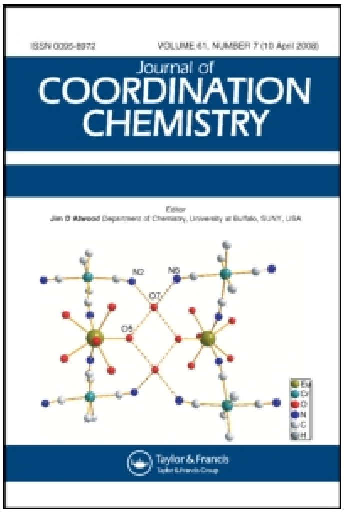

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Syntheses and crystal structures of two 2D coordination polymers of cobalt(II) and nickel(II) with the Malonate Dianion Ligand

Xu-Da Wang[a]; Li-Cun Li[ab]; Dai-Zheng Liao[a]; Zong-Hui Jiang[a]; Shi-Ping Yan[a]; Peng Cheng[a]
[a] Department of Chemistry, Nankai University, Tianjin 300071, P.R. China [b] State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, P.R. China

To cite this Article Wang, Xu-Da , Li, Li-Cun , Liao, Dai-Zheng , Jiang, Zong-Hui , Yan, Shi-Ping and Cheng, Peng(2004) 'Syntheses and crystal structures of two 2D coordination polymers of cobalt(II) and nickel(II) with the Malonate Dianion Ligand', Journal of Coordination Chemistry, 57: 17, 1577 — 1585

To link to this Article: DOI: 10.1080/00958970412331307198

URL: http://dx.doi.org/10.1080/00958970412331307198

J. Coord. Chem., Vol. 57, No. 17–18,
20 November–15 December 2004, pp. 1577–1585

Taylor & Francis
Taylor & Francis Group

SYNTHESES AND CRYSTAL STRUCTURES OF TWO 2D COORDINATION POLYMERS OF COBALT(II) AND NICKEL(II) WITH THE MALONATE DIANION LIGAND

XU-DA WANG[a], LI-CUN LI[a,b,*], DAI-ZHENG LIAO[a,*], ZONG-HUI JIANG[a], SHI-PING YAN[a] and PENG CHENG[a]

[a]*Department of Chemistry, Nankai University, Tianjin 300071, P.R. China;*
[b]*State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, P.R. China*

Two 2D complexes, [Co(mal)(phen)$(H_2O)_2$] (**1**) and [Ni(mal)(phen)$(H_2O)_2$] (**2**) (mal = malonate dianion; phen = 1,10-phenanthroline), have been synthesized by the reaction of $Co(ClO_4)_2 \cdot 6H_2O$ and $Ni(ClO_4)_2 \cdot 6H_2O$ with disodium malonate and 1,10-phenanthroline in MeOH/H_2O solution. Their crystal structures have been determined by X-ray diffraction. The structures of Complexes **1** and **2** show that each metal ion is coordinated by one 1,10-phenanthroline, two water molecules and a malonate ligand forming a distorted octahedral environment and each mononuclear fragment forms a 2D supramolecular network through H-bonding interactions.

Keywords: Nickel(II); Cobalt(II); Crystal structures; Malonato complexes; Hydrogen bond

INTRODUCTION

There has been considerable interest in the design and synthesis of complexes with carboxylate ligands because carboxylates can give rise to different coordination modes with metal ions and increase recognition of the metal's role in biological systems [1–3]. The malonate ligand, with two neighbouring carboxylate groups, is a very flexible ligand [4–9], it can adopt several chelating bidentate coordination modes (bidentate [η^5-chelation], bidentate [η^5-chelation]–unidentate, bidentate [η^5-chelation]–bis(unidentate)) and/or different carboxylato-bridging coordination modes such as *syn–syn*, *syn–anti*, and *anti–anti* [8]. On the other hand, the malonate ligand occupies one or two coordination positions, allowing the inclusion of other ligands in the coordination sphere of the metal. These complementary ligands can act as bridging or blocking ligands, contributing to the interconnection or isolation of the metal ions. Thus, combining malonate with other bridging and/or blocking ligands, monomers, dimers [10], trimers [11,12], infinite chains [13,14], 2D and 3D [15] complexes have been obtained and studied. In the present work we report the syntheses and X-ray

