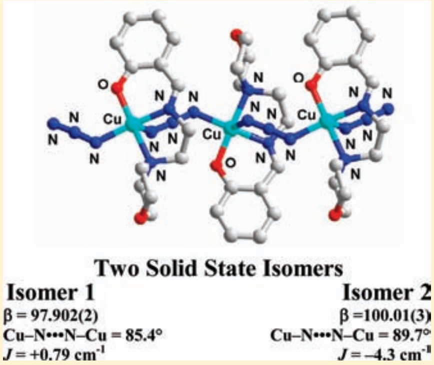
Inorganic Chemistry
ARTICLE
pubs.acs.org/IC

Syntheses, Structures, and Magnetic Properties of Three One-Dimensional End-to-End Azide/Cyanate-Bridged Copper(II) Compounds Exhibiting Ferromagnetic Interaction: New Type of Solid State Isomerism

Sujit Sasmal,[†] Sohini Sarkar,[†] Núria Aliaga-Alcalde,*[,‡] and Sasankasekhar Mohanta*[,†]

[†]Department of Chemistry, University of Calcutta, 92 A. P. C. Road, Kolkata 700 009, India
[‡]ICREA-Departament de Química Inorgànica, Universitat de Barcelona, Diagonal 647, 08028 Barcelona, Spain

Supporting Information



ABSTRACT: The work in this paper presents the syntheses, structures, and magnetic properties of three end-to-end (EE) azide/cyanate-bridged copper(II) compounds $[Cu^{II}L^1(\mu_{1,3}\text{-NCO})]_n\cdot 2nH_2O$ (**1**), $[Cu^{II}L^1(\mu_{1,3}\text{-N}_3)]_n\cdot 2nH_2O$ (**2**), and $[Cu^{II}L^2(\mu_{1,3}\text{-N}_3)]_n$ (**3**), where the ligands used to achieve these species, HL^1 and HL^2, are the tridentate Schiff base ligands obtained from [1 + 1] condensations of salicylaldehyde with 4-(2-aminoethyl)-morpholine and 3-methoxy salicylaldehyde with 1-(2-aminoethyl)-piperidine, respectively. Compounds **1** and **2** crystallize in the monoclinic $P2_1/c$ space group, while compound **3** crystallizes in the orthorhombic *Pbca* space group. The metal center in **1**−**3** is in all cases pentacoordinated. Three coordination positions of the metal center in **1**, **2**, or **3** are satisfied by the phenoxo oxygen atom, imine nitrogen atom, and morpholine (for **1** and **2**) or piperidine (for **3**) nitrogen atom of one deprotonated ligand, $[L^1]^-$ or $[L^2]^-$. The remaining two coordination positions are satisfied by two nitrogen atoms of two end-to-end bridging azide ligands for **2** and **3** and one nitrogen atom and one oxygen atom of two end-to-end bridging cyanate ligands for **1**. The coordination geometry of the metal ion is distorted square pyramidal in which one EE azide/cyanate occupies the apical position. Variable-temperature (2−300 K) magnetic susceptibilities of **1**−**3** have been measured under magnetic fields of 0.05 (from 2 to 30 K) and 1.0 T (from 30 to 300 K). The simulation reveals a ferromagnetic interaction in all three compounds with J values of $+0.19 \pm 0.01$, $+0.79 \pm 0.01$, and $+1.25 \pm 0.007$ cm^{-1} for **1**, **2**, and **3**, respectively. Compound **1** is the sole example of a ferromagnetically coupled EE cyanate-bridged 1-D copper(II) system. In addition, a rare example of supramolecular isomerism and a nice example of magnetic isomerism have been observed and most interestingly a new type of solid state isomerism has emerged as a result of the comparison of the structure and magnetic properties of **2** with a previously published compound (**2A**) having the same composition and even the same crystal system and space group (*New J. Chem.* **2001**, *25*, 1203−1207).

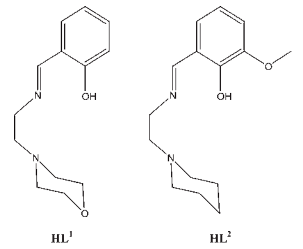
INTRODUCTION

Supramolecular chemistry/crystal engineering[1−5] and molecular magnetism[3,5−24] of coordination compounds are two research areas of current age vast fascination. Design of suitable building blocks and utilization of coordinate bonds and noncovalent interactions to generate self-assemblies of various dimensions having aesthetic beauty and properties for possible use as functional materials are the major objectives in supramolecular chemistry/crystal engineering. On the other hand, important aspects in molecular magnetism are the determination of magneto−structural correlations[3,6,7] and utilization of the correlations to design magnetic materials.[3,5,6a,8−10] In this context, 1-D exchange-coupled compounds are important for the establishment of structure−property correlations[3,6g] and also as magnetic materials;[9] although 1-D compounds should not be associated with real 3-D magnetic order, some 1-D systems are known to exhibit slow magnetic relaxation and also a hysteresis loop and thus behave as single-chain magnets (SCMs).[9]

In both of the above-mentioned research areas, pseudohalide (e.g., azide, cyanate)[3,5,6a,6d,6f−6h,9,10,12−24] bridged systems have occupied dominating positions. Metallo−azide species, in particular, have been always of great interest due to its versatile bridging modes (e.g., $\mu_{1,1}$,[3,6a,6f,6h,9,10a,10b,12−16] $\mu_{1,3}$-,[3,6a,6g,10c−10e,13,17−20d] $\mu_{1,1,1}$,[14] $\mu_{1,1,3}$,[15] $\mu_{1,1,1,1}$,[21a] and $\mu_{1,1,3,3}$[21b]) as well as due to its ability to mediate ferro- or antiferromagnetic interactions among metal centers. Having various bridging modes, several dinuclear, oligonuclear cluster, and polymeric (1-D, 2-D, and 3-D) metallo−azide compounds have been reported, and magnetic studies of many such systems have been carried out resulting in the emergence of a few interesting magneto−structural

Received: March 7, 2011
Published: May 27, 2011

Scheme 1. Chemical Structures of HL^1 and HL^2



correlations[3,6a,6f−6h,7] and a few magnetic materials.[9,10] In contrast to azide, another pseudo-halide, cyanate, appears to be less versatile; so far, only two common bridging modes, $\mu_{1,1}$[6d,11b,22] and $\mu_{1,3}$,[23,24] and two rarely bridging modes, $\mu_{1,1,3}$[25a] and $\mu_{1,1,1,1}$,[25b] have been observed for the cyanato anion. Although much less in comparison to the azide systems, a number of cyanate-bridged dinuclear, oligonuclear cluster, and 1-D metal complexes have been reported, and their structure-dependent magnetic properties have been investigated.

In spite of extensive research previously carried out, it is difficult to judge the nature of a metallo−pseudo-halide product to be obtained from a reaction mixture; for a particular pseudo-halide, the composition, topology, and nuclearity of the product depend on the metal ion and its simple salt, organic ligand, solvent, stoichiometric ratio of the reactants, etc., and therefore, new topologies may be attained by modifying these parameters. The tridentate Schiff base ligands, HL^1 and HL^2 (Scheme 1), have been previously used to derive some copper(II) and nickel(II) azide compounds.[17,19a,26,27] Derived from HL^2, only one metal−azide compound, which is a 1-D copper(II)−azide system, has been reported.[27] Interestingly, by changing the reaction conditions or starting metal salt of the same 1:1:1 mixture of HL^1, metal ion, and azide, one mononuclear and two different 1-D copper(II)-azide compounds have been obtained.[19a,26,27] On the other hand, a unique single end-to-end ($\mu_{1,3}$) azide-bridged cyclic tetranickel(II) cluster[17] has been obtained from a 1:1:4 mixture of HL^1, metal ion (Ni^{II}), and azide. With the aim of getting interesting topologies that can exhibit appealing magnetic properties as well, we utilized HL^1/HL^2 to derive copper(II)−pseudo-halide compounds from the corresponding 1:1:4 reaction mixture of the ligand, metal ion, and pseudo-halide and isolated three one-dimensional end-to-end pseudo-halide-bridged compounds of composition $[Cu^{II}L^1(\mu_{1,3}\text{-NCO})]_n\cdot 2nH_2O$ (**1**), $[Cu^{II}L^1(\mu_{1,3}\text{-N}_3)]_n\cdot 2nH_2O$ (**2**), and $[Cu^{II}L^2(\mu_{1,3}\text{-N}_3)]_n$ (**3**). Herein, we report the syntheses, characterization, crystal structures, and magnetic properties of **1**−**3** along with supramolecular isomerism and the emergence of a new type of solid state isomerism.

