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Synthesis and characterization of coordination polymers with interpenetrated frameworks: M(adipate)(1,2-bis(4-pyridyl)ethane) and M(adipate)(trans-1,2-bis(4-pyridyl)ethene), M = Co, Mn

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Abstract

Four novel coordination polymers: M(adipate)(1,2-bis(4-pyridyl)ethane) (1, 2) and M(adipate)(*trans*-1,2-bis(4-pyridyl)ethene) (3, 4), M = Co (1, 3) or Mn (2, 4), were synthesized by the self-assembly of Co²⁺ or Mn²⁺, adipate, and 1,2-bis(4-pyridyl)ethane or *trans*-1,2-bis(4-pyridyl)ethene. Their crystal structures were determined by X-ray diffraction, showing that they have similar structures. Each structure of 1–4 contains two sets of interpenetrated open frameworks, which are built by M(adipate) 2-D networks connected by N,N'-dipyridyl ligands. Magnetic studies indicate 1–4 follow Curie–Weiss law and become antiferromagnetic at low temperatures.

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Keywords: Coordination polymers; Crystal structure; Self-assembly; Interpenetrated; Antiferromagnetic

1. Introduction

Crystal engineering has become an intriguing field, continuing to generate new materials [1]. To date, selfassembly of metal ions and multidentate organic ligands have achieved great success in forming coordination polymers [2-8] that can be potentially applied as catalysts [3], or possess interesting properties such as molecular sorption [4], electric conductivities [5], magnetism [6] and optical properties [7]. The architecture of the hybrid inorganic-organic networks is determined by the geometrical preference of the metal ions as well as organic ligand building blocks, which exhibit remarkable variety in their molecular structures. Rigid polycarboxylates, such as 1,3,5-benzenetricarboxylates, 1,3,5-cyclohexanetricarboxylates, 1,4-benzenedicarboxylate and 4,4'-biphenyldicarboxylate, have been used as anionic linkers to stabilize many structures with open frameworks [8]. In order to verify if the length and shape of building blocks determines the topologies of the

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with a long and flexible polycarboxylate, adipate [9], and one of the two N,N'-bidentate ligands with similar structures, 1,2-bis(4-pyridyl)ethane and *trans*-1,2-bis(4pyridyl)ethene (Scheme 1). In this work we report such combinations resulted in the formation of similar interpenetrated frameworks under the same synthetic conditions. By choosing the two N,N'-bidentate ligands with different π -conjugation system, we attempted to investigate if the subtle structural difference of ligands imposes any effect on the coupling of the magnetic centers. A variable temperature magnetic susceptibility investigation shows that the metal centers in the complexes are antiferromagnetically coupled.

products, we compare the self-assemblies of metal ions

2. Experimental

 $Co(NO_3)_2 \cdot 6H_2O$, $Mn(NO_3)_2 \cdot 4H_2O$ (Riedel-de Haën), $CoCl_2 \cdot 6H_2O$ (Showa), $MnCl_2 \cdot 4H_2O$ (Showa), 1,2-bis(4pyridyl)ethane (Aldrich), *trans*-1,2-bis(4-pyridyl)ethene (Aldrich), were used as obtained, without further purification. Infrared spectra (IR) were recorded from

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Scheme 1.

KBr pellets on a Perkin–Elmer PC 16 FTIR spectrometer. Thermogravimetric analysis (TGA) was performed under air flow at a heating rate of 10 °C min⁻¹ using a Shimadzu TGA-50 system. X-ray powder diffraction (XRPD) data were recorded on a Shimadzu XRD-6000 diffractometer.

