

Microwave-assisted synthesis, spectroscopy, and crystal structures of $[(\text{H}_2-(4,4'\text{-bipy}))^{2+} [\text{Cr}_2\text{O}_7]^{2-}]$ and one-dimensional polymeric $\{[\text{Mn}(4,4'\text{-bipy})(\text{Cr}_2\text{O}_7)(\text{H}_2\text{O})_2]\}_n$ compounds

Hirihattaya PHETMUNG^{1,*}, Muneer WATEH¹ Chaveng PAKAWATCHAI²

¹*Inorganic and Materials Chemistry Research Unit, Department of Chemistry, Thaksin University, Songkhla, 90000, THAILAND*

e-mail: tayaphetmung@yahoo.com

²*Department of Chemistry, Prince of Songkla University, Hat Yai, 90112, THAILAND*

Received: 12.04.2011

A compound (**1**), $[\text{H}_2-(4,4'\text{-bipy})]^{2+} [(\text{Cr}_2\text{O}_7)]^{2-}$ and a metal organic-inorganic coordination framework (**2**), $[\text{Mn}(4,4'\text{-bipy})(\text{Cr}_2\text{O}_7)(\text{H}_2\text{O})_2]$ (4,4'-bipy=4,4'-bipyridine) were successfully synthesized by microwave method. Their characterization was performed by single crystal X-ray crystallography and FT-IR spectroscopy. The crystal structure of **1** revealed a diprotonated 4,4'-bipyridium dichromate compound while compound **2** is an onedimensional (1D) polymer in which $(\text{Cr}_2\text{O}_7)^{2-}$ acts as a bridging ligand supporting the formation of infinite $\{[\text{Mn}(4,4'\text{-bipy})(\text{Cr}_2\text{O}_7)(\text{H}_2\text{O})_2]\}_n$ polymeric chains. The geometry of the 4,4'-bipy ring in **1** is typical coplanar, but twists in **2**. In the free molecule **1**, dichromate ligand adopts an eclipsed conformation, but adopts a staggered conformation in complex. The principal features of the crystal supramolecularity of **1** and **2** are non-covalent weak interactions which occurred via N-H...O and C-H...O hydrogen bonding.

Key Words: Microwave assisted synthesis, organic-inorganic framework, diprotonated 4,4'-bipyridium, eclipsed conformation

Introduction

For the discovery of new compounds in recent years, the technique referred to by critics as 'mix and wait' may not be sufficient.¹ In this decade, performing chemical reactions using microwave irradiation has become

*Corresponding author

increasingly popular owing to higher yields, selectivity and speeds than conventional methods. Moreover, it is an environmentally benign method for chemical synthesis due to its high efficiency and homogeneous heating.^{2,3} This technique being widely used in various areas such as for reducing the time in organic chemical synthesis^{4,5} polymerization reactions^{6,7} biomedical research and clinical diagnosis^{8,9} and test medical devices.¹⁰ Microwave assisted synthesis has also been used to design and synthesize organic-inorganic polymer hybrids.¹ Very recently, our group has successfully synthesized an organic-inorganic polymer hybrid containing 4,4'-bipyridine (4,4'-bipy) using this method.¹¹ Since 4,4'-bipy is an excellent ligand containing two 4-pyridyl units, it is liable to have some weak intermolecular interactions such as non-covalent bridging modes: hydrogen bridging and π, π -tacking bridging modes. It has commonly been employed as building blocks in designing coordination polymers and constructing supramolecular architectures.^{12,13}

Chromium and its oxoanion are essential trace elements not only in biological fluids¹⁴ but also for industrial purposes.¹⁵ Oxoanions such as dichromate containing chromium can act as terminal and/or bridging ligands to construct multidimensional compounds.¹⁵⁻¹⁸ The chemistry of dichromate and N-donor atoms as ligands has been reported.¹⁵⁻¹⁸ Much of the work on bipyridine dichromate metal compounds focuses on the reaction with Co^{15b} Ni and U metal atoms.^{18b-c} Although the chemistry of manganese has received considerable attention in recent years, much of the work concentrates on the catalytically active in a variety of metalloenzymes.¹⁹

We have been pursuing synthetic work to study dichromate as a bridging ligand. We investigated bipyridium dichromate $[(H_2-C_{10}H_8N_2)]^{2+}[Cr_2O_7]^{2-}$ and the metal organic-inorganic hybrid $[Mn(4,4'-bipy)(Cr_2O_7)(H_2O)_2]$ under microwave irradiation for the first time. The title compounds were evaluated by single crystal X-ray determination and Fourier transform infrared (FT-IR) spectroscopy.