EXPERIMENTAL SECTION

Materials and Physical Measurements. All reagents and solvents were purchased from commercial sources and used as received. Elemental (C, H, and N) analyses were performed on a Perkin-Elmer 2400 II analyzer. IR spectra were recorded in the region 400−4000 cm^{-1} on a Bruker-Optics Alpha-T spectrophotometer with samples as KBr disks. Magnetic measurements were carried out in the "Unitat de Mesures Magnètiques (Universitat de Barcelona)" on polycrystalline samples with a Quantum Design SQUID MPMS-XL magnetometer working in the 2−300 K range under magnetic fields of 0.05 T (from 2 to 30 K) and 1.0 T (from 30 to 300 K). The diamagnetic corrections were evaluated from Pascal's constants. The fit was performed minimizing the function R (agreement factor, defined as $\Sigma_i[(\chi_M T)_{obs(i)} - (\chi_M T)_{calcd(i)}]^2 / \Sigma_i[(\chi_M T)_{obs(i)}]^2$).

Syntheses. *$[Cu^{II}L^1(\mu_{1,3}\text{-NCO})]_n\cdot 2nH_2O$ (**1**).* A solution of 4-(2-aminoethyl)-morpholine (0.130 g, 1 mmol) and salicylaldehyde (0.122 g, 1 mmol) in 30 mL of MeOH was refluxed for 2 h. Then the volume of the resulting red-colored solution was reduced to 10 mL and added dropwise to a methanol solution (5 mL) of $Cu(ClO_4)_2\cdot 6H_2O$ (0.371 g, 1 mmol) under continuous stirring. The color of the solution changed from red to green. To the green solution, an aqueous solution (5 mL) of NaNCO (0.260 g, 4 mmol) was added dropwise under stirring. After a few minutes a blue precipitate started to deposit. Stirring was continued for 2 h, and then the blue precipitate was collected by filtration and washed with cold methanol. Recrystallization from methanol produced a blue crystalline compound containing diffraction-quality single crystals. Yield: 0.319 g (85%). Anal. Calcd for $C_{14}H_{21}N_3O_5Cu$: C, 44.85; H, 5.65; N, 11.21. Found: C, 44.70; H, 5.68; N, 11.28. Selected FT-IR data on KBr (cm^{-1}): $\nu(H_2O)$, 3362 m; ν(OCN), 2197 vs; ν(C=N), 1641 vs.

*$[Cu^{II}L^1(\mu_{1,3}\text{-N}_3)]_n\cdot 2nH_2O$ (**2**).* This compound was prepared following a similar procedure to that used for the synthesis of **1**, except that NaN_3 was added instead of NaNCO. Color: blue. Yield: 0.300 g (80%). Anal. Calcd for $C_{13}H_{21}N_5O_4Cu$: C, 41.65; H, 5.65; N, 18.68. Found: C, 41.70; H, 5.68; N, 18.58. Selected FT-IR data on KBr (cm^{-1}): $\nu(H_2O)$, 3378 m; ν(azide), 2051 vs; ν(C=N), 1641 s.

*$[Cu^{II}L^2(\mu_{1,3}\text{-N}_3)]_n$ (**3**).* This compound was prepared following a similar procedure to that used for the synthesis of **1**, except that 1-(2-aminoethyl)-piperidine, 3-methoxy salicylaldehyde, and NaN_3 were used instead of 4-(2-aminoethyl)-morpholine, salicylaldehyde, and NaNCO, respectively. Color: blue. Yield: 0.311 g (85%). Anal. Calcd for $C_{15}H_{21}N_5O_2Cu$: C, 49.1; H, 5.77; N, 19.09. Found: C, 49.20; H, 5.70; N, 19.15. Selected FT-IR data on KBr (cm^{-1}): ν(azide), 2045 vs; ν(C=N), 1635 s.

Crystal Structure Determination of 1−3. The crystallographic data for **1**−**3** are summarized in Table 1. Diffraction data were collected on a Bruker-APEX II SMART CCD diffractometer at 296 K using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). For data processing and absorption correction the packages SAINT[28a] and SADABS[28b] were used. The structures were solved by direct and Fourier methods and refined by full-matrix least-squares based on F^2 using the SHELXTL[28c] and SHELXL-97 packages.[28d] Four water hydrogen atoms of **1** and **2** were not located from difference Fourier maps, and therefore, all these hydrogen atoms were not considered in the refinement process. All other hydrogen atoms in **1** and **2** were inserted at calculated positions with isotropic thermal parameters and refined. All hydrogen atoms of **3** were located from difference Fourier maps. Using anisotropic treatment for the non-hydrogen atoms and isotropic treatment for the hydrogen atoms, the final refinements converged to R_1 values ($I > 2\sigma(I)$) of 0.0420, 0.0467, and 0.0292 for **1**, **2**, and **3** respectively.

RESULTS AND DISCUSSION

Description of Structures of 1−3. Crystal structures of $[Cu^{II}L^1(\mu_{1,3}\text{-NCO})]_n\cdot 2nH_2O$ (**1**), $[Cu^{II}L^1(\mu_{1,3}\text{-N}_3)]_n\cdot 2nH_2O$ (**2**), and $[Cu^{II}L^2(\mu_{1,3}\text{-N}_3)]_n$ (**3**) are shown in Figures 1, 2, and 3, respectively, while selected bond lengths and angles of the three compounds are listed in Table 2. The crystal structures of the three compounds reveal that these are one-dimensional copper(II) compounds containing one crystallographically distinct copper(II) center, which is pentacoordinated. The three coordination positions of the metal center in **1**, **2**, or **3** are satisfied by the phenoxo oxygen atom, imine nitrogen atom, and morpholine

Table 1. Crystallographic Data for 1−3

	1	2	3
empirical formula	$C_{14}H_{17}N_3O_5Cu$	$C_{13}H_{17}N_5O_4Cu$	$C_{15}H_{21}N_5O_2Cu$
fw	370.85	370.86	366.91
cryst color	blue	blue	blue
cryst syst	monoclinic	monoclinic	orthorhombic
space group	$P2_1/c$	$P2_1/c$	$Pbca$
a [Å]	9.3725(15)	9.4934(15)	13.0218(6)
b [Å]	9.1324(15)	9.2962(14)	9.6216(5)
c [Å]	19.663(3)	18.377(3)	25.4583(12)
V [Å^3]	1656.0(5)	1606.4(4)	3189.7(3)
α [deg]	90.00	90.00	90.00
β [deg]	100.290(5)	97.902(2)	90.00
γ [deg]	90.00	90.00	90.00
Z	4	4	8
temperature [K]	296(2)	296(2)	296(2)
2θ [°]	4.22−56.00	4.34−52.00	3.20−56.00
μ [mm^{-1}]	1.346	1.386	1.387
λ (Mo K$_\alpha$) [Å]	0.71073	0.71073	0.71073
ρ_{calcd} [g cm^{-3}]	1.487	1.533	1.528
$F(000)$	764	764	1528
abs corr	multiscan	multiscan	multiscan
index ranges	$-11 \le h \le 12$	$-11 \le h \le 11$	$-17 \le h \le 16$
	$-12 \le k \le 12$	$-11 \le k \le 11$	$-12 \le k \le 12$
	$-25 \le l \le 24$	$-19 \le l \le 22$	$-33 \le l \le 33$
no. of reflns collected	21 278	11 637	41 990
no. of independent reflns (R_{int})	3896(0.0275)	3125(0.0402)	3851(0.0425)
$R_1{}^a$/ w$R_2{}^b$ ($I > 2\sigma(I)$)	0.0420/0.1470	0.0467/0.1078	0.0292/0.0936
$R_1{}^a$/ w$R_2{}^b$ (for all data)	0.0519/0.1548	0.0623/0.1137	0.0423/0.1129

[a] $R_1 = [\Sigma||F_o| - |F_c||/\Sigma|F_o|]$. [b] $wR_2 = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma wF_o{}^4]^{1/2}$.

