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3D Hydrogen-Bonded Network Built from Copper(II) Complexes of 1,3-Propanediamine

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A reação entre $Cu(NO_3)_2.3H_2O$ e 1,3-propanodiamina (pn), na presença de NaN_3, conduziu à obtenção de um co-cristal 1:1 formado por $[Cu(NO_3)_2(pn)_2]$ e $[Cu(N_3)(NO_3)(pn)_2]$ (**1** e **2**), os quais foram caracterizados por análise elementar, espectroscopia no IV e difração de raios X por monocristal. Em ambos os compostos, os átomos de cobre(II) encontram-se em um ambiente octaédrico distorcido, com quatro ligações no plano basal formadas por quatro átomos de N de dois ligantes pn bidentados enquanto que as ligações axiais são formadas por dois átomos de O do ligante nitrato em **1** e por um átomo de O do ligante nitrato e um átomo de N do íon azida em **2**. A estrutura cristalina consiste em dois complexos (**1** e **2**) cristalograficamente independentes, que se unem por uma série de ligações de hidrogênio do tipo N–H···O e N–H···N bem como interações por C–H···O. Novos *synthons* supramoleculares foram identificados pela ocorrência de dois modos geometricamente distintos de reconhecimento molecular envolvendo o íon NO_3^- e grupos amino dos ligantes pn.

The reaction of $Cu(NO_3)_2.3H_2O$ with 1,3-propanediamine (pn), in the presence of NaN_3, afforded a 1:1 co-crystal formed by $[Cu(NO_3)_2(pn)_2]$ and $[Cu(N_3)(NO_3)(pn)_2]$ (**1** and **2**), which were characterized by elemental analysis, IR spectroscopy and single crystal X-ray diffraction. In both compounds, the copper(II) centers are in a distorted octahedral environment, formed by four N atoms of two bidentate pn ligands in the basal plane, whereas the axial bonds are formed by two O atoms from the nitrate ligands in **1** and one O atom from the nitrate ligand and one N atom from the azide ion in **2**. The asymmetric unit of the crystal consists of two crystallographically independent **1** and **2** complexes, which are held together in a 3D network by a series of N–H···O and N–H···N hydrogen bonds, as well C–H···O interactions. New supramolecular synthons are identified by the occurrence of two geometrically distinct molecular recognition patterns involving the NO_3^- ion and amino groups from pn ligands.

Keywords: copper(II) complexes, hydrogen bonds, supramolecular chemistry

Introduction

Much attention has been devoted to the investigation of transition metal-based supramolecular frameworks due to theoretical and challenging aspects in controlling the self-assembly processes, as well the potential uses of such materials in sensing, gas adsorption, magnetic devices, molecular electronics, porous and nanosized materials.[1] Among the non-covalent interactions, which play a significant role in the molecular self-recognition of the components, within the crystal, the hydrogen bonding is the most important interaction type, since it combines directionality with strength.[2] Within this context, a large number of well-ordered architectures has been successfully built up by assembling discrete coordination compounds via hydrogen bonding motifs.[3]

In our recent works,[4] we have obtained a series of multidimensional supramolecular systems based on the self-assembly of discrete $[Pd(SCN)_2(3,5\text{-dimethylpyrazole})_2]$, and $[M(NCS)_2(pyrazole)_4]$ (M = Co, Ni) by means of intermolecular hydrogen bonds, type N–H···NCS-Pd and N–H···SCN-M, respectively.

As part of our ongoing investigations on the coordination and supramolecular chemistry of metal pseudohalides complexes,[4,5] we report herein the

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preparation and crystallographic studies on the co-crystal of $[Cu(NO_3)_2(pn)_2]$ $[Cu(N_3)(NO_3)(pn)_2]$.

Experimental

Synthesis of $[Cu(NO_3)_2(pn)_2][Cu(N_3)(NO_3)(pn)_2]$

To a solution of $Cu(NO_3)_2.3H_2O$ (0.29 g, 1.20 mmol) in ethanol (6.0 cm^3) was added 1,3-propanediamine (0.23 cm^3, 2.76 mmol), followed by dropwise addition of an aqueous solution of NaN_3 (0.16 g, 2.43 mmol). The obtained deep blue solution was stirred for 30 min and then kept at 4 °C. After five days, blue crystals suitable for X-ray analysis were collected. Yield: 40%. The results of C, H, N and Cu elemental analysis were in agreement with the formula. (Calc. for $C_{12}H_{40}N_{14}Cu_2O_9$: C, 22.12; H, 6.19; N, 30.09; Cu, 19.50%, Found: C, 21.94; H, 6.49; N, 29.89; Cu, 19.45).