2.1. Synthesis

2.1.1. Co(adipate)(1,2-bis(4-pyridyl)ethane)

 $Co(NO_3)_2 \cdot 6H_2O$ (0.145 g, 0.500 mmol) and a mixture of adipic acid (0.073 g, 0.500 mmol)-1,2-bis(4-pyridyl)ethane (0.276 g, 1.50 mmol) were first dissolved in 5 and 10 ml distilled water, respectively, at 80 °C. The two solutions were mixed and sealed in a 30 ml test tube, forming a clear pink solution with pH 3.84. The solution was kept at 80 °C for 4 days until many parallelepiped purple crystals of 1 were observed. The final pH value was 4.90. Crystals (0.168 g) were collected after filtration and several washings with distilled water and acetone in 86.8% yield (based on Co). IR(KBr, cm^{-1}): 3064(w), 2944(m), 2856(w), 1602(s), 1568(s), 1552(m), 1498(w), 1456(m), 1422(s), 1330(w), 1296(w), 1218(m), 1128(m), 1072(w), 1016(m), 922(w), 872(w), 834(s), 816(w), 802(w), 634(m), 554(s), 500(w), 418(w), 404(w). Anal. Calc. for CoO₄N₂C₁₈H₂₀: C, 55.82; H, 5.20; N, 7.23. Found: C, 55.57; H, 5.18; N, 7.32%.

2.1.2. Mn(adipate)(1,2-bis(4-pyridyl)ethane)

Mn(NO₃)₂·4H₂O (0.126 g, 0.500 mmol) and a mixture of adipic acid (0.073 g, 0.500 mmol)–1,2-bis(4-pyridyl)ethane (0.368 g, 2.00 mmol) were first dissolved in 5 and 10 ml distilled water, respectively, at 80 °C. The two solutions were mixed and sealed in a 30 ml test tube, forming a colorless solution with pH 3.69. The solution was kept at 80 °C for 4 days until many colorless crystals of **2** were observed. The final pH value was 5.29. Crystals (0.096 g) were collected after filtration and several washings with distilled water and acetone in 86.8% yield (based on Mn). IR(KBr, cm⁻¹): 3062(w), 3034(w), 2944(s), 2856(w), 1596(s), 1564(s), 1500(w), 1456(w), 1422(s), 1330(w), 1294(m), 1216(m), 1186(m), 1126(s), 1068(w), 1012(s), 920(m), 876(w), 832(s), 814(m), 772(w), 694(w), 632(s), 550(s), 494(m). *Anal.* Calc. for $MnO_4N_2C_{18}H_{20}$: C, 56.40; H, 5.26; N, 7.31. Found: C, 55.99; H, 5.25; N, 7.41%.

2.1.3. Co(adipate)(trans-1,2-bis(4-pyridyl)ethene)

CoCl₂·6H₂O (0.119 g, 0.500 mmol) were first dissolved in 5 ml distilled water and a mixture of adipic acid (0.073 g, 0.500 mmol)-trans-1,2-bis(4-pyridyl)ethene (0.364 g, 2.00 mmol) were first dissolved in 5 ml distilled water-5 ml ethanol at 80 °C. The two solutions were mixed and sealed in a 30 ml test tube, forming a clear pink solution with pH 4.50. The solution was kept at 80 °C for 3 days until many parallelepiped red crystals of 3 were observed. The final pH value was 5.31. Crystals (0.169 g) were collected after filtration and several washings with distilled water and acetone in 87.7% yield (based on Co). IR(KBr, cm⁻¹): 3066(w), 3040(w), 3008(w), 2948(m), 2854(w), 1600(s), 1564(s), 1500(w), 1458(m), 1424(s), 1330(w), 1294(w), 1248(m), 1208(m), 1128(w), 1066(w), 1012(m), 988(m), 922(w), 862(m), 832(s), 802(w), 762(w), 624(m), 554(s), 506(w), 470(w), 426(w). Anal. Calc. for CoO₄N₂C₁₈H₁₈: C, 56.12; H, 4.71; N, 7.27. Found: C, 55.91; H, 4.69; N, 7.24%.

