# Enantiospecific inclusion of chiral 1,2-dichloroethane rotamers in the crystal lattice of chiral square-pyramidal Cu(II) complexes with perfectly polar alignment of guest and host molecules

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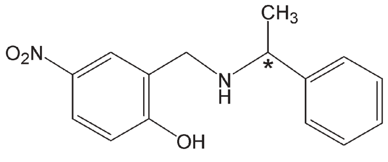
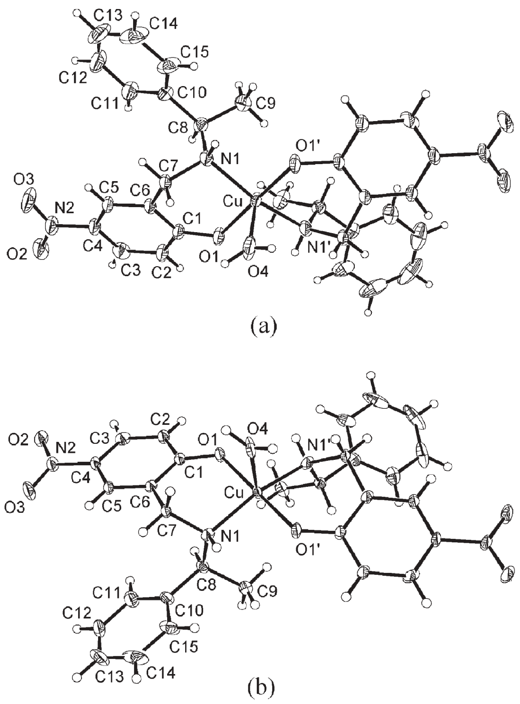
**The inclusion compounds, $[CuL^1{}_2(H_2O)]\cdot(P)\text{-}C_2H_4Cl_2$ and $[CuL^2{}_2(H_2O)]\cdot(M)\text{-}C_2H_4Cl_2$ ($HL^1$ = *N*-(2-hydroxy-5-nitrobenzyl)-(*R*)-α-methylbenzylamine and $HL^2$ = *N*-(2-hydroxy-5-nitrobenzyl)-(*S*)-α-methylbenzylamine), crystallise in the non-centrosymmetric space group *C*2; intermolecular hydrogen bonding leads to a perfectly polar alignment of both host and guest molecules with enantioselectivity.**

Polar and non-centrosymmetric organization of molecules in the crystalline state is a prerequisite for molecular materials having technologically important physical properties such as ferro-, pyro- or piezoelectricity and nonlinear optical effects.[1] Inclusion of chirality in the molecule is a common approach to ensure non-centrosymmetric organization in the crystals.[2] On the other hand, perfectly polar assembly in the crystal lattice is rare and requires special design strategies.[3] Synthesis of inclusion compounds having polar host frameworks that can confine and align guest molecules in a polar order is one of the successful strategies.[4] In this regard, it may well be noted that the synthesis of host frameworks with chiral cavities is a noteworthy challenge as these solids also have potential applications in the separation of enantiomers and in asymmetric catalysis.[5] In this work, we report the enantioselective isolation of the right handed (*P*) and the left-handed (*M*) *gauche* form of 1,2-dichloroethane in the host lattices formed by the chiral square-pyramidal Cu(II) complexes having the general formula $[CuL^n{}_2(H_2O)]$ ($HL^1$ = *N*-(2-hydroxy-5-nitrobenzyl)-(*R*)-α-methylbenzylamine and $HL^2$ = *N*-(2-hydroxy-5-nitrobenzyl)-(*S*)-α-methylbenzylamine, H represents the dissociable phenolic proton) with perfectly polar alignment of both guest and host molecules.



($HL^n$)

