Use of Different Unsaturated Dicarboxylates Toward the Design of New 3D and 2D Networks of Copper(II)

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Two new polymeric complexes of copper(II), $[Cu(L1)(\mu\text{-}fum)(\mu\text{-}H_2O)]_n$ (**1**) (fum = fumarate dianion; L1 = *N*,*N′*-dimethylethane-1,2-diamine) and $[Cu(L2)(\mu\text{-}tp)]_n$ (**2**) [tp = terephthalate dianion; L2 = *N*-(2-aminoethyl)-3-amino-1-propanol], have been synthesized. The molecular structures are determined by X-ray crystallography. Complex **1** is a fumarato-bridged zig-zag 1D chain of Cu^{II}–L1, which is extended to a 3D coordination polymer through bridging water molecules. Complex **2** is a chain of Cu^{II} in which the terephthalate anions bridge in alternate bis(bidentate) and bis(monodentate) fashions. The coexistence of such types of bridging modes of terephthalate ions in a single molecule is unprecedented. The chelating terephthalate ion is linked to an equatorial and an axial site of consecutive metal ions, while the other terephthalate ion is axially linked to Cu^{II} centers. Both the complexes are characterized by variable-temperature susceptibility measurements at room temperature down to 4 K. Fitting of the magnetic data reveals the existence of weak antiferromagnetic interactions through the bridging dicarboxylate pathways.

Introduction

Construction of molecules with covalent and noncovalent motifs has recently become a rapidly growing area of research as it pursues to establish principles that will ultimately lead to the development of new state-of-the-art functional materials.[1−6] Among the noncovalent motifs, hydrogen bonding[2,3] and π-π stacking[7] have been employed as synthetic paradigms to rationally design superstructures. Recent progress in this area has generated examples in which the design of network structures has produced crystals with (a) one-dimensional (1D) molecular networks composed of hydrogen bonding,[8,9] metal−ligand coordination,[10,11] or a combination of these and other interactions, referred to as hybrid interactions;[12] (b) 2D networks comprising either hydrogen bonding[13]/metal−ligand coordination[14] or hybrid interactions; and (c) 3D networks composed of hydrogen bonding[15] or metal−ligand coordination.[16] These approaches seek to establish structural relationships between the molecular and supramolecular networks and look for molecular features, such as functional groups, that can interfere and modify the arrangements of molecules in crystals, a task that remains a considerable challenge at present.

Recently, di- and polycarboxylates have become one of the most demanding spacers to the material chemist, and especially to the inorganic chemist, for the synthesis of compounds that have potential useful applications as molecular-based magnetic materials as well as materials that mimick zeolite with host-guest behavior.[17−19] Different types of dicarboxylates like terephthalate, malonate, succinate, and oxalates are widely used by these chemists, but use of fumarate is relatively less frequent due to poor solubility of its coordination complexes in common solvents. We have reported a new method of crystallization of Cu^{II} complexes of fumarate that uses ammonia as solvent.[20] With this procedure we have already obtained and reported on some interesting molecular architectures.[20,21] We are currently exploring the design of molecules that use suitable metal ions and ligands capable of forming H-bonds as well as π-π interactions as directional motifs to extend the dimensionality of the molecule. The present article contributes to the synthesis, crystal structure, and variable-temperature magnetic behavior of two Cu^{II} complexes with unsaturated dicarboxylate as bridging ligands, namely $[Cu(L1)(\mu\text{-}fum)(\mu\text{-}H_2O)]_n$ (**1**) and $[Cu(L2)(\mu\text{-}tp)]_n$ (**2**) [fum = fumarate dianion; tp = terephthalate dianion; L1 = *N*,*N′*-dimethylethane-1,2-diamine; L2 = *N*-(2-aminoethyl)-3-amino-1-pro-