Instrumentation

The IR spectrum of the co-crystal was recorded as KBr pellets on a Nicolet IMPACT 400 spectrophotometer in the 4000-400 cm^{-1} wavelength range, at a resolution of 4 cm^{-1}. C, H, and N analysis were carried out with a CE Instruments EA1110 CHNS-O microanalyzer. The Cu content was determined following the literature procedure.[6]

Crystal structure determination

The data collections for a single crystal were carried out on an Enraf Nonius CAD4 diffractometer, using graphite monochromated MoK_α (λ = 0.71073Å) radiation. Twenty five reflections (12.41 < θ < 18.06) were used to determine the cell parameters, at room temperature. During the data collection 3 standard reflections were used with no significant decay. Intensities were corrected by absorption factors [$\mu(MoK_\alpha)$ = 1.643 mm^{-1}] using the PSISCAN method.[7] Information concerning crystallographic data collection and refinement of the structure are given in Table 1. The structures were solved using the WinGX system[8] by SIR92,[9] and refined by full matrix least squares and difference Fourier synthesis using SHEL97.[10] The final residual electronic density, is located around the copper atom. The hydrogen atoms were located in their ideal positions and not refined, with the thermal vibration parameters equal to 1.3 times the isotropic equivalent U of the attached atom. All non-hydrogen atoms were refined anisotropically. The structural analysis was performed by PLATON system.[11]

Results and Discussion

During our attempts to synthesize new Cu^{II} azido-complexes from the reaction between copper(II) nitrate and 1,3-propanediamine (pn) with two equivalents of NaN_3, in an ethanol:water mixture, we have obtained

Table 1. Summary of data collection and refinement conditions

	$[Cu(NO_3)_2(pn)_2]$ $[Cu(NO_3)(N_3)(pn)_2]$
Empirical formula	$C_6H_{20}CuN_6O_6$, $C_6H_{20}CuN_8O_3$
Molecular weight	651.68
Temperature/ K	293
K_α Mo, λ/ Å	0.71073
Crystal system	monoclinic
Space Group	$P2_1/n$
a/Å	8.4624(8)
b/Å	10.7404(12)
c/Å	29.7142(34)
β/ (°)	91.636(9)
Volume/ Å^3; Z	2699(2); 4
D_c / (Mg m^{-3})	1.603
μ /mm^{-1}	1.643
F (000)	1360
Crystal size/ mm	0.225 × 0.350 × 0.500
θ range/ (°)	2.5, 25.2
hk*l*(min:max.)	10:10; 0:12; 0: 35
Reflections collected; unique; R_{int}	4891; 4796; 0.033
Reflections observed (I >2σ(I))	3845
Refinement method	Full-matrix least-squares on F2
NPAR	334
Speed scan(°/min) (min:max.)	2.74: 16.48
R; wR_2; S	0.0321, 0.0872, 1.05
Largest diff. peak and hole/ (e Å^{-3})	0.522; -0.391

physical and analytical evidences of the formation of an unusual compound. Repeated elemental analysis results of the sample were consistent with a $C_{12}H_{40}N_{14}Cu_2O_9$ formulation. The X-ray structural determination of this species was undertaken in order to get a better knowledge of its structure.

X-ray crystallographic studies

The co-crystallization of two different monomeric compounds in the asymmetric unit, $[Cu(NO_3)_2(pn)_2]$ (**1**) and $[Cu(N_3)(NO_3)(pn)_2]$ (**2**), was definitely proved by the crystal and molecular structure X-ray analysis, corroborating the important structural features suggested by IR spectroscopy.

The molecular structures of the complexes $[Cu(NO_3)_2(pn)_2]$ (**1**) and $[Cu(N_3)(NO_3)(pn)_2]$ (**2**), together with the crystallographic labeling scheme, are shown in Figures 1 and 2, respectively. Selected bond lengths and angles with their estimated standard deviations in parentheses are listed in Table 2 and 3, respectively.