$HL^1$ and $HL^2$ were prepared by condensation reactions of one mole equivalent of 5-nitrosalicylaldehyde with one mole equivalent of the corresponding enantiomerically pure α-methylbenzylamine in methanol followed by reduction with $NaBH_4$. Reactions of $CuCl_2\cdot 2H_2O$, $HL^n$ and LiOH (1:2:2 mole ratio) in methanol produce the complexes, $[CuL^1{}_2(H_2O)]$ (**1**) and $[CuL^2{}_2(H_2O)]$ (**2**) in good yields.‡ X-Ray quality single crystals were grown by slow evaporation of 1,2-dichloroethane solutions of the complexes. Both complexes crystallise as $[CuL^n{}_2(H_2O)]\cdot C_2H_4Cl_2$ in the non-centrosymmetric space group *C*2 with essentially identical unit cell parameters.§ The molecular structures of **1** and **2** are mirror images of each other (Fig. 1). In each complex molecule, the metal centre is in a distorted square-pyramidal $N_2O_3$ coordination sphere. Two bidentate chelating ligands form the $N_2O_2$ basal plane and the water oxygen occupies the apical site. The bidentate ligands are related by a crystallographically imposed two-fold axis passing through the Cu and the apical water O. Both atoms are at special positions on the *b*-axis. The dihedral angles between the plane defined by Cu, N1 and O1 and that defined by Cu, N1′ and O1′ are 18.41(4)° and 18.97(5)° for **1** and **2**, respectively. These values indicate a tetrahedral distortion of the $N_2O_2$ basal plane.



(a)

(b)

**Fig. 1** Molecular structures of (a) $[CuL^1{}_2(H_2O)]$ (**1**) and (b) $[CuL^2{}_2(H_2O)]$ (**2**) with the atom-labelling schemes. All non-hydrogen atoms are represented by their 35 and 50% probability thermal ellipsoids for **1** and **2**, respectively.

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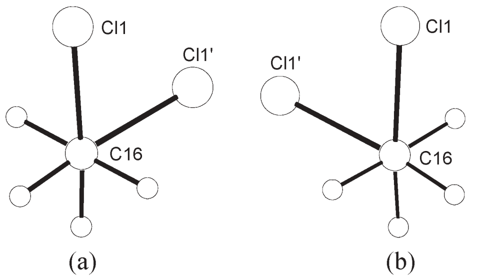
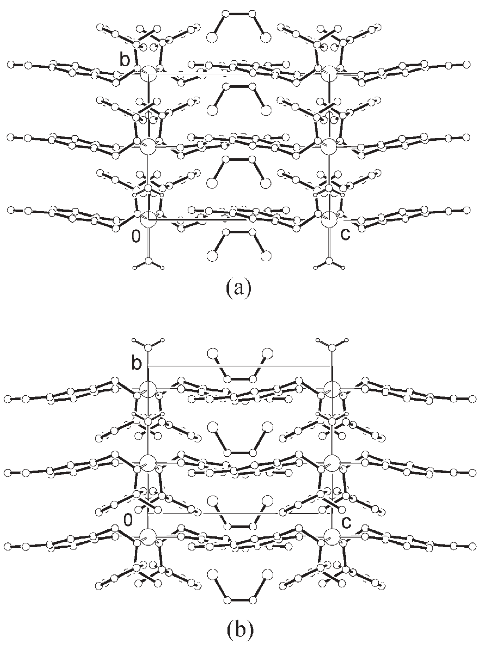
The bond parameters associated with the Cu(II) centres in **1** and **2** are unexceptional.[6]

Three rotamers are possible for 1,2-dichloroethane. These are the *trans* or *anti*, the *cis* or eclipsed and the *gauche* forms. The eclipsed form is energetically most unfavorable. Between the *trans* and the *gauche* forms the former is more stable (by ~1 kcal mol$^{-1}$).[7] The *gauche* form is chiral and also polar. One of the enantiomers has the right-handed (*P*) form and the other one has the left-handed (*M*) form. In the structures of **1**·$C_2H_4Cl_2$ and **2**·$C_2H_4Cl_2$, the asymmetric unit contains one-half of the 1,2-dichloroethane molecule. The other half can be generated by rotation about a two-fold axis passing through the mid-point of the C–C bond. The molecule is in *gauche* form in each structure (Fig. 2). The torsion angles involving Cl–C–C–Cl are 63(1)° and 64.6(9)° in **1**·$C_2H_4Cl_2$ and **2**·$C_2H_4Cl_2$, respectively. The molecule is trapped in the *P*-form in **1**·$C_2H_4Cl_2$ (Fig. 2a). On the other hand, in the case of **2**·$C_2H_4Cl_2$ only the *M*-form of it exists (Fig. 2b). Thus the chiral host complexes **1** and **2** produce the appropriate frameworks in the crystal lattice for exclusive accommodation of the *P*- and *M*-forms of 1,2-dichloroethane, respectively.



(a) (b)

**Fig. 2** (a) The right-handed (*P*) and (b) the left-handed (*M*) forms of 1,2-dichloroethane in **1**·$C_2H_4Cl_2$ and **2**·$C_2H_4Cl_2$, respectively.

