

Metal-organic frameworks from chiral square-pyramidal copper(II) complexes: Enantiospecific inclusion and perfectly polar alignment of guest and host molecules

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Abstract

The physical properties of $[\text{CuL}_2(\text{H}_2\text{O})]$ (**1**) and $[\text{CuL}'_2(\text{H}_2\text{O})]$ (**2**) and preparation and crystal structures of the inclusion compounds $\mathbf{1} \cdot (P)\text{-C}_2\text{H}_4\text{Br}_2$, $\mathbf{2} \cdot (M)\text{-C}_2\text{H}_4\text{Br}_2$, $\mathbf{1} \cdot \text{CH}_3\text{CN}$ and $\mathbf{2} \cdot \text{CH}_3\text{CN}$ are described. HL^1 and HL^2 (H represents the dissociable phenolic proton) are the N,O-donor chiral reduced Schiff bases *N*-(2-hydroxy-5-nitrobenzyl)-(*R*)- α -methylbenzylamine and *N*-(2-hydroxy-5-nitrobenzyl)-(*S*)- α -methylbenzylamine, respectively. All the compounds crystallize in the non-centrosymmetric space group *C*2. In the crystal lattice, the host $[\text{CuL}_2(\text{H}_2\text{O})]$ (**1** and **2**) molecules connected by O–H \cdots O and C–H \cdots O interactions form perfectly polar two-dimensional networks. In these chiral and polar host frameworks, enantiospecific inclusion with polar ordering of the right-handed (*P*) and the left-handed (*M*) *gauche* form of 1,2-dibromoethane as well as polar alignment of acetonitrile molecules are observed. The host and guest molecules are linked by C–H \cdots O interactions. The O-atoms of the nitro substituent on the ligands of **1** and **2** act as the acceptors in all these intermolecular O–H \cdots O and C–H \cdots O interactions. The structures reported in this work provide rare examples of enantiospecific trapping of the chiral rotamers of 1,2-dibromoethane as well as perfectly polar alignment of both guest and host molecules.

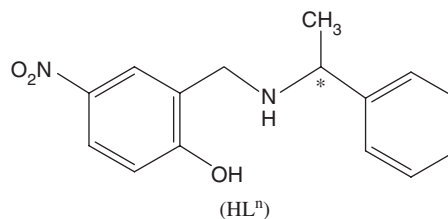
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Keywords: Chiral copper(II) complexes; Host-guest compounds; Crystal structures; Non-covalent interactions; Enantiospecific inclusion; Polar alignment

1. Introduction

Metal-organic frameworks are of immense current interest owing to their potential applications in a variety of research areas which include catalysis, separation science, gas storage, drug delivery, optoelectronics and molecule-based metals and magnets [1–13]. Synthesis of frameworks containing chiral cavities is a noteworthy challenge as these solids can be very useful for enantiospecific separation and catalysis [6–13]. A further challenging task is the generation of frameworks via polar and non-centrosymmetric assembly of host molecules which also can confine and align guest molecules in polar order [14]. Such species are of particular significance for some technologically important physical properties such as ferro-, pyro- or piezoelectricity and nonlinear optical effects

[15,16]. Inclusion of chirality in the molecule is a common strategy for non-centrosymmetric organization in the crystal lattice [17,18]. However, perfectly polar assemblies in the crystal lattice are rare [19–25]. Recently we have reported an enantiomeric pair of square-pyramidal copper(II) complexes, $[\text{CuL}_2(\text{H}_2\text{O})]$ (**1**) and $[\text{CuL}'_2(\text{H}_2\text{O})]$ (**2**) ($\text{HL}^1 = N$ -(2-hydroxy-5-nitrobenzyl)-(*R*)- α -methylbenzylamine and $\text{HL}^2 = N$ -(2-hydroxy-5-nitrobenzyl)-(*S*)- α -methylbenzylamine, H represents the dissociable phenolic proton) [25].



