Hydrothermal Syntheses and Crystal Structures of Ni(II), Co(II), and Cu(II), Bis(*trans*-4-pyridylacrylate) Interpenetration Networks

Yen-Hsiang Liu,* Chia-Shiang Lin,† Shiang-Ying Chen,† Hui-Lien Tsai,‡
Chuen-Her Ueng,†,1 and Kuang-Lieh Lu*,1

Institute of Chemistry, Academia Sinica, Taipei 115, Taiwan; †Department of Chemistry, National Taiwan Normal University, Taipei 106, Taiwan; and ‡Department of Chemistry, National Cheng Kung University, Tainan 701, Taiwan

Three metal–organic polymeric networks, $Ni(C_8H_6NO_2)_2(H_2O)_2$ (**1**), $Co(C_8H_6NO_2)_2$ (**2**), and $Cu(C_8H_6NO_2)_2(H_2O)_2$ (**3**), were synthesized by the hydrothermal method. Single-crystal X-ray analysis revealed that within these compounds metal centers are linked through *trans*-4-pyridylacrylate ligands to form interpenetrating infinite networks. The Ni(II) and Cu(II) compounds possess an overlay of interpenetrating square grid layers, whereas the Co(II) compound possesses interpenetrating diamondoid networks. Comparing these three compounds, the formation of cavities potentially for guest molecule inclusion within the interpenetrating networks could be achieved by taking advantage of the coordination nature of metals. Crystal structures of all three compounds were determined by single-crystal X-ray diffraction methods and solved by direct method. Crystal data for **1**: orthorhombic, space group *Pbcn*, $a = 13.735(3)$ Å, $b = 6.995(2)$ Å, $c = 16.723(3)$ Å, $V = 1606.7(6)$ Å^3, $Z = 4$, final refinement ($I > 2\sigma(I)$): $R1 = 0.0296$, w$R2 = 0.0843$. Crystal data for **2**: monoclinic, space group *Cc*, $a = 11.5717(9)$ Å, $b = 21.2838(16)$ Å, $c = 8.5504(7)$ Å, $\beta = 130.5210(10)°$, $V = 1600.8(2)$ Å^3, $Z = 4$, final refinement ($I > 2\sigma(I)$): $R1 = 0.0347$, w$R2 = 0.0879$. Crystal data for **3**: orthorhombic, space group *Pbcn*, $a = 13.6844(13)$ Å, $b = 7.5053(8)$ Å, $c = 15.929(4)$ Å, $V = 1636.0(5)$ Å^3, $Z = 4$, final refinement ($I > 2\sigma(I)$), $R1 = 0.0299$, w$R2 = 0.0787$. © 2001 Academic Press

Key Words: hydrothermal; nickel; cobalt; copper; metal–organic framework; interpenetration; coordination polymer; porous material; crystal structure.

INTRODUCTION

One of the major challenges for chemists in the field of materials science is to design and synthesize compounds with specific shape and prescribed functions such as luminescence, sorption, and catalysis (1). Taking advantage of the rich coordination nature of metal–organic coordination compounds, transition metal-directed polymeric networks possessing chain, layer, and open frameworks could be achieved by way of crystal engineering (2). Extensive studies have concentrated on exploiting neutral donating ligands (e.g., pyrazine, 4,4′-bipyridine, etc.) or pure dianionic ligands (e.g., carboxylates) to generate metal–organic frameworks (3, 4), and successful examples have demonstrated the synthesis of polymeric networks possessing porous structures that are potentially useful for size-selective and functional-group-selective sorption (5). However, there remain difficulties in building framework structures with large pore size because large open spaces within crystals will result in interpenetration phenomenon (6). This negative impact will block and eliminate the framework cavity. In the literature, there are not many systematic and theoretical discussions of the relationship between the porosity and interpenetration of open frameworks (7). In an effort to study the relationship between network interpretation and cavities, we report the synthesis of three polymeric metal–organic networks, $Ni(C_8H_6NO_2)_2(H_2O)_2$ (**1**), $Co(C_8H_6NO_2)_2$ (**2**), and $Cu(C_8H_6NO_2)_2(H_2O)_2$ (**3**). *trans*-4-Pyridylacrylic acid (tpda) ligand is employed in this work. In addition to its valuable feature of intermolecular electron asymmetry (the "push–pull" effect), it can also balance the charge of metal centers to avoid counterions occupying the open spaces. Most importantly, this type of ligand could simultaneously provide more flexible coordination modes such as monodentate, bidentate chelating, bidentate bridging, and tridentate binding fashion while combining with metal centers to result in diverse neutral building blocks (8). Our results show that these three polymeric networks are categorized into two different network interpenetration topologies. We carefully evaluate these interpenetrating network structures showing that the formation of cavities for guest molecule inclusion within the interpenetrating networks could be achieved by taking advantage of the coordination nature of metals.