2.1.4. *Mn(adipate)(trans-1,2-bis(4-pyridyl)ethene)*

MnCl₂·4H₂O (0.099 g, 0.500 mmol) were first dissolved in 5 ml distilled water and a mixture of adipic acid (0.073 g, 0.500 mmol)-trans-1,2-bis(4-pyridyl)ethene (0.364 g, 2.00 mmol) were first dissolved in 5 ml distilled water-5 ml ethanol at 80 °C. The two solutions were mixed and sealed in a 30 ml test tube, forming a colorless solution with pH 2.94. The solution was kept at 80 °C for 3 days until many parallelepiped vellow crystals of 4 were observed. The final pH value was 4.35. Crystals (0.096 g) were collected after filtration and several washings with distilled water and acetone in 50.1% yield (based on Mn). IR(KBr, cm^{-1}): 3064(w), 3008(w), 2948(m), 2858(w), 2362(w), 1704(w), 1592(s), 1562(s), 1456(w), 1424(s), 1330(w), 1294(m), 1248(w), 1210(m), 1128(m), 1064(w), 1010(s), 988(s), 920(m), 892(w), 866(w), 830(s), 802(m), 764(m), 628(s), 554(s), 504(w). Anal. Calc. for MnO₄N₂C₁₈H₁₈: C, 56.70; H, 4.76; N, 7.35. Found: C, 56.61; H, 4.77; N, 7.39%.

2.2. Structure determination

Single crystals of 1–4 were mounted on the tops of glass fibers. The crystallographic works were performed on a Bruker P4 automatic diffractometer with graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Initial unit cells for 1–4 were determined from 20 reflections randomly located from hemisphere search. Unit cell constants and orientation matrices for data collection were refined from 25 carefully centered

reflections around $2\theta = 25^{\circ}$. Three standard reflections were measured periodically every 97 reflections. No significant decay was observed. An empirical ψ -scan absorption correction was applied to all the data. The structures were solved with direct method (SHELXS-86) [10], and were refined by a full-matrix least-square technique available in the SHELXL-93 [11] crystallographic software package. All the non-hydrogen atoms were refined with anisotropic thermal parameters. All the hydrogen atoms bonded to carbon atoms at calculated idealized positions were included in structure factor calculation but were not refined. The crystallographic data and detailed information of structure solution and refinement are listed in Table 1.

2.3. Magnetic measurement

Variable-temperature dc magnetic susceptibility data were collected for polycrystalline samples of 1-4 in an applied filed of 1.0 kG, and in the temperature range of 2.0-300.0 K, which were measured by a squid magnetometer (Quantum Design, MPMS-7). The samples were embedded in eicosane wax to prevent any torquing of the polycrystalline in the magnetic field. Pascal's constants [12] were used to estimate the diamagnetic corrections.

3. Results and discussion

3.1. Synthesis

The crystals of 1 suitable for single-crystal X-ray diffraction studies were obtained from a reaction with stoichiometric amount of starting reagents, Co^{2+} :adipic

Table 1

acid:bpe = 1:1:1, under the same reaction parameters mentioned in the experimental section. However the yield obtained from such ratio was very low at 24.8%. During the efforts to optimize the yield, we found the yield can be improved significantly to 86.8% by increasing the amount of N,N'-dipyridyl ligands to more than 3 equiv. The addition of more dipyridyl ligands was observed to increase the crystal growing rates at the sacrifice of crystallinity and crystal size. During the preparation of **3** and **4**, appropriate amount of ethanol was added in order to promote the crystallization of the products. The addition of too much ethanol resulted in the formation of polycrystalline products in a shorter reaction period.

3.2. Crystal structures

Compounds 1, 2 and 3, 4 are two pairs of isostructures, with similar three-dimensional frameworks. Each 3-D framework is formed by two sets of interpenetrated networks offset by (1/2, 1/2, 1/2), as shown in Fig. 1. Each set of 3-D network is composed of parallel 2-D M(adipate) nets perpendicular to $[\bar{1}11]$ direction, as shown schematically in Fig. 2, cross-linked by bridging 1,2-bis(pyridyl)ethane in 1 and 2, or by bridging trans-1,2-bis(pyridyl)ethene in 3 and 4. All the dipyridyl rings are parallel, with the bpe ligands running along the [011] direction. The linkage of M^{2+} ions, adipates and dipyridyl ligands results in large parallelepipeds with dimensions of $13.7 \times 10.8 \times 13.7$ Å for 1, $13.7 \times 10.9 \times 10.9$ 13.9 Å for **2**, $13.3 \times 10.8 \times 13.6$ Å for **3** and $13.4 \times$ 10.9×13.9 Å for 4, respectively, whereas little void space is obtained due to interpenetration. Fig. 3(a) and (b) show the distorted octahedral coordination environment of the metal centers. Among the four oxygen