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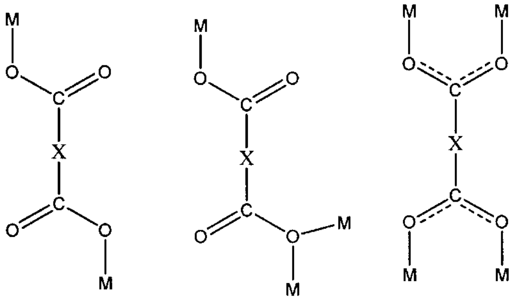
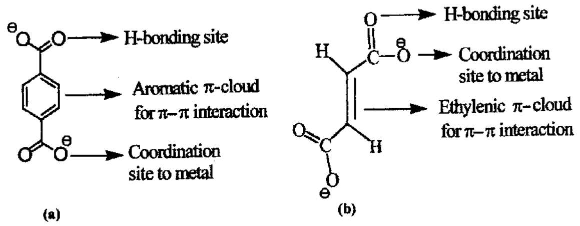
panol]. The results of the structural analysis of complex **1** reveals a 3D network and that of **2** a chain with alternating bis(bidentate) and bis(monodentate) bridging modes of terephthalate, which results in a molecule with a unique topology. The coexistence of terephthalate ligands with different bridging fashions inside a single molecule has not been reported earlier. These unsaturated dicarboxylates are chosen as spacers because of the following reasons: (i) fumarate and terephthalate show versatile coordination modes (Scheme 1); (ii) they coordinate metal ions to form unidimensional coordination chains, which, in general, can enlarge the dimensionality through H-bonding; and (iii) they have ethylenic and phenyl moieties that are capable of forming π-π stacking as a directional motif (Scheme 2).



Scheme 1. [X = $-CH{=}CH-$ or $-C_6H_4-$ (1,4)]



Scheme 2. Possible sites for coordination as well as supramolecular interaction in terephthalate (a) and fumarate (b)

Results and Discussion

Description of the Structures

[Cu(L1)(μ-fum)(μ-H_2O)]$_n$ (1)

The crystal structure of **1** consists of Cu^{II}(L1) units connected through bridging amphi-monodentate fumarate dianions to form polymeric chains with a zig-zag arrangement (Figure 1). Each copper atom is located on a twofold crystallographic axis with an elongated octahedral geometry that involves the diamine ligand donors N(1) and the carboxylic oxygen atom O(2) in the equatorial positions, and two water molecules as axial ligands. The former distances [Cu−O(2) 1.973(2), Cu−N(1) 2.022(2) Å] are significantly shorter than those involving the water molecule [2.481(2) Å]. A selection of bond lengths and angles is reported in Table 1. The dicarboxylate anion spans the metal atoms with a distance of 8.857 Å, a distance similar to those of 8.653 and 8.666 Å observed in two dinuclear fumarate-bridged Cu^{II} complexes.[22,23] It is worthwhile to note the

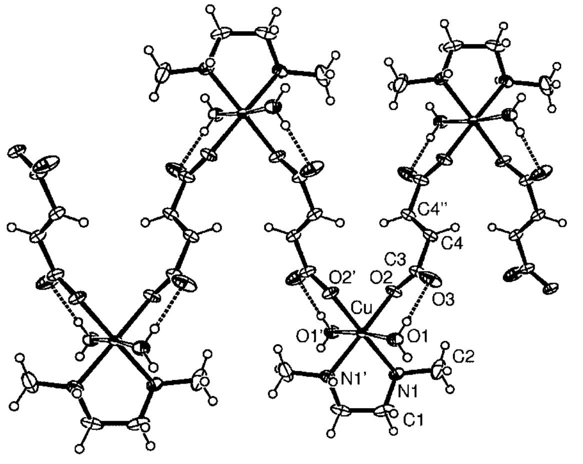


Figure 1. ORTEP drawing (thermal ellipsoid at 40% probability level) of the polymeric arrangement of **1** with atom labeling scheme; dotted lines indicate intrachain H-bonds

Table 1. Selected bond lengths [Å] and angles [°] for complex [Cu(L1)(μ-fum)(μ-H_2O)] (**1**)

Cu−O(2)	1.973(2)	O(2)−C(3)	1.265(3)
Cu−N(1)	2.022(2)	O(3)−C(3)	1.234(3)
Cu−O(1)	2.481(2)	C(4)−C(4′′)[a]	1.311(5)
O(2)−Cu−N(1′)[a]	174.88(8)	N(1′)−Cu−N(1)	85.4(1)
O(2)−Cu−N(1)	93.60(9)	N(1)−Cu−O(1)	90.13(8)
O(2)−Cu−O(1)	98.48(7)	N(1)−Cu−O(1′)	86.54(8)
O(2)−Cu−O(1′)	84.80(7)	O(2)−Cu−O(2′)	87.9(1)
O(1′)−Cu−O(1)	175.5(2)	C(3)−O(2)−Cu	123.3(2)

[a] Symmetry operations: (′): 1.25 − *x*, 0.25 − *y*, *z*; (′′): 1 − *x*, −*y*, 1 − *z*.