Experimental

Materials and methods

All starting chemical reagents were commercially available in analytic grade except for 4,4'-bipyridine in reagent grade. The Fourier Transform Infrared (FT-IR) spectra for **1** and **2** were recorded from 400 to 4000 cm^{-1} on a Perkin-Elmer 783 spectrometer using KBr pellets. Melting points were measured on a Büchi melting point B-540 apparatus. The X-ray diffraction data were collected on SMART Bruker 1000 CCD area-detector diffractometer.²⁰

Synthesis

Compound $[(H_2-(4,4'-bipy))]^{2+}[Cr_2O_7]^{2-}$ (**1**)

A mixture of $MnCl_2 \cdot 4H_2O$ (0.250 g, 1.0 mmol), anhydride of chromic acid or chromic(VI) oxide (0.100 g, 0.10 mmol), 4,4'-bipy (0.156 g, 1.0 mmol), and water (6 mL) in 1:1:1:333 stoichiometries was stirred at room temperature until all the starting materials dissolved. The resulting solution was irradiated using a domestic microwave oven for 2 min. The radiation frequency was 2450 MHz which affects only the molecular rotation or movement and is not sufficient to cleave molecular bonds or affect molecular structure.²¹ After microwave irradiation, clear orange needle crystals were obtained. The melting point is about 214.8-219.5 °C. Yield 67%.

IR ν_{max}/cm^{-1} : 3300, 1597, 1534, 1487, 1324, 1218, 1069, 1016, 1001, 960, 930, 873, 812, 784, 673, 624, 484.

Compound $[\text{Mn}(4,4'\text{-bipy})(\text{Cr}_2\text{O}_7)(\text{H}_2\text{O})_2]$, (**2**)

This compound was prepared in the same way as **1** by using **1** as a starting material. The mixture of compound **1** (0.374 g, 1.0 mmol), $\text{MnCl}_2\cdot 4\text{H}_2\text{O}$ (0.250 g, 1.0 mmol), and water (6 mL) in the ratios of 1:1:333 was stirred completely at room temperature. Black crystals were obtained upon microwave irradiation. Yield 55%. IR ν_{max}/cm^{-1} : 3300, 3097, 2949, 1620, 1591, 1486, 1376, 119, 933, 767, 541.

Measurements

Crystallography

An orange needle crystal of **1** and a black prismatic crystal of **2** were mounted on a glass fiber. X-ray data were collected on a SMART Bruker 1000 CCD area-detector diffractometer equipped with a graphite-monochromated Mo K_α radiation ($\lambda = 0.71073 \text{ \AA}$) at 566(2) K.

A full sphere of data was obtained for each using the omega scan method. Data were collected, processed, and corrected for Lorentz and polarization effects using a SMART Bruker 1000 CCD area-detector diffractometer and SAINT software. Absorption corrections were based on multiple scans and were also applied using SABABS.²¹ Space group *Pmna* was selected and confirmed by the subsequent structure analysis. The *ADDSYM* option in PLATON revealed no additional symmetry.²² Structure was solved *via* direct methods and refined by full matrix least squares on F^2 using the SHELXTL program package.²³ All non-hydrogen atoms were refined anisotropically. The O(3) and O(5) atoms in compound (**2**) were disordered over those 2 positions and had 50% site occupancy ration. The hydrogen atoms were located from a difference electron-density map and refined isotropically. All packing diagrams and thermal ellipsoid plots were produced using the Diamond software program.²⁴ The crystallographic data are shown in Table 1.

Results and discussion

Synthesis

Although compound **1** has already been studied by the conventional method,²⁵ we tried a different route to synthesis using a microwave-assisted method and different starting chemical. Dramatic differences in the crystal packing were seen. Moreover, additional work on IR spectroscopy and crystal packing will be discussed.

Crystallographic structure

Compound $[(\text{H}_2\text{-}(4,4'\text{-bipy}))^{2+} + [\text{Cr}_2\text{O}_7]^{2-}]$ (**1**)

The crystal structure of **1** as illustrated in Figure 1, presents an orthorhombic space group *Pnma* (no#62) which is about the same space group as *Pcmn* (no#62) found in previous work.²⁵ This caused by the interchange of the unit cell dimensions between *a* and *c* axes. Space group *Pcmn* is the *cba* setting of *Pnma*.

The crystal structure of **1** consists of a 4,4'-bipyridium $[\text{H}_2\text{-}4,4'\text{-bipy}]^{2+}$ dication and a dichromate $[\text{Cr}_2\text{O}_7]^{2-}$ anion. The cation is an essential planar with the torsion angles $\text{C}(2)\#1\text{-C}(3)\text{-C}(4)\text{-C}(5)\#1$ of

Table 1. Crystallographic data for **1** and **2**.