These two complexes crystallize in the non-centrosymmetric space group *C*2 with 1,2-dichloroethane molecules as the

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guest. The structures of $1 \cdot (P)\text{-C}_2\text{H}_4\text{Cl}_2$ and $2 \cdot (M)\text{-C}_2\text{H}_4\text{Cl}_2$ illustrate how the position and orientation of the nitro substituent on the enantiomeric ligands of **1** and **2** participating in the non-covalent interactions lead to not only the perfectly polar alignment of the host molecules but also help in polar and enantiospecific confinement of the right-handed (*P*) and the left-handed (*M*) *gauche* form of 1,2-dichloroethane in the crystal lattice. To examine whether this polar and enantiospecific confinement can be extended to 1,2-dibromoethane and the polar alignment to an achiral guest such as acetonitrile, we have prepared the 1:1 inclusion compounds of **1** and **2** with the said solvent molecules. Herein, we have described the X-ray crystal structures of these inclusion compounds and shown the versatility of the host frameworks formed by **1** and **2** for the enantiospecific trapping and perfectly polar alignment of guest molecules.

2. Experimental

2.1. Materials

The chiral reduced Schiff bases (HL^1 and HL^2) and the corresponding square-pyramidal copper(II) complexes, $[\text{CuL}_2^1(\text{H}_2\text{O})]$ (**1**) and $[\text{CuL}_2^2(\text{H}_2\text{O})]$ (**2**), have been synthesized by following the procedures reported previously [25,26]. The crystals of 1:1 inclusion compounds $1 \cdot \text{C}_2\text{H}_4\text{Br}_2$, $2 \cdot \text{C}_2\text{H}_4\text{Br}_2$, $1 \cdot \text{CH}_3\text{CN}$ and $2 \cdot \text{CH}_3\text{CN}$ were obtained in 90–95% yields by slow evaporation of the solutions of amorphous **1** and **2** in the corresponding solvents in air at room temperature (298 K).

2.2. Physical measurements

Microanalytical (C, H, N) data were obtained with a Thermo Finnigan Flash EA1112 series elemental analyzer.

Solution electrical conductivities were measured with a Digisun DI-909 conductivity meter. Magnetic susceptibilities were measured using a Sherwood Scientific balance. Diamagnetic corrections calculated from Pascal's constants [27] were used to obtain the molar paramagnetic susceptibilities. Infrared spectra were collected by using KBr pellets on a Jasco-5300 FT-IR spectrophotometer. A Shimadzu 3101-PC UV/vis/NIR spectrophotometer was used to record the electronic spectra. EPR spectra were recorded on a Jeol JES-FA200 spectrometer.

2.3. X-ray crystallography

Unit cell parameters and the intensity data for each of the four inclusion crystals were obtained on a Bruker-Nonius SMART APEX CCD single-crystal diffractometer, equipped with a graphite monochromator and a $\text{MoK}\alpha$ fine-focus sealed tube ($\lambda = 0.71073 \text{ \AA}$) operated at 2.0 kW. The detector was placed at a distance of 6.0 cm from the crystal. Data were collected at 298 K with a scan width of 0.3° in ω and an exposure time of 15 s/frame. The θ range of the data collected was $2\text{--}28.3^\circ$. The SMART software was used for data acquisition and the SAINT-Plus software was used for data extraction [28]. The absorption corrections were performed with the help of SADABS program [29]. All the inclusion compounds crystallize in the non-centrosymmetric space group *C2*. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares procedures. In each structure, all the non-hydrogen atoms were refined using anisotropic thermal parameters. The hydrogen atoms of the metal coordinated water molecule and the secondary amine *N*-atoms were located in the corresponding difference maps and refined with fixed O–H distances and H–O–H angles for