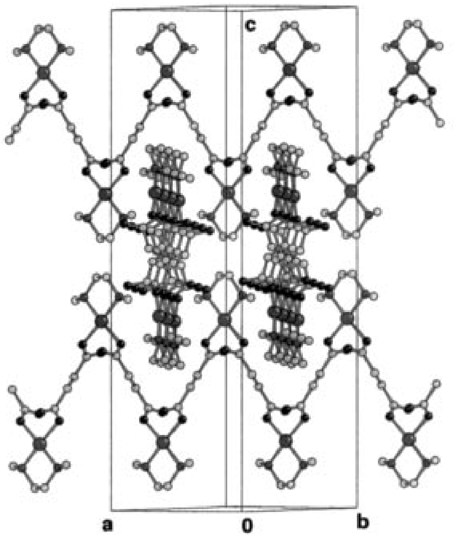


Figure 2. Perspective view of the packing of **1** showing the intersecting Cu(L1)(fum) chains (water molecules not shown for clarity)

packing shown by the X-ray structural analysis, in which the coordination polymers present an intersecting arrangement (Figure 2). The dimensionality of the network is enlarged to 3D through the axially coordinated water molecules that bridge consecutive metal ions as depicted in Figure 3. These $-(\mathrm{Cu-H_2O})_n-$ chains are characterized by a metal−metal separation of 4.512 Å and a $\mathrm{Cu-OH_2-Cu''}$ bond angle of 130.6(1)°. The dicarboxylate skeleton is not coplanar, and instead, a O(3)−C(3)−C(4)−C(4′′) torsion angle of 145.0(4)° is observed. This conformational feature is likely assumed in order to favor the intrachain H-bond formation between the coordinated water molecule and the fumarate oxygen atom O(3) (Figure 3; O−O 2.651 Å). However, the C(4)−C(4′′) bond length of 1.311(5) Å still indicates a larger double-bond character relative to that of the C(3)−C(4) bond [1.491(3) Å].

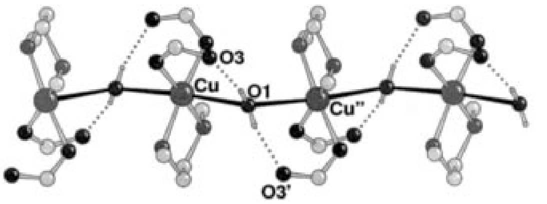


Figure 3. Bridging water molecules connecting the coordination polymers to form a 3D network in **1**; dotted lines indicate H-bonds [O(3′) at 1.75 − *x*, *y*, 0.75 − *z*; Cu′′ at 0.5 + *x*, 0.25 − *y*, 0.75 − *z*]

[Cu(L2)(μ-tp)]$_n$ (2)

The structure of complex **2** consists of 1D polymeric chains formed by Cu(L2) moieties [L2 = *N*-(2-aminoethyl)-3-amino-1-propanol] bridged by terephthalate anions. The polymeric motifs, together with the atom numbering scheme, is shown in Figure 4, and a selection of bond lengths and angles is given in Table 2. The metal environment can be described as a distorted octahedron in which the equatorial positions are occupied by the hydroxy-diamine ligand donors and by the carboxyl oxygen atom O(2), while the oxygen atoms O(4) and O(3) of different bridging terephthalate anions complete the coordination sphere. The latter distances [Cu−O(4) 2.300(4), Cu−O(3) 2.553(4) Å] are significantly longer with respect to those in the basal plane [range 1.971(4)−2.027(5) Å]. The distortions from the octahedral geometry are indicated by the small bite angle of the carboxylate group O(2)−Cu−O(3) [56.7(2)°] and by the O(4)−Cu−O(3) angle [153.3(1)°]. The four equatorial donors are coplanar ±0.086(3) Å, with the metal atom slightly displaced by 0.164(3) Å from their mean plane towards O(4). Thus, along the chain, two terephthalate anions, both having the phenyl ring located about a crystallographic symmetry center, connect Cu(L2) units, alternatively in a bis(monodentate) and a chelating bis(bidentate) fashion (Figure 4). The simultaneous presence of terephthalate ligands with different bridging fashions gives rise to an unprecedented coordination chain. The dihedral angle formed by the anions with the equatorial coordination plane is 45.9(1) and 80.3(2)°, the latter indicating a nearly perpendicular orientation for the bis(bidentate) terephthalate. The respective *intra*molecular Cu−Cu distances spanned by the anions are 10.998(5) and 10.830(3) Å; the small difference appears to be caused by the ligand coordination mode. In fact, making allowance for packing and for the different ligands bound at the metal atom, distances of about 11.0 Å were found for copper ions bridged by bis(monodentate) terephthalate anions,[24−26] while a separation of 10.710 Å was reported in $[(\mathrm{CuL''})_2\mathrm{tp}](\mathrm{ClO_4})_2$ (L'' = pentaethyldiethylenetriamine)[27] in which the anion bridges in a chelating bis(bidentate) fashion. The carboxylate group C(6)/O(2)/O(3) is nearly coplanar with the phenyl ring [4.9(3)°], while C(10)/O(4)/O(5) exhibits a tilt of 24.0(5)°. This dihedral angle was tentatively taken into account to assess the magnetic exchange coupling with structural parameters in transition metal ions bridged by a tp ligand.[28] The described polymers are held together through strong hydrogen bonds that occur between the hydroxy group O(1)−H and the carboxylate oxygen atom O(5) [2.678 Å, O(1)−H···O(5) 159.07°] to yield a layered structure (Figure 5) in which the shortest *inter*chain Cu−Cu distance is 5.532(1) Å. Moreover, the phenyl groups of the bis(bidentate) terephthalate are not coplanar with