---

*Authors for correspondence. E-mail: coord@nankai.edu.cn

ISSN 0095-8972 print: ISSN 1029-0389 online
DOI: 10.1080/00958970412331307198

crystal structures of two new 2D complexes, [Co(mal)(phen)(H_2O)$_2$] (**1**) and [Ni(mal)(phen)(H_2O)$_2$] (**2**).

EXPERIMENTAL

Synthesis

[Co(mal)(phen)(H_2O)$_2$] (1)

An aqueous solution (5 cm^3) of disodium malonate (0.148 *g*, 1 mmol) was added dropwise to a methanolic solution (15 cm^3) of Co(ClO_4)$_2$ · 6H_2O (0.170 *g*, 1 mmol) with constant stirring for 30 mins. To the resulting reaction mixture a methanolic solution (10 cm^3) of phen (0.156 g, 1 mmol) was added slowly and the reaction mixture was stirred for 2 h, then filtered. After several days, red, single crystals were obtained by slow evaporation of the filtrate.

[Ni(mal)(phen)(H_2O)$_2$] (2)

This complex was prepared with Ni(ClO_4)$_2$ · 6H_2O in a way similar to that of **1** and blue, single crystals were obtained.

Physical Measurements

Infrared spectroscopy using KBr pellets was performed on a Shimadzu IR-408 spectrophotometer in the 4000–400 cm^{-1} region.

Crystal Structure Determinations

Single crystals of Complexes **1** and **2** were mounted on a Bruker Smart 1000 diffractometer with a CCD area detector and a graphite-monochromated Mo Kα radiation source ($\lambda = 0.71073$ Å). Data collection was performed at room temperature. The structures were solved by direct methods using the SHELXS-97 program [16] and refined with SHELXS-97 [17] by full-matrix least-squares methods on F^2. Further details of the structural analyses are summarized in Table I. Atomic coordinates and equivalent isotropic displacement parameters for **1** and **2** are listed in Tables II and III. Selected bond distances and bond angles are given in Table IV. Crystallographic data for the structures of the two complexes reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC-234642 (**1**) and CCDC-234643 (**2**). Copies of the data can be obtained free of charge from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

IR Spectra

IR spectra of both compounds **1** and **2** show a broad band in the region 3100–3400 cm^{-1}, which can be assigned to the stretching vibrations, ν(O–H), of the

TABLE I Crystallographic data and structure refinement details for **1** and **2**

	1	**2**
Formula	[Co(mal)(phen)(H_2O)$_2$]	[Ni(mal)(phen)(H_2O)$_2$]
Formula weight	377.21	376.99
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å)	10.431(3)	10.592(3)
b (Å)	9.609(3)	9.464(3)
c (Å)	15.512(5)	15.519(5)
β (°)	106.286(5)	107.874(5)
V (Å^3)	1492.4(8)	1480.5(8)
Z	4	4
D_{calc} ($\mathrm{g\,cm^{-3}}$)	1.679	1.691
Crystal size (mm)	0.26 × 0.20 × 0.14	0.20 × 0.16 × 0.1
$F(000)$	772	776
Absorption coefficient ($\mathrm{mm^{-1}}$)	1.186	1.347
θ range for data collection	2.52 to 26.44	2.56 to 26.38
Reflections collected	8366	8284
Unique reflections	3047	3022
R (int)	0.0300	0.0302
Observed reflections [$I > 2\sigma(I)$]	3047	3022
No. of refined parameters	217	217
GOF	1.015	1.033
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.0286, 0.0629	0.0291, 0.0679
$R1$, $wR2$ (all data)	0.0463, 0.0684	0.0419, 0.0726
Largest diff. peak and hole	0.272, −0.260	0.323, −0.382