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[1] To whom correspondence should be addressed. Fax: + 886-2-27831237. E-mail: lu@chem.sinica.edu.tw.

EXPERIMENTAL

Materials and Methods

Nickel(II) chloride hexahydrate, cobalt(II) chloride hexahydrate, copper(II) nitrate dihydrate, triethylamine, and KOH were purchased from ACROS and used without further purification. *trans*-4-Pyridylacrylic acid (tpda) is synthesized according to the literature procedure (9).

Synthesis of Ni(trans-4-pyridylacrylate)$_2$(H$_2$O)$_2$ (1)

In a typical synthesis, *trans*-4-pyridylacrylic acid (89.4 mg, 0.61 mmol) and KOH (34.2 mg, 0.60 mmol) were throughly mixed in distilled water (7 mL) until completely dissolved, and then 3 mL of aqueous NiCl$_2$·6H$_2$O (35.0 mg, 0.31 mmol) solution was slowly added dropwise into it. The solution was sealed in a Teflon-lined acid digestion autoclave and heated hydrothermally at 140°C under autogenous pressure. After 48 h of heating, the reaction vessel was cooled continuously at 3°C/h to room temperature. Green columnar crystals were obtained. *Anal. Calcd.* for NiC$_{16}$H$_{16}$N$_2$O$_6$: C, 49.15; H, 4.14; N, 7.16. Found: C, 49.08; H, 4.28; N, 7.10.

Synthesis of Co(trans-4-pyridylacrylate)$_2$ (2)

A procedure similar to the synthesis of **1** was adopted. An aqueous solution (3 mL) of CoCl$_2$·6H$_2$O (35 mg, 0.30 mmol) was added dropwise into the aqueous solution (7 mL) of *trans*-4-pyridylacrylic acid (89.4 mg, 0.60 mmol) and triethylamine (0.60 mmol), and then treated hydrothermally at 140°C under autogenous pressure for 48 h followed by cooling to room temperature at 3°C/h. Reddish-purple columnar crystals were obtained. *Anal. Calcd.* for CoC$_{16}$H$_{12}$N$_2$O$_4$: C, 54.10; H, 3.41; N, 7.88. Found: C, 53.70; H, 3.50; N, 7.81.

Synthesis of Cu(trans-4-pyridylacrylate)$_2$(H$_2$O)$_2$ (3)

A mixture of *trans*-4-pyridylacrylic acid (122.3 mg, 0.82 mmol) and KOH (34.2 mg, 0.60 mmol) was thoroughly mixed in distilled water (7 mL) until completely dissolved, and then Cu(NO$_3$)$_2$·2H$_2$O (99.1 mg, 0.41 mmol) in 3 mL of water–ethanol (2:1 v/v) solution was slowly added dropwise into it. The solution was sealed in a Teflon-lined acid digestion autoclave and heated hydrothermally at 110°C under autogenous pressure. After 72 h of heating, the reaction vessel was cooled to room temperature. Bulk products of dark blue columnar crystals of **3** were obtained in a yield of 25.9%. *Anal. Calcd.* for CuC$_{16}$H$_{16}$N$_2$O$_6$: C, 48.55; H, 4.07; N, 7.07. Found: C, 48.80; H, 3.94; N, 7.08.