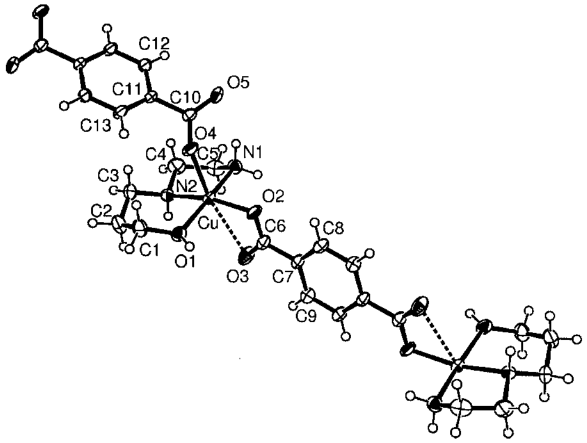


Figure 4. ORTEP drawing (thermal ellipsoid drawn at 40% probability level) of the polymeric chain of **2** with atom labeling scheme; the broken lines indicate the weak interaction between the copper and carboxyl oxygen O(3) atoms

Table 2. Selected bond lengths [Å] and angles [°] of [Cu(L2)-(μ-tp)] (**2**)

Cu−O(1)	2.006(4)	Cu−O(4)	2.300(4)
Cu−O(2)	1.971(4)	O(2)−C(6)	1.273(7)
Cu−N(1)	1.997(5)	O(3)−C(6)	1.231(7)
Cu−N(2)	2.027(5)	O(4)−C(10)	1.265(7)
Cu−O(3)	2.553(4)	O(5)−C(10)	1.246(7)
O(1)−Cu−O(2)	89.4(2)	N(1)−Cu−N(2)	84.6(2)
O(1)−Cu−N(1)	172.6(2)	N(1)−Cu−O(3)	95.7(2)
O(1)−Cu−N(2)	89.2(2)	N(1)−Cu−O(4)	94.1(2)
O(1)−Cu−O(3)	82.6(2)	N(2)−Cu−O(3)	109.1(2)
O(1)−Cu−O(4)	90.5(2)	N(2)−Cu−O(4)	96.4(2)
O(2)−Cu−N(1)	95.7(2)	O(4)−Cu−O(3)	153.3(1)
O(2)−Cu−N(2)	165.7(2)	C(10)−O(4)−Cu	128.7(4)
O(2)−Cu−O(3)	56.7(2)	C(6)−O(2)−Cu	102.8(4)
O(2)−Cu−O(4)	97.7(2)	C(6)−O(3)−Cu	76.9(3)

aromatic rings of neighboring chains, but are perpendicular. As a consequence, the phenyl centroid of the latter is at a distance of 2.66 Å from the H−C group of the adjacent aromatic ring leading to a C−H···π interaction (Figure 5).