TABLE II Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) for **1**

Atom	x/a	y/b	z/c	U(eq)
Co(1)	1577(1)	3938(1)	2335(1)	24(1)
N(1)	3504(2)	3042(2)	2927(1)	30(1)
N(2)	2722(2)	5707(2)	2972(1)	29(1)
C(1)	3876(3)	1724(2)	2895(2)	39(1)
C(2)	5152(3)	1249(3)	3337(2)	46(1)
C(3)	6076(3)	2161(3)	3813(2)	50(1)
C(4)	5733(2)	3570(3)	3867(2)	41(1)
C(5)	6626(3)	4597(3)	4360(2)	57(1)
C(6)	6225(3)	5911(3)	4408(2)	56(1)
C(7)	4897(3)	6351(2)	3954(2)	41(1)
C(8)	4434(3)	7715(3)	3978(2)	51(1)
C(9)	3157(3)	8044(3)	3508(2)	51(1)
C(10)	2336(2)	7018(2)	2999(2)	39(1)
C(11)	3987(2)	5378(2)	3445(1)	29(1)
C(12)	4415(2)	3955(2)	3410(1)	30(1)
O(1)	1934(2)	4314(2)	1110(1)	33(1)
O(2)	1708(2)	3824(2)	−322(1)	34(1)
O(3)	802(2)	2033(1)	1833(1)	30(1)
O(4)	−436(2)	703(2)	759(1)	53(1)
C(13)	1327(2)	3742(2)	376(1)	26(1)
C(14)	56(2)	2928(2)	322(1)	30(1)
C(15)	154(2)	1794(2)	1018(1)	28(1)
O(5)	−260(2)	5087(2)	1982(1)	34(1)
O(6)	992(2)	3445(2)	3484(1)	38(1)

U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

TABLE III Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for **2**

Atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*(eq)
Ni(1)	6591(1)	1111(1)	2349(1)	23(1)
O(1)	6945(2)	708(2)	1154(1)	30(1)
O(2)	6689(2)	1128(2)	−294(1)	33(1)
O(3)	5786(2)	3007(2)	1852(1)	29(1)
O(4)	4529(2)	4343(2)	754(1)	49(1)
O(5)	4777(2)	0(2)	1971(1)	32(1)
O(6)	6060(2)	1591(2)	3488(1)	37(1)
N(1)	8456(2)	2019(2)	2911(1)	29(1)
N(2)	7681(2)	−666(2)	2984(1)	27(1)
C(1)	8821(3)	3350(3)	2865(2)	38(1)
C(2)	10 107(3)	3831(3)	3291(2)	44(1)
C(3)	11 042(3)	2910(3)	3770(2)	48(1)
C(4)	10 702(2)	1485(3)	3840(2)	40(1)
C(5)	11 602(3)	438(3)	4337(2)	53(1)
C(6)	11 205(3)	−893(3)	4403(2)	52(1)
C(7)	9868(2)	−1328(3)	3961(2)	38(1)
C(8)	9406(3)	−2701(3)	4005(2)	49(1)
C(9)	8121(3)	−3035(3)	3537(2)	49(1)
C(10)	7291(2)	−1988(2)	3023(2)	37(1)
C(11)	8959(2)	−335(2)	3449(1)	29(1)
C(12)	9379(2)	1097(2)	3398(1)	29(1)
C(13)	6333(2)	1260(2)	402(1)	24(1)
C(14)	5086(2)	2115(2)	317(1)	28(1)
C(15)	5145(2)	3247(2)	1024(1)	26(1)