Crystal Structure Determination

Crystals of **1**, **2**, and **3** suitable for single-crystal X-ray diffraction with sizes 0.40 mm × 0.25 mm × 0.10 mm, 0.26 mm × 0.20 mm × 0.16 mm, and 0.35 mm × 0.29 mm × 0.20 mm respectively were selected and mounted on the end of a glass fiber.

For compounds **1** and **3**, structural analyses were performed on a Nonius-CAD4 diffractometer equipped with graphite-monochromated MoKα ($\lambda = 0.71073$ Å) radiation. Least-squares refinement of their setting angles in the 2θ range between 21.3–26.7° gave rise to the unit cell parameters. The diffracted intensities were corrected for Lorentz, polarization, decay, and background effects. Empirical absorption correction was applied to both compounds, based on Ψ-scans of suitable reflections having χ values close to 90°. The calculations were performed using the WINGX program (10). The structures were solved by a combination of direct methods (SHELX-97) (11) and difference Fourier methods and refined by full-matrix least-squares on F^2. All nonhydrogen atoms were refined anisotropically. All hydrogen atom positions were located from the difference Fourier map and introduced in the final stages of refinement as fixed atom contributions riding on their parent atoms. Crystal data and details associated with data collections and structure refinements are also given in Table 1.

For compound **2**, a hemisphere of data was collected at room temperature on a Bruker SMART CCD platform diffractometer (12) equipped with graphite-monochromated MoKα radiation ($\lambda = 0.71073$ Å). The frames were integrated in the Bruker SAINT software package (13), and the data were corrected for absorption using the SADABS

TABLE 1
Crystal Data and Structure Refinement for 1, 2, and 3

Empirical formula	C$_{16}$H$_{16}$N$_2$O$_6$Ni	C$_{16}$H$_{12}$N$_2$O$_4$Co	C$_{16}$H$_{16}$N$_2$O$_6$Cu
a, Å	13.735(3)	11.5717(9)	13.6844(13)
b, Å	6.9950(14)	21.2838(16)	7.5053(8)
c, Å	16.723(3)	8.5504(7)	15.929(4)
α, deg	90	90	90
β, deg	90	130.5210(10)	90
γ, deg	90	90	90
V, Å^3	1606.7(6)	1600.8(2)	1636.0(5)
Z	4	4	4
Fw	391.02	355.21	395.85
Space group	Pbcn	Cc	Pbcn
Temp, °C	25(2)	25(2)	25(2)
λ, Å	0.71073	0.71073	0.71073
ρ_{calc}, g/cm^3	1.616	1.474	1.607
μ, cm^{-1}	12.44	10.92	13.71
Goodness-of-fit	1.049	1.045	1.033
$R1$, [$I > 2\sigma(I)$]	0.0296	0.0347	0.0299
w$R2$, [$I > 2\sigma(I)$]	0.0843	0.0879	0.0787

Note. $R1 = \sum \|F_o| - |F_c\| / \sum |F_o|$. w$R2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$.

program (14). The structure was solved using the SHELXTL V. 5.10 package (15) and refinement was carried out by full-matrix least-squares calculations on F^2. All the nonhydrogen atoms were located and refined anisotropically. Hydrogen atoms were located from the difference Fourier maps and refined isotropically. The final results were given in Table 1. Molecular drawings were produced by the SHELXTL-XP program (15).
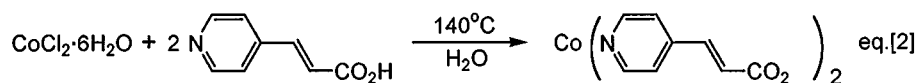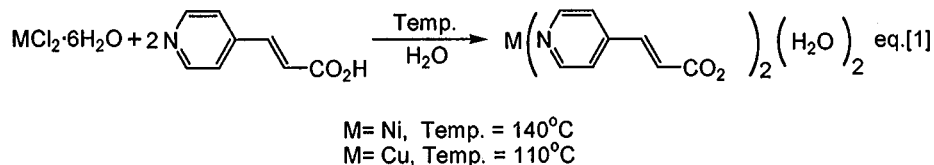
Magnetism Measurement

The magnetic susceptibilities were measured on polycrystalline samples of compound **3** at a field of 1000 G and at temperatures ranging from 2 to 300 K embedded in an eicosane matrix.

