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Honeycomb Nets with Interpenetrating Frameworks Involving Iminodiacetato–Copper(II) Blocks and Bipyridine Spacers: Syntheses, Characterization, and Magnetic Studies

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Three coordination polymers of copper(II), viz. $\{[\mathrm{Cu(ida)(4,4'\text{-}bipyH)}]\mathrm{ClO_4}\}_\infty$ (**1**), $\{[\mathrm{Cu_2(ida)_2}(\mu\text{-}4,4'\text{-}\mathrm{bipy})]\cdot 2\mathrm{H_2O}\}_\infty$ (**2**), and $[\mathrm{Cu_2(ida)_2(bpa)}]_\infty$ (**3**) have been synthesized by the process of self-assembly using Cu(ida) [ida = iminodiacetate(2-)] as the building block and 4,4′-bipyridyl and 1,2-bis(4-pyridyl)ethane (bpa) as linkers. Crystals of **1** are orthorhombic, of space group $Pna2_1$, with $a = 13.8956(12)$ Å, $b = 16.3362(16)$ Å, $c = 7.3340(12)$, and $Z = 4$. Both compounds **2** and **3** crystallize in monoclinic space group $P2_1/a$ with $a = 10.1887(8)$ Å (9.6779(10) Å for **3**), $b = 8.0008(11)$ Å (9.1718(10) Å), $c = 11.6684(9)$ Å (12.9144(12) Å), $\beta = 98.307(11)°$ (102.796(18)°), and $Z = 2$ (2). Compound **1** has a zigzag chain structure with an extensive hydrogen-bonded network while compounds **2** and **3** are honeycomb (6,3) nets with interpenetrating structures. Variable temperature (2–300 K) magnetic study indicates the presence of weak antiferromagnetic interactions ($J = 0.82 \pm 0.01$ cm^{-1}) in **1** and ferromagnetic in **2** ($J = -0.45 \pm 0.05$ cm^{-1}) and **3** ($J = -0.21 \pm 0.02$ cm^{-1}). The extent of planarity of the bridging “Cu–O–C–O–Cu” moiety, acting as the super-exchange pathway between the neighboring copper centers, probably controls the sign of the magnetic exchange coupling in these compounds.

Introduction

The principle of self-assembly[1] has been extensively utilized to generate numerous metal-organic ligand networks with fascinating structural topologies.[2] Generally, the complexation processes involve more than one metal ions and multidentate ligands with heterodonor atoms, capable of providing steric and interactive interactions inscribed in them.[3,4] For the construction of a specific supramolecular architecture with one-, two-, and three-dimensional extended networks, design of the ligands and selection of metal ions are extremely crucial.[5] This problem was addressed by many researchers over the years to develop many aesthetically pleasing molecular networks such as molecular grids,[6] bricks,[7] herringbones,[8] ladders,[9] rings,[10] boxes,[11] diamondoids,[12] honeycombs,[13] helicates,[14] and other uncommon frameworks.[15] The synthetic strategies which have been used

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to ensemble the arrays include use of covalent bonding,[5b] hydrogen bonding,[16] and other weak intermolecular attractions.[17] The structures of coordination polymers constructed from rigid linear ligand arms generally have predictable networks. Ligands with more flexibility often give rise to less predictable structures, sometimes with interpenetrations,[18] and have interesting material properties.[19,20] Over the years, this information has prompted the syntheses of transition-metal coordination polymers with interpenetrating structures.[18,21]

Polycarboxylate ligands have been extensively employed in recent time in the preparation of carboxylato bridged coordination polymers with multidimensional networks.[22] Herein, we report copper(II) complexes with extended structural networks, involving iminodiacetate(2−) (ida) ligand in the presence of 4,4′-bipyridyl and 1,2-bis(4-pyridyl)ethane (bpa) as spacers. One of these compounds has self-assembled as a 1D chain (**1**) while the remaining two (**2** and **3**) have 2D structures with honeycomb-type extended architectures. The compounds have been characterized by X-ray diffraction analyses, variable temperature magnetic measurements, and X-band EPR analyses.

Experimental Section

Materials. 4,4′-Bipyridyl and 1,2-bis(4-pyridyl)ethane were purchased from Aldrich. All other reagents and solvents were commercially available and used as received. Sodium salt of iminodiacetate was prepared as follows.

An aqueous solution of iminodiacetic acid was treated with an aqueous solution of sodium hydroxide in 1:2 molar proportions. The resultant solution was heated on a water bath to near to dryness. It was then cooled to room temperature and diluted with absolute alcohol to obtain a white powder, which was collected by filtration, redissolved in a minimum amount of hot water, and finally diluted again with absolute ethanol to obtain the ultimate purified product.

Preparation of Complexes. **$\{[Cu(ida)(4,4'\text{-}bipyH)]ClO_4\}_\infty$ (1).** About 0.09 g (0.5 mmol) of sodium iminodiacetate (Na_2ida) was taken in 20 mL of water. To this stirred solution was added dropwise a solution of copper(II) perchlorate hexahydrate (0.18 g, 0.5 mmol), dissolved in 25 mL of methanol, when a blue solution was obtained. It was stirred for 1 h and then combined with a methanolic solution (10 mL) of 4,4′-bipyridyl (0.08 g, 0.5 mmol), during which a navy blue solution was obtained. It was stirred for another 30 min when a flocculent sky-blue compound was precipitated out, which was removed by filtration. The filtrate was kept in the air and filtered time and again to remove any unwanted amorphous precipitate. After ca. 4−5 weeks time, a blue crystalline compound began to appear, which was collected by filtration, washed with acetone, and dried in vacuo. A few X-ray diffraction quality crystals were picked up from this product. Yield: 0.06 g (25%). Anal. Calcd for $C_{14}H_{14}ClCuN_3O_8$: C, 37.22; H, 3.10; N, 9.30. Found: C, 37.10; H, 3.22; N, 9.45%. IR (KBr disk, cm^{-1}): ν(N−H), 3552, 3472, 3415; ν_{asym}(COO), 1607; ν_{sym}(COO), 1377; ν_{asym}(Cl−O), 1086; δ(O−Cl−O), 629. μ_{eff}/monomeric unit, 1.86 μ_B.