U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

TABLE IV Bond lengths (Å) and angles (°) for **1** and **2**

Co(1)–O(3)	2.0632(14)	Ni(1)–O(3)	2.0348(15)
Co(1)–O(1)	2.0691(15)	Ni(1)–O(1)	2.0380(15)
Co(1)–O(6)	2.0933(15)	Ni(1)–O(6)	2.0631(16)
Co(1)–N(1)	2.1415(18)	Ni(1)–N(1)	2.0835(18)
Co(1)–O(5)	2.1452(15)	Ni(1)–O(5)	2.1098(16)
Co(1)–N(2)	2.1523(17)	Ni(1)–N(2)	2.1053(18)
O(3)–Co(1)–N(1)	91.54(6)	O(3)–Ni(1)–O(1)	89.55(6)
O(6)–Co(1)–N(1)	90.39(7)	O(3)–Ni(1)–N(1)	91.61(7)
O(3)–Co(1)–O(5)	97.63(6)	O(1)–Ni(1)–N(1)	92.44(7)
O(1)–Co(1)–O(5)	93.02(6)	O(6)–Ni(1)–N(1)	91.36(7)
O(6)–Co(1)–O(5)	83.21(6)	N(2)–Ni(1)–O(5)	93.08(7)
O(1)–Co(1)–N(2)	93.67(6)	O(3)–Ni(1)–O(5)	95.38(6)
N(1)–Co(1)–N(2)	77.73(7)	N(1)–Ni(1)–N(2)	79.69(7)
O(5)–Co(1)–N(2)	92.95(6)	O(6)–Ni(1)–O(5)	83.33(6)
O(1)–Co(1)–O(6)	172.87(6)	N(1)–Ni(1)–O(5)	170.93(6)
O(3)–Co(1)–N(2)	169.25(6)	O(1)–Ni(1)–O(6)	174.55(6)

hydroxyl group in water molecules. The next group of bands appears at around 2800–2900 cm^{-1} and corresponds to the stretching vibration, ν(C–H), of the malonate ligand [18]. The malonate ion shows a strong ν_{as}(OCO) band at 1700 cm^{-1} and a ν_{s}(OCO) band at 1450 cm^{-1}. These frequencies are significantly shifted to lower frequencies in both the complexes on coordination to cobalt(II) and nickel(II) ions. In Complex **1** ν_{as}(OCO) and ν_{s}(OCO) appear at 1619 and 1429 cm^{-1}, respectively, and for Complex **2** at 1628 and 1430 cm^{-1}. The significant shift to lower frequency indicates the coordination of the carboxylate. Finally, the δ(C=O) bending vibration is observed in the 1180–1300 cm^{-1} range for both compounds. The medium intensity bands around 1620–1510 cm^{-1} are due to ν(C=N) and ν(C=C) stretches of coordinated phen molecules.

Crystal Structures

The molecular structure of **1** is illustrated in Fig. 1 with the atom labelling. The cobalt(II) ion has a distorted octahedral coordination environment. Equatorial positions are occupied by N(1) and N(2) [Co–N(1), 2.1415(18) Å; Co–N(2), 2.1523(17) Å] from phen and O(3) [Co–O(3), 2.0632(14) Å] from the malonate ligand and O(5) [Co–O(5), 2.1452(15) Å] from one water molecule. *Trans* axial positions are occupied by O(1) and O(6) [Co–O(1), 2.0691(15) Å; Co–O(6), 2.0933(15) Å] of the malonate and a second water molecule, respectively. The main distortion arises from the bond angles [97.63(6)°, 77.73(7)°, 83.21(6)° for O(3)–Co(1)–O(5), N(1)–Co(1)–N(2), O(6)–Co(1)–O(5), respectively]. There are strong hydrogen bonding interactions in this complex. The oxygen atoms O(2), O(3), O(4) from the malonate ligand act as acceptors and coordinated water molecules O(5), O(6) as donors. The average O$\cdots$O distance is 2.754 Å [2.790 Å, 2.797 Å, 2.822 Å, 2.608 Å for O(5)–H(5A)–O(3), O(5)–H(5B)–O(2), O(6)–H(6A)–O(2), O(6)–H(6B)–O(4)], respectively, and the range of angles ∠DHAis from 166.03° to 177.16° (Table V). By the hydrogen-bond interactions, each monomer links six neighbouring monomers resulting in an infinite 2D supramolecular network (Fig. 3). The shortest Co$\cdots$Co distance is 5.925 Å. The phen moieties show a face-to-face π–π interaction (Fig. 4); the interplanar distance between phen rings of adjacent molecules is 3.827 Å, and the dihedral angle is 23.3°.