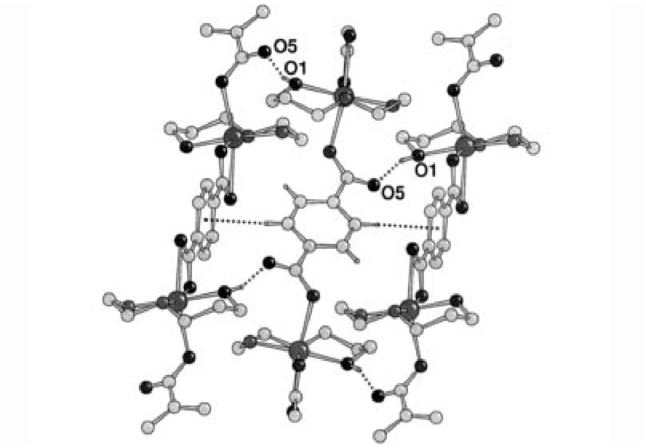


Figure 5. Perspective view of the layered structure in **2** (along axis *a*) showing the interchain H-bonding scheme and the C−H···π interactions

Magnetic Properties

[Cu(L1)(μ-fum)(μ-H$_2$O)]$_n$ (1)

The magnetic behavior of complex **1** was investigated using a SQUID magnetometer in the temperature region 280−4 K within an applied magnetic field of 5 kOe. The $\chi_M T$ product first decreases smoothly and then abruptly when cooling down from $T = 280$ K. It reaches a value close to zero at $T = 4$ K. The $\chi_M = f(T)$ plot is shown in Figure 6. These magnetic data are consistent with the presence of a weak antiferromagnetic interaction between the Cu^{II} ions within the compound even though the shorter Cu−Cu distance is larger than 6 Å. The susceptibility data, using the 1D chain model of the Cu^{II} system, was fitted, resulting in a J value of -2.6 cm^{-1}. This value is satisfactory, since it is of the same order of magnitude as that from a previously reported communication in which a 3D interlocked network of Cu^{II} ions has a bridging fumarate ion that is linked in a similar manner to that in the present complex.[21] From a structural point of view, each copper atom, located on a twofold crystallographic axis, shows an elongated octahedral geometry involving the diamine ligand donors and a carboxylic oxygen atom in the equatorial positions, and two water molecules at the axial sites. Due to this axially elongated geometry of Cu^{II} centers, the magnetically active unpaired electron on each Cu^{II} atom is located on the basal $d_{x^2-y^2}$ orbital, whereas the d_{z^2} orbital is occupied by paired electrons. Since each bridging water is bound to the d_{z^2} (nonmagnetic) orbital of two Cu^{II} centers, the coupling interaction through the aqua bridging pathway may be considered to be zero. Therefore, in the fitting, we did not consider the coupling interaction through the water bridging pathway, and rather, for magnetic study, the compound was considered as a 1D coordination chain.

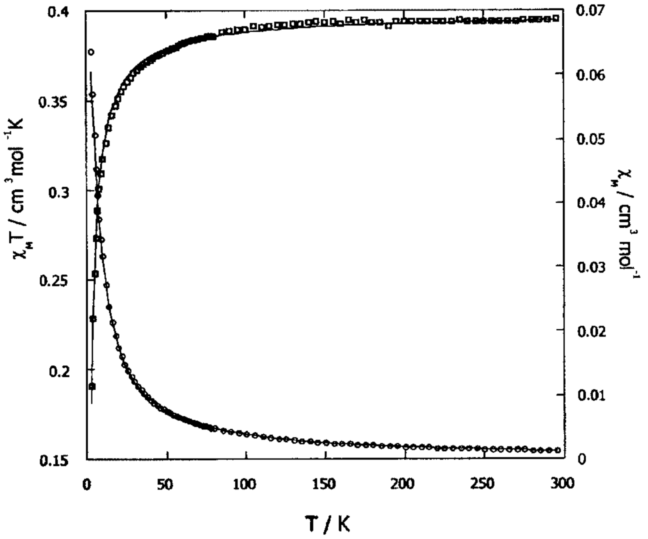


Figure 6. Plot of $\chi_M T$ vs. T (squares) and χ_M vs. T (circles) data; solid lines show the best fit obtained considering a uniform chain of $S = 1/2$ local spin states

[Cu(L2)(μ-tp)] (2)

The structural analysis reveals a 1D chain with dicarboxylate anions in a different alternating bridging mode. We have considered that an axial−axial bridging terephthalate ion has no influence on magnetic coupling since the unpaired electron on the Cu^{II} atom is not concentrated in axial orbital regions. The $\chi_M T$ vs. T plot shows a gradual decrease in $\chi_M T$ values with decreasing temperature (Figure 7), which indicates the existence of antiferromagnetic interactions within the complex. The $\chi_M T$ vs. T data are fitted using the Bleaney−Bowers formula[29] of the Cu^{II} local spin state. The results of the best fit are $J = -6$ cm^{-1}, $\rho = 0.007$, $g = 2.01$, $R = 1.8 \cdot 10^{-5}$, which are similar to those previously reported for a similar type of bridging tp core.[25]