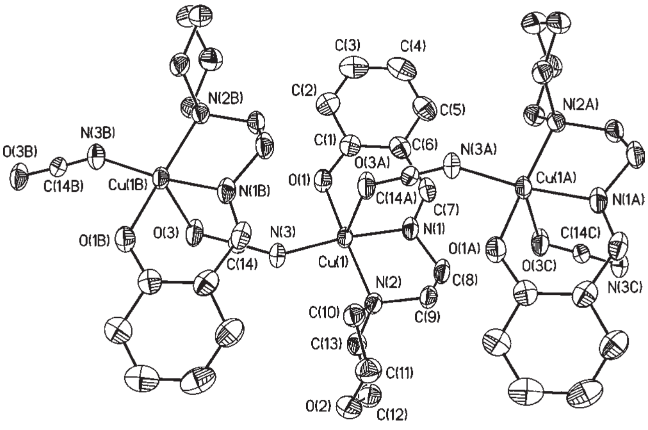


Figure 1. Crystal structure of $[Cu^{II}L^1(\mu_{1,3}\text{-}NCO)]_n \cdot 2nH_2O$ (**1**). Hydrogen atoms and water molecules are not shown for clarity. Symmetry codes: A, −*x*, −0.5 + *y*, 0.5 − *z*; B, −*x*, 0.5 + *y*, 0.5 − *z* ; C, *x*, −1 + *y*, *z*.

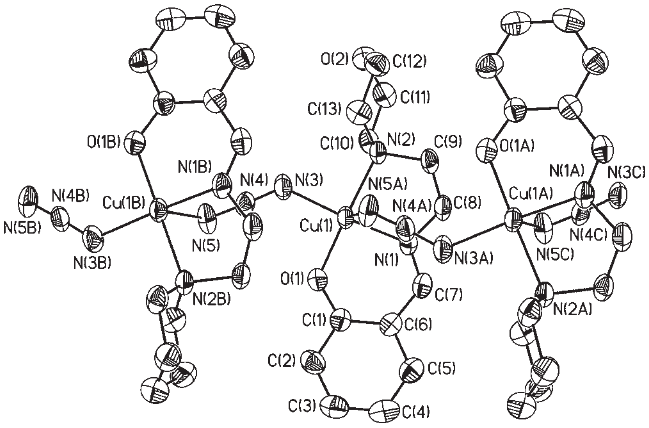


Figure 2. Crystal structure of $[Cu^{II}L^1(\mu_{1,3}\text{-}N_3)]_n \cdot 2nH_2O$ (**2**). Hydrogen atoms and water molecules are not shown for clarity. Symmetry codes: A, 1 − *x*, 0.5 + *y*, 0.5 − *z*; B, 1 − *x*, −0.5 + *y*, 0.5 − *z*; C, *x*, 1 + *y*, *z*.

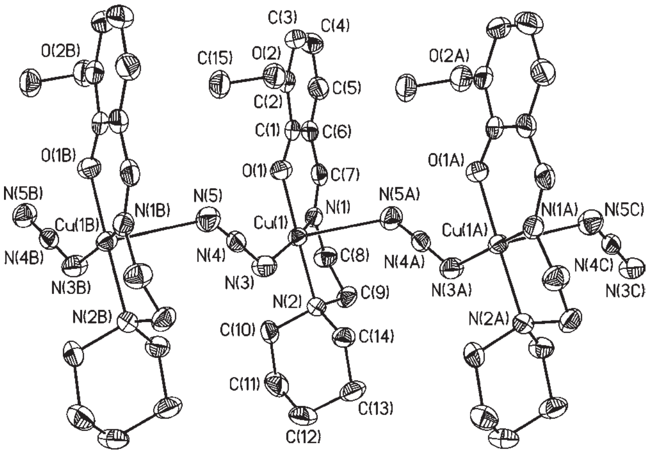


Figure 3. Crystal structure of $[Cu^{II}L^2(\mu_{1,3}\text{-}N_3)]_n$ (**3**). Hydrogen atoms are not shown for clarity. Symmetry codes: A, 0.5 − *x*, −0.5 + *y*, *z*; B, 0.5 − *x*, 0.5 + *y*, *z*; C, *x*, −1 + *y*, *z*.

(for **1** and **2**) or piperidine (for **3**) nitrogen atom of one deprotonated ligand, $[L^1]^-$ or $[L^2]^-$. The remaining two coordination positions are satisfied by two nitrogen atoms of two end-to-end bridging azide ligands for **2** and **3** and one nitrogen atom and one oxygen atom of two end-to-end bridging cyanate ligands for **1**. The other ends of these two azides (for **2** and **3**) or two cyanates (for **1**) coordinate to two different copper(II) ions to result in the formation of a one-dimensional chain. The chains in all three structures propagate along the crystallographic *b* axes.

The coordination geometry of the metal center in **1**−**3** is distorted square pyramidal. The basal plane is defined by two nitrogen atoms (N(1) and N(2)) and one oxygen atom (O(1)) of the Schiff base ligand and one nitrogen atom (N(3)) of the azide (for **2** and **3**) or cyanate (for **1**) ligand, while the apical position is occupied by one azide nitrogen atom (N(5A)) for **2** and **3** and by the cyanate oxygen atom (O(3A)) for **1**. The bond distances involving the atoms in the basal plane lie in almost identical ranges for the three compounds, 1.931(2)−2.093(2) Å for **1**, 1.916(3)−2.079(3) Å for **2**, and 1.9021(13)−2.0709(15) Å for **3**. In contrast, the apical bond distance is significantly longer, 2.468, 2.495, and 2.583 Å for **1**, **2**, and **3**, respectively. The two transoid angles in the basal plane are 170.75(10)° and

Table 2. Selected Bond Lengths (Angstroms) and Angles (degrees) of 1−3

1		2		3
Cu(1)−N(1)	1.9389(19)	Cu(1)−N(1)	1.942(3)	1.9413(18)
Cu(1)−N(2)	2.093(2)	Cu(1)−N(2)	2.079(3)	2.0709(15)
Cu(1)−N(3)	1.932(2)	Cu(1)−N(3)	1.960(3)	1.9701(16)
Cu(1)−O(1)	1.9312(19)	Cu(1)−O(1)	1.916(3)	1.9021(13)
Cu(1)−O(3A)	2.468	Cu(1)−N(5A)	2.495	2.583
N(1)−Cu(1)−N(3)	170.75(10)	N(1)−Cu(1)−N(3)	169.09(16)	165.07(7)
N(2)−Cu(1)−O(1)	174.92(7)	N(2)−Cu(1)−O(1)	172.82(13)	178.65(6)
N(1)−Cu(1)−N(2)	84.31(9)	N(5A)−Cu(1)−N(1)	86.41	85.36
N(1)−Cu(1)−O(1)	91.88(9)	N(5A)−Cu(1)−N(2)	88.86	90.26
N(1)−Cu(1)−O(3A)	89.3	N(5A)−Cu(1)−N(3)	103.00	108.90
N(2)−Cu(1)−N(3)	92.32(9)	N(5A)−Cu(1)−O(1)	97.45	88.96
N(2)−Cu(1)−O(3A)	92.9	N(1)−Cu(1)−N(2)	84.54(13)	84.83(6)
N(3)−Cu(1)−O(1)	90.94(10)	N(1)−Cu(1)−O(1)	92.42(13)	94.00(6)
N(3)−Cu(1)−O(3A)	99.5	N(2)−Cu(1)−N(3)	90.11(14)	90.55(7)
O(1)−Cu(1)−O(3A)	90.4	N(3)−Cu(1)−O(1)	91.78(14)	90.75(6)

174.92(7)° for **1**, 169.09(16)° and 172.82(13)° for **2**, and 165.07(7)° and 178.65(6)° for **3**, while the ranges of the cisoid angles in **1**, **2**, and **3** are 84.31(9)−99.5°, 84.54(13)−103.00°, and 84.83(6)−108.90°, respectively. From the corresponding least-squares basal plane, the average deviation of the constituted atoms is 0.04, 0.02, and 0.12 Å, while the metal center is displaced by 0.11, 0.14, and 0.12 Å for **1**, **2**, and **3**, respectively. The dihedral angle between the basal planes of two neighboring metal ions in the 1-D chain is 20.19°, 21.00°, and 50.68°, while the metal···metal separation is 5.71, 5.59, and 6.01 Å for **1**, **2**, and **3**, respectively.