CCDC deposition number	760023	760084
Empirical formula	C ₁₀ H ₁₀ Cr ₂ N ₂ O ₇	C ₂₀ H ₂₀ Cr ₂ Mn N ₄ O ₉
Formula weight	374.20	619.34
Wavelength (Å)	0.71073	0.71073
Crystal system	Orthorhombic	Triclinic
Space group	<i>Pnma</i>	<i>P</i> – 1
<i>a</i> (Å)	20.898(5)	7.491(2)
<i>b</i> (Å)	12.345(3)	8.250(2)
<i>c</i> (Å)	5.0650(12)	10.292(1)
α (°)	90.00	83.19(1)
β (°)	90.00	86.09(1)
γ (°)	90.00	71.18(2)
<i>V</i> (Å ³)	1306.7(5)	597.4(3)
<i>Z</i>	4	1
<i>D_c</i> (g/cm ³)	1.902	1.721
Absorption coefficient (mm ⁻¹)	1.698	1.472
<i>F</i> (000)	752	313
Crystal size (mm ³)	0.032 × 0.024 × 0.010	0.402 × 0.402 × 0.294
Reflections collected	10,716	2946
Independent reflections	1702 [<i>R</i> _{int} = 0.0362]	2946 [<i>R</i> _{int} = 0.0000]
Absorption correction	Semi-empirical	Semi-empirical
<i>T</i> _{min} , <i>T</i> _{max}	0.952, 0.983	0.559, 0.649
Goodness-of-fit on <i>F</i> ²	1.049	1.073
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0337, <i>wR</i> ₂ = 0.0954	<i>R</i> ₁ = 0.0448, <i>wR</i> ₂ = 0.1135
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0497, <i>wR</i> ₂ = 0.1038	<i>R</i> ₁ = 0.0477, <i>wR</i> ₂ = 0.1159
Extinction coefficient	-	0.041(5)
Largest diff. peak and hole (eÅ ⁻³)	0.542 and -0.322	0.687 and -0.667

0.1(5)° and C(2)^{#1}-C(3)-C(4)-C(5)^{#1} of -179.8(3)°. The anion adopts twists of about 6° away from a perfectly eclipsed conformation with the torsion angles O(1)-Cr(1)-O(4)-Cr(1)^{#1} of 176.97(18) and C(1)-C(2)-C(3)-C(4) of -179.9(3). The Cr(IV) geometry is a typical tetrahedral illustrated by the bond angles as shown in Table 2. Consideration of Figures 2 and 3 suggests that each cation is surrounded by 4 anions and each anion by 4 cations. The compound adopts 4:4 coordination number ratios as some cations bridge cations located in adjacent unit cells as shown in Figure 3.

Comparison of the structures of **1** to the previous study found that the structure parameters are slightly different.²⁵ The greatest differences may come from the slightly longer bridging oxygen atoms in our work with the Cr-O(4) of 1.7996(12) Å, but making an impact in different crystal packing.

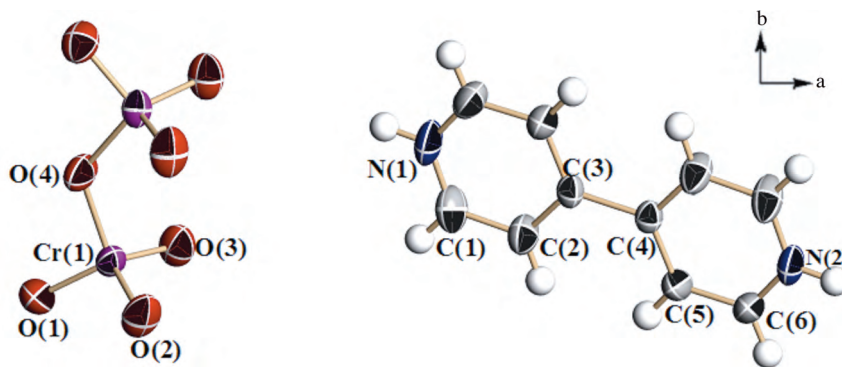


Figure 1. A molecular structure of $[(\text{H}_2\text{-(4,4'-bipy)})]^{2+} \text{Cr}_2\text{O}_7]^{2-}$ along c axis. Unlabeled atoms are related by an inversion center to the labeled atoms.

Table 2. Selected bond distances (\AA), bond angles and torsion angles ($^\circ$) for **1**.

N(1)-C(1)	1.316(3)	N(2)-C(6)	1.319(3)
C(3)-C(4)	1.502(4)	C(4)-C(5) ^{#1}	1.382(3)
C(4)-C(5)	1.382(3)	Cr ···Cr	3.220
Cr(1)-O(2)	1.594(2)	Cr(1)-O(4)	1.801(1)
Cr(1)-O(1)	1.608(2)	N(1)-C(1)	1.316(3)
Cr(1)-O(3)	1.610(2)	C(4)-C(5)	1.382(3)
C(5)-C(4)-C(3)	121.2(2)	N(2)-C(6)-C(5)	120.0(3)
C(6)-C(5)-C(4)	120.1(3)	O(1)-Cr(1)-O(4)	105.8(1)
O(2)-Cr(1)-O(1)	110.4(1)	C(1) ^{#1} -N(1)-C(1)	122.6(3)
O(2)-Cr(1)-O(3)	109.7(1)	Cr(1)-O(4)-Cr(1) ^{#1}	127.0(2)
O(1)-Cr(1)-O(4)-Cr(1) ^{#1}	177.0(2)	C(1)-C(2)-C(3)-C(4)	-179.9(3)
C(2) ^{#1} -C(3)-C(4)-C(5) ^{#1}	0.1(5)	C(2) ^{#1} -C(3)-C(4)-C(5)	-179.8(3)

Symmetry transformations used to generate equivalent atoms: ^{#1} $x, -y + 1/2, z$