Table 1
Crystal and refinement data

	$1 \cdot (P)\text{-C}_2\text{H}_4\text{Br}_2$	$2 \cdot (M)\text{-C}_2\text{H}_4\text{Br}_2$	$1 \cdot \text{CH}_3\text{CN}$	$2 \cdot \text{CH}_3\text{CN}$
Chemical formula	$\text{CuC}_{32}\text{H}_{36}\text{N}_4\text{O}_7\text{Br}_2$	$\text{CuC}_{32}\text{H}_{36}\text{N}_4\text{O}_7\text{Br}_2$	$\text{CuC}_{32}\text{H}_{35}\text{N}_5\text{O}_7$	$\text{CuC}_{32}\text{H}_{35}\text{N}_5\text{O}_7$
Formula weight	812.01	812.01	665.21	665.21
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>C2</i>	<i>C2</i>	<i>C2</i>	<i>C2</i>
<i>a</i> (Å)	20.444(1)	20.441(2)	20.078(2)	20.080(2)
<i>b</i> (Å)	8.1977(6)	8.1984(7)	8.1722(8)	8.1754(8)
<i>c</i> (Å)	13.0089(9)	13.009(1)	12.701(1)	12.702(1)
β (deg.)	129.099(1)	129.104(1)	127.937(1)	127.938(1)
<i>V</i> (Å ³)	1691.9(2)	1691.8(2)	1643.6(3)	1644.5(3)
<i>Z</i>	2	2	2	2
ρ_{calcd} (g cm ⁻³)	1.594	1.594	1.344	1.343
μ (mm ⁻¹)	3.059	3.059	0.717	0.717
Unique reflections	3972	3966	3850	3844
Reflections [$I \geq 2\sigma(I)$]	3458	3595	3403	3633
Data/restraints/parameters	3972/7/218	3966/7/218	3850/2/214	3844/2/214
GOF on F^2	1.046	1.054	1.069	1.062
R_1, wR_2 [$I \geq 2\sigma(I)$]	0.0674, 0.1814	0.0674, 0.1821	0.0486, 0.1057	0.0345, 0.0840
R_1, wR_2 [all data]	0.0766, 0.1907	0.0734, 0.1889	0.0550, 0.1093	0.0365, 0.0853
Flack parameter	0.05(2)	0.04(2)	0.018(14)	0.016(9)
Largest peak and hole (e Å ⁻³)	0.996, -1.722	0.991, -1.731	0.841, -0.232	0.383, -0.308

$1 \cdot \text{C}_2\text{H}_4\text{Br}_2$ and $2 \cdot \text{C}_2\text{H}_4\text{Br}_2$, and fixed N–H distances for $1 \cdot \text{CH}_3\text{CN}$ and $2 \cdot \text{CH}_3\text{CN}$. Except the disordered hydrogen atoms of the acetonitrile methyl group in $1 \cdot \text{CH}_3\text{CN}$ and $2 \cdot \text{CH}_3\text{CN}$, rest of the hydrogen atoms in all the structures were included in the structure factor calculation at idealized positions by using a riding model. The SHELX-97 programs [30] of the WinGX package [31] were used for structure solution and refinement. The ORTEX6a [32] and Platon packages [33] were used for molecular graphics. Significant crystal data for all the inclusion compounds are listed in Table 1.

3. Results and discussion

3.1. Some properties of 1 and 2

Complexes **1** and **2** were synthesized in good yields ($\sim 74\%$) by reacting $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, HL^n ($n = 1$ and 2) and $\text{LiOH} \cdot \text{H}_2\text{O}$ (in 1:2:2 mole ratio) in methanol [25]. The elemental analysis data for **1** and **2** are satisfactory for the general molecular formula $[\text{CuL}_2^2(\text{H}_2\text{O})]$ (Table 2). Both complexes are moderately soluble in common organic solvents, affording electrically non-conducting solutions. The room temperature (298 K) effective magnetic moments (1.88 and $1.87 \mu_{\text{B}}$ for **1** and **2**, respectively) are consistent with an $S = 1/2$ spin state and hence the $+2$ oxidation state of the metal ion in both complexes.

As **1** and **2** are the enantiomeric pair, the infrared as well as the electronic spectroscopic features of them are essentially identical. The broad band observed near 3460 cm^{-1} in the infrared spectra of **1** and **2** is assigned to the metal coordinated water molecule. The N–H stretch appears as a sharp band at $\sim 3270 \text{ cm}^{-1}$. The ν_{asym} and ν_{sym} stretches of the NO_2 group are observed as two strong bands at ~ 1597 and $\sim 1293 \text{ cm}^{-1}$, respectively. Two medium to strong bands near 1564 and 1476 cm^{-1} are possibly due to the C=C stretches from the aromatic fragments of the ligands.

The electronic spectra were collected using chloroform solutions of **1** and **2**. A weak absorption observed at 645 nm is followed by four strong absorptions in the range 377 – 237 nm (Table 2). The weak absorption is attributed to the d-d transition. The occurrence of this absorption in this region is consistent with square-based coordination geometry around the copper(II) center [34–36]. The strong absorptions are in all probability due to ligand-to-metal charge transfer and ligand centered transitions.