The N(cyanate)−Cu−O(cyanate) or N(azide)−Cu−N(azide) angle in **1**, **2**, and **3** is 99.50°, 103.00°, and 108.90°, respectively, indicating a cis arrangement of the azide or cyanate ligand in the title compounds. The end-to-end azide or cyanate bridges the metal ions in a significantly bent way as evidenced by the Cu(1)−N(3)−N(4) (128.08° for **2** and 123.74° for **3**) and Cu(1)−N(5A)−N(4A) (122.53° for **2** and 128.78° for **3**) angles in **2** and **3** and the Cu(1)−N(3)−C(13) (149.77°) and Cu(1)−O(3A)−C(14A) (125.07°) angles in **1**, indicating that 1-D chains are zigzag (Figures 1−3). The Cu−N···N−Cu torsion angles in **2** and **3** are 85.4° and 56.1°, respectively, while the Cu−N···O−Cu torsion angle in **1** is −57.6°, indicating that the bridging moieties are significantly twisted.

There are a few intrachain/interchain C−H···N/C−H···O/O−H···O hydrogen bonds in the structures of **1**−**3**. The interchain hydrogen bonds and also the supramolecular topologies in both the cyanate-bridged compound **1** and the azide-bridged compound **2** are similar. Of the two solvated water molecules in **1** and **2**, one is hydrogen bonded with its symmetry-related counterpart to form a water dimer. This water dimer acts as a bridge to interlink two 1-D chains in the crystallographic *bc* plane due to formation of O−H···O hydrogen bonds between the two water molecules of the water dimer and phenoxo oxygen atoms. Another 2-D sheet in the crystallographic *ab* plane is formed due to one C−H···O hydrogen bond involving a hydrogen atom of the iminoethyl moiety and an oxygen atom of the morpholine ring. Thus, the overall supramolecular topology in both **1** and **2** is 3-D. The chain-to-chain distances in the *ab* plane (9.372 Å for **1** and 9.493 Å for **2**) and *bc* plane (10.203 Å for **1** and 10.132 Å for **2**) indicate that the chains are well isolated. The supramolecular topology of the second azide-bridged compound, **3**, is 2-D in the crystallographic *ab* plane, which is generated due to an interchain C−H···N hydrogen bond involving a hydrogen atom of the iminoethyl moiety and an azide nitrogen atom. The chain-to-chain distance of 6.534 Å indicates that the chains are also well isolated in **3**. A more detailed description along with figures (Figures S1 and S2, Supporting Information, for **2**, Figures S3 and S4, Supporting Information, for **1**, and Figure S5, Supporting Information, for **3**) and a table (Table S1, Supporting Information) of the supramolecular interactions/topologies are presented in the Supporting Information.

Syntheses and FT-IR Spectra. The three compounds **1**−**3** were readily prepared in high yield on reacting copper(II) perchlorate hexahydrate and sodium cyanate (for **1**)/sodium azide (for **2** and **3**) with the solution containing salicylaldehyde (for **1** and **2**)/3-methoxysalicylaldehyde (for **3**) and 4-(2-aminoethyl)-morpholine (for **1** and **2**)/1-(2-aminoethyl)-piperidine (for **3**). On condensing the corresponding aldehyde and amine in methanol, isolation in very high yields of both ligands HL^1 and HL^2 has been reported previously.[27] As the yields of HL^1 and HL^2 could be greater than 95%,[27] we did not attempt to isolate the ligands in their solid state forms but proceeded with the refluxed solutions of the corresponding aldehyde and amine for the syntheses of the metal complexes, which is a widely followed general approach. Eventually, we obtained the recrystallized products of **1**−**3** in 80% or more than 80% yields.

No base was added during the syntheses of **1**−**3**, indicating metal-assisted deprotonation of both HL^1 and HL^2 takes place to produce the title compounds. As already discussed, all three compounds are 1-D polymers containing a 1:1:1 stoichiometric ratio of Cu^{II}, [L^1]$^-$/[L^2]$^-$, and azide/cyanate. All three donor centers, phenolate oxygen atom and imine and morpholine/piperidine nitrogen atoms, of a Schiff base ligand are monodentate and coordinate to one metal center, while the azide or cyanate moiety acts as a bridging ligand.

The characteristic azide stretching in **2** and **3** is very strong and appears at 2051 and 2045 cm^{-1}, respectively, while the characteristic cyanate stretching in **1** appears as a very strong signal at 2197 cm^{-1}. The imine stretching is observed as a strong intensity band at 1641 cm^{-1} for **1** and **2** and at 1635 cm^{-1} for **3**.

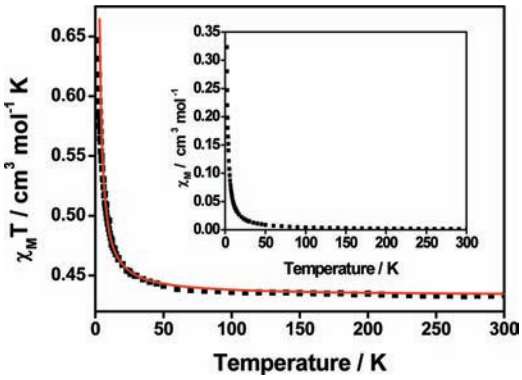


Figure 4. Fittings of the $\chi_M T$ vs T of $[\mathrm{Cu^{II}L^1}(\mu_{1,3}\text{-}\mathrm{N_3})]_n\cdot 2n\mathrm{H_2O}$ (**2**) between 2.0 and 300.0 K. The experimental data are shown as black squares, and the red line corresponds to the theoretical values. (Inset) χ_M vs T data.

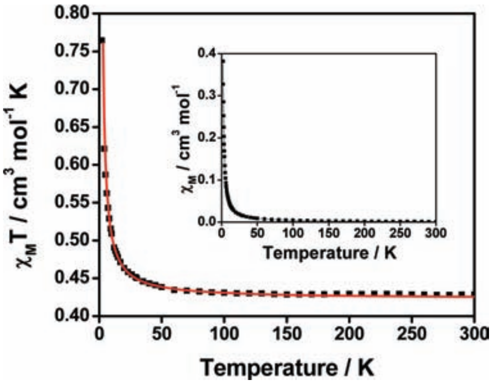


Figure 5. Fittings of the $\chi_M T$ vs T of $[\mathrm{Cu^{II}L^2}(\mu_{1,3}\text{-}\mathrm{N_3})]_n$ (**3**) between 2.0 and 300.0 K. The experimental data are shown as black squares, and the red line corresponds to the theoretical values. (Inset) χ_M vs T data.

The presence of water molecules is evident from the appearance of a medium-intensity band at 3362 and 3378 cm^{-1} for **1** and **2**, respectively.

Magnetic Properties of 1−3. Solid-state, variable-temperature (2−300 K) magnetic susceptibility data using 0.05 (from 2 to 30 K) and 1.0 T (from 30 to 300 K) fields were collected on polycrystalline samples of compounds **2** and **3**. The resulting data are plotted in Figures 4 and 5 as $\chi_M T$ vs T and χ_M vs T (inset), respectively. In both compounds, the molar magnetic susceptibility shows an overall intrachain ferromagnetic behavior, with $\chi_M T$ increasing with decreasing temperature. Compound **2** exhibits a $\chi_M T$ value at 300 K of 0.43 cm^3 mol^{-1} K, higher than that ($\chi_M T = 0.375$ cm^3 mol^{-1} K assuming $g = 2.0$) expected for a magnetically isolated $S = 1/2$ system; this value is maintained upon cooling until approximately 40 K (0.44 cm^3 mol^{-1} K) and rapidly increases to 0.64 cm^3 mol^{-1} K at 2 K (Figure 4). Similarly, compound **3** presents a value of 0.43 cm^3 mol^{-1} K at 300 K too that rises abruptly as previously, reaching a value of 0.76 cm^3 mol^{-1} K at 2 K.