In both compounds, the metal ion exhibits an elongated and distorted *trans*-octahedral geometry. The coordination polyhedron is defined by four nitrogen atoms at the equatorial plane from two chelating 1,3-propanediamine ligands: N1, N2, N3 and N4 at Cu1, for complex **1** and N1a, N2a, N3a and N4a at Cu2, for **2**, with average Cu-N distances of 2.023(2) and 2.031(2) Å, respectively. The six-membered chelate rings formed by 1,3-propanediamine adopt the expected chair conformation. The atoms that constitute the basal plane do not deviate significantly from planarity, with the largest deviations being -0.133(3) Å for N1 and N3 and 0.137(2) Å and 0.129(2) Å for N2 and N4 respectively. The Cu1 and Cu2 ions are displaced from the basal planes by -0.1232(3) Å and 0.1657(3) Å, respectively. The axial positions of **1** are occupied by the O5 and O3 atoms of the monodentate nitrate (Cu1-O3 = 2.927(3) and Cu1-O5 = 2.458(3) Å) and, for the compound **2**, they are

Table 2. Selected bond lengths (Å) for the co-crystal

Cu1	O3	2.927(3)	Cu2	O9	2.990(4)	N1	C1	1.464(4)
Cu1	O5	2.458 (3)	Cu2	N1A	2.020(2)	N2	C3	1.478(4)
Cu1	N1	2.019(2)	Cu2	N2A	2.035(2)	N3	C4	1.466(3)
Cu1	N2	2.031(2)	Cu2	N3A	2.040(2)	N4	C6	1.468(4)
Cu1	N3	2.007(2)	Cu2	N4A	2.028(2)	N1A	C1A	1.467(4)
Cu1	N4	2.036(2)	Cu2	N5A	2.333(2)	N2A	C3A	1.477(3)
O1	N5	1.248(3)	O6	N6	1.219(3)	N3A	C4A	1.477(3)
O2	N5	1.239(3)	O7	N7	1.252(3)	N4A	C6A	1.479(3)
O3	N5	1.232(3)	O8	N7	1.199(4)	N5A	N6A	1.171(3)
O4	N6	1.224(4)	O9	N7	1.196(4)	N6A	N7A	1.169(3)
O5	N6	1.243(3)						

Table 3. Selected angles (°) for the co-crystal

O3	Cu1	O5	163.64(7)	N1A	Cu2	N4A	169.44(8)
O3	Cu1	N1	81.44(7)	N1A	Cu2	N5A	95.59(8)
O3	Cu1	N2	73.62(7)	N2A	Cu2	N3A	171.50(8)
O3	Cu1	N3	84.72(8)	N2A	Cu2	N4A	91.47(8)
O3	Cu1	N4	107.01(8)	N2A	Cu2	N5A	91.88(8)
O5	Cu1	N1	82.68(8)	N1A	Cu2	N2A	86.46(8)
O5	Cu1	N2	102.34(8)	N1A	Cu2	N3A	90.27(8)
O5	Cu1	N3	111.37(8)	N4A	Cu2	N5A	94.83(8)
O5	Cu1	N4	78.10(9)	N3A	Cu2	N4A	90.32(9)
N1	Cu1	N2	89.42(8)	N3A	Cu2	N5A	96.26(8)
N1	Cu1	N3	165.62(8)	Cu2	N1A	C1A	116.1(2)
N1	Cu1	N4	94.38(9)	Cu2	N2A	C3A	115.6(2)
N2	Cu1	N3	90.43(8)	Cu2	N3A	C4A	118.6(2)
N2	Cu1	N4	176.20(9)	Cu2	N4A	C6A	118.8(2)
N3	Cu1	N4	85.91(9)	Cu2	N5A	C6A	112.2(2)
Cu1	O3	N5	126.6(2)	O1	N5	O2	119.8(2)
Cu1	O5	N6	115.3(2)	O1	N5	O3	119.5(2)
Cu1	N1	C1	119.6(2)	O2	N5	O3	120.7(2)
Cu1	N2	C3	120.0(2)	O4	N6	O5	117.3(2)
Cu1	N3	C4	115.7 (2)	O4	N6	O6	123.6(3)
Cu1	N4	C6	117.1(2)	O5	N6	O6	119.1(2)
N5A	N6A	N7A	178.5(2)	O8	N7	O9	125.9(3)
O7	N7	O9	114.4 (3)	O7	N7	O8	119.7(3)

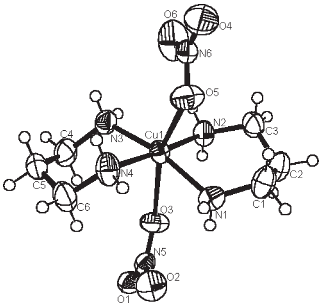


Figure 1. The ORTEP representation of the molecular structure with labeling scheme for $[Cu(NO_3)_2(pn)_2]$ **1**. Ellipsoids are shown at 50% probability level.

