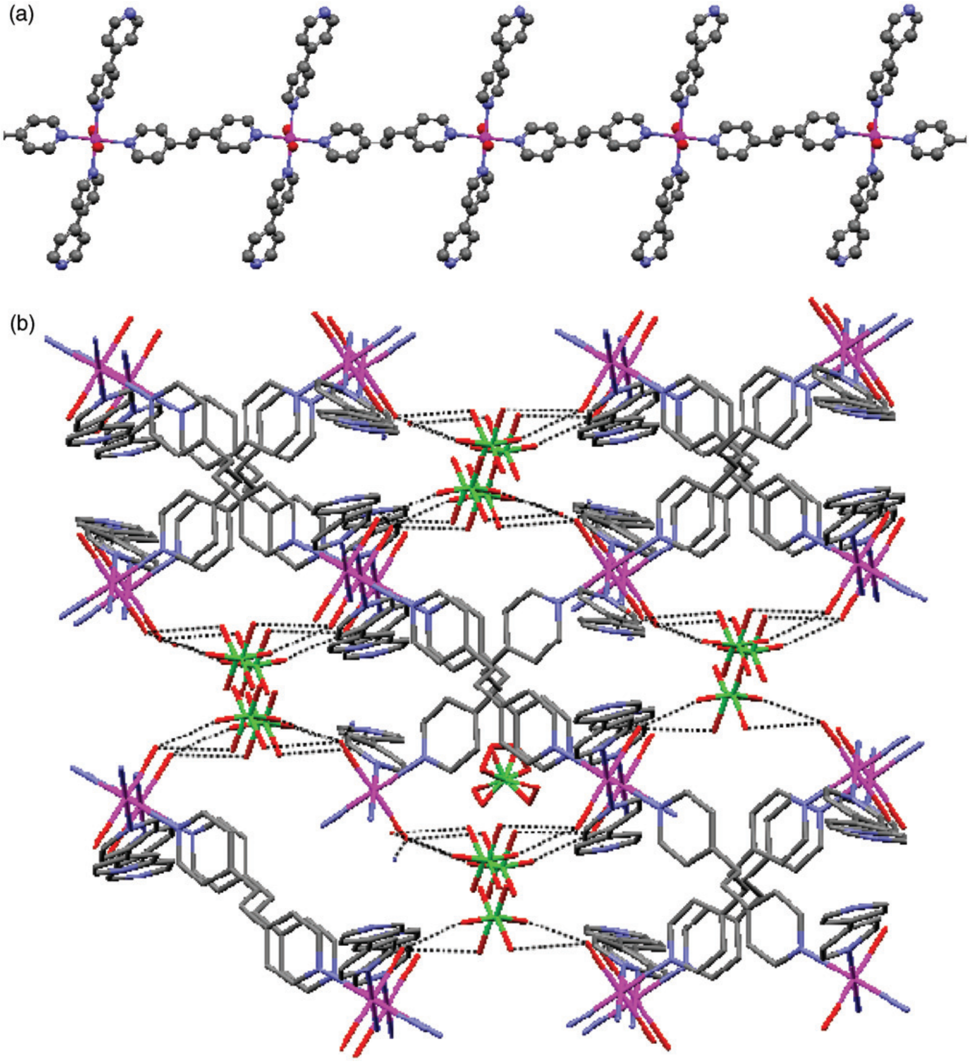

Figure 2. (a) 1D and (b) hydrogen bonding and 3-D-network of $\{[Cd(\mu\text{-bpa})(4,4'\text{-bipy})_2(H_2O)_2]\cdot(ClO_4)_2\}_n$.

systematic studies of mixed-ligand coordination polymers with different metal ions are ongoing in our laboratory and may offer new insights into metal-organic supramolecular assembly.

Supplementary material

The crystallographic data (excluding structure factors) for **1** have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication number CCDC-687580. Copies of the data can be obtained, free of charge, by application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; Email: data_request@ccdc.cam.ac.uk or via the internet: http://www.ccdc.cam.ac.uk/products/csd/request).