Both **1** and **2** in frozen (120 K) chloroform solutions display very similar EPR spectra. The spectral features are typical for an axial spectrum commonly displayed by mononuclear copper(II) complexes having square-based coordination geometry [35,37]. The A_{\parallel} , g_{\parallel} and g_{\perp} values are $\sim 170 \text{ G}$, ~ 2.26 and ~ 2.03 , respectively.

3.2. Description of molecular structures

As observed for the 1:1 inclusion compounds of $[\text{CuL}_2^1(\text{H}_2\text{O})]$ (**1**) and $[\text{CuL}_2^2(\text{H}_2\text{O})]$ (**2**) with 1,2-dichloroethane [25], crystals of analogous inclusion compounds $1 \cdot \text{C}_2\text{H}_4\text{Br}_2$, $2 \cdot \text{C}_2\text{H}_4\text{Br}_2$, $1 \cdot \text{CH}_3\text{CN}$, and $2 \cdot \text{CH}_3\text{CN}$ were readily obtained by slow evaporation of the solutions of **1** and **2** in the respective solvents (1,2-dibromoethane and acetonitrile). All these inclusion compounds crystallize in the same non-centrosymmetric space group $C2$. The host complex molecules (**1** and **2**) are square-pyramidal (Fig. 1). In the N,O-donor reduced Schiff bases, HL^1 and HL^2 , the chiral C-center has absolute configuration R and S , respectively. After complexation with the metal center the N-atom of the deprotonated monoanionic ligand becomes chiral. In **1**, the absolute configuration of the N-center is found to be R while in **2**, it is found to be S . Thus the generation of the new chiral center is homogeneous with respect to the original chiral C-center in both cases. In each complex molecule, two bidentate chelating ligands form the N_2O_2 basal plane and the water O-atom occupies the apical site. The bidentate ligands are related by a crystallographically imposed two-fold axis which happens to be also the molecular dipole axis passing through the metal center

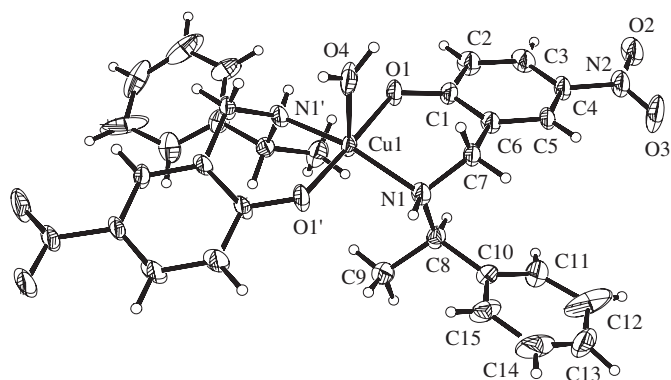


Fig. 1. Molecular structure of $[\text{CuL}_2^1(\text{H}_2\text{O})]$ (**1**). All non-hydrogen atoms are represented by their 35% probability thermal ellipsoids.

Table 2
Elemental analysis^a and electronic spectroscopic^b data

Complex	%C	%H	%N	λ_{max} (nm) ($10^{-3} \times \epsilon$ ($\text{M}^{-1} \text{cm}^{-1}$))
$[\text{CuL}_2^1(\text{H}_2\text{O})]$ (1)	57.84 (57.73)	5.10 (5.17)	8.92 (8.98)	645 ^c (0.19), 377 (22.4), 337 ^c (16.5), 306 ^c (11.5), 237 (13.7)
$[\text{CuL}_2^2(\text{H}_2\text{O})]$ (2)	57.65 (57.73)	5.11 (5.17)	8.87 (8.98)	645 ^c (0.25), 377 (22.5), 337 ^c (16.3), 306 ^c (11.3), 237 (14.0)

^aThe calculated values are in parentheses.

^bIn chloroform.