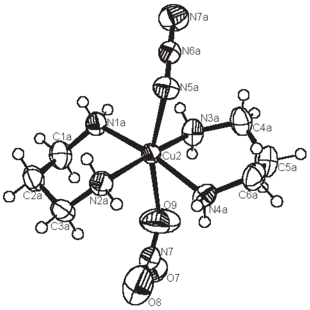


Figure 2. The ORTEP representation of the molecular structure with labeling scheme for $[Cu(N_3)(NO_3)(pn)_2]$ **2**. Ellipsoids are shown at 50% probability level.

occupied by the N5a atom of the terminal azide and O9 of the other monodentate nitrate (Cu2-N5a = 2.333(2) and Cu2-O9 = 2.990(4) Å).

The average Cu-N(pn) distances of 2.023(2) (**1**) and 2.031(2) Å (**2**) are comparable with those found[12] for $[Cu(NO_3)_2(dmpn)_2]$ (dmpn = bis(1,3-diamino-2,2-dimethylpropane), 2.018 Å and slightly longer than the values found[13] for $[Cu_2(N_3)_4(pn)_2]$, 2.000 Å. The Cu-N(azido) length of compound **2** of 2.333(2) Å is significantly longer than those found[14] for $[Cu(N_3)(NCO)(tmen)]_2$ (tmen = *N,N,N´,N´*-tetramethylethylenediamine), 2.000(1) Å; $[Cu(N_3)(L)_4]ClO_4$ (L = β-collidine)[15], 2.141(6) Å; but comparable with the axial Cu-N(azide) bond distances found[16] for $[Cu(N_3)_2(diEten)]_2$ (diEten = *N,N,*-diethylethylenediamine), 2.333(3) Å and $[Cu(N_3)_2(tmen)]_n$, 2.346(3) Å.[14] The azide group is essentially linear (N5a-N6a-N7a = 178.5(2)º).

In compound **1**, the two axial Cu-O bond distances are very different from each other: Cu1-O3 = 2.927(3) Å and Cu1-O5 = 2.458(3) Å. The former apical Cu-O bond distances for **1** as well that found for **2** (Cu2-O9 = 2.990(4) Å) indicated the existence of very weak covalent interactions between one of the oxygen atom from the nitrate and Cu(II) ion. Despite the fact that these bond lengths are slightly longer than the sum of van der Waals radii of copper and oxygen (2.90 Å), Cu-O values within the range of 2.5-3.0 Å have been considered as long coordination distances for copper(II) complexes.[17] For instance, Valdéz-Martinez *et al.*[18] considered the coordination of the NO_3^- groups at the axial positions of $[Cu(NO_3)_2(MeTSC)_2]$, which exhibited Cu-O bond length of 2.864(3) Å. Copper-oxygen bond of 2.906(7) Å was also considered significant in the molecular structure of $[Cu(NO_3)_2(py)_2]_2 \cdot py$ (py = pyridine).[19] Anyway, if one takes into account that Cu1-O3 and Cu2-O9 are non-bonding distances, the metal coordination polyhedron in **1** and **2** could alternatively be described as distorted square pyramidal.

The azide and nitrate groups participate in a series of hydrogen bonds which are responsible for the stabilization of the crystal structure. Table 4 lists the distances and angles of hydrogen bonds and C–H···O interactions in the co-crystal.