The crystallographic data of these two species, **2** and **3**, depict 1-D systems formed by equally spaced Cu^{II} ions (5.594 Å for **2** and 6.014 Å for **3**, respectively); each chain is well separated from the others and displays a zigzag shape due to coordination in a cis manner of the two azido groups attached to each Cu^{II} center. Hence, correlation of the magnetic data was performed in both cases using an expression for this type of chains[6a,29] for which the final equation is derived from the Hamiltonian $H = -J\Sigma SA_i\cdot SA_{i+1}$.[6a,29] The best-fit parameters for **2** and **3** were found as $J = +0.79 \pm 0.01$ cm^{-1}, $g = 2.15 \pm 0.01$, and $R = 9 \times 10^{-4}$ and $J = +1.25 \pm 0.007$ cm^{-1}, $g = 2.12 \pm 0.01$, and $R = 2 \times 10^{-4}$ in that order. Their ferromagnetic behavior, indicated by the positive signs of the coupling exchanges, are also supported by the rapid saturation of the reduced magnetization of each complex when they are measured at 2 K and different fields (from 0 to 50000 G); the experimental data tend fast to 1.0 Nμ_B for both species, not following the Brillouin formula for $S = 1/2$, a clear indication of ferromagnetic interactions within a chain (Figure 6 for **2** and Figure S6 in the Supporting Information for **3**).[20b]

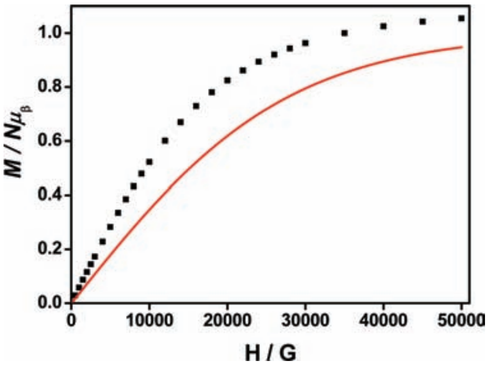


Figure 6. Plot of the reduced magnetization (M/Nμ_β) versus H/G at 2 K for $[\mathrm{Cu^{II}L^1}(\mu_{1,3}\text{-}\mathrm{N_3})]_n\cdot 2n\mathrm{H_2O}$ (**2**). Black squares represent the experimental values, and the solid red line is the simulation obtained using the Brillouin formula for $S = 1/2$ and $g = 2.15$.

The average g values determined for compounds **2** and **3** are comparable to those of the other similar Cu^{II} complexes in the literature,[19,20d] and the positive values for the exchange couplings were already expected in the description of their experimental data above.[10d,17,20] It should be stressed that the ferromagnetic nature of the interaction through EE azido pathways is not very common. In general, the most commonly observed coordination mode which provides antiferromagentic interaction is the one involving EE ($\mu_{1,3}$) bridging azido group,[3,6a,6g,10c,10e,13,17−19] whereas EO ($\mu_{1,1}$) is normally the one giving a ferromagnetic interaction.[3,6a,6f,6h,9,10a,10b,12−15] However, detailed studies have proved that an antiferromagnetic interaction is possible in Cu^{II} and Ni^{II} systems containing azido groups with EO mode of coordination[6h,7a,16] and similarly, it is viable to find ferromagnetic behavior in complexes with EE azido groups.[10d,17,20] From those works, it has been established that the nature of the coupling parameter of this type of compounds is strongly dependent on the nature of magnetic orbitals involved in the binding, the M−N−N angles, and the M−N···N−M torsion angle.

In this regard, for compounds **2** and **3**, one side of the bridging azido group is linked to an equatorial position of one Cu^{II} while the other extreme of the same ligand is coordinated to an axial position of the neighboring Cu^{II} center. Hence, the magnetic orbitals involved are $d_{x^2-y^2}$ and d_{z^2}, respectively, which diminish the antiferromagnetic component of the exchange coupling (which is proportional to the sum of the squares of the energy difference between the symmetric and the antisymmetric combinations of MOs, $\Sigma\Delta^2$) and favors a ferromagnetic behavior (see Figure S7, Supporting Information, for a general scheme of the

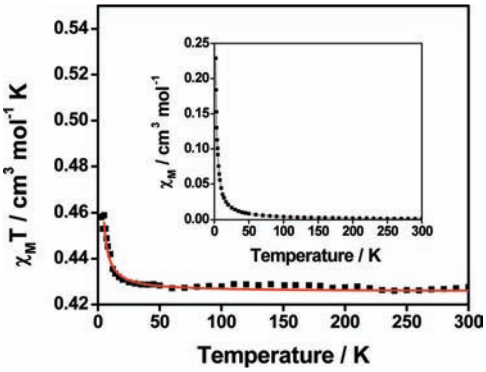


Figure 7. Fittings of the $\chi_M T$ vs T of $[Cu^{II}L^1(\mu_{1,3}\text{-NCO})]_n \cdot 2nH_2O$ (**1**) between 2.0 and 300.0 K. The experimental data are shown as black squares, and the red line corresponds to the theoretical values. (Inset) χ_M vs T data.

distribution of the magnetic orbitals). In addition, the two Cu−N−N bond angles, with values of 122.53° and 128.08° for **2** and 123.74° and 128.78° for **3**, are clearly larger than 108° (calculated value where the antiferromagnetic component of the coupling maximizes),[3,6g,17,18b] facilitating ferromagnetic interaction as well. Lastly, the Cu−N···N−Cu torsion angles, 94.58° (or 85.42°) for **2** and ±123.91° (or ±56.09°) for **3**, are high and deviate significantly from 180° (or 0°), thus leading toward a ferromagnetic exchange too.[3,6g,17,18b] Differences between **2** and **3** in these respects do not exhibit huge changes in their corresponding coupling constant, resulting in J values of the same order. Overall, these two compounds exhibit ferromagnetic behaviors that can be perfectly explained taking into account the structural features of such systems. It is relevant to mention at this point that the sign of the exchange coupling constants in **2** and **3** agrees well with the previously established density functional theoretical magneto−structural correlations on single end-to-end azide-bridged metal complexes.[17]

On the other hand, the EE cyanate-bridged compound **1** displays a similar pattern to the two previous species, **2** and **3**. The $\chi_M T$ values for this complex are plotted in Figure 7 (χ_M versus T plot is shown in the inset). Here again, the $\chi_M T$ versus T curve shows that the global magnetic interaction in this complex is ferromagnetic in nature, with a $\chi_M T$ value of 0.43 cm^3 mol^{-1} K at 300 K that increases to 0.48 cm^3 mol^{-1} K at the lowest temperature (2 K). Eluding the obvious differences like the nature of the bridging ligands (now cyanate instead of azide) and the corresponding distances and angles that will be discussed below, this 1-D system was magnetically treated as done previously. The results of the best fit (from 5 to 300 K), shown as the line in Figure 7, were $J = +0.19 \pm 0.01$ cm^{-1}, $g = 2.13 \pm 0.01$, and $R = 1.4 \times 10^{-5}$. The discussion of the ferromagnetic nature of the exchange interaction could follow the same arguments explained above (see Figure S7, Supporting Information, for a general scheme of the distribution of the magnetic orbitals). As in the cases of **2** and **3**, the reduced magnetization versus field (Figure S8, Supporting Information) also shows deviations from Brillouin's formula, indicating ferromagnetic interaction.[20b] The Cu−O−C and Cu−N−C angles of 125.07° and 149.77°, respectively, differ greatly from 108°, which will provide antiferromagnetic interaction, and the torsion angle of −57.61° (or 122.39°) leads toward ferromagnetic interaction. There are three examples in the literature of 1-D systems containing Cu^{II} ions bonded through single EE cyanate bridges.[23,30] Of those three, two have been magnetically studied, both exhibiting antiferromagnetic behavior.[23] Hence, compound **1** is the first Cu−cyanate chain exhibiting ferromagnetic interaction.