^cShoulder.

and the apical water O-atom. Both Cu- and O-atom are at special positions on the *b*-axis. In none of the structures, the N₂O₂ basal plane is exactly planar. The dihedral angle between the planes defined by Cu, N1, and O1 and Cu, N1' and O1' is in the range 8.76(5)–18.97(5)°. These values indicate a tetrahedral distortion of the N₂O₂ basal plane around the metal center due to twisting of the two bidentate chelating ligands. It is interesting to note that in the case of **1**, the ligands show the right-handed (Δ or *P*) helicity, while in the case of **2**, the ligands exhibit left-handed (Λ or *M*) helicity. Perhaps the configurations of the C- and the N-centers of the ligands in **1** (*R,R*) and **2** (*S,S*) lead to the opposite helicity of the CuN₂O₂ fragments [26]. In all the structures, the bond parameters associated with the copper centers are consistent with the +2 oxidation state of the metal ion [25,38–40]. The intraligand bond parameters are comparable with those reported for structures of complexes with reduced Schiff bases [25,26,38–41].

The asymmetric units of **1**·C₂H₄Br₂ and **2**·C₂H₄Br₂ contain one-half of the guest 1,2-dibromoethane molecule. In each case, the other half of the chiral *gauche* form of 1,2-dibromoethane can be generated by rotation about a two-fold axis passing through the mid-point of the C–C bond. This two-fold axis is the molecular dipole axis of 1,2-dibromoethane. The Br–C–C–Br torsion angles are 54.1° and 52.7° in **1**·C₂H₄Br₂ and **2**·C₂H₄Br₂, respectively. The 1,2-dibromoethane is in right handed or *P*-form in **1**·C₂H₄Br₂ and in left handed or *M*-form in **2**·C₂H₄Br₂ (Fig. 2). Before we reported the structures of **1**·(*P*)-C₂H₄Cl₂ and **2**·(*M*)-C₂H₄Cl₂ [25] there was only one report on the inclusion crystal of a nearly eclipsed (Cl–C–C–Cl torsion angle is 36°) chiral 1,2-dichloroethane with a chiral (*S*) organic host [42]. Cambridge crystallographic database (version 5.27) search reveals there are only eight structures with 1,2-dibromoethane as the guest molecule in the crystal lattice. In five of these structures, either the guest molecule is disordered or the atomic coordinates are not available. In two structures, the molecule is *trans* or *anti* and two halves of the molecule are related by an inversion center (Br–C–C–Br torsion angle is 180°) [43,44]. The third structure contains both *trans* or

anti (Br–C–C–Br torsion angle is 179.3°) and nearly eclipsed (Br–C–C–Br torsion angle is 20.9°) forms of 1,2-dibromoethane [45]. All the three structures are in centrosymmetric space groups. Thus the structures of **1**·(*P*)-C₂H₄Br₂ and **2**·(*M*)-C₂H₄Br₂ provide the first examples of enantiospecific isolation of chiral rotamers of 1,2-dibromoethane. In the cases of **1**·CH₃CN and **2**·CH₃CN, the *N*- and the two C-atoms of CH₃CN lie on the two-fold axis. This model requires that the methyl group hydrogen atoms be disordered.

3.3. Crystal packing and non-covalent interactions

In the crystal lattice of each structure, the host copper(II) complex molecules, as well as the guest solvent (1,2-dihaloethane and acetonitrile) molecules are aligned in a perfectly polar order along the *b*-axis (Fig. 3). Both host and guest molecules are involved in intermolecular non-covalent interactions. The geometrical parameters related to these interactions are listed in Table 3. In the O–H···O interactions, the apically coordinated water molecule acts as donor and the O-atoms of the nitro groups of the neighboring molecules act as acceptors. The same O-atom of the nitro group participates in another C–H···O interaction involving the methylene group of the bidentate ligand. These O–H···O and C–H···O interactions connect the complex molecules and a polar two-dimensional layered structure is formed (Fig. S1) [25]. In the channels between these parallel layers the guest molecules are trapped and oriented in a polar order. As observed for 1,2-dichloroethane [25], the methylene group of 1,2-dibromoethane in both **1**·C₂H₄Br₂ and **2**·C₂H₄Br₂ is involved in C–H···O interaction with the other O-atom of the ligand nitro group (Fig. S2, Table 3). In the cases of **1**·CH₃CN and **2**·CH₃CN, the same O-atom of the nitro group is very close to the methyl C-atom of the acetonitrile (Table 3). Although the H-atoms of this methyl group are disordered but a C–H···O type interaction can not be ruled out considering the observed C···O distances. These C–H···O interactions involving the host and the guest molecules bridge the parallel layers of the complex molecules and a polar three-dimensional network of host and guest molecules is formed (Figs. S2 and S3).