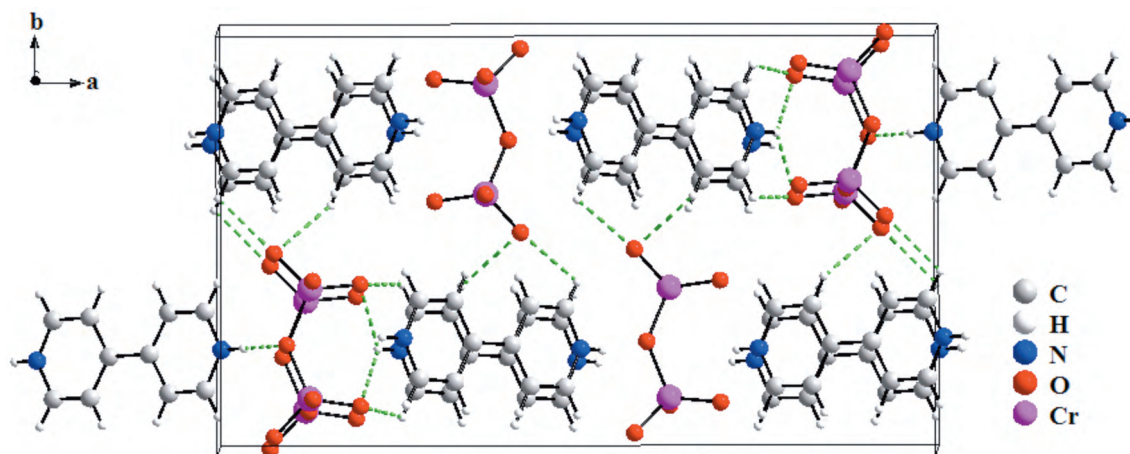


Figure 2. A unit cell of **1** projected approximately along the c axis illustrating the weak interactions.

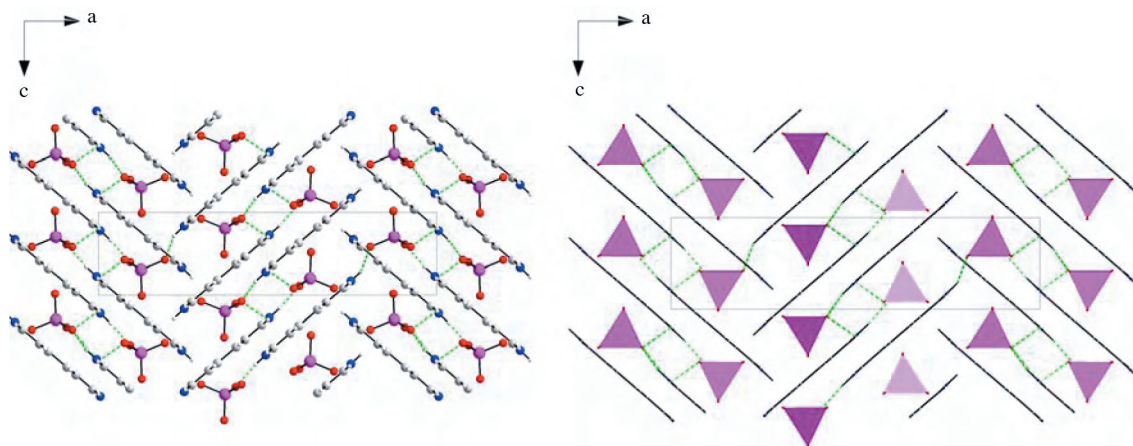


Figure 3. A packing diagram of **1** projected approximately along the *b* axis showing hydrogen bond interactions (left) and dichromate polyhedra (right).

To simplify the diagrams in crystal packing (Figure 3 right), the cations are depicted as elongated lines on the *b* axis. It is important to realize that the interactions made by the cations and anions with the viewing direction vary greatly from structure to structure. Both oxygen atoms of dichromate act as hydrogen acceptors, being involved in hydrogen bonds with the bifurcated N atoms of 4,4'-bipy ligands as shown in Table 3, just about the same as reported in previous work.²⁵ In addition, the C-H...O interactions play an important role in crystal packing which occurred via intermolecular weak interactions to consolidate the whole architecture. Previous work led us to expect only 1 C-H...O interaction at about 2.996 Å, but we found 2 more interactions at about 3.020 Å and 3.013 Å as shown in Table 3 and Figures 2 and 3. These C-H...O interaction values are lower than those found in the literature for any chromium(VI) compounds with organic bases.²⁵

Table 3. All of the relevant hydrogen bonding values and symmetry codes of **1**.

D-H...A	d(D-H) (Å)	d(H...A) (Å)	d(D...A) (Å)	<DHA (°)
N(1)-H(1A)...O(3) # ¹	0.860	2.397	2.990	126.55
N(1)-H(1A)...O(3) # ²	0.860	2.397	2.990	126.55
N(2)-H(2A)...O(4) # ³	0.860	1.828	2.686	174.69
C(6)-H(6)...O(1)	0.930	2.507	3.020	114.0
C(1)-H(1)...O(3)	0.930	2.559	3.125	115.2
C(2)-H(2)...O(1)	0.930	2.515	3.013	128.5

Symmetry codes: #¹ $[-x + 3/2, -y + 1, z - 1/2]$, #² $[-x + 3/2, y - 1/2, z - 1/2]$, #³ $[x - y, x, z + 1/6]$ #⁴ $[y, -x + y, z - 1/6]$, #⁵ $[-x + y + 1, -x + 1, z - 1/3]$

Compound $[\text{Mn}(4,4'\text{-bipy})(\text{Cr}_2\text{O}_7)(\text{H}_2\text{O})_2]$, (**2**)

The structural determination revealed that compound **2** crystallizes in the centrosymmetric space group $P-1$. The dichromate oxygen O(3) atom contains only a half atom in unit cell. The asymmetric unit structure

with the atomic numbering scheme is shown in Figure 4. Selected bond lengths, bond angles, and torsion angles are shown in Table 4.