$\{[Cu_2(ida)_2(\mu\text{-}4,4'\text{-}bipy)]\cdot 2H_2O\}_\infty$ (2). To an aqueous solution of sodium iminodiacetate (0.09 g, 0.5 mmol) was added dropwise a solution of copper(II) acetate dihydrate (0.10 g, 0.5 mmol) in 30

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mL of hot methanol. The resultant solution was stirred for 30 min during which a blue solution was obtained. This was treated with 4,4′-bipyridyl (0.04 g, 0.25 mmol), dissolved in 10 mL of methanol, when a deep blue solution was obtained. It was stirred for ca. 10 min when a sky-blue compound was precipitated out. It was removed by filtration. The filtrate was diluted with 15 mL of water. The resultant solution was left in the air for slow evaporation. After ca. 4−5 weeks, a blue crystalline compound was obtained along with X-ray diffraction quality crystals. It was filtered, washed with acetone, and dried in vacuo. Yield: 0.05 g (30%). Anal. Calcd for $C_{18}H_{22}Cu_2N_4O_{10}$: C, 37.15; H, 3.78; N, 9.63. Found: C, 37.34; H, 3.71; N, 9.48%. IR (KBr disk, cm^{-1}): ν(O−H), 3443; ν_{asym}(COO), 1634, 1603; ν_{sym}(COO), 1376. μ_{eff}/monomeric unit, 1.84 μ_B.

$[Cu_2(ida)_2(bpa)]_\infty$ (3). Sodium iminodiacetate (0.09 g, 0.5 mmol) in 20 mL of water was combined with a methanolic solution (20 mL) of copper(II) perchlorate hexahydrate (0.18 g, 0.5 mmol) to obtain a blue solution, which was stirred for 1 h and then treated with a methanolic solution (10 mL) of 1,2-bis(4-pyridyl)ethane (bpa) (0.05 g, 0.25 mmol). The mixture was filtered after 30 min. The filtrate was kept in the air for ca. 2 weeks to obtain a blue crystalline compound along with X-ray diffraction quality crystals. The product was collected by filtration, washed with acetone, and dried in vacuo. Yield: 0.04 g (28%). Anal. Calcd for $C_{20}H_{22}Cu_2N_4O_8$: C, 41.84; H, 3.83; N, 9.76. Found: C, 42.37; H, 3.94; N, 9.76%. IR (KBr disk, cm^{-1}): ν_{asym}(COO), 1643, 1608; ν_{sym}(COO), 1383. μ_{eff}/monomeric unit, 1.86 μ_B.

Physical Measurements. The IR spectra and elemental analyses were done using the same instrumentation facilities as described elsewhere.[23] Magnetic susceptibility and magnetization measurements on powdered samples were performed on a Cryogenics S600 SQUID magnetometer. The data were corrected for the diamagnetic contributions using Pascals' constants. X-band EPR spectra were recorded at temperatures between 4 and 298 K on a Varian E-9 spectrometer equipped with an Oxford instruments ESR helium flux cryostat.

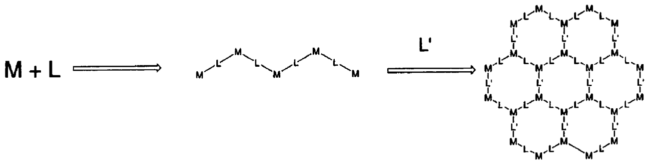
X-ray Crystallography. Crystals of dimensions 0.14 × 0.16 × 0.43 mm (**1**), 0.35 × 0.19 × 0.43 mm (**2**), and 0.07 × 0.29 × 0.31 mm (**3**) were mounted on glass fibers without protection. Cell dimensions were determined at 23 °C from the setting angles of an Enraf-Nonius CAD-4 diffractometer for 25 centered reflections in the ranges of θ, 13.3−14.8° (**1**), 13.3−14.9° (**2**), and 14.0−15.0° (**3**). Crystallographic parameters and residuals are given in Table 1. Programs in the TEXSAN suite[24] were used for data reduction for all crystals, and for structure solution (SIR92)[25] and refinement for **2** and **3**. The structure solution and refinement for **1** was performed by means of SHELX97.[26] In all cases, absorption corrections based on azimuthal ("ψ") scans were applied. The hydrogen atoms in **1** and **2** were located and refined isotropically. For compound **3**, hydrogen atoms were included at positions recalculated after each cycle of refinement [$B(H) = 1.2B_{eq}(C)$; $d(C-H) = 0.95$ Å]. In the case of **1**, difference map indicated disorder of the perchlorate anion, and two sets of oxygen atoms about a common chlorine atom were refined with weights 0.60 and 0.40. Inspection of coordinates and packing diagram for **1** confirmed the absence of a crystallographic mirror plane normal to *c*, and the correct polarity was confirmed by refinement of a Flack parameter to 0.02(5).

Table 1. Crystal Data, Data Collections, and Refinement Parameters for the Complexes **1**, **2**, and **3**

	1	**2**	**3**
formula	$C_{14}H_{14}ClCuN_3O_8$	$C_{18}H_{22}Cu_2N_4O_{10}$	$C_{20}H_{22}Cu_2N_4O_8$
fw	451.27	581.5	573.5
T (K)	296	296	296
cryst size (mm)	0.14 × 0.16 × 0.43	0.035 × 0.19 × 0.43	0.07 × 0.29 × 0.31
cryst syst	orthorhombic	monoclinic	monoclinic
space group	$Pna2_1$	$P2_1/a$	$P2_1/a$
a (Å)	13.8956(12)	10.1887(8)	9.6779(10)
b (Å)	16.3362(16)	8.0008(11)	9.1718(10)
c (Å)	7.3340(12)	11.6684(9)	12.9144(12)
α (deg)	90	90	90
β (deg)	90	98.307(11)	102.796(18)
γ (deg)	90	90	90
V (Å^3)	1664.8(3)	941.2(2)	1117.9(2)
Z	4	2	2
ρ_{calcd} (g cm^{-3})	1.800	2.052	1.704
$F(000)$	916	592	584
radiation used	Mo Kα	Mo Kα	Mo Kα
μ (mm^{-1})	15.2	23.3	19.6
$2\theta_{max}$ (deg)	50	55	60
no. of independent reflns: total	1589	2451	3445
observed [$I \geq \sigma(I)$]	1320 [$I \geq 2\sigma(I)$]	1848	2621
no. of params	280	181	154
R(F),[a] wR(F^2)[b]	0.058, 0.157	0.028, 0.067	0.043, 0.114
S[c]	1.10	1.49	2.28