RESULTS AND DISCUSSION

Synthesis

Compound **1** was obtained as green columnar crystals by a hydro(solvo)thermal reaction between $NiCl_2 \cdot 6H_2O$ and tpda in water at 140°C (Eq. [1]). Compound **2** was prepared by mixing $CoCl_2 \cdot 6H_2O$ and tpda in water and maintaining the temperature at 140°C (Eq. [2]). Similarly, compound **3** could be obtained in a mixture of water and ethanol at lower temperature (110°C).
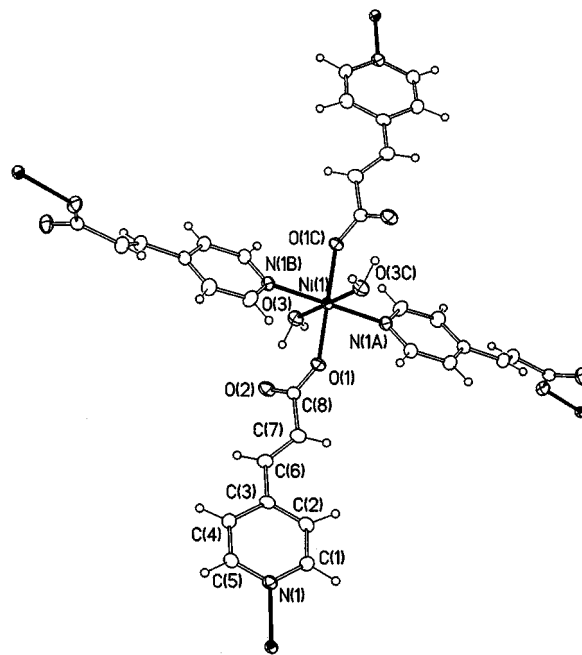

FIG. 1. ORTEP drawing of **1** with 40% ellipsoids.

trate, and their relative arrangement gives rise to various H-bonding interactions, for example, those between water molecules from one net and carboxylate tails from the other.

M= Ni, Temp. = 140°C
M= Cu, Temp. = 110°C

Crystal Structures

In the crystal structure of **1**, octahedral geometry is observed around the nickel(II) center, which is coordinated with four tpda ligands and two water molecules (Fig. 1). From the literature we learned that a tpda ligand can be utilized as a longer spacer ligand in comparison with isonicotinate ligand to form more porous materials as indicated in the case of bis(isonicotinate)zinc and bis(4-pyridylacrylato)cadmium compounds (8b). As shown in Fig.2a, these nickel centers are interlinked by tpda ligands forming porous two-dimensional chess-board-like nets with a nickel-to-nickel distance of about 11.4 Å. However, large open spaces destabilized the molecular packing in crystals. To compensate this negative impact, these nets interpene-

As shown in Figs. 2b and 2c, two different sets of parallel nets formed an overlay inclined-interpenetration arrangement. Within the networks, two nets from different sets only cross each other once along the intersection line. Consequently, the porosity of nets was eliminated due to the interpenetration.