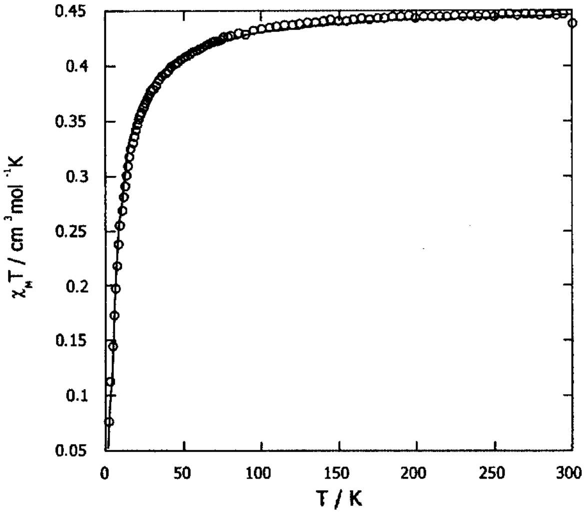


Figure 7. Fitting of $\chi_M T$ vs. T data using the dimeric model of $S = {}^1/_2$ local spins; solid line shows the best fit obtained

Conclusions

This article presents the synthesis, single-crystal structure, and magnetic behavior of two dicarboxylate-bridged metal complexes. Complex **1** is a 3D network of Cu^{II} in which both a fumarate ion and a water molecule function as a bridging ligand. Cu−fumarate zig-zag chains are involved in the bridging by water molecules to form a 3D network. On the other hand, complex **2** is a 1D chain of Cu^{II}−terephthalate in which the dicarboxylate is alternately bridged in a bis(bidentate) and a bis(monodentate) fashion in an axial−axial and equatorial−equatorial mode to form a unique molecule since such an alternate coordination fashion has not been reported earlier for terephthalate systems. Furthermore, the solid-state structure of complex **2** is stabilized by C−H···π interactions. Here, the role of the chemically different dicarboxylates upon the formation of the superstructure is a crucial aspect open to theoretical speculations. Low-temperature magnetic susceptibility data of **1** were fitted to the equation of a chain of $S = {}^{1}/_{2}$ local spins, which reveal the existence of weak antiferromagnetic interactions along the fumarate pathway. In the case of **2**, the variable-temperature magnetic data were fitted to a dimeric formula of $S = {}^{1}/_{2}$ spin state, which indicates a weak antiferromagnetic interaction along the terephthalate pathway.

Experimental Section

Synthesis of Cu(L1)(μ-fum)(μ-H$_2$O)] (1): 1 mmol of *N*,*N*′-dimethylethane-1,2-diamine was slowly added drop by drop to an aqueous solution of $CuCl_2·2H_2O$ (5 mL, 1 mmol, 0.1705 g), resulting in a deep blue solution. An aqueous solution of Na_2−fumarate (10 mL, 1 mmol, 0.160 g) was added with continuous stirring and the stirring continued for 40 min and then filtered. Suitable blue single crystals for X-ray analysis were obtained after 15 d on keeping the deep blue filtrate in a refrigerator. $C_8H_{16}CuN_2O_5$ (283.77): calcd. C 33.80, H 5.63, N 9.86; found C 32.17, H 5.73, N 10.14. IR: ν(COO^-) = 1392, 1562 cm^{-1}; ν(N−H) = 3000 cm^{-1}; ν(O−H) = 3450−3370 cm^{-1}.

Synthesis of [Cu(L2)(μ-tp)] (2): A methanolic solution of a mixture of terephthalic acid (1 mmol) and triethylamine (2 mmol) was layered on a blue aqueous solution of $Cu(ClO_4)_2·6H_2O$ (1 mmol) and *N*-(2-aminoethyl)-3-amino-1-propanol (1 mmol). After a month, a microcrystalline blue complex with suitable single crystals for X-ray diffraction were obtained. The crystals were separated by a needle. $C_{13}H_{18}CuN_2O_5$ (345.83): calcd. C 45.10, H 5.20, N 8.09; found C 44.87, H 5.33, N 9.84. IR: ν(COO^-) = 1372, 1543 cm^{-1}; ν(N−H) = 3050 cm^{-1}; ν(O−H) = 3400−3350 cm^{-1}.

Physical Measurements: IR spectra were recorded with a Nicolet 520 FTIR spectrometer using KBr pellets. Magnetic measurements were carried out on a polycrystalline sample with a SQUID magnetometer operating in the 2−300 K temperature range with an applied field of 5 kOe. Diamagnetic corrections were estimated from Pascal constants.