[a] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR(F^2) = [\sum w(|F_o|^2 - |F_c|^2)^2/\sum w|F_o|^4]^{1/2}$. [c] $S = [\sum w(|F_o| - |F_c|)^2/(N - V)]^{1/2}$.

Scheme 1. Synthetic Strategy for the Construction of Honeycomb Complexes **2** and **3**



Results and Discussion

Synthesis. Dicarboxylic acid attached to a rigid frame and polypyridine-type molecules used as a cross-linker are popular among the inorganic chemists to use them as potential bridging ligands to synthesize coordination polymers. Many of these complexes have novel structural topologies.[27] Our strategy to generate interesting molecular networks using Cu(II)−iminodiacetate as the building block is displayed in Scheme 1. Reaction of Cu(II) with iminodiacetate ligand (L) in an aqueous methanolic medium generates a zigzag molecular chain, propagated by a bridging carboxylate group of the ligand that binds the two adjacent copper centers in syn−anti mode[28] as revealed from X-ray

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crystallography (see latter). In the second stage, two such chains are connected by the ancillary linker (L′ = 4,4′-bipy and bpa) to generate extended 2D structures with puckered honeycomb network **2** and **3**. With 4,4′-bipy the cross-linking reaction fails in the presence of $Cu(ClO_4)_2 \cdot 6H_2O$ and the product obtained (**1**) has a 1D zigzag chain structure involving a 4,4′-bipy molecule with one of its N atoms remaining protonated (eq 1). Traces of free acid present in the copper(II) perchlorate precursor is believed to be the source of proton in this case. At higher pH (using copper(II) acetate dihydrate as the metal ion precursor), cross-linking proceeds, leading to the generation of extended honeycomb structure (eq 2). With bpa as the linker, however, the only product is **3** irrespective of the associated anion of the metal ion precursor (eq 3).

$$Cu(ClO_4)_2 + Na_2ida + 4,4'\text{-bipy} + H^+ \rightarrow \{[Cu(ida)(4,4'\text{-bipyH})]ClO_4\} + NaClO_4 + Na^+ \quad (1)$$

$$2Cu(OAc)_2 + 2Na_2ida + 4,4'\text{-bipy} + 2H_2O \rightarrow \{[Cu_2(ida)_2(4,4'\text{-bipy})]\cdot 2H_2O\} + 4NaOAc \quad (2)$$

$$2Cu(X)_2 + 2Na_2ida + bpa \rightarrow [Cu_2(ida)_2(bpa)] + 4NaX \quad (X = ClO_4, OAc) \quad (3)$$

All the complexes reported here are formed by the process of self-assembly, through a slow crystallization step. Sometime it takes about a month to isolate the desired product. Moreover, reported complexes are sparingly soluble in common organic solvents. We have tried to crystallize the products from an optimum dilution so that we could strike a balance between the improved crystal quality and the time of crystallization.

IR spectra of the complexes **1**−**3** display all the characteristic bands of the coordinated iminiodiacetate ligand. These include a pair of strong bands at ca. 1635 and 1380 cm^{-1} corresponding to ν_{asym}(COO) and ν_{sym}(COO) vibrations, respectively, of an unidentate carboxylate group with characteristically large $\Delta\nu$ values (ca. 250 cm^{-1}).[29] For the syn−anti bridged carboxylate group, ν_{asym}(COO) band shows up at ca. 1610 cm^{-1}. The corresponding band due to ν_{sym} stretch is not traceable. In the high-frequency region, a sharp band is observed in the 3195−3160 cm^{-1} range due to ν(N−H) vibration of the ligand. Prominent bands in **1** also include three sharp bands at 3550, 3473, and 3415 cm^{-1}, corresponding to the NH proton of the 4,4′-bipyH$^+$ moiety, which remains hydrogen-bonded to carboxylate oxygen from a nearby chain, thus generating a supramolecular assembly as revealed from X-ray crystallography (see latter). Also, a couple of strong bands at 1086 and 629 cm^{-1} indicates the presence of ionic perchlorate in **1**.

Description of Crystal Structures. The X-ray crystal structure of the fundamental building unit of **1** is shown in Figure 1 and the relevant metrical parameters in Table 2. The imino nitrogen N1 and two carboxylate oxygen atoms O1 and O3 from iminodiacetate take up the basal positions around Cu(II) along with the nonprotonated N2 atom of the 4,4′-bipyH$^+$ ligand. A carboxylate oxygen O2^i of an adjacent molecule (not shown in Figure 1) occupies the apical position, leading to a square pyramidal geometry around the metal center. As a result, chains of Cu(ida) units occur along each crystallographic 2_1 axis in space group $Pna2_1$. One such chain is shown in Figure 2. Unlike the Cu−N distances, the Cu−O distances here are disperate. The axial Cu−O2^i distance (2.313(9) Å) is much longer than the basal distances (Cu−O1, 1.946(10) Å; Cu−O3, 1.947(9) Å), as expected for a Jahn−Teller ion. The trans angles O1−Cu−O3 and N1−Cu−N2 are 165.0(3)° and 170.5(5)°, respectively, and the Cu atom is displaced by 0.128(4) Å from the least-squares basal plane toward the apical oxygen atom O2^i and makes no short contacts on the open side. Cross-linking into a sheet structure (Figure 3) results from protonated nitrogen atoms N2 of the ancillary 4,4′-bipy ligands, extending on both sides of each chain acting as proton donors to iminodiacetate O atoms of adjacent chains. Details of hydrogen-bonding