The molecular structure of **2** is illustrated in Fig. 2 with the atom labelling. The structure of **2** is quite similar to that of **1**. The distorted octahedral nickel(II) centre is linked to a chelated malonate, one phen and two water molecules. The two nitrogen atoms N(1) and N(2) [Ni–N(1), 2.0835(18) Å; Ni–N(2), 2.1053(18) Å] of the phen ligand and the two oxygen atoms O(3) and O(5) [Ni–O(3), 2.0348(15) Å; Ni–O(5), 2.1098(16) Å] from the malonate and a water molecule, respectively, form the equatorial plane around nickel(II) and the *trans* axial positions are occupied by the O(1) and O(6)

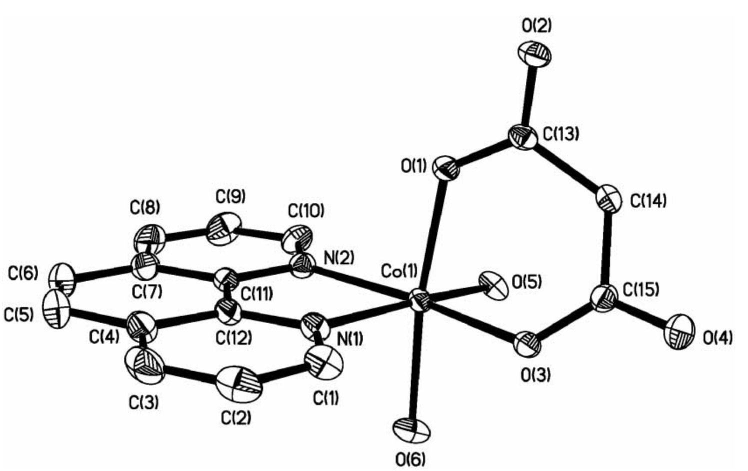

FIGURE 1 The molecular structure and atom labelling scheme for **1**.

TABLE V Hydrogen bond data for Complex **1**

D–H	*d*(*D–H*)	*d*(*H*···*A*)	$<DHA$	*d*(*D*···*A*)	*A*
O5–H5A	0.850	1.943	174.62	2.790	O3 $[-x,\ y+1/2,\ -z+1/2]$
O5–H5B	0.850	1.963	166.62	2.797	O2 $[-x,\ -y+1,\ -z]$
O6–H6A	0.850	1.990	166.03	2.822	O2 $[x,\ -y+1/2,\ z+1/2]$
O6–H6B	0.850	1.759	177.16	2.608	O4 $[-x,\ y+1/2,\ -z+1/2]$