Table 4. Hydrogen bonds distances and angles for the co-crystal (Å, °)

D–H····A	D–H/ Å	H····A/ Å	D····A/ Å	D–H····A/ (°)
N1 – H1N1··· N7A	0.90	2.30	3.17(4)	166
N1 – H2N1··· N7A[a]	0.90	2.61	3.33(4)	138
N2 – H2N2··· O1[b]	0.90	2.14	3.00(3)	161
N4A – H1A4··· O7[c]	0.90	2.22	3.07(4)	159
N4A – H2A4··· O4[d]	0.90	2.28	3.02(4)	139
N2A – H1A2··· O7[c]	0.90	2.58	3.32(4)	140
N2A – H2A2··· O1[a]	0.90	2.24	3.09(3)	159
N2 – H1N3··· O7	0.90	2.14	3.02(4)	166
N3 – H2N3··· O1[b]	0.90	2.57	3.39(3)	152
N3 – H2N3··· O3[b]	0.90	2.36	3.19(4)	154
N3A – H1A3··· O9[d]	0.90	2.25	2.92(4)	130
N1A – H11A··· O2[a]	0.90	2.44	3.33(4)	169
N3A – H2A3··· O5	0.90	2.47	3.33(4)	160
N4 – H1N4··· N7A	0.90	2.07	2.97(4)	178
N4 – H2N4··· O8	0.90	2.57	3.46(5)	171
N1A – H21A··· O5	0.90	2.27	3.16(4)	168
C4A – H2B4··· O8	0.97	2.53	3.28(5)	134
C1 – H1C1··· O2[a]	0.97	2.51	3.12(4)	120

Symmetry code: a = -1-x,-y,1-z; b = 1-x,-1-y,1-z; c = x,1+y,z; d = 3/2-x,1/2+y,-z;

As can be observed in Figure 3, each molecule of $[Cu(NO_3)_2(pn)_2]$ (**1**) and $[Cu(N_3)(NO_3)(pn)_2]$ (**2**) of the asymmetric unit are assembled by N–H···O and N–H···N intermolecular hydrogen bonds. One oxygen atom from the NO_3^- group of **1** takes part in two hydrogen bonds with two amino groups from distinct pn ligands of **2**, leading to the formation of R_2^1 (6) rings (N1a···O5 = 3.16(4) Å, N3a···O5 = 3.33(4) Å). Similarly, the N1 and N4 atoms from 1,3-propanediamine ligands in **1** form two hydrogen bonds with N7a atom from the N_3^- group of **2**, affording the hydrogen-bond pattern R_2^1 (6).

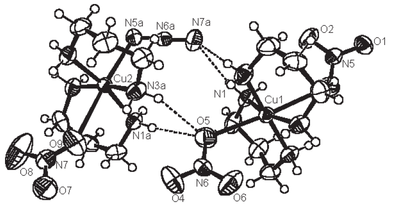


Figure 3. Packing view of the asymmetric unit of the co-crystal $[Cu(NO_3)_2(pn)_2][Cu(NO_3)(N_3)(pn)_2]$.

The association of $[Cu(NO_3)_2(pn)_2]$ molecules *via* N–H···O intermolecular hydrogen bonds (Figure 4) is also noticed. The hydrogen-bonding motif $R_2^2(8)$ is formed by the O1* and O3* atoms from the NO_3^- group of a monomer involved in two hydrogen bonds with H2(N2) and H2(N3), respectively, from pn ligands of the adjacent monomer and *vice-versa* (N2···O1* = 3.00(3) Å, N3···O3* = 3.19(4)). These molecules are also connected by bifurcated hydrogen bonds between O1* and O3* and H2(N3) atoms.

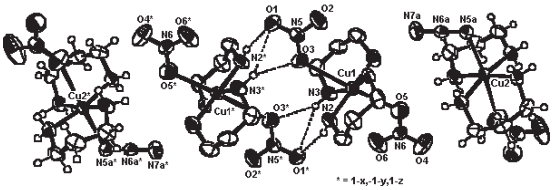


Figure 4. ORTEP representation of two molecules of **1** and **2** showing N–H···O intermolecular hydrogen bonds.

Hydrogen bonding motifs of the type $R_2^2(8)$ are also present in the assembly of $[Cu(NO_3)_2(pn)_2]$ (**1**) and $[Cu(N_3)(NO_3)(pn)_2]$ (**2**) molecules (Figure 5). The O1 and O2 atoms from a nitrate group of **1** take part in two intermolecular hydrogen bonds between H2(N2a*) and H1(N1*a) atoms, respectively, of two pn ligands of a neighboring molecule of **2** (N2a*···O1 = 3.09(3) Å, N1a*···O2 = 3.33(4)). In addition, monomers of **1** are connected by intermolecular contacts of the type C1*–H1···O2 (C1*···O2 = 3.12(4) Å, C1*–H···O2 = 120°).