Crystal Data Collection and Refinement: The data set for **1** and **2** were collected at room temperature using the ω-2θ scan technique with an Enraf−Nonius MACH 3 and a CAD4 Enraf−Nonius single-crystal diffractometer, respectively, equipped with a graphite monochromator and Mo-K_α radiation (λ = 0.71073 Å). Three standard reflections, measured at regular intervals throughout the data collection, showed no noticeable variation in intensity. An absorption correction based on the ψ-scan method was applied (max./min. T = 0.9988/0.8316 for **1** and 0.9971/0.8035 for **2**). The structure was solved by conventional Patterson and Fourier analyses and refined on F^2 by full-matrix anisotropic least-squares method using the SHELXL-97 package.[30] All the calculations were performed using the WinGX System, Ver 1.63.[31] Crystal data and refinement details are given in Table 3. X-ray crystallographic data in CIF format for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. CCDC-236904 and -236905 contain these data, which can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 3. Crystal data and structure refinement for complexes [Cu(L1)(μ-fum)(μ-H$_2$O)] (**1**) and [Cu(L2)(μ-tp)] **(2)**

	1	**2**
Empirical formula	$C_8H_{16}CuN_2O_5$	$C_{13}H_{18}CuN_2O_5$
M	283.77	345.83
T [K]	293(2)	293(2)
Crystal system	orthorhombic	monoclinic
Space group	*Fddd* (choice 2)	$P2_1/n$
a [Å]	9.016(4)	7.437(3)
b [Å]	16.322(6)	9.367(2)
c [Å]	30.908(8)	20.103(5)
β [°]	90.00	94.07(4)
V [Å^3]	4548(4)	1396.8(7)
Z	16	4
$D_{calcd.}$ [g cm^{-1}]	1.685	1.644
μ(Mo-K_α) [mm^{-1}]	1.929	1.587
Reflections collected	4929	4307
Unique reflections	1316	3976
R(int)[a]	0.0689	0.0638
$R1$	0.0322	0.0633
$wR2$	0.0720	0.1709
GOF	1.016	1.207
Residuals [e·Å^{-3}]	0.281/−0.427	1.483/−0.742

[a] $R = ||F_o| - |F_c||/|F_o|$; $Rw = \{[w(F_o^2 - F_c^2)^2]/[w(F_o^2)^2]\}^{1/2}$.

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[1] D. Braga, F. Grepioni, A. G. Orpen, *Crystal Engineering: From Molecules and Crystals to Materials*, NATO Science Series, Mathematical and Physical Sciences, vol. 538, Kluwer Academic Publishers, Dordrecht, The Netherlands, **1999**.

[2] R. K. Seddon, M. Zaworotko, *Crystal Engineering: The Design and Application of Functional Solids*, NATO Science Series,

Mathematical and Physical Sciences, vol. 539, Kluwer Academic Publishers, Dordrecht, The Netherlands, **1999**.

[3] G. R. Desiraju, *Crystal Engineering: The Design of Organic Solids*, Elsevier Science Publishers, Amsterdam, The Netherlands, **1989**.

[4] D. N. Chin, J. A. Zerkowski, J. C. MacDonald, G. M. Whitesides, *Organized Molecular Assemblies in the Solid State*, John Wiley and Sons, New York, **1999**, pp. 185−253.

[5] M. Fujita, *Molecular Self-Assembly − Organic versus Inorganic Approaches*, Structure and Bonding, vol. 96, Springer-Verlag, Berlin, Heidelberg, Germany, **2000**.

[6] J. M. Lehn, *Supramolecular Chemistry − Concepts and Perspectives*, VCH, Weinheim, Germany, **1995**.

[7] [7a] I. G. Dance, in: *The Crystals as a Supramolecular Entity* (Ed.: G. R. Desiraju), John Wiley, NewYork, **1996**. [7b]D. J. Hill, M. J. Mio, R. B. Prince, T. S. Hughes, J. S. Moore, *Chem. Rev.* **2001**, *101*, 3893. [7c] D. Ghoshal, T. K. Maji, G. Mostafa, T. H. Lu, N. Ray Chaudhuri, *Cryst. Growth Des.* **2003**, *3*, 9. [7d] A. K. Ghosh, D. Ghoshal, T. H. Lu, G. Mostafa, N. Ray Chaudhuri, *Cryst. Growth Des.* **2004**, *4*, 851. [7e] D. Ghoshal, T. K. Maji, G. Mostafa, S. Sain, J. Ribas, E. Zangrando, T. H. Lu, N. Ray Chaudhuri, *Dalton Trans.* **2004**, 1687.