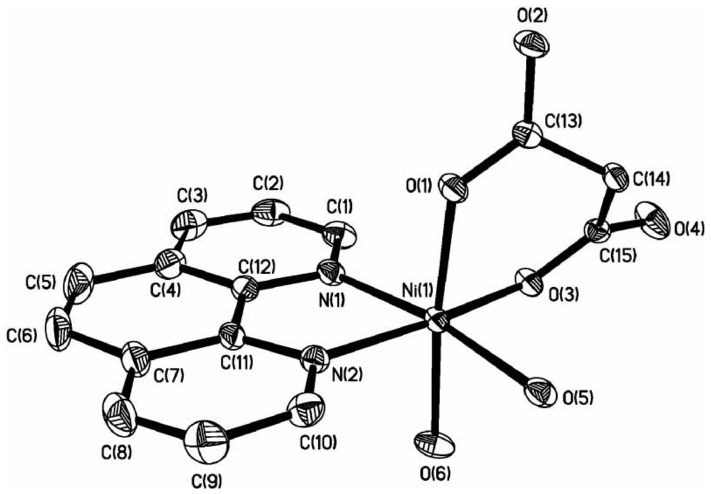

FIGURE 2 The molecular structure and atom labelling scheme for **2**.

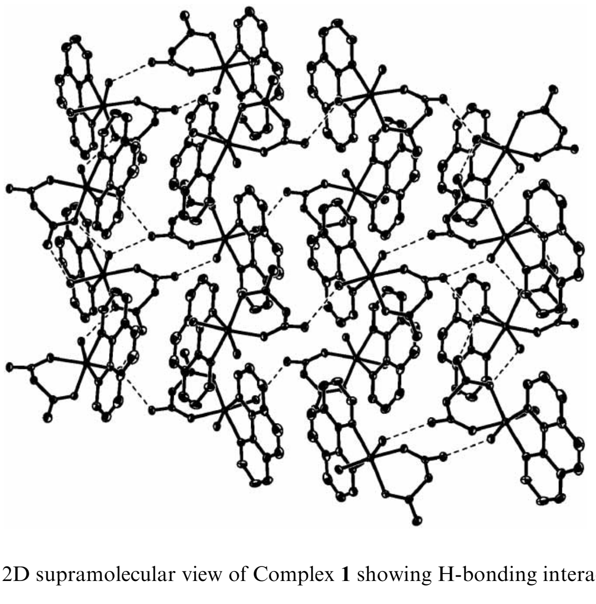

FIGURE 3 Infinite 2D supramolecular view of Complex **1** showing H-bonding interactions in the *ab* plane.

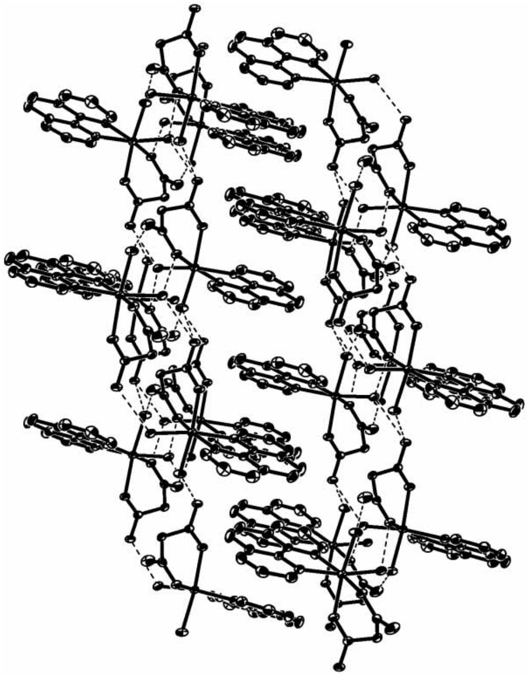

FIGURE 4 Network, showing π–π interactions between the H-bonded 2D sheets of Complex **1**.