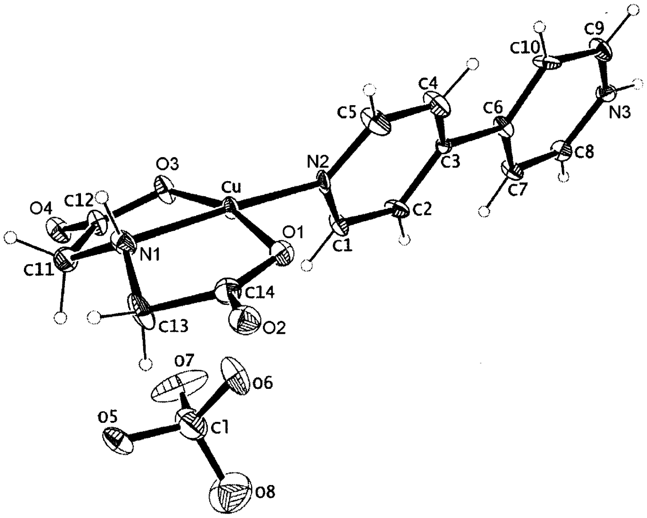

Figure 1. Molecular structure and atom numbering scheme for the mononuclear unit of complex $\{[Cu(ida)(4,4'\text{-bipyH})]ClO_4\}_\infty$ (**1**).

Table 2. Interatomic Distances (Å) and Angles (deg) for Complexes **1**, **2**, and **3**[a]

	1	2	3
Bond Lengths			
Cu−O1	1.946(10)	1.950(2)	1.954(2)
Cu−O2^i	2.313(9)	2.343(2)	2.236(2)
Cu−O3	1.947(9)	1.959(2)	1.969(2)
Cu−N1	1.977(9)	1.999(2)	1.999(2)
Cu−N2	1.980(7)	2.000(2)	1.983(2)
Bond Angles			
O1−Cu−O2^i	90.0(3)	107.47(7)	98.2(1)
O1−Cu−O3	165.0(3)	156.81(7)	158.11(9)
O1−Cu−N1	83.1(5)	84.25(7)	84.45(9)
O1−Cu−N2	104.1(5)	94.03(7)	93.40(1)
O2^i−Cu−O3	99.4(4)	93.38(7)	101.96(9)
O2^i−Cu−N1	92.6(3)	94.02(8)	98.65(9)
O2^i−Cu−N2	93.6(3)	90.55(8)	90.80(1)
O3−Cu−N1	84.8(5)	84.27(7)	84.18(8)
O3−Cu−N2	87.1(5)	95.85(7)	94.70(9)
N1−Cu−N2	170.5(5)	175.41(8)	170.50(1)

[a] The symmetry transformations i for **1**: $2 - x$, $1 - y$, $-0.5 + z$. The symmetry transformations i for **2** and **3**: $0.5 + x$, $1.5 - y$, z.

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(29) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd ed.; Wiley-Interscience: New York, 1978.

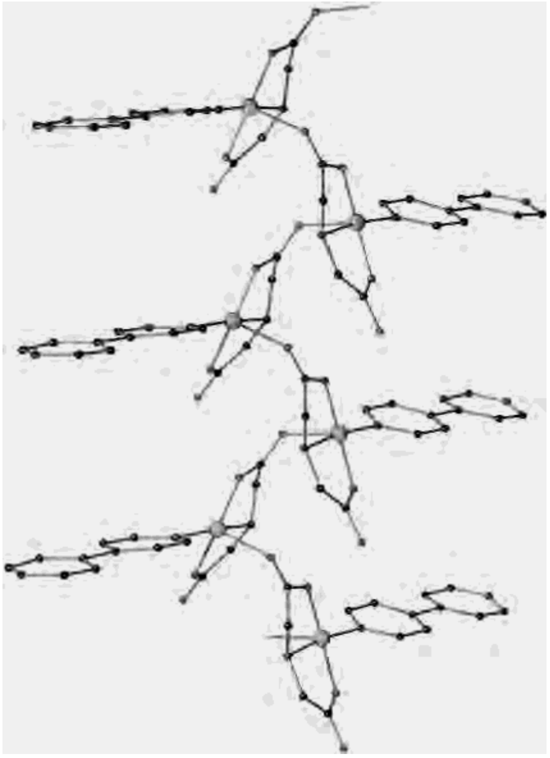

Figure 2. View of an infinite 1D coordination chain of $\{[Cu(ida)(4,4'\text{-}bipyH)]ClO_4\}_\infty$ (**1**) propagated along the crystallographic 2_1 axis.

parameters are summarized in Table 3. Voids in the network contain disordered ClO_4 anions.

Compounds **2** and **3** both crystallize in space group $P2_1/a$ with closely related structures. Their relevant interatomic parameters are summarized in Table 2. As in **1**, each copper atom is bonded to the N1 atom and two carboxylate oxygen atoms (O1 and O3) of an ida ligand along with an N atom of a bridging bipyridine ligand (4,4′-bipy for **2** and bpa for **3**), which lies across a crystallographic center of symmetry (Figures 4 and 5). In addition, the copper atom forms a somewhat longer bond (2.343(2) Å for **2** and 2.236(2) Å for **3**) to the $O2^i$ atom of another Cu(ida) unit generated by the *a* glide operation. As a consequence, the coordination geometry is square pyramidal around copper atom. The trans angles O1−Cu−O3 and N1−Cu−N2 are 156.81(7)° (158.11(9)° for **3**) and 175.41(8)° (170.50(1)°), respectively, and the Cu atom is displaced by 0.235(1) Å (0.257(1) Å) from the least-squares basal plane toward the apical oxygen atom. Infinite zigzag chains, thus generated by the bridging syn−anti carboxylate moiety, extended in the *a* direction. The ligand 4,4′-bipy (bpa in **3**) cross-links the Cu atoms of the chains to give pleated sheets containing (6,3) rings of a honeycomb network[13,18] as displayed in Figures 6 and 7. The individual hexagonal ring of this network is made up of six Cu(ida) units connected together by two cross-linker ligands leading to a puckered ring structure involving six copper centers each acting as a node. The sheets repeat at intervals of three unit cells in the *b* direction. Each pleated sheet is interwoven with two others, offset by the $+b$ and $-b$ translations but sharing the same mean plane (parallel to *ab*), which makes only weak contacts with the first sheet, and with the adjacent interwoven sets along the *c* direction. Three-dimensional interlocked structures obtained by parallel interpenetration of (6,3) nets of **2** and **3** are shown in Figures 8 and 9, respectively. Few such interwoven nets have been reported recently in the literature.[4a,18,30]