Table 3. Magnetic and Structural Parameters of the Single EE Cyanate-Bridged *cis*-1D Copper(II) Compounds

parameters	present work	ref23a	ref23b
Cu^{II}···Cu^{II} (Å)	5.709	5.825	5.80
Cu−O−C (deg)	125.07	117.5	118.5
Cu−N−C (deg)	149.77	167.55	161.2
torsion angle (deg)	−57.61	25.017	64.44
Cu−O (Å)	2.468	2.568	2.663
Cu−N (Å)	1.932	1.937	1.952
J (cm^{-1})	+0.19	−0.19	−1.26

Magnetic and relevant structural parameters of **1** and two previously published similar compounds are compared in Table 3. There is a clear difference in the Cu−O−C and Cu−N−C angles among these three compounds, where **1** has the most appropriate values to present ferromagnetism. Also, Cu^{II}···Cu^{II} and Cu−O distances are much smaller in **1** than those in the two others, facilitating the ferromagnetic exchange even though this is very weak. At the same time, **1**, **2**, and **3** show comparable structural parameters, points that stress the similarity in their magnetic behavior. It also should be noted that the cyanate bridge acts in a very similar manner to the azide group, except that the magnitude of the magnetic exchange has been always found to be lower than those of the azide cases, which, in turn, basically arises due to the asymmetry of the cyanate versus the azide (larger Cu−O distance compared to Cu−N distances).[31]

Comparison of the Structure and Properties of Single EE Azide-Bridged *cis*-1-D Copper(II) Systems. The synthesis and crystal structure of a compound having a composition the same as that of $[Cu^{II}L^2(\mu_{1,3}\text{-N}_3)]_n$ (**3**) have been reported previously.[27] Comparison of crystallographic data and structural parameters of the two compounds in Tables S2 and S3, Supporting Information, reveal that the two systems are the same compound. However, the magnetic property of **3** was not investigated previously. On the other hand, the synthesis, crystal structure, and magnetic properties of a compound (**2A**) having a composition the same as that of $[Cu^{II}L^1(\mu_{1,3}\text{-N}_3)]_n \cdot 2nH_2O$ (**2**) have been reported previously.[19a] The azide-bridged one-dimensional topology of both **2** and **2A** are the same. Most of the crystallographic data (Table S2, Supporting Information) and some structural parameters (Table S3, Supporting Information) of **2** and **2A** may also be considered as almost identical. However, some differences are also there. For example, (1) the β values of **2** and **2A** are 97.9° and 100.0°, respectively; (2) the Cu−N··· N−Cu torsion angle is 94.6° (or 85.4°) in **2** but 89.7° in **2A**; (3) the dihedral angle between two neighboring basal planes of the metal ions is 21.0° for **2** but 17.0° for **2A**; (4) the apical Cu−azide bond distance is 2.495 Å for **2** but 2.563 Å for **2A**; (5) the N(morpholine)−Cu−O(phenoxo) bond angle is 172.8° for **2** but 175.1° for **2A**; (6) the location of two water molecules in **2** and **2A** are different (Supporting Information for discussion and Figure S9), the distances between the metal ion and two water molecules are 4.008 and 4.317 Å in **2** but 4.063 and 6.553 Å in **2A**; (7) although the water molecules in both **2** and **2A** act as bridges between the 1-D chains in both **2** and **2A** to generate a 2-D sheet, two water molecules are involved in hydrogen-bonding

Table 4. Cambridge Structural Database Refcodes[36] and Magnetic and Structural Parameters of the Single EE Azide-Bridged *cis*-1D Copper(II) Compounds

compound/CSD refcode	Cu−N···N−Cu (deg)	Cu−N−N (deg)	Cu···Cu (Å)	J (cm^{-1})	ref
2	85.4	122.53, 128.08	5.594	+0.79	this work
3	56.1	123.74, 128.78	6.014	+1.25	this work
2A/BACHAP	89.7	122.60, 129.00	5.638	−4.3	19a
QOZGER	88.4	125.60, 135.70	5.773	+1.36	20a
FIFZUQ	−88.0	136.37, 141.21	6.086	+1.6	20b
LUBLAV	−30.8	133.78, 137.72	5.594	+2.69	20c
LUBLEZ	77.3	122.49, 135.11	5.735	+2.02	20c
OFAYOJ	82.2	126.60, 131.25	5.685	+2.15	20d
OFAYUP	−49.9	131.19, 139.14	5.630	+3.61	20d
QAKRAW	81.7	119.09, 126.95	5.530	+6.7	20e
QAKREA	70.9	120.99, 124.39	5.393	+4.64	20e
QAKREA01	−75.9, −73.3	116.32, 125.19, 123.97, 122.28	5.139, 5.525	−22.5	19b
RAWHUT	75.8	128.00, 143.35	6.074	+ 0.70	20f

interactions in different ways in the two compounds (see Supporting Information for discussion and figures; Figure S10 for **2A**); (8) the overall supramolecular topology in **2** is 3-D, while that in **2A** is 2-D. As the R_1 values of structure determination are quite good, 0.0467 for **2** and 0.042 for **2A**, and as most of the unit cell parameters and some structural parameters are almost identical, the above-mentioned differences should be considered as significant, indicating that compounds **2** and **2A** are isomers. The two compounds are definitely supramolecular isomers[32] because of the differences in supramolecular interactions and topologies (points 7 and 8 above). On the other hand, other differences (points 1−6 above) are not matched either with any of the classical isomerism[33] or any of the recently addressed nonclassical isomerisms, namely, supramolecular isomerism,[32] molecular isomerism due to a difference in the number of interstitial solvent molecules,[34] or catenation isomerism.[35] Therefore, compounds **2** and **2A** also represent a new type of solid state isomerism, which could be called crystallographic isomerism. The fact that **2** and **2A** are not the same compound but isomers is further evident from their drastically different magnetic behavior; while **2** exhibits a ferromagnetic interaction with $J = +0.79$ cm^{-1}, **2A**[19a] exhibits an antiferromagnetic interaction with $J = -4.3$ cm^{-1}. Thus, **2** and **2A** are nice examples of magnetic isomers as well.

Magnetic and relevant structural parameters of compounds **2**, **3**, and other previously published single EE azide-bridged *cis*-1-D copper(II) compounds are summarized in Table 4. Most, except two, of these compounds are ferromagnetically coupled. The Cu−N−N angles in these compounds range between ca. 116° and ca. 143°. Except in one case for which the Cu−N···N−Cu torsion angle (τ) is 30.8°, this torsion angle ranges between ca. 50° and ca. 90° in other examples. However, while the complex with $\tau = 30.8°$ is ferromagnetic, two complexes with τ of ca. 74° and ca. 90° are antiferromagnetic. Clearly, the nature of the interaction is more a composite effect of bridging moieties.

CONCLUSIONS

The syntheses, structures, and magnetic properties of two (**2** and **3**) EE azide-bridged and one (**1**) EE cyanate-bridged 1-D copper(II) compounds have been described in this investigation. Compound **1** is only the third example and, interestingly, the sole example exhibiting a ferromagnetic interaction in the family of EE cyanate-bridged 1-D copper(II) compounds. Although the crystal structures and magnetic properties of 11 other, EE azide-bridged 1-D copper(II) compounds have been previously reported, some significant aspects have emerged from the studies of the two compounds, **2** and **3**, in this investigation. The composition/topology, crystal system/space group, and most of the unit cell parameters and bond lengths/angles of compound **2** are identical or almost identical with a previously reported compound, **2A**, derived from the same ligand. However, some definite differences exist between the two structures in the one unit cell angle (β), Cu−N···N−Cu torsion angle, dihedral angle between two neighboring basal planes of metal ions, apical Cu−azide bond distance, location of the two solvated water molecules, and supramolecular interactions and topologies. The magnetic exchange interactions in **2** and **2A** are also drastically different: ferromagnetic in **2** ($J = +0.79$ cm^{-1}) and antiferromagnetic in **2A** ($J = -4.3$ cm^{-1}). In spite of the many similarities, the definite differences are quite interesting. Because of the differences in supramolecular interactions/topologies and magnetic properties, **2** and **2A** represent rarely observed supramolecular isomerism and magnetic isomerism, respectively. On the other hand, other differences result in the emergence of a new type of solid-state isomerism which could be called crystallographic isomerism. Comparison of the structures and magnetic properties of **2**, **3**, and 11 other previously published related compounds also reveals that the magnetic exchange in such systems is governed by composite effects of several parameters.

ASSOCIATED CONTENT

Supporting Information. Crystallographic data of **1**−**3** in CIF format; discussion on supramolecular topology in **1**−**3** and **2A**. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: sm_cu_chem@yahoo.co.in; nuria.aliaga@icrea.cat.

ACKNOWLEDGMENT

Financial support from the Government of India through the Department of Science and Technology, the Government of

India (SR/S1/IC-12/2008), and the University Grants Commission (fellowship to S. Sasmal and S. Sarkar) is gratefully acknowledged. Crystallography was performed at the DST-FIST, India-funded Single Crystal Diffractometer Facility at the Department of Chemistry, University of Calcutta. N.A.-A. thanks the Ministerio de Educación y Ciencia (CTQ2009-06959/BQU) and ICREA (Institució Catalana de Recerca i Estudis Avançats) for financial support.