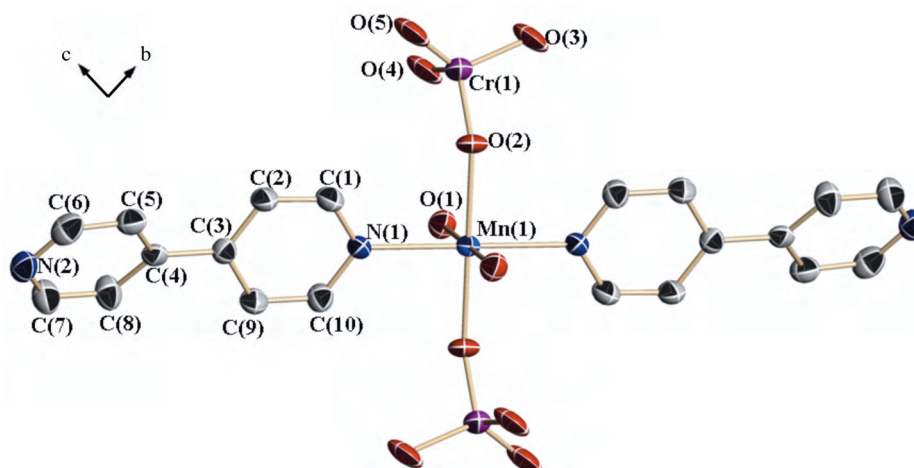


Figure 4. A molecular structure of mononuclear compound **2** with the atoms numbering scheme. Unlabeled atoms are related by an inversion center to the labeled atoms. Hydrogen atoms on rings have been omitted for clarity.

Table 4. Selected bond distances (Å), bond angles and torsion angles (°) for **2**.

Mn(1)-O(1)	2.210(3)	Cr(1)-O(2)	1.630(4)
Mn(1)-O(2)	2.140(4)	Cr(1)-O(3)	1.788(8)
Mn(1)-N(1)	2.261(4)	Cr(1)-O(4)	1.520(5)
N(1)-C(2)	1.338(6)	Cr(1)-O(5)	1.549(5)
C(3)-C(4)	1.481(6)	Cr(1)-O(3)#2	1.829(7)
N(2)-C(6)	1.324(7)	Cr...Cr	3.311
O(1)-Mn(1)-O(1)#1	180.0	Cr(1)-O(3)-Cr(1)#2	132.5(4)
O(2)-Mn(1)-O(1)	92.1(2)	O(1)#1-Mn(1)-N(1)#1	87.8(1)
O(2)#1-Mn(1)-O(1)	87.9(2)	Cr(1)-O(2)-Mn(1)	145.6(1)
C(1)-N(1)-C(10)	116.1(4)	O(1)#1-Mn(1)-N(1)#1	87.8(1)
C(2)-C(3)-C(4)	122.4(4)	Cr(1)-O(2)-Mn(1)	145.6(1)
C(5)-C(4)-C(3)	121.8(4)		
O(2)-Cr(1)-O(3)-Cr(1)#1	-92.8(1)	O(3A)-Cr(1)-O(3)-Cr(1)#1	0.00
C(2)-C(3)-C(4)-C(5)	-22.8(1)	C(2)-C(3)-C(4)-C(8)	158.1(1)

Symmetry transformations used to generate equivalent atoms: #1 $-x + 1, -y + 1, -z + 1$ #2 $-x, -y + 2, -z + 1$

Compound **2** is in a *trans* form as found in Ni compound with dichromate in the bridging fashion.^{18b,26} The Mn(1) contributes its 6 empty orbitals to accommodate the lone pair of electrons from 2 oxygen atoms of the dichromate anion, 2 terminal nitrogen atoms of 4,4'-bipy and 2 terminal oxygen atoms of water. The coordination sphere of the manganese atom can be regarded as a slightly distorted octahedral of $[\text{MnO}_4\text{N}_2]^{2+}$

where the Mn-O(1), Mn-O(2), and Mn-N(1) bond distances are 2.210(3), 2.140(4) and 2.261(4) Å respectively. The slight distortion of this octahedron can be demonstrated further by the bond angles of the coordinated atoms, O(2)-Mn(1)-O(1) of 92.10(15)° and O(2)[#]-Mn(1)-O(1) of 87.90(15)°, obviously deviating from the ideal octahedron value of 90°.