Crystal structures of related copper(II)−ida complexes involving 2,4′- and 2,2′-bipy as ancillary ligands have already been reported in the literature.[31,32] These molecules show interesting diversity in their molecular structures with the type of incorporated bipy ligands. Thus, with 2,4′-bipy, the product $\{[Cu(ida)(2,4'\text{-}bipy)]\cdot H_2O\}_\infty$ has an extended polymeric structure.[31] The Cu atom displays a distorted square pyramidal geometry with attached ida^{2-} ligand in a mer-tridentate chelating mode and uses a syn−anti bridging carboxylate group to provide polymeric chains as observed in **1**−**3**. 2,4′-bipy ligand binds the metal center by its N4 donor. Nearly planar pyridyl rings of this molecule play an interesting role to generate a bilayered 2D framework through interligand $\pi-\pi^*$ stacking. Closely similar stacking of *N*-heterocyclic ligands is observed in **1** (Figure 3). With 2,2′-bipy, however, the product isolated $[Cu(ida)(2,2'\text{-}bipy)]\cdot 6H_2O$ is a mononuclear compound[32] involving a square pyramidal copper(II) center with ida^{2-} ligand acting as terdentate, exhibiting a fac- chelation unlike in **1**−**3**. The Cu−N and Cu−O bond distances in these molecules are in the ranges comparable to the corresponding distances in **1**−**3**.

Magnetism and EPR. The EPR spectra recorded on polycrystalline samples of compounds **1**−**3** are displayed in Figures S1 (Supporting Information) and 10, which show no temperature dependence in the temperature range studied (6−298 K). The spectra were simulated using a standard simulation program[33] by assuming simple $S = {}^1/_2$ paramagnetic behavior, including (slight) *g* value anisotropy. This fitting procedure yielded $g_{//} = 2.31$, $g_\perp = 2.05$, $\langle g \rangle = 2.14$, and a line width of 25 G for **1**; $g_{//} = 2.29$, $g_\perp = 2.12$, $\langle g \rangle = 2.17$, and a line width of 95 G for **2**; and $g_{//} = 2.25$, $g_\perp = 2.10$, $\langle g \rangle = 2.15$, and a line width of 300 G for **3**. The errors in the *g* values are estimated to be ±0.01 for **1** and **2** and ±0.05 for **3**. The fact that the order $g_{//} > g_\perp > 2.03$ indicates a $d_{x^2-y^2}$ (or less likely a d_{xy}) based ground state for these molecules.[34]

The $\chi_M T$ product versus T curve for **1** (Figure 11) shows that the $\chi_M T$ value is 0.43 emu K/mol expected for a noncoupled Cu(II) ion $[(N_A g^2 \mu_B{}^2/3k)S(S + 1)]$ taking the $\langle g \rangle = 2.14$ from the EPR spectra (see above). A $1/\chi_M$ vs T (Curie) plot shows a straight line down to very low temperatures. Fitting this curve to the Curie−Weiss law $[1/\chi_M = (T - \theta)/C]$ gives a Curie constant $C = 0.432 \pm 0.001$ emu K/mol and a Weiss temperature θ of -0.72 ± 0.07 K, the latter of which is indicative of (weak) antiferromagnetic

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[31] Tribet, M.; Covelo, B.; Choquesillo-Lazarte, D.; Gonjález-Pérez, J. M.; Castiñeiras, A.; Niclós-Gutiérrez, J. *Inorg. Chem. Commun.* **2003**, *6*, 343.

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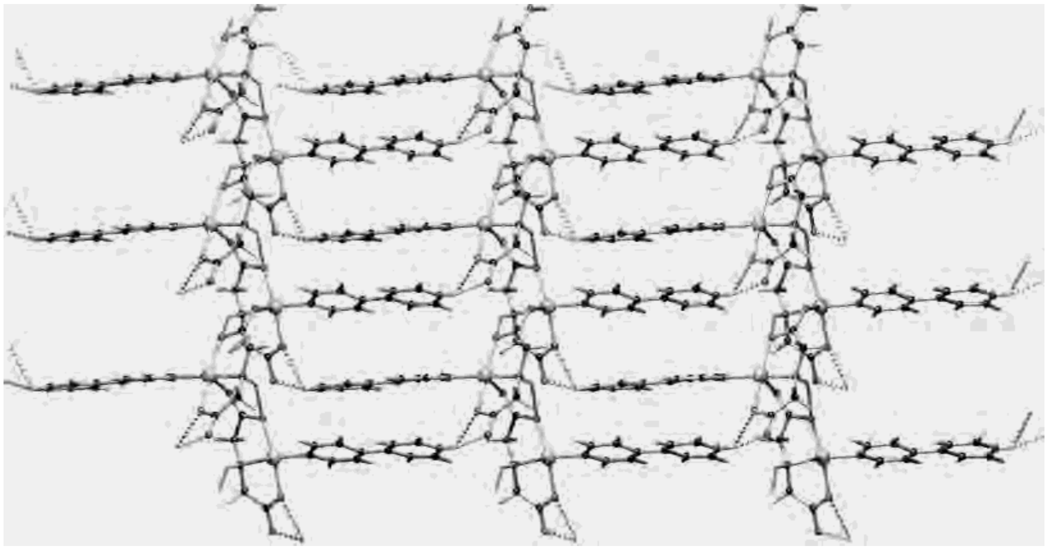

Figure 3. View of an infinite 2D supramolecule, generated by the cross-linking of $\{[Cu(ida)(4,4'\text{-bipyH})]ClO_4\}_\infty$ (**1**) chains into a sheet structure through extensive hydrogen bonding.