These intermolecular forces are responsible for the self-assembly of the 1D chains of **1** and **2** into a three-dimensional supramolecular network, which is illustrated in Figure 6.

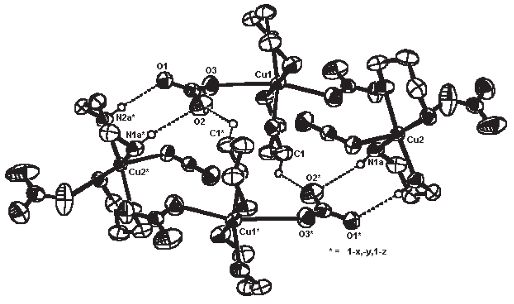


Figure 5. ORTEP representation of four molecules of **1** and **2** showing N–H···O intermolecular hydrogen bonds and C–H···O interactions.

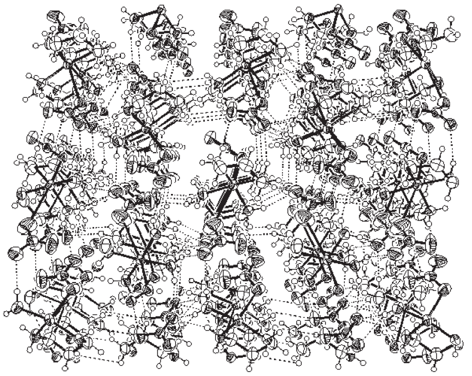
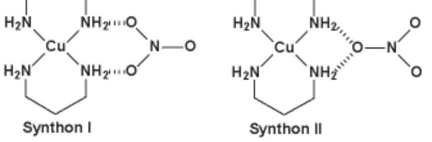


Figure 6. Perspective view of the 3D supramolecular network in the co-crystal.

From the crystal engineering point of view, the crystal structure described in this paper clearly demonstrated two geometrically distinct supramolecular synthons (synthons I and II) which are generated from the molecular recognition between the hydrogen bond donating NH_2 groups from chelating 1,3-propanediamine ligands and HB-accepting site of nitrate group (Scheme 1).



Scheme 1.

IR spectroscopy

The IR spectrum of the co-crystal $[Cu(NO_3)_2(pn)_2]$ and $[Cu(N_3)(NO_3)(pn)_2]$ (**1** and **2**) displayed a number of absorption bands attributed to vibrational modes of 1,3-propanediamine at 3262 cm^{-1} ($\nu_{as}NH_2$), 3157 cm^{-1} ($\nu_s NH_2$) and 1580 cm^{-1} (δNH_2). However, the main interest in IR spectrum of the compounds **1**-**2** lies in the bands associated with the vibrational modes of N_3 and NO_3^- groups as they can be very useful for the diagnosis of their coordination mode. The first feature of the IR spectrum of the co-crystal was the occurrence of a strong band at 2032 cm^{-1} assigned to $\nu_{ass}N_3$ and indicative of azide group terminally coordinated to the copper atom.[17] The presence of the nitrate group is evidenced by the appearance of a strong and narrow band at 1383 cm^{-1} (νONO).

Conclusions

In this work, we describe the X-ray structural characterization of an unusual 1:1 co-crystal of $[Cu(NO_3)_2(pn)_2]$ (**1**) and $[Cu(N_3)(NO_3)(pn)_2]$ (**2**). The crystal structure consists of 1D hydrogen-bonded chains of **1** and **2** which are interconnected by N–H···O and N–H···N hydrogen bonds and C–H···O contacts to yield a three-dimensional supramolecular array.

In the context of supramolecular chemistry and crystal engineering of the transition metal-based species, it is of vital importance to identify and understand the role played by new inorganic supramolecular synthons in the molecular aggregation within the crystal since they can be important tools in the rational construction of well-ordered structures. A systematic work on the creation of novel supramolecular architectures is currently underway in our laboratory.

Acknowledgments

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Supplementary Information

Additional materials, consisting of atomic coordinates and equivalent isotropic displacement parameters for nonhydrogen atoms, H-atom coordinates and isotropic displacement parameters, bond lengths and interbond angles have been deposited with the Cambridge Crystallographic Data Centre, CCDC, No. CCDC **276281**. Copies of available material can be obtained on application to CCDC, 12, Union Road, Cambridge CB2 IEZ, UK (fax 44-1223-336033 or e-mail:deposit@ccdc.cam.ac.uk).

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