■ REFERENCES

(1) (a) Neumann, R.; Dahan, M. *Nature* **1997**, *388*, 353–355. (b) Beer, P. D.; Gale, P. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 486–516. (c) Lehn, J.-M. *Supramolecular Chemistry*; VCH: Weinheim, 1995. (d) Robson, R. *J. Chem. Soc., Dalton Trans.* **2000**, 3735–3744. (e) Song, Y.; Massera, C.; Roubeau, O.; Gamez, P.; Manotti-Lanfredi, A. M.; Reedijk, J. *Inorg. Chem.* **2004**, *43*, 6842–6847.

(2) (a) In *Transition Metals in Supramolecular Chemistry*; Sauvage, J.-P., Ed.; Perspectives in Supramolecular Chemistry 5; Wiley: London, 1999. (b) Blake, A. J.; Champness, N. R.; Hubberstey, P.; Withersby, M. A.; Schröder, M. *Coord. Chem. Rev.* **1999**, *183*, 117–138. (c) Lin, H.-H.; Mohanta, S.; Lee, C.-J.; Wei, H.-H. *Inorg. Chem.* **2003**, *42*, 1584–1589.

(3) Ribas, J.; Escuer, A.; Monfort, M.; Vicente, R.; Cortés, R.; Lezama, L.; Rojo, T. *Coord. Chem. Rev.* **1999**, *193*−*195*, 1027–1068.

(4) (a) Nayak, M.; Koner, R.; Lin, H.-H.; Flörke, U.; Wei, H.-H.; Mohanta, S. *Inorg. Chem.* **2006**, *45*, 10764–10773. (b) Hazra, S.; Koner, R.; Nayak, M.; Sparkes, H. A.; Howard, J. A. K.; Mohanta, S. *Cryst. Growth Des.* **2009**, *9*, 3603–3608. (c) Nayak, M.; Jana, A.; Fleck, M.; Hazra, S.; Mohanta, S. *CrystEngComm.* **2010**, *12*, 1416–1421. (d) Sasmal, S.; Majumder, S.; Hazra, S.; Sparkes, H. A.; Howard, J. A. K.; Nayak, M.; Mohanta, S. *CrystEngComm.* **2010**, *12*, 4131–4140. (e) Bhattacharya, S.; Mondal, S.; Sasmal, S.; Sparkes, H. A.; Howard, J. A. K.; Nayak, M.; Mohanta, S. *CrystEngComm.* **2011**, *13*, 1029–1036.

(5) (a) Verdaguer, M.; Bleuzen, A.; Marvaud, V.; Vaissermann, J.; Seuleiman, M.; Desplanches, C.; Scuiller, A.; Train, C.; Garde, R.; Galley, G.; Lomenech, C.; Rosenman, I.; Veillet, P.; Cartier, C.; Villain, F. *Coord. Chem. Rev.* **1999**, *190*−*192*, 1023–1047. (b) Ohba, M.; Ōkawa, H. *Coord. Chem. Rev.* **2000**, *198*, 313–328. (c) Batten, S. R.; Murray, K. S. *Coord. Chem. Rev.* **2003**, *246*, 103–130.

(6) (a) Kahn, O. *Molecular Magnetism*; VCH Publications: New York, 1993. (b) Thompson, L. K.; Mandal, S. K.; Tandon, S. S.; Bridson, J. N.; Park, M. K. *Inorg. Chem.* **1996**, *35*, 3117–3125. (c) Nanda, K. K.; Thompson, L. K.; Bridson, J. N.; Nag, K. *J. Chem. Soc., Chem. Commun.* **1994**, 1337–1338. (d) Arriortua, M. I.; Cortés, R.; Mesa, J. L.; Lezama, L.; Rojo, T.; Villeneuve, G. *Transition Met. Chem.* **1988**, *13*, 371–374. (e) Mohanta, S.; Nanda, K. K.; Thompson, L. K.; Flörke, U.; Nag, K. *Inorg. Chem.* **1998**, *37*, 1465–1472. (f) Koner, R.; Hazra, S.; Fleck, M.; Jana, A.; Lucas, C. R.; Mohanta, S. *Eur. J. Inorg. Chem.* **2009**, 4982–4988. (g) Vicente, R.; Escuer, A.; Ribas, J.; Fallah, M. S. E.; Solans, X.; Font-Bardía, M. *Inorg. Chem.* **1995**, *34*, 1278–1281. (h) Tandon, S. S.; Thompson, L. K.; Manuel, M. E.; Bridson, J. N. *Inorg. Chem.* **1994**, *33*, 5555–5570.

(7) (a) Ruiz, E.; Cano, J.; Alvarez, S.; Alemany, P. *J. Am. Chem. Soc.* **1998**, *120*, 11122–11129. (b) Manca, G.; Cano, J.; Ruiz, E. *Inorg. Chem.* **2009**, *48*, 3139–3144. (c) Triki, S.; Gómez-García, C. J.; Ruiz, E.; Sala-Pala, J. *Inorg. Chem.* **2005**, *44*, 5501–5508.

(8) (a) Lin, P.-H.; Burchell, T. J.; Ungur, L.; Chibotaru, L. F.; Wernsdorfer, W.; Murugesu, M. *Angew. Chem., Int. Ed.* **2009**, *48*, 9489–9492. (b) Freedman, D. E.; Jenkins, D. M.; Iavarone, A. T.; Long, J. R. *J. Am. Chem. Soc.* **2008**, *130*, 2884–2885. (c) Yoshihara, D.; Karasawa, S.; Koga, N. *J. Am. Chem. Soc.* **2008**, *130*, 10460–10461. (d) Ohkoshi, S.-i.; Ikeda, S.; Hozumi, T.; Kashiwagi, T.; Hashimoto, K. *J. Am. Chem. Soc.* **2006**, *128*, 5320–5321.

(9) (a) Liu, T.-F.; Fu, D.; Gao, S.; Zhang, Y.-Z.; Sun, H.-L.; Su, G.; Liu, Y.-J. *J. Am. Chem. Soc.* **2003**, *125*, 13976–13977. (b) Sun, H.-L.; Wang, Z.-M.; Gao, S. *Chem.—Eur. J.* **2009**, *15*, 1757–1764.

(10) (a) Feng, P. L.; Stephenson, C. J.; Amjad, A.; Ogawa, G.; Barco, E. d.; Hendrickson, D. N. *Inorg. Chem.* **2010**, *49*, 1304–1306. (b) Gu, Z.-G.; Song, Y.; Zuo, J.-L.; You, X.-Z. *Inorg. Chem.* **2007**, *46*, 9522–9524. (c) Gao, E.-Q.; Liu, P.-P.; Wang, Y.-Q.; Yue, Q.; Wang, Q.-L. *Chem. —Eur. J.* **2009**, *15*, 1217–1226. (d) Liu, X.-T.; Wang, X.-Y.; Znang, W.-X.; Cui, P.; Gao, S. *Adv. Mater.* **2006**, *18*, 2852–2856. (e) Leibeling, G.; Demeshko, S.; Dechert, S.; Meyer, F. *Angew. Chem., Int. Ed.* **2005**, *44*, 7111–7114.

(11) (a) Jana, A.; Majumder, S.; Carrella, L.; Nayak, M.; Weyhermueller, T.; Dutta, S.; Schollmeyer, D.; Rentschler, E.; Koner, R.; Mohanta, S. *Inorg. Chem.* **2010**, *49*, 9012–9025. (b) Hazra, S.; Koner, R.; Lemoine, P.; Sañudo, E. C.; Mohanta, S. *Eur. J. Inorg. Chem.* **2009**, 3458–3466.

(12) (a) Yang, C.-I.; Wernsdorfer, W.; Lee, G.-H.; Tsai, H.-L. *J. Am. Chem. Soc.* **2007**, *129*, 456–457. (b) Milios, C. J.; Inglis, R.; Vinslava, A.; Prescimone, A.; Parsons, S.; Perlepes, S. P.; Christou, G.; Brechin, E. K. *Chem. Commun.* **2007**, 2738–2740.

(13) Demeshko, S.; Leibeling, G.; Dechert, S.; Meyer, F. *Dalton Trans.* **2006**, 3458–3465.