It is interesting to note that the guest molecules in all these inclusion compounds are found at the same position of the host lattices. The consistency in the crystal packing of these inclusion compounds as described above is also reflected by the small variations in their unit cell parameters. In fact for each enantiomeric pair of inclusion compounds having a particular guest they are essentially identical (Table 1 and Ref. [25]). Calculations using the Squeeze program [46] of the Platon package show that the effective volumes available for inclusion of the guest are in the range 14.6–16.0% of the total crystal volume in these structures. Thus, the very similar cell parameters and the effective volumes for the inclusion of the guest molecules indicate that the host frameworks having the opposite

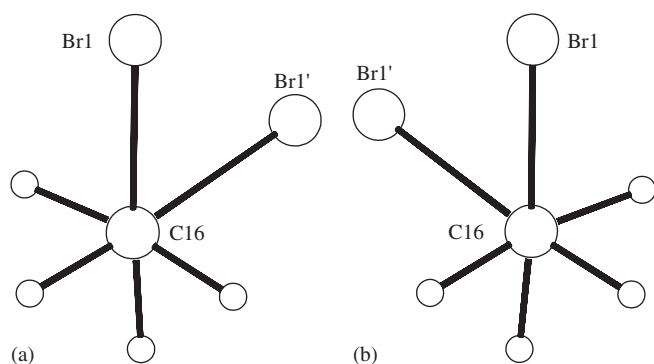


Fig. 2. (a) The right-handed (*P*) and (b) the left-handed (*M*) forms of 1,2-dibromoethane in **1**·(*P*)-C₂H₄Br₂ and **2**·(*M*)-C₂H₄Br₂, respectively.

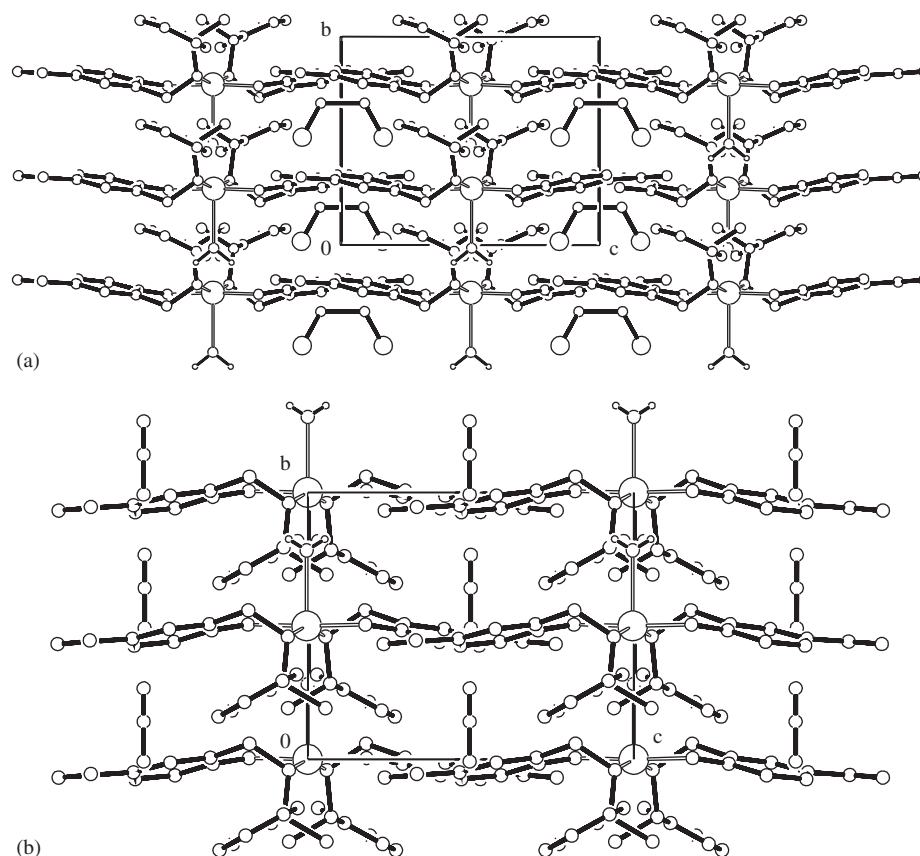


Fig. 3. Polar alignments (a) $1 \cdot (P)\text{-C}_2\text{H}_4\text{Br}_2$ and (b) $2 \cdot \text{CH}_3\text{CN}$ viewed along the a -axis. Except the hydrogen atoms of the metal coordinated H_2O all other hydrogen atoms are omitted for clarity.