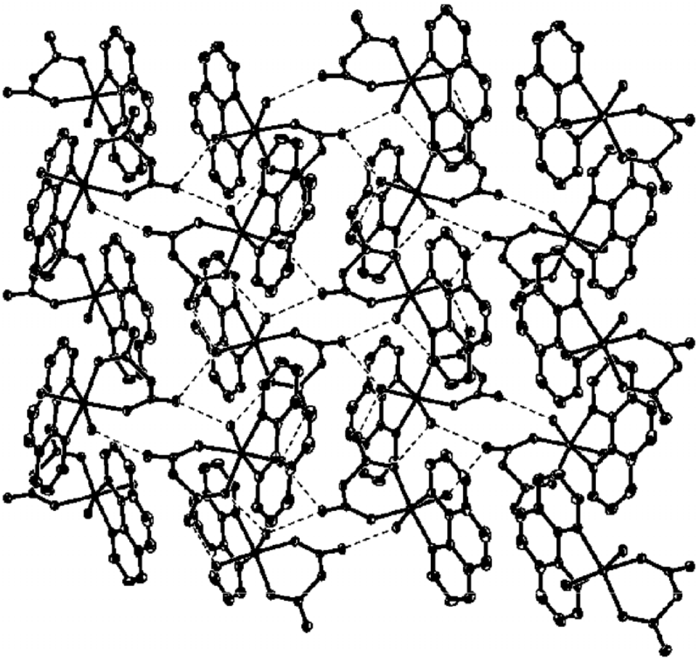

FIGURE 5 Infinite 2D supramolecular view of complex 2 showing H-bonding interaction in the *ab* plane.

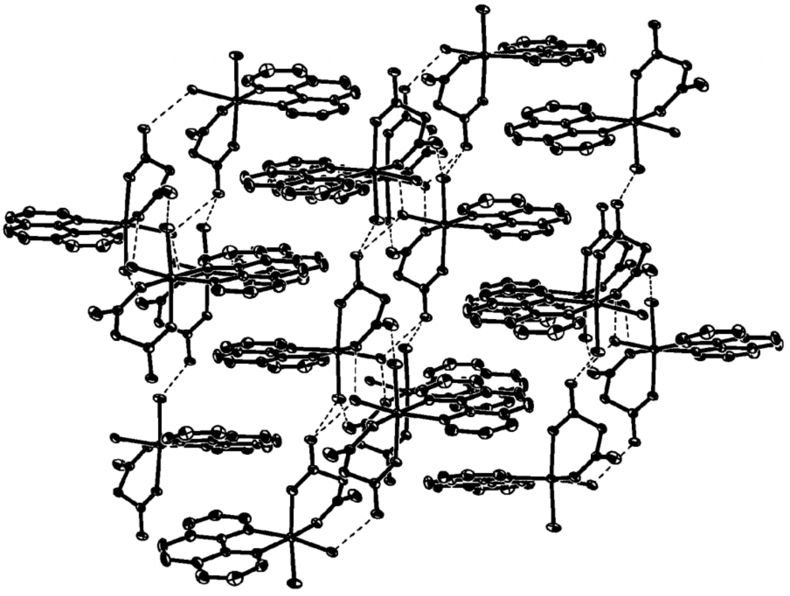

FIGURE 6 Network showing π–π interaction between the H-bonded 2D sheets of complex 2.

TABLE VI Hydrogen bond data for Complex **2**

D–H	*d(D–H)*	*d(H...A)*	$<DHA$	*d(D...A)*	*A*
O5–H1A	0.852	1.974	163.32	2.800	O2 $[-x+1, -y, -z]$
O5–H1B	0.853	1.970	170.52	2.814	O3 $[-x+1, y-1/2, -z+1/2]$
O6–H2A	0.842	1.977	171.11	2.812	O2 $[x, -y+1/2, z+1/2]$
O6–H2B	0.850	1.749	175.55	2.598	O4 $[-x+1, y-1/2, -z+1/2]$

[Ni–O(1), 2.0380(15) Å; Ni–O(6), 2.0631(16) Å] of the malonate and the second water molecule. The main distortion arises from the bond angles [95.38(6)°, 79.69(7)°, 83.33(6)° for O(3)–Ni(1)–O(5), N(1)–Ni(1)–N(2), O(6)–Ni(1)–O(5), respectively]. O(2), O(3) and O(4) acceptors of the malonate ligand engage in strong hydrogen-bonding interactions with water molecules [2.800, 2.814, 2.812, 2.598 Å for O(5)–H(1A)–O(2), O(5)–H(1B)–O(3), O(6)–H(2A)–O(2), O(6)–H(2B)–O(4), respectively]. The average O···O distance is 2.583 Å, and the range of angles $<$DHA is from 163.32° to 175.55° (Table VI). Therefore, neighboring mononuclear fragments form the same 2D supramolecular network (Fig. 5). The Ni···Ni distance is 5.911 Å, and the distance between adjacent phen rings is about 3.614 Å (Fig. 6); the dihedral angle is about 24.7° between phen rings.