(14) Milios, C. J.; Prescimone, A.; Sanchez-Benitez, J.; Parsons, S.; Murrie, M.; Brechin, E. K. *Inorg. Chem.* **2006**, *45*, 7053–7055.

(15) Demeshko, S.; Leibeling, G.; Maringgele, W.; Meyer, F.; Mennerich, C.; Klauss, H.-H.; Pritzkow, H. *Inorg. Chem.* **2005**, *44*, 519–528.

(16) Mukherjee, P. S.; Maji, T. K.; Mostafa, G.; Mallah, T.; Chaudhuri, N. R. *Inorg. Chem.* **2000**, *39*, 5147–5150.

(17) Sasmal, S.; Hazra, S.; Kundu, P.; Majumder, S.; Aliaga-Alcalde, N.; Ruiz, E.; Mohanta, S. *Inorg. Chem.* **2010**, *49*, 9517–9526.

(18) (a) Massoud, S. S.; Mautner, F. A.; Vicente, R.; Gallo, A. A.; Ducasse, E. *Eur. J. Inorg. Chem.* **2007**, 1091–1102. (b) Hong, C. S.; Koo, J.-e.; Son, S.-K.; Lee, Y. S.; Kim, Y.-S.; Do, Y. *Chem.—Eur. J.* **2001**, *7*, 4243–4252. (c) Kersting, B.; Steinfeld, G.; Siebert, D. *Chem.—Eur. J.* **2001**, *7*, 4253–4258. (d) Meyer, F.; Demeshko, S.; Leibeling, G.; Kersting, B.; Kaifer, E.; Pritzkow, H. *Chem.—Eur. J.* **2005**, *11*, 1518–1526.

(19) (a) Mukherjee, P. S.; Dalai, S.; Mostafa, G.; Lu, T.-H.; Rentschler, E.; Chaudhuri, N. R. *New J. Chem.* **2001**, *25*, 1203–1207. (b) Adhikary, C.; Mal, D.; Okamoto, K.-I.; Chaudhuri, S.; Koner, S. *Polyhedron* **2006**, *25*, 2191–2197.

(20) (a) Maji, T. K.; Mukherjee, P. S.; Mostafa, G.; Mallah, T.; Cano-Boquerac, J.; Chaudhuri, N. R. *Chem. Commun.* **2001**, 1012–1013. (b) Sarkar, S.; Mondal, A.; Ribas, J.; Drew, M. G. B.; Pramanik, K.; Rajak, K. K. *Inorg. Chim. Acta* **2005**, *358*, 641–649. (c) Dalai, S.; Mukherjee, P. S.; Drew, M. G. B.; Lu, T.-H.; Chaudhuri, N. R. *Inorg. Chim. Acta* **2002**, *335*, 85–90. (d) Mukherjee, P. S.; Maji, T. K.; Escuer, A.; Vicente, R.; Ribas, J.; Rosair, G.; Mautner, F. A.; Chaudhuri, N. R. *Eur. J. Inorg. Chem.* **2002**, 943–949. (e) Jiang, Y.-B.; Kou, H.-Z.; Wang, R.-J.; Cui, A.-L. *Eur. J. Inorg. Chem.* **2004**, 4608–4615. (f) Wen, H.-R.; Wang, C.-F.; Song, Y.; Zuo, J.-L.; You, X.-Z. *Inorg. Chem.* **2005**, *44*, 9039–9045.

(21) (a) Papaefstathiou, G. S.; Escuer, A.; Vicente, R.; Font-Bardía, M.; Solans, X.; Perlepes, S. P. *Chem. Commun.* **2001**, 2414–2415. (b) Meyer, F.; Kircher, P.; Pritzkow, H. *Chem. Commun.* **2003**, 774–775.

(22) (a) Habib, M.; Karmakar, T. K.; Aromi, G.; Ribas-Ariño, J.; Fun, H.-K.; Chantrapromma, S.; Chandra, S. K. *Inorg. Chem.* **2008**, *47*, 4109–4117. (b) Nicola, C. D.; Effendy.; Fazaroh, F.; Pettinari, C.; Skelton, B. W.; Somers, N.; White, A. H. *Inorg. Chim. Acta* **2005**, *358*, 720–734. (c) Clemente-Juan, J. M.; Mackiewicz, C.; Verelst, M.; Dahan, F.; Bousseksou, A.; Sanakis, Y.; Tuchagues, J.-P. *Inorg. Chem.* **2002**, *41*, 1478–1491. (d) Goher, M. A. S.; Mautner, F. A. *J. Chem. Soc., Dalton Trans.* **1999**, 1923–1924.

(23) (a) Talukder, P.; Datta, A.; Mitra, S.; Rosair, G.; Fallah, M. S. E.; Ribas, J. *Dalton Trans.* **2004**, 4161–4167. (b) Vicente, R.; Escuer, A.; Peñalba, E.; Solans, X.; Font-Bardía, M. *J. Chem. Soc., Dalton Trans.* **1994**, 3005–3008.

(24) Escuer, A.; Font-Bardía, M.; Peñalba, E.; Solans, X.; Vicente, R. *Inorg. Chim. Acta* **1999**, *286*, 189–196.

(25) (a) Luo, J.; Zhou, X.-G.; Weng, L.-H.; Hou, X.-F. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **2003**, *59*, m519–m522. (b) Boudalis, A. K.; Sanakis, Y.; Clemente-Juan, J. M.; Donnadieu, B.; Nastopoulos, V.; Mari, A.; Coppel, Y.; Tuchagues, J.-P.; Perlepes, S. P. *Chem.—Eur. J.* **2008**, *14*, 2514–2526.

(26) Cheng, K.; Zhu, H.-L.; Gao, Y.-H. *Synth. React. Inorg., Met.-Org., Nano. Met. Chem.* **2006**, *36*, 477–480.

(27) Hou, P.; You, Z.-L.; Zhang, L.; Ma, X.-L.; Ni, L. L. *Transition Met. Chem.* **2008**, *33*, 1013–1017.

(28) (a) *APEX-II, SAINT-Plus, and TWINABS*; Bruker−Nonius AXS Inc.: Madison, Wisconsin, 2004. (b) Sheldrick, G. M. *SAINT* (Version 6.02); *SADABS* (Version 2.03); Bruker AXS Inc.: Madison, WI, 2002. (c) *SHELXTL* (version 6.10); Bruker AXS Inc.: Madison, WI, 2002. (d) Sheldrick, G. M. *SHELXL-97, Crystal Structure Refinement Program*; University of Göttingen: Göttingen, 1997.

(29) Baker, G. A.; Rushbrooke, G. S.; Guilbert, H. E. *Phys. Rev.* **1964**, *135*, A1272–A1277.

(30) (a) Valach, F.; Dunaj-Jurco, M.; Handlovic, M. *J. Cryst. Mol. Struct.* **1980**, *10*, 61–66. (b) Valach, F.; Dunaj-Jurco, M. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1982**, *38*, 2145–2148.

(31) Cortés, R.; Urtiaga, M. K.; Lezama, L.; Larramendi, J. I. R.; Arriortua, M. I.; Rojo, T. *J. Chem. Soc., Dalton Trans.* **1993**, 3685–3694.

(32) (a) Ring, D. J.; Aragoni, M. C.; Champness, N. R.; Wilson, C. *CrystEngComm.* **2005**, *103*, 621–623. (b) Zhang, J.-P.; Kitagawa, S. *J. Am. Chem. Soc.* **2008**, *130*, 907–917.

(33) (a) Purcell, K. F.; Kotz, J. C. In *An Introduction to Inorganic Chemistry*; Saunders College Publishing: Philadelphia, 1980. (b) von Zelewsky, A. In *Stereochemistry of Coordination Compounds*; Wiley: New York, 1996.

(34) Poulsen, R. D.; Overgaard, J.; Schulman, A.; Østergaard, C.; Murillo, C. A.; Spackman, M. A.; Iversen, B. B. *J. Am. Chem. Soc.* **2009**, *131*, 7580–7591.

(35) Ma, L.; Lin, W. *J. Am. Chem. Soc.* **2008**, *130*, 13834–13835.

(36) *The Cambridge Structural Database (CSD)*, Version 5.31; The Cambridge Crystallographic Data Center: Cambridge, U.K., 2009.