In the crystal structure of **2**, cobalt(II) centers adopt a distorted octahedral geometry by coordinating to two pyridyl nitrogen atoms and chelating to two carboxylate groups of tpda ligands (Fig. 3). Unlike compound **1**, carboxylate ligands chelate to the metal centers and occupied all the coordination sites, thereby altering the coordination geometry. If the chelating carboxylates are treated as one connecting point, the cobalt(II) centers in **2** form a pseudotetrahedral geometry. Therefore, cobalt(II) centers
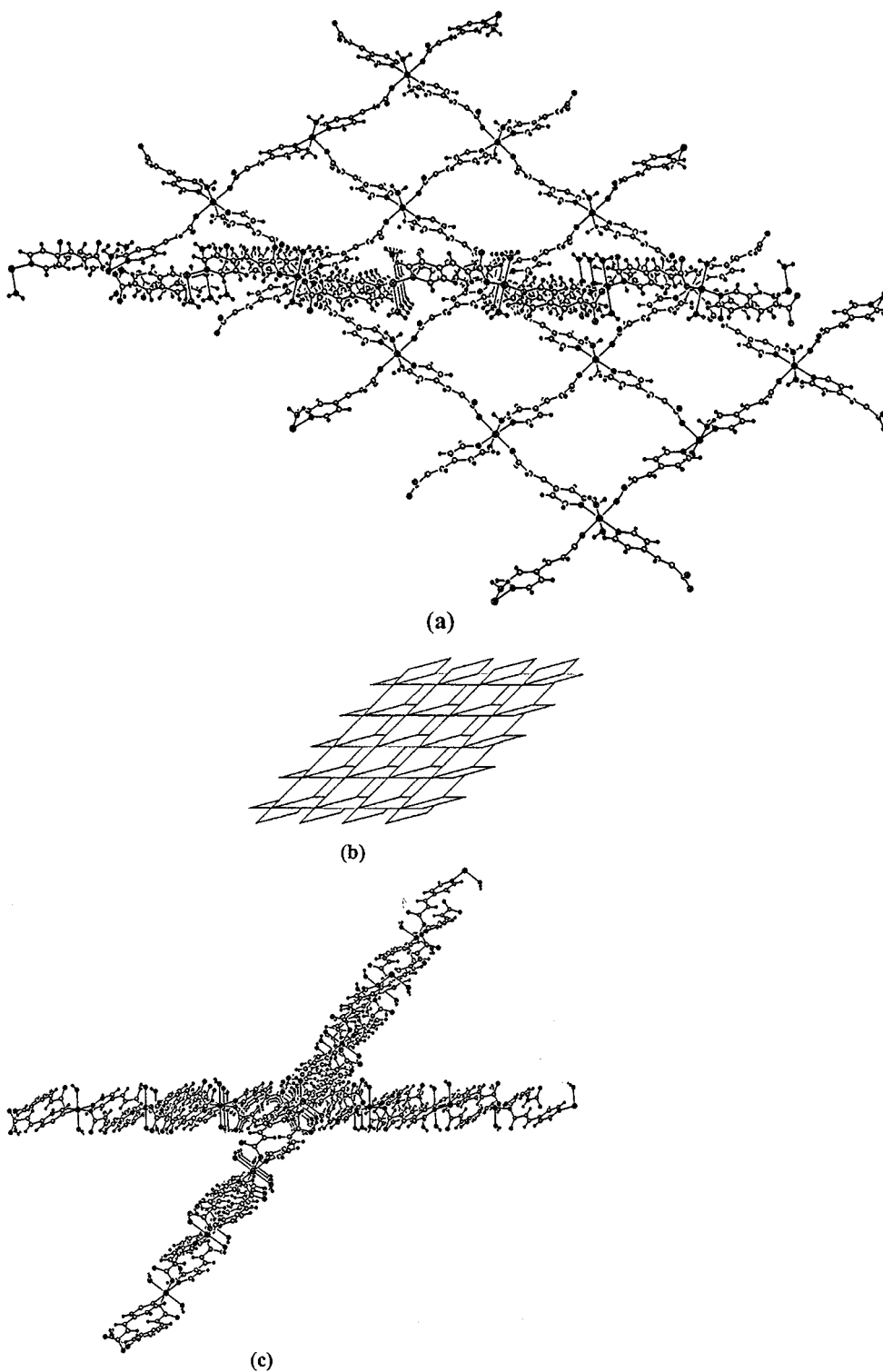
(a)

(b)

(c)

FIG. 2. (a) View of the porous Ni(tdpa) sheets of **1**: two sheets interpenetrating once along a line of intersection of the two planes. (b) Pictorial representation of the two stacks of inclined interpenetrating sheets. (c) Side view of the two inclined interpenetrating sheets.