Acknowledgment

This work was supported by the National Natural Science Foundation of China (No. 20331010, No. 20471032).

References

[1] V.L. Pecoraro (Ed.), *Manganese Redox Enzymes* (VCH, New York, 1992).

[2] G. Christou, *Acc. Chem. Res.* **22**, 328 (1989).

[3] K. Wieghardt, *Angew. Chem., Int. Ed. Engl.* **28**, 1153 (1989).

[4] D. Chattopadhyay, S.K. Chattopadhyay, P.R. Lowe, C.H. Schwalke, S.K. Mazumber, A. Rana and S. Ghosh, *J. Chem. Soc., Dalton Trans.* 913 (1993).

[5] I. Gil de Muro, F.A. Mautner, M. Insausti, L. Lezama, M.I. Arriortua and T. Rojo, *Inorg. Chem.* **37**, 3243 (1998).

[6] C. Ruiz-Pérez, J. Sanchiz, M. Hernández-Molina, F. Lloret and M. Julve, *Inorg. Chim. Acta* **298**, 202 (2000).

[7] E. Suresh and M.H. Bhadbhade, *Acta Crystallogr.* **C53**, 193 (1997).

[8] C. Ruiz-Pérez, M. Hernández-Molina, P. Lorenzo-Luis, F. Lloret, J. Cano and M. Julve, *Inorg. Chem.* **39**, 3845 (2000).

[9] C. Ruiz-Pérez, J. Sanchiz, M. Hernández-Molina, F. Lloret and M. Julve, *Inorg. Chem.* **39**, 1363 (2000).

[10] S. Sain, T.K. Maji, G. Mostafa, T.-H. Lu and N.R. Chaudhuri, *Inorg. Chim. Acta* **31**, 12 (2003).

[11] Y.-G. Wei, S.-W. Zhang, M.-C. Shao, Q. Liu and Y.-Q. Tang, *Polyhedron* **15**, 4303 (1996).

[12] C. Ruiz-Pérez, M. Hernández-Molina, J. Sanchiz, T. López, F. Lloret and M. Julve, *Inorg. Chim. Acta* **298**, 245 (2000).

[13] C. Ruiz-Pérez, J. Sanchiz, M. Hernández-Molina, F. Loret and M. Julve, *Inorg. Chem.* **39**, 1363 (2000); C. Ruiz-Pérez, J. Sanchiz, M. Hernández-Molina, F. Loret and M. Julve, *Inorg. Chim. Acta* **298**, 202 (2000).

[14] S.H. Saadeh, K.L. Trojan, J.W. Kampf, W.E. Hatfield and V.L. Peroraro, *Inorg. Chem.* **32**, 3034 (1993).

[15] T.K. Maji, T. Sain, G. Mostafa, T.-H. Lu, J. Ribas, M. Monfort and N.R. Chaudhuri, *Inorg. Chem.* **42**, 709 (2003).

[16] G.M. Sheldrick, SHELXS-97, *Program for the Solution of Crystal Structures* (University of Göttingen, Germany, 1997).

[17] G.M. Sheldrick, SHELXL-97, *Program for the Refinement of Crystal Structures* (University of Göttingen, Germany, 1997).

[18] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds* (Wiley-Interscience, New York, 1978), 3rd Edn., pp. 227, 232, 371, 380.