Coordination seems to affect the geometries of the 4,4'-bipy and dichromate moieties in this crystal (**2**). The geometry of 4,4'-bipy is not coplanar which is different from compound **1** but twists with the torsion angles C(2)-C(3)-C(4)-C(5) of -22.78 (0.77)° and C(2)-C(3)-C(4)-C(8) of 158.12(0.49)°. The dichromate geometry adopts a staggered conformation with the torsion angles O(2)-Cr(1)-O(3)-Cr(1)[#] of -92.75(0.65)°. Its conformation differs from an eclipsed conformation in diprotonated 4,4'-bipyridium (**1**), caused by the complexation as seen in similar structures.^{16,18b}

In correspondence with the typical coordination mode, dichromate anion acts as a bridging ligand to form 1D $\{(\text{Cr}_2\text{O}_7)^{2-} - [\text{Mn}(4,4'\text{-bipy})(\text{H}_2\text{O})_2]^{2+} - (\text{Cr}_2\text{O}_7)^{2-}\}$ chains running along the crystallographic *b* axis.^{18b} The relative propagation directions of the chain lie parallel to one another as shown in Figures 5 and 6.

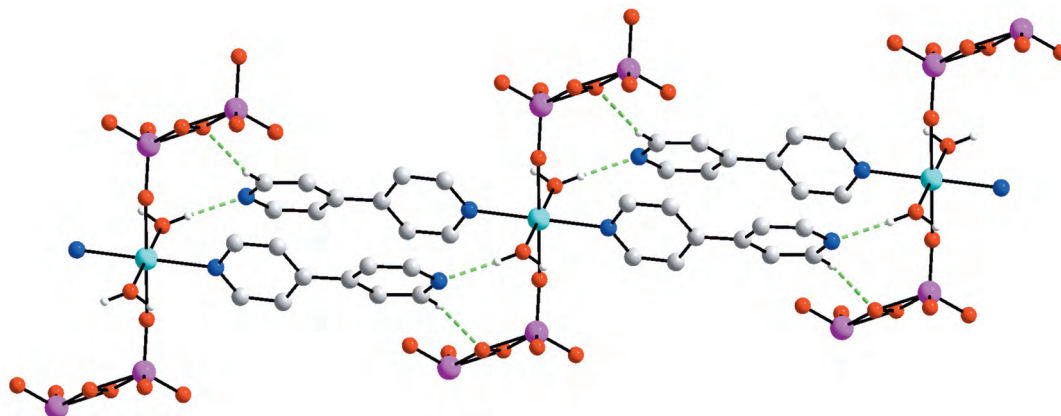


Figure 5. The intermolecular interactions are in **2**. Some of the hydrogen atoms not involving interactions have been omitted for clarity.

The most intriguing features of crystal structures arise from the interactions at supramolecular level. As shown in Figures 5 and 6 and Table 5, there are intermolecular hydrogen bonds to link the molecules into a 2D network structure. In this network, the uncoordinated N donor atoms of 4,4'-bipy ligands exhibit a connection mode with one Ow (oxygen atom of water ligand) to form N-H...Ow, (1.937 Å), with the neighboring chain making 2D supramolecular assembly networks as seen in a previous study.²⁷ Moreover there is a point that deserve to be emphasized which is a C-H...O interaction between bipyridine ring and one bridging oxygen atom from dichromate anion (2.937 Å). This additional network may come from the half site occupancy of bridging oxygen atoms.