are linked through tpda ligands to become a three-dimensional diamondoid network. Reports in the literature have shown that the construction of functional coordination polymers based on diamondoid structures is of particular interest owing to the general robustness of three-dimensionally interconnected diamondoid networks (16). Although these diamondoid nets interpenetrate (Fig. 4) due to the large porosity (average cobalt-to-cobalt distance about
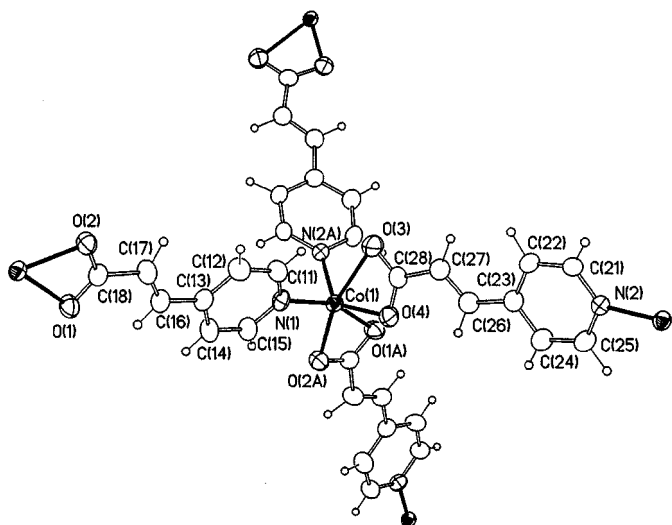
FIG. 3. ORTEP drawing of **2** with 40% ellipsoids.

11.1 Å), a void analysis result from the PLATON (17) program (analysis of the accessible volume not occupied by the framework atoms (Cu, N, C, O)) indicated that a void volume of 69.9 Å^3 (ca. 4.4% of a unit cell volume) could

allow guest molecules inclusion (18). Due to electron neutrality of the host framework itself, small molecules with sizes comparable to those of water molecules still possessed the possibility to act as potential guest molecules in occupying these free spaces.

Compound $Cu(C_8H_6NO_2)_2(H_2O)_2$ (**3**) is structurally isomeric to compound $Ni(C_8H_6NO_2)_2(H_2O)_2$ (**1**). It possesses the same overlay interpenetrating square grid network topology. However, due to the Jahn–Teller effect of the copper center, the difference in bond lengths between the metal and the axial coordinated water molecule (2.103(2) Å and 2.588(3) Å for **1** and **3**, respectively) could be observed.

Magnetic Properties

Magnetic studies of compound **3** showed that the magnetic susceptibility data in the temperature range 2–300 K can be fitted to a Curie–Weiss law with $\theta = +0.286$ K, and $C = 0.412$ emu K/mol (Fig. 5). The Curie constant agrees well with the reasonable value of $g = 2.10$ for copper(II) one-spin electron configuration, which corresponds to an effective magnetic moment (μ_{eff}) per copper ion of 1.82 BM. The very weak ferromagnetic interaction with
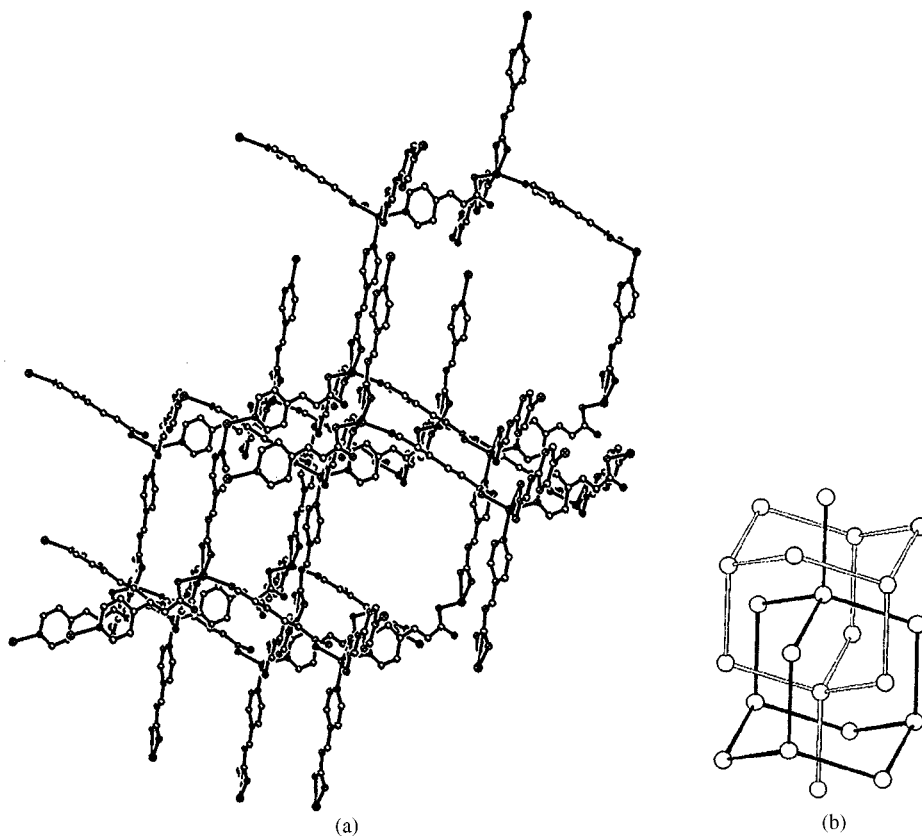