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References

[1] Y.H. Liu, Y.L. Liu, H.C. Wu, J.C. Wang, K.L. Lu. *Inorg. Chem.*, **413**, 2592 (2002).
[2] S.M. Kuznicki, V.A. Bell, S. Nair, H.W. Hillhouse, R.M. Jacubinas, C.M. Braunbarth, B.H. Toby, M. Tsapatsis. *Nature*, **412**, 720 (2001).
[3] S.A. Bourne, J. Lu, A. Mondal, B. Moulton, M.J. Zaworotko. *Angew. Chem. Int. Ed.*, **40**, 2111 (2001).
[4] J. Lu, A. Mondal, B. Moulton, M.J. Zaworotko. *Angew. Chem. Int. Ed.*, **40**, 2113 (2001).
[5] M. Aoyagi, K. Biradha, M. Fujita. *J. Am. Chem. Soc.*, **121**, 7457 (1999).
[6] C.V.K. Sharma, S.T. Griffin, R.D. Rogers. *Chem. Commun.*, **2**, 215 (1998).
[7] S.R. Batten, B.F. Hoskins, R. Robson. *J. Am. Chem. Soc.*, **117**, 385 (1995).
[8] A.N. Khlobystov, A.J. Blake, N.R. Champness, D.A. Lemenovskii, A.G. Majouga, N.V. Zyk, M. Schroder. *Coord. Chem. Rev.*, **222**, 155 (2001).
[9] J. Christoph. *Dalton Trans.*, **14**, 2781 (2003).
[10] A. Erxleben. *Coord. Chem. Rev.*, **246**, 203 (2003).
[11] M.G. Amiri, A. Morsali. *Z. Anorg. Allg. Chem.*, **632**, 1419 (2006).
[12] M.G. Amiri, A. Morsali. *Z. Anorg. Allg. Chem.*, **632**, 2371 (2006).
[13] M.L. Tong, J.W. Cai, X.L. Yu, X.M. Chen, S.W. Ng, T.C.W. Mak. *Aust. J. Chem.*, **51**, 637 (1998).
[14] J.D. Woodward, R.V. Backov, K.A. Abboud, D.R. Talham. *Polyhedron*, **25**, 2605 (2006).
[15] G. Ferguson, C. Glidewell, E.S. Lavender. *Acta Crystallogr., B*, **55**, 591 (1999).
[16] C.Y. Sun, L.C. Li, L.P. Jin. *Polyhedron*, **25**, 3017 (2006).
[17] A. Aslani, A. Morsali, M. Zeller. *Solid State Sci.*, **10**, 854 (2008).
[18] Y.H. Wang, Y.W. Li, W.L. Chen, Y.G. Li, E.B. Wang. *J. Mol. Struct.*, **877**, 56 (2008).
[19] B. Moulton, M.J. Zaworotko. *Chem. Rev.*, **101**, 1629 (2001).
[20] L.J. Farrugia. *J. Appl. Crystallogr.*, **30**, 565 (1997).
[21] J.C. Collings, K.P. Roscoe, E.G. Robins, A.S. Batsanov, L.M. Stimson, J.A.K. Howard, S.J. Clark, T.B. Marder. *New J. Chem.*, **26**, 1740 (2002).
[22] X.H. Miao, L.G. Zhu. *Inorg. Chim. Acta*, in press (2008).
[23] G. Tian. *J. Mol. Struct.*, **787**, 45 (2006).
[24] M. Felloni, A.J. Blake, N.R. Champness, P. Hubberstey, C. Wilson, M. Schräder. *J. Supramol. Chem.*, **2**, 163 (2002).
[25] S.C. Manna, J. Ribas, E. Zangrando, N.R. Chaudhuri. *Inorg. Chim. Acta*, **360**, 2589 (2007).
[26] S. Zhang, Z. Wang, H. Zhang, Y. Cao, Y. Sun, Y. Chen, C. Huang, X. Yu. *Inorg. Chim. Acta*, **360**, 2704 (2007).
[27] G. Tian, G. Zhu, Q. Fang, X. Guo, M. Xue, J. Sun, S. Qiu. *J. Mol. Struct.*, **787**, 45 (2006).
[28] S.M. Ying, J.G. Mao, Y.Q. Sun, H.Y. Zeng, Z.C. Dong. *Polyhedron*, **22**, 3097 (2003).