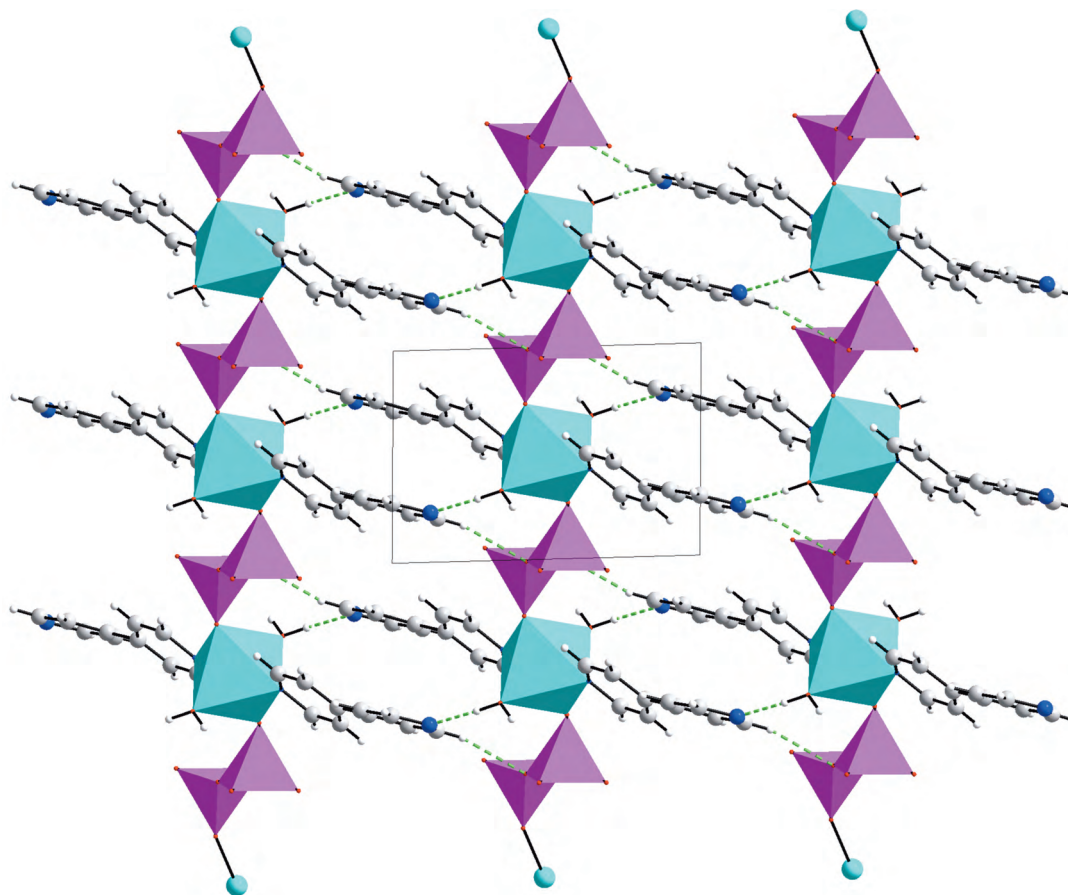


Figure 6. Crystal packing of polymeric $[\text{Mn}(4,4'\text{-bipy})_2(\text{Cr}_2\text{O}_7)(\text{H}_2\text{O})_2]$ shows weak interactions and the geometries around Mn and Cr atoms.

Table 5. All of the relevant hydrogen bonding values and symmetry codes of **2**.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<DHA
O(1)-H(1A)...O(4) ^{#1}	0.820	2.266	3.080	172.30
O(1)-H(1B)...N(2) ^{#2}	0.896	1.396	2.824	170.49
C(6)-H(6)...O(3)	0.930	2.514	3.011	167.0

Symmetry codes: ^{#1} $[-x, -y + 1, -z + 1]$ ^{#2} $[x, y + 1, z - 1]$

The infrared spectra

The infrared spectrum of **1** and **2** are consistent with their chemical formulae. The IR bands at 3279 cm^{-1} and 1486 cm^{-1} are assigned to the N-H stretching and N-H bending vibrations in **1**, respectively, confirming the $[\text{H}_2\text{-4,4'-bipy}]^{2+}$ pyridinium group.²⁵ The other characteristic bands of $[\text{H}_2\text{-4,4'-bipy}]^{2+}$ are the 2 medium intensity bands at 1620 cm^{-1} and 1591 cm^{-1} , which are attributed to the C=C and C=N stretching modes.

These characteristic absorption bands of **2** are shifted to lower wave numbers compared to the free ligand (**1**).²⁸ The weak bands observed at *ca.* 1200-1000 cm⁻¹ in all spectra were assigned to in-plane C-H deformations.

The characteristic bands of dichromate groups are observed. Both compounds exhibit bands at around 560-540 cm⁻¹ and 770-740 cm⁻¹, which belong to the symmetric and antisymmetric stretching modes of the Cr-O-Cr stretching and bending vibrations, respectively.²⁹ On the other hand, all spectra show frequencies in *ca.* 900-880 cm⁻¹ and 965-930 cm⁻¹ regions corresponding to the symmetric and antisymmetric Cr-O terminal bond stretching vibrations, which are in good agreement with those reported for K₂Cr₂O₇.²⁸ Furthermore, both compounds exhibit a band in a *ca.* 490-450 cm⁻¹ region, which is assigned to the bending mode of vibration of the Cr-O terminal bonds.²⁶ Finally, the strong band at *ca.* 490-460 cm⁻¹ in **2** is attributed to the stretching vibrations of the M-O and Mn-N bonds.^{11,25}

Conclusions

To sum up, microwave-assisted synthesis is a feasible method to synthesize such compounds containing dichromate and 4,4'-bipy ligands, confirmed by the quite high percent yields of 67 and 55 for compounds **1** and **2**, respectively. These 2 compounds were characterized by FT-IR spectroscopy and X-ray crystal structure analysis. Compound **1**, [(H₂-C₁₀H₈N₂)(Cr₂O₇)], is a centrosymmetric structure that contains a diprotonated 4,4'-bipyridium dichromate. Compound **2**, [Mn(4,4'-bipy)(Cr₂O₇)(H₂O)₂], is a chain of vertex-linked [Cr₂O₇]²⁻ and [CuN₂O₄]²⁺ units to form 1D polymer. The intermolecular hydrogen bonds constructed a 2D supramolecular assembly network differing from the previous similar work.

Acknowledgement

We acknowledge the department of chemistry, Thaksin University, for a partial support to MW.

Supplementary data

CCDC data 760023 and 760084 contain the supplementary crystallographic data for **1**. These 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.