Table 3
Geometrical parameters for intermolecular interactions

Compound	Interaction	H...A (Å)	D...A (Å)	$\angle \text{DHA}$ (°)
$1 \cdot (P)\text{-C}_2\text{H}_4\text{Br}_2$	O4–H...O2	2.07(5)	2.866(6)	146(8)
	C7–H...O2	2.56	3.403(8)	146
	C16–H...O3	2.43	3.35(4)	157
$2 \cdot (M)\text{-C}_2\text{H}_4\text{Br}_2$	O4–H...O2	2.04(4)	2.863(6)	152(7)
	C7–H...O2	2.56	3.408(8)	146
	C16–H...O3	2.44	3.35(4)	157
$1 \cdot \text{CH}_3\text{CN}$	O4–H...O2	2.20(4)	2.824(3)	167(7)
	C7–H...O2	2.55	3.392(5)	146
	C16–H...O3 ^a	—	3.339(4)	—
$2 \cdot \text{CH}_3\text{CN}$	O4–H...O2	2.19(3)	2.827(2)	163(5)
	C7–H...O2	2.54	3.390(4)	146
	C16–H...O3 ^a	—	3.347(3)	—

^aThe H-atoms of the acetonitrile methyl group (C16) are disordered.

chirality created by **1** and **2** are highly rigid and can accommodate different guest molecules at the same position and in the same fashion.

4. Conclusion

Intermolecular non-covalent interaction assisted self-assembly is one of the most potent tools for the design and synthesis of metal-organic framework having desired network and properties. The spatial disposition of the

functional group participating in non-covalent interactions can play important role in such endeavors. Our previous report [25] on the structures of $[\text{CuL}_2^1(\text{H}_2\text{O})] \cdot (P)\text{-C}_2\text{H}_4\text{Cl}_2$ (**1** · $(P)\text{-C}_2\text{H}_4\text{Cl}_2$) and $[\text{CuL}_2^2(\text{H}_2\text{O})] \cdot (M)\text{-C}_2\text{H}_4\text{Cl}_2$ (**2** · $(M)\text{-C}_2\text{H}_4\text{Cl}_2$), and the structures of the analogous inclusion compounds of **1** and **2** with 1,2-dibromoethane and acetonitrile reported in this work provide good models for the above. The O–H...O and C–H...O interactions involving one of the two O-atoms of the nitro substituent on the ligands as acceptor perhaps play a crucial role in the perfectly polar organization of the host enantiomeric square-pyramidal copper(II) complexes (**1** and **2**). The participation of the other O-atom of the nitro group in the C–H...O interaction with the guest molecule possibly facilitates not only the enantiospecific inclusion of the chiral 1,2-dihaloethane rotamers but also the polar alignment of these rotamers and achiral guest molecules such as acetonitrile. We are currently engaged in exploring the patterns of frameworks generated by copper(II) complexes with the reduced Schiff bases HL¹ and HL² containing nitro as well as other substituents at different positions of the same aromatic ring.

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Appendix A. Supporting information available

Crystallographic data (excluding structure factors) for $1 \cdot (P)\text{-C}_2\text{H}_4\text{Br}_2$, $2 \cdot (M)\text{-C}_2\text{H}_4\text{Br}_2$, $1 \cdot \text{CH}_3\text{CN}$ and $2 \cdot \text{CH}_3\text{CN}$ have been deposited with the Cambridge Crystallographic Data Centre (deposition numbers: CCDC 602464–602467). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Appendix B. Supplementary materials

Supplementary figures (S1, S2 and S3) associated with this article can be found in the online version at doi:10.1016/j.jssc.2006.10.002.

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