Table 3. Hydrogen Bonding Interactions for Complex **1**[a]

	D	H	A	D....A	D−H	H....A	∠D−H....A
1	N1	H1A	O1 #1	3.092(13)	0.91	2.3300	141.00
	N3	H3A	O3 #2	2.841(15)	0.86	2.5000	105.00
	N3	H3A	O4 #2	2.606(12)	0.86	1.7700	163.00

[a] Symmetry transformations used to generate equivalent atoms. (#1) $-x, -y, -{}^1/_2 + z$; (#2) $1 - x, -y, -{}^1/_2 + z$.

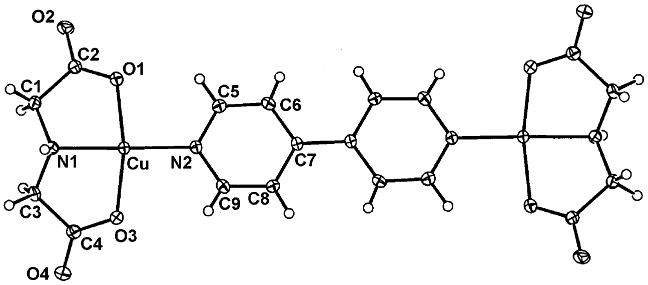

Figure 4. Molecular structure and atom numbering scheme for the centrosymmetric binuclear fundamental unit of $\{[Cu_2(ida)_2(\mu\text{-}4,4'\text{-bipy})]\cdot 2H_2O\}_\infty$ (**2**).

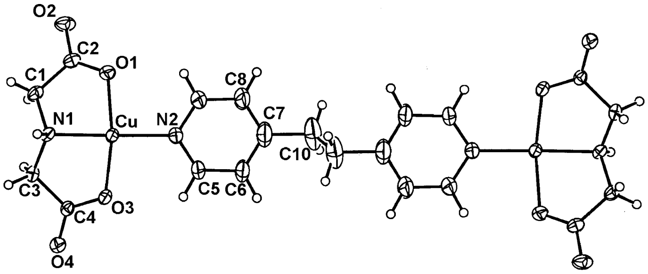

Figure 5. Molecular structure and atom numbering scheme for the centrosymmetric binuclear fundamental unit of $[Cu_2(ida)_2(bpa)]_\infty$ (**3**).

interactions, in agreement with the decrease in $\chi_M T$ going to low temperatures. The data were also fitted to the numerical expression[35] obtained from the Bonner−Fisher uniform antiferromagnetic Heisenberg chain model.[36] Using the effective spin Hamiltonian $\mathbf{H} = J\mathbf{S}_i\mathbf{S}_{i+1}$, this takes the form (eq 4)

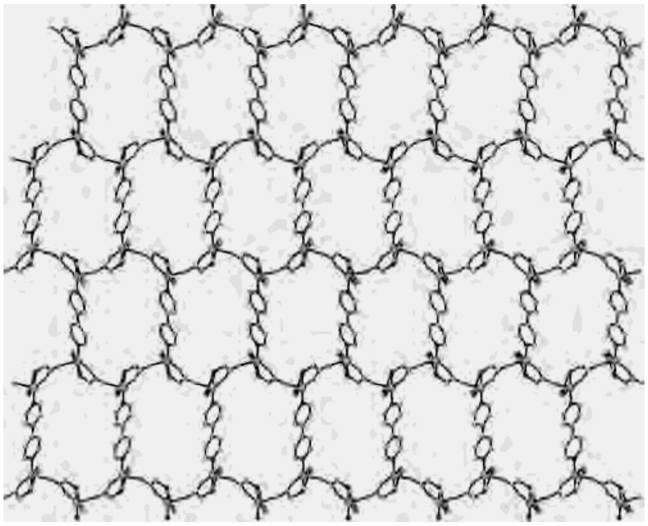

Figure 6. Pleated honeycomb architecture involving a (6,3) net formed by the cross-connection of the $\{[Cu_2(ida)_2(\mu\text{-}4,4'\text{-bipy})]\cdot 2H_2O\}_\infty$ (**2**) strands through a 4,4′-bipy bridge.

$$\chi_M T = \frac{Ng^2\mu_B^{\,2}}{k_B}\,\frac{0.25 + 0.074975x + 0.075235x^2}{1.0 + 0.9931x + 0.172135x^2 + 0.757825x^3} \tag{4}$$

where $x = |J|/k_BT$. From the fitting an exchange interaction parameter $J = 0.82 \pm 0.01$ cm^{-1} was obtained.

In the case of **2**, the $\chi_M T$ value at high temperatures is 0.42 emu K/mol (Figure 12), which is also close to the value expected for a noninteracting Cu(II) ion with $\langle g\rangle = 2.17$. On decreasing the temperature, the $\chi_M T$ value increases, which indicates predominant ferromagnetic exchange interactions. The parameters, obtained from a Curie plot, are $C = 0.413 \pm 0.001$ emu K/mol and an almost negligible Weiss temperature of 0.16 ± 0.13 K. The positive sign of the Weiss temperature indicates ferromagnetic interactions within the chain. To obtain the exchange interaction constant, the data

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(35) Estes, W. E.; Gavel, D. P.; Hatfield, W. E.; Hodgson, D. J. *Inorg. Chem.* **1978**, *17*, 1415.

(36) Bonner, J. C.; Fisher, M. E. *Phys. Rev. A* **1964**, *135*, 640.