References

1. Yaghi, O. M.; O'Keeffe, M.; Ockwig, N. W.; Chae, H. K.; Eddaoudi, M.; Kim J. *Nature* **2003**, *423*, 705-714.
2. Parodi, F. *SPIE Proceedings* **1998**, *4017*, 2-17.
3. Committee on microwave processing of materials, *National materials advisory board, Microwave processing of materials*, National Academy Press, Washington, D.C., 1994.
4. Giguere, R. J.; Bray, T. L.; Duncan, S. M. *Tetrahedron Lett.* **1986**, *27*, 4945-4948.

5. Baxendale, I. R.; Ley, S. V. *Nat. Rev. Drug. Disc.* **2002**, *1*, 573-586.
6. Tan, Y.; Cai, S.; Liao, L.; Wang, Q.; Liu, L. *Polym. J.* **2009**, *41*, 899-928.
7. Kajiwara, Y.; Nagai A.; Chujo, Y. *Polym. J.* **2009**, *41*, 1080-1084.
8. Doran, T. J.; Lul, P. J.; Vanier, G. S.; Collins, M. J.; Wu, B.; Lu, Q. L. *Gene. Ther.* **2009**, *16*, 119-126.
9. Horcajada, P.; Chalati, T.; Serre, C.; Gillet, B.; Sebrie, C.; Baati, T.; Eubank, J. F.; Heurtaux, D.; Clayette, P.; Kreuz, C.; Chang, J. S.; Hwang, Y. K.; Marsaud, V.; Bories, P. N.; Cynober, L.; Gil, S.; Férey, G.; Couvreur, P.; Gref, R. *Nat. Mat.* **2010**, *9*, 172-178.
10. Stears, R.L.; Martinsky, T.; Schena, M. *Nat. Med.* **2003**, *9*, 140-145.
11. Phetmung, H.; Wongsawat, S.; Pakawatchai; C.; Harding, D. R. *Inorg. Chim. Acta.* **2009**, *362*, 2435-2439.
12. Roesky, H. W.; Ruh, M. *Coordin. Chem. Rev.* **2003**, *236*, 91-119.
13. Woodward, J. D.; Backov, R.; Abboud, K. A.; Ohnuki, H.; Meisel, M. W.; Talham, D. R. *Polyhedron* **2003**, *22*, 2821-2829.
14. Rodman, D. L.; Carrington; N. A.; Xue, Z. L. *Talanta* **2006**, *70*, 668-675.
15. a) Cieslak-Golonka; M.; Daszkiewicz, M. *Coordin. Chem. Rev.* **2005**, *249*, 2391-2407; b) Sharma, R. P.; Sharma, R.; Bala, R.; Salas; J. M.; Quiros M. *J. Chem. Crystallogr.* **2005**, *35*, 769-775.
16. Gili P.; Lorenzo-Luis, P. A. *Coordin. Chem. Rev.* **1999**, *193*, 747-768.
17. Chen, X. Y.; Zhao, B.; Cheng, P.; Ding, B.; Liao, D. Z.; Yan; S. P.; Jiang, Z. H. *Eur. J. Inorg. Chem.* **2004**, *3*, 562-569.
18. a) Kopf, A. L.; Maggard, P. A.; Stern; C. L.; Poeppelmeier, K. R. *Acta Cryst.* **2005**, *C61*, m165-m168; b) Karmakar, R.; Choudhury, C. R.; Gramlich V.; Mitra, S. *Inorg. Chim. Acta.* **2004**, *357*, 3785-3788; c) Krivovichev, S. V.; Tananaev, I. G.; Kahlenberg, V.; Myasoedov, B. F. *Radiochemistry* **2006**, *48*, 213-216.
19. a) Pecoraro, V. L. *Manganese Redox Enzymes* VCH Publishers Inc., New York, 1992; b) Wiegardt, K. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1153-1172; c) Christou, G. *Acc. Chem. Res.* **1989**, *22*, 328-335.
20. SMART Version 5.618, Madison, Wisconsin, USA, 2002; Bruker AXS Inc., SAINT Version 6.02a.
21. Kingston, H. M.; *Introduction to Microwave Sample Preparation Theory and Practice*, American Chemical Society Publishing: Washington DC, 1988.
22. Spek, A. L. *PLATON* Version of June 2002, University of Utrecht, The Netherlands, 2002.
23. Sheldrick, G. M. *SHELXL-97 Program for the Refinement of Crystal Structures* University of Göttingen, Germany, 1997.
24. Brandenburg, K.; Putz, H. *Diamond Version 3* Crystal Impact, Germany, 2005.
25. Martin-Zarza, P.; Gili, P.; Rodriguez-Romero, F. V.; Ruiz-Pere; C.; Solans, X. *Polyhedron* **1995**, *14*, 2907-2917.
26. Mestres, J.; Duran, M.; Martin-Zarza, P.; Medina de la Rosa; E.; Gili, P. *Inorg. Chem.* **1993**, *32*, 4708-4713.
27. Brandon; J. K.; Brown, I. D. *Can. J. Chem.* **1968**, *46*, 933-941.
28. Nedelcu, A.; Zak, Z.; Madalan, A. M.; Pinkas, J.; Ruh, M. *Polyhedron* **2003**, *22*, 789-794.
29. Dave, B. C.; Czernuszewicz, R. S. *Inorg. Chem.* **1994**, *33*, 847-848.