	1	2	3	4
Formula	CoO ₄ N ₂ C ₁₈ H ₂₀	MnO ₄ N ₂ C ₁₈ H ₂₀	CoO ₄ N ₂ C ₁₈ H ₁₈	MnO ₄ N ₂ C ₁₈ H ₁₈
Formula weight	387.29	383.30	385.27	381.28
Space group	$P\bar{1}$ (number 2)	$P\bar{1}$ (number 2)	$P\bar{1}$ (number 2)	$P\bar{1}$ (number 2)
a (Å)	8.482(1)	8.433(1)	8.297(1)	8.217(1)
b (Å)	9.374(1)	9.406(1)	9.096(2)	9.150(1)
a (Å)	11.409(1)	11.476(2)	11.343(2)	11.384(3)
α (°)	98.42(1)	97.02(1)	96.96(1)	95.88(1)
β(°)	95.17(1)	94.66(2)	96.24(2)	95.65(2)
γ (°)	106.07(1)	105.15(1)	103.40(1)	102.54(1)
$V(Å^3)$	854.1(2)	866.0(2)	818.3(3)	824.6(2)
Z	2	2	2	2
Temperature (K)	298	298	298	298
λ (Å) (Mo K α)	0.71073	0.71073	0.71073	0.71073
$\rho_{\rm calc} ({\rm g}{\rm cm}^{-3})$	1.506	1.470	1.564	1.524
μ (Mo K α , cm ⁻¹)	10.30	7.87	10.75	8.20
$R_1^{a}/wR_2^{b} (I > 2\sigma(I))$	0.0484/0.0690	0.0478/0.0761	0.0944/0.1430	0.0425/0.0592

^a $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|.$

^b $wR_2(F) = [\Sigma w (F_o^2 - F_c^2)^2 / \Sigma w (F_o^2)^2]^{1/2}.$

Crystallographic data for 1-4



(b)



Fig. 1. (a) Packing diagram of a single set of interpenetrated frameworks. (b) Schematic presentation of two sets of interpenetrated frameworks.

atoms bound to M, two are from a bidentate COO⁻ group and two are from two monodentate COO⁻ of three different adipates. Selected bond lengths and angles are given in Table 2. M and the four oxygen atoms bound to it are almost in the same plane. The O(1)-M-O(2) angles of the oxygen atoms from the bidentate COO⁻ are close to 60° while the O(3)-M-O(4) angles of the oxygen atoms from two monodentate COO^{-} are close to 120° The bond lengths of the metal to the oxygen atoms of the bidentate COO⁻ are longer than those between the metal and the oxygen atoms of the monodentate COO⁻. Two dipyridyl ligands are at *trans* positions with nearly linear N(1)-M-N(2) angles $(177.4(1)^{\circ}$ **1**, $174.44(9)^{\circ}$ **2**, $176.4(3)^{\circ}$ **3**, $173.21(9)^{\circ}$ **4**) and average Co-N and Mn-N distances of 2.156 and 2.281 Å, respectively. The similarity of these bond lengths and angles data in 1-4 reflects the fact that 1,2-bis(pyridyl)

ethane and *trans*-1,2-bis(pyridyl)ethene are building blocks of similar size and shape in constructing these frameworks.

3.3. Thermal analysis

TGA experiments performing under air flow indicate 1-4 are thermally stable up to 274, 237, 292 and 276 °C for 1-4, respectively, followed by one-step exothermic decomposition, resulting in Co₃O₄ or Mn₂O₃ residues based on XPRD measurements.

3.4. Magnetic studies

The magnetic susceptibilities of complexes were measured in the range of 2.0–300.0 K. The inverse magnetic susceptibilities (χ^{-1}) and effective magnetic



Fig. 2. ORTEP diagram of the 2-D framework of M(adipate), M = Co, Mn.