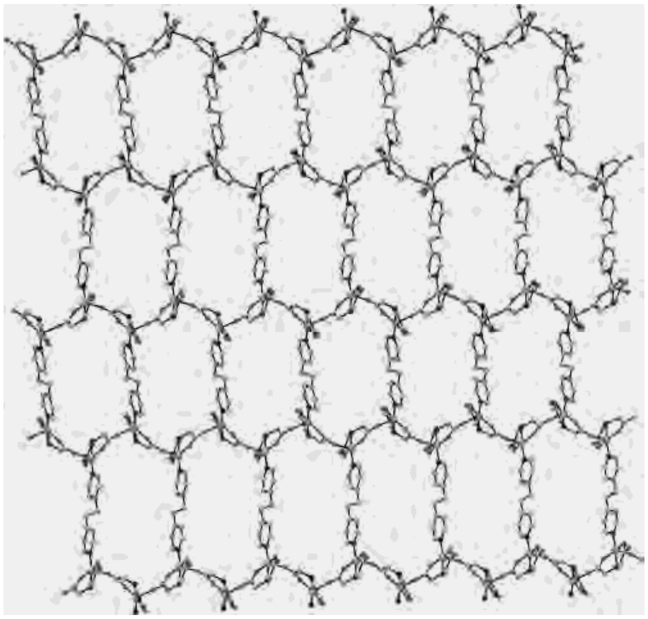

Figure 7. Pleated honeycomb architecture involving a (6,3) net formed by the cross-connection of the $[Cu_2(ida)_2(bpa)]_\infty$ (**3**) strands through a bpa bridge.

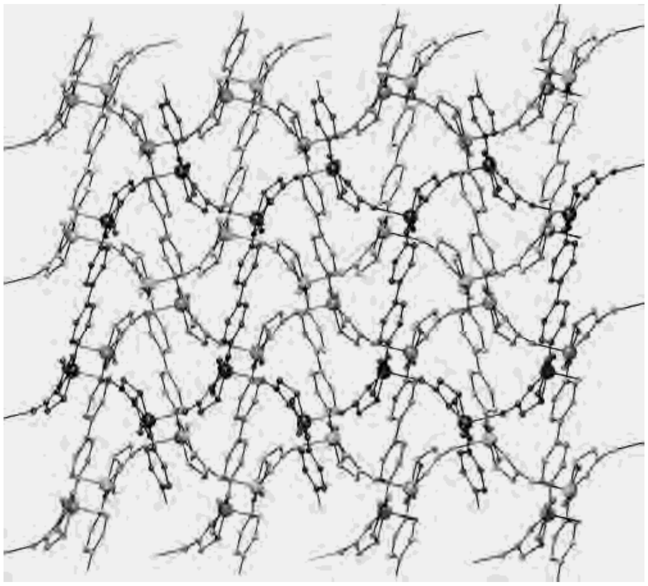

Figure 8. Perspective view of the crystal packing showing the three interpenetrated sheets of **2** down the *c*-axis.

were fitted to the numerical equation obtained by Baker et al.[37] for ferromagnetic $S = {}^1/_2$ Heisenberg chains:

$$\chi_M T = \frac{Ng^2\mu_B^{\,2}}{4k_B}([1.0 + 5.7979916x + 16.902653x^2 + 29.376885x^3 + 29.832959x^4 + 14.036918x^5]/[1.0 + 2.7979916x + 7.0086780x^2 + 8.653644x^3 + 4.5743114x^4]) \qquad \text{where } x = J/2k_BT \quad (5)$$

The fitting procedure resulted in a ferromagnetic exchange interaction constant $J = -0.45 \pm 0.05$ cm^{-1}.

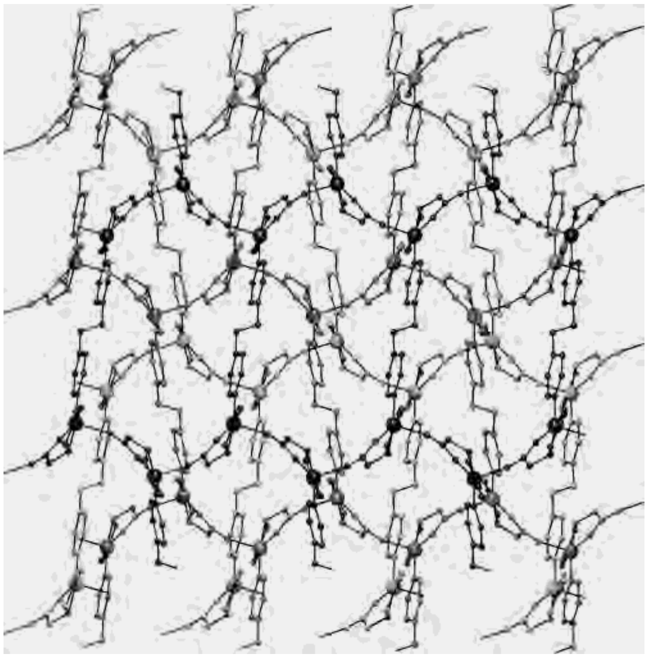

Figure 9. Perspective view of the crystal packing showing the three interpenetrated sheets of **3** down the *c*-axis.

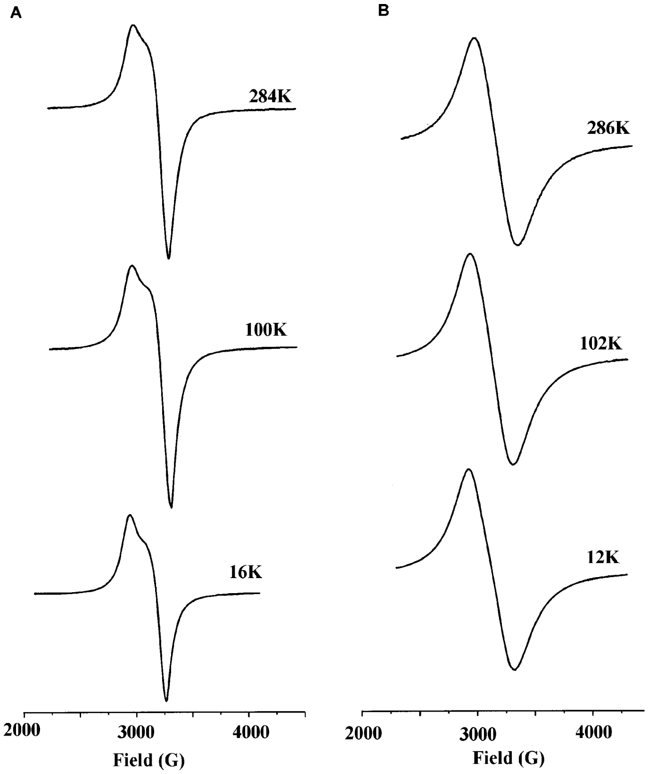

Figure 10. Variable temperature X-band EPR spectra of (A) compound **2** and (B) compound **3** in the solid state.