(a)

(b)

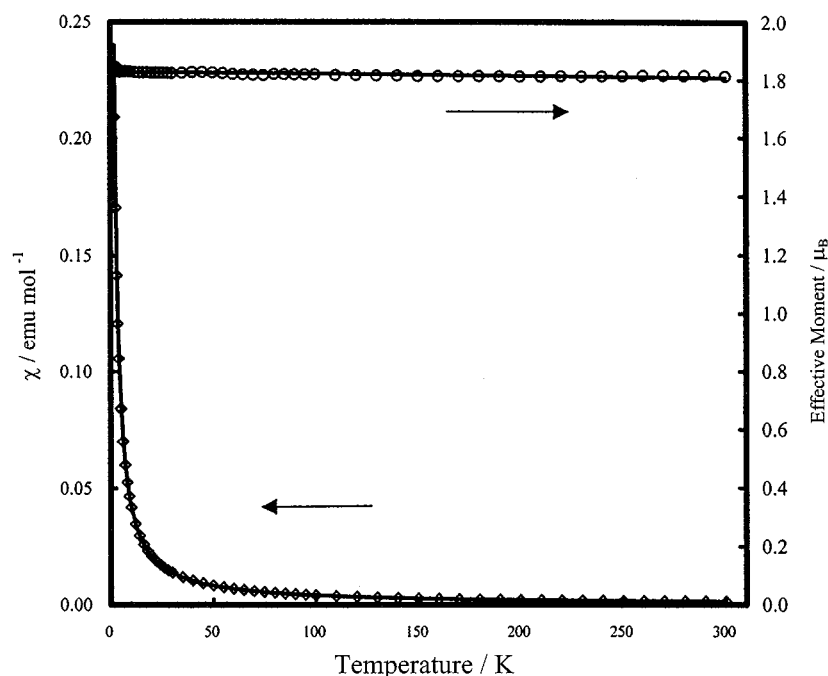**FIG. 4.** (a) Diamondoid interpenetrating nets of **2**. (b) Pictorial representation.

FIG. 5. Experimental μ_{eff} and χ versus temperature plots for compound **3** at a field of 1000 G.

$\theta = +0.286$ K indicates that there is no strong metal–metal interaction behavior within frameworks.

To summarize this work, we were able to demonstrate a feasible method taking advantage of the coordination nature of various metals to result in the change of the network building block arrangement. Therefore, gaining porosity potentially for guest molecule inclusion within interpenetrating networks could be achieved. Further study in altering and optimizing the metal-to-ligand coordination nature from monodentate, bidentate chelating and bridging to more rigid cluster-type coordination in order to construct large-pore networks with firm packing to avoid interpenetration is currently in progress.

ACKNOWLEDGMENTS

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