[8] [8a] S. Palacin, D. N. Chin, E. E. Simanek, J. C. MacDonald, G. M. Whitesides, M. T. McBride, G. T. R. Palmore, *J. Am. Chem. Soc.* **1997**, *119*, 11807. [8b] K. E. Schwiebert, D. N. Chin, J. C. MacDonald, G. M. Whitesides, *J. Am. Chem. Soc.* **1996**, *118*, 4018.

[9] Y. L. Chang, M. A. West, F. W. Fowler, J. W. Lauher, *J. Am. Chem. Soc.* **1993**, *115*, 5991.

[10] S. L. James, *Chem. Soc., Rev.* **2003**, *32*, 276.

[11] B. Moulton, M. J. Zaworotko, *Chem. Rev.* **2001**, *101*, 1629.

[12] C. K. Kuehl, F. M. Tabellion, A. M. Arif, P. J. Stang, *Organometallics* **2001**, *20*, 1956.

[13] S. S. Kuduva, D. Bläser, R. Boese, G. R. Desiraju, *J. Org. Chem.* **2001**, *66*, 1621.

[14] R. H. Groeneman, L. R. MacGillivray, J. L. Atwood, *Chem. Commun.* **1998**, 2735.

[15] K. T. Holman, A. M. Pivotar, J. A. Swift, M. D. Ward, *Acc. Chem. Res.* **2001**, *34*, 107.

[16] T. J. Prior, M. J. Rosseinsky, *Chem. Commun.* **2001**, 495.

[17] [17a] M. Eddaoudi, H. Li, O. M. Yaghi, *J. Am. Chem. Soc.* **2000**, *122*, 1391. [17b] M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keeffe, O. M. Yaghi, *Acc. Chem. Res.* **2001**, *34*, 319.

[18] T. M. Reineke, M. Eddaoudi, M. Fehr, D. Kelley, O. M. Yaghi, *J. Am. Chem. Soc.* **1999**, *121*, 1651.

[19] S. S.-Y. Chui, S. M.-F. Lo, J. P. H. Charmant, A. G. Orpen, I. D. Williams, *Science* **1999**, *283*, 1148.

[20] P. S. Mukherjee, T. K. Maji, G. Mostafa, T. Mallah, N. Ray Chaudhuri, *Inorg. Chem.* **2000**, *39*, 5147.

[21] P. S. Mukherjee, S. Dalai, G. Mostafa, E. Zangrando, G. Rogez, T. Mallah, N. Ray Chaudhuri, *Chem. Commun.* **2001**, 1346.

[22] P. Charpin, G. Chevrier, M. Lance, D. Vigner, *Acta Crystallogr., Sect. C* **1987**, *43*, 216.

[23] C. E. Xanthopoulos, M. P. Sigalas, G. A. Katsoulos, C. A. Tsipis, A. Terzis, A. Hountas, *Inorg. Chim. Acta* **1993**, *214*, 153.

[24] P. Chaudhuri, K. Oder, K. Wieghardt, S. Gehring, W. Haase, B. Nuber, J. Weiss, *J. Am. Chem. Soc.* **1988**, *110*, 3657.

[25] E. G. Bakalbassis, A. P. Bozopoulos, J. Mrozinski, P. J. Rentzeperis, C. A. Tsipis, *Inorg. Chem.* **1988**, *27*, 529.

[26] E. Bakalbassis, C. Tsipis, A. Bozopoulos, W. Dreissig, H. Hartl, J. Mrozinski, *Inorg. Chim. Acta* **1991**, *186*, 113.

[27] M. Verdaguer, J. Gouteron, S. Jeannin, Y. Jeannin, O. Kahn, *Inorg. Chem.* **1984**, *23*, 4291.

[28] J. Cano, G. De Munno, J. L. Sanz, R. Ruiz, J. Faus, F. Lloret, M. Julve, A. Caneschi, *J. Chem. Soc., Dalton Trans.* **1997**, 1915.

[29] [29a] B. Bleaney, K. D. Bowers, *Proc. R. Soc., London, Ser. A* **1952**, *214*, 415. [29b] O. Kahn, *Molecular Magnetism*, VCH, Heidelberg, **1993**.

[30] G. M. Sheldrick, *SHELXL 97, Program for the Solution of Crystal Structure*, University of Göttingen, Germany, **1997**.

[31] WinGX − A Windows Program for Crystal Structure Analysis: L. J. Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 837.

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