Compound **3** is very similar to **2** in behavior. Thus, the Curie plot (Figure S2, inset) gave $C = 0.428 \pm 0.001$ emu K/mol and $\theta = -0.01 \pm 0.01$ K. The sign of this latter value suggests a predominant antiferromagnetic exchange interaction, but since the error from the fit is larger than the value, no definite conclusions can be drawn. Fitting $\chi_M T$ vs T (Figure S2) to expression 5 yields a ferromagnetic exchange interaction constant $J = -0.21 \pm 0.02$ cm^{-1}.

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(37) Baker, G. A., Jr.; Rushbrooke, G. S.; Gilbert, H. E. *Phys. Rev. A* **1964**, *135*, 1272.

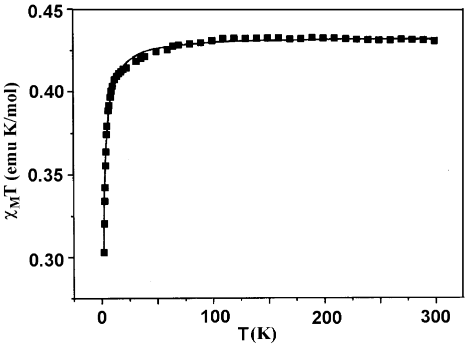

Figure 11. Thermal dependence of $\chi_M T$ for complex **1**. The solid line represents the best fit of the experimental data (see text).

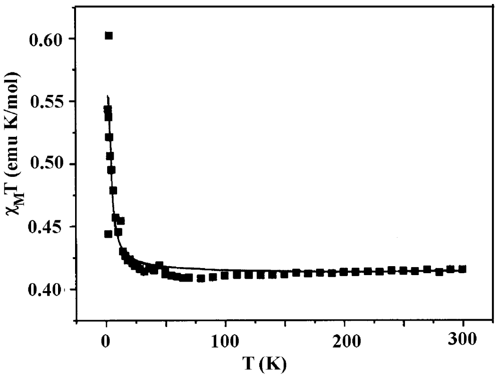

Figure 12. Thermal dependence of $\chi_M T$ for complex **2**. The solid line represents the best fit of the experimental data (see text).

In carboxylate bridged Cu(II) complexes, the exchange coupling between the participating metal centers is largely determined by the coordination mode of the bridging ligand.[38−45] In complexes where the metal ions are bridged in a syn−syn manner, the exchange coupling is large and antiferromagnetic ($J \approx 300$ cm^{-1})[38] while for the anti−anti bridge, the coupling is always weak antiferromagnetic.[39] There are only a few fully characterized carboxylato bridged copper(II) complexes with syn−anti bridging conformations.[40−45] They display either antiferromagnetic[40−42] or ferromagnetic behavior[43−45] with weak exchange coupling ($J \leq 5.0$ cm^{-1}).

The compounds reported in this paper (**1**−**3**) show diverse magnetic behavior; while **1** is antiferromagnetic ($J = 0.82 \pm 0.01$ cm^{-1}), the remaining two compounds **2** and **3** are ferromagnetic in nature ($J = -0.45 \pm 0.05$ for **2** and -0.21 ± 0.02 for **3**). As previously noted, in all these complexes the square pyramidal Cu(II) centers are sequentially bridged by carboxylate groups of syn−anti conformation, via an equatorial position of one to the apical position of the other. The magnetic orbitals here are predominantly of the $d_{x^2-y^2}$ type with a minor contribution from the d_{z^2} orbital in the axial direction. In compound **1** where adjacent copper centers are only connected by a syn−anti carboxylate bridge, the planarity of the super exchange pathway “Cu−O−C−O−Cu” allow enough overlap of the magnetic orbitals to display weak antiferromagnetic interactions. In compounds **2** and **3**, formation of honeycomb networks needs participation of the bipyridine ligands that fix the copper atoms in a rigid molecular frame. This probably disturbs the planarity of the “Cu−O−C−O−Cu” moiety (due to pleated structure) as the copper atoms are pushed out of the plane comprising the super exchange pathway. Net result is a decrease in antiferromagnetic contribution to such an extent that the ferromagnetic term becomes prominent[44a] in the latter two compounds.

Concluding Remarks

Coordination polymers **1**−**3** have been synthesized by the process of self-assembly using Cu(ida) as the building block and bipyridine ligands as linkers. Compound **1** has a 1D zigzag chain structure while **2** and **3** have 2D puckered honeycomb (6,3) net structures. Interpenetration of these nets generates 3D structures for the latter two compounds. Adjacent copper centers in all these compounds are linked by carboxylate groups of syn−anti conformation. Variable temperature magnetic study (2−300 K) indicates weak antiferromagnetic interaction ($J = 0.82 \pm 0.01$ cm^{-1}) in **1** while ferromagnetic contribution becomes dominant in **2** ($J = -0.45 \pm 0.05$ cm^{-1}) and **3** ($J = -0.21 \pm 0.02$ cm^{-1}), respectively. The extent of planarity of the “Cu−O−C−O−Cu” bridging moiety, acting as the super exchange pathway between the adjacent copper(II) centers, probably controls the sign of the magnetic exchange coupling in these compounds.

Acknowledgment. Financial support received from the Council of Scientific and Industrial Research (CSIR), New Delhi, is gratefully acknowledged. P.B.C. and D.M. also thank CSIR for the award of Junior Research Fellowships. We thank Dr. Rakesh Ganguly for helpful discussions.

Supporting Information Available: Figures S1 and S2. X-ray crystallographic files in CIF format for compounds **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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