Fig. 3. ORTEP diagram and labeling scheme of 1 (a) and 3 (b). Note that 2 and 4 are isostructural to 1 and 3, respectively, and are not given here.

moment (μ_{eff}) versus temperature plots are shown in Fig. 4. When the temperature is lowered, the value of μ_{eff} is decreased, indicative of overall antiferromagnetic

Table 2 Selected bond lengths (Å) and angles (°) for 1-4

	1	2	3	4
M-O(1)	2.164(3)	2.231(2)	2.122(7)	2.216(3)
M-O(2)	2.261(3)	2.341(2)	2.283(7)	2.342(3)
M-O(3)	2.023(2)	2.106(2)	2.011(6)	2.103(3)
M-O(4)#1	2.023(2)	2.101(2)	2.009(6)	2.094(3)
M-N(1)	2.156(2)	2.277(2)	2.152(7)	2.269(3)
M - N(2)	2.158(3)	2.295(2)	2.156(7)	2.283(3)
O(1) - M - O(2)	58.7(1)	56.68(8)	57.9(3)	56.7(1)
O(1) - M - O(3)	92.5(1)	92.64(9)	92.2(3)	91.8(1)
O(1)-M-O(4)#1	147.3(1)	144.63(9)	145.3(3)	142.8(1)
O(1) - M - N(1)	91.5(1)	93.67(9)	92.8(3)	95.8(1)
O(1) - M - N(2)	88.3(1)	88.21(9)	88.9(3)	88.2(1)
O(2) - M - O(3)	150.9(1)	149.09(9)	149.8(3)	148.3(1)
O(2)-M-O(4)#1	88.7(1)	88.09(9)	87.6(3)	86.3(1)
O(2) - M - N(1)	93.3(1)	95.81(9)	94.3(3)	96.4(1)
O(2) - M - N(2)	88.8(1)	89.60(9)	89.3(3)	90.3(1)
O(3)-M-O(4)#1	119.8(1)	122.15(9)	122.0(3)	124.7(1)
O(3) - M - N(1)	91.0(1)	89.36(8)	90.5(3)	89.5(1)
O(3) - M - N(2)	86.4(1)	85.32(8)	86.2(3)	85.0(1)
O(4)#1 - M - N(1)	93.1(1)	92.95(9)	92.8(3)	92.3(1)
O(4)#1 - M - N(2)	88.6(1)	88.52(9)	87.7(3)	87.8(1)
N(1)-M-N(2)	177.4(1)	174.44(9)	176.4(3)	173.21(9)

Symmetry transformations used to generate equivalent atoms: #1, -x, -y, -z; #2, x, y-1, z-1; #3, x, y+1, z+1; #4, -x+1, -y, -z+1; #5, -x+1, -y+1, -z.



Fig. 4. Magnetic effective moment vs. temperature plots for $1(\bigcirc)$, $2(\Box)$, $3(\triangle)$, and $4(\diamondsuit)$ and inverse magnetic susceptibility vs. temperature plots for $1(\bigcirc)$, $2(\blacksquare)$, $3(\triangle)$, and $4(\diamondsuit)$. The solid lines represent the best fitting to the Curie–Weis law for data of 60–300 K.

coupling between magnetic centers. For cobalt complexes 1 and 3, the μ_{eff} values at 300 K are 4.32 and 4.48 μ_B , and decrease smoothly upon cooling to about 30 K, and then decrease rapidly to 1.37 and 1.67 μ_B at 2.0 K, respectively. For manganese complexes 2 and 4, the μ_{eff} values at 300 K are 5.80 and 5.78 μ_B , and decrease

smoothly upon cooling to about 30 K, and then decrease rapidly to 1.54 and 1.51 μ_B at 2.0 K, respectively. From the magnetic properties of complexes **1**, **2**, **3**, and **4**, the different π -conjugation system in the two N,N'-bidentate ligands does not play an important role in the pathway of magnetic coupling interaction.

In Fig. 4, the plots of χ^{-1} versus *T* for complexes 1–4 give straight lines, which can be fitted to the Curie–Weiss law. The best linear fits of $\chi^{-1}(T)$ data above 60 K yield C = 2.446, 4.067, 2.623 and 4.307 emu mol⁻¹ and $\theta = -14.3$, -7.9, -14.9, and -9.4 K for complexes 1–4, respectively. The values of θ indicate the antiferromagnetic interactions between the metal centers, and there is stronger antiferromagnetic coupling between two Co than Mn.

4. Supplementary material

The X-ray crystallographic files in CIF format is available free of charge via the internet.

Acknowledgements

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