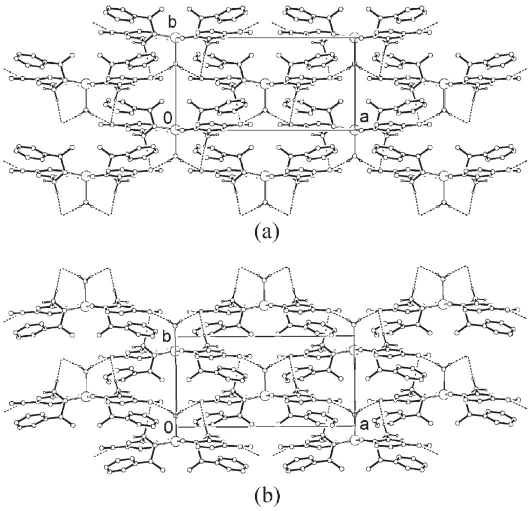


(a)

(b)

**Fig. 3** Polar alignments of (a) **1**·(*P*)-$C_2H_4Cl_2$ and (b) **2**·(*M*)-$C_2H_4Cl_2$ viewed along the *a*-axis; H-atoms of the ligands and 1,2-dichloroethane are omitted for clarity.

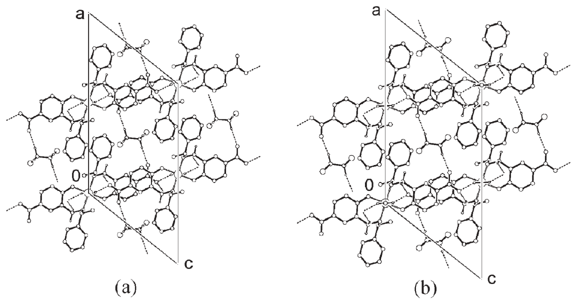
Reports of inclusion crystals of optically active and polar rotamers of 1,2-dichloroethane with a chiral host compound are very rare.[8] There are no reports on inclusion crystals of a chiral rotamer of 1,2-dichloroethane with polar alignment of the guest molecules in the host framework. The crystals of **1**·$C_2H_4Cl_2$ and **2**·$C_2H_4Cl_2$ provide examples, not only of enantioselective isolation of the *P*- and *M*-forms of the chiral rotamers, but also of the unprecedented, perfectly polar alignment of both host and guest molecules in the crystal lattice. In each case, the polar alignments of host and guest molecules are along the *b*-axis. It may be noted that for **1** and **2**, and also for (*P*)-$C_2H_4Cl_2$ and (*M*)-$C_2H_4Cl_2$, the molecular dipole axis is along the *b*-axis or parallel to the *b*-axis. The polar alignments are in opposite directions due to the enantiomeric relationship between the two host molecules and that between the two guest molecules in **1**·(*P*)-$C_2H_4Cl_2$ and **2**·(*M*)-$C_2H_4Cl_2$ (Fig. 3). In the crystal lattice of each structure, the apical water molecule of the complex is involved in hydrogen bonding interactions with the nitro groups of the neighboring molecules. Most likely these O–H···O interactions are primarily responsible for the alignment of the host molecules in a head-to-tail manner along the *b*-axis. For **1** the O4–H, H···O2 and O4···O2 distances and O4–H···O2 angle are 0.86(6), 2.03(7) and 2.846(3) Å and 160(9)°, respectively. For **2** the values of these parameters are 0.89(5), 1.98(6) and 2.816(3) Å and 156(7)°, respectively. In both cases, the same O-atom of the nitro group participates in an additional weak intermolecular C–H···O interaction involving one of the methylene hydrogens.[9] The C7···O2 distance and the C7–H···O2 angle are 3.388(4) Å and 146° and 3.336(4) Å and 147° for **1** and **2**, respectively. These O–H···O and C–H···O interactions connect the complex molecules and a polar two-dimensional layered structure is formed (Fig. 4). In the channels formed by the parallel layers of the complex molecules, the 1,2-dichloroethane molecules are trapped and oriented in a polar order. The methylene groups of the 1,2-dichloroethane are involved in intermolecular C–H···O interactions with the other O-atom of the nitro group (Fig. 5). The C16···O3 distance and the C16–H···O3 angle are 3.285(14) Å and 150° and 3.195(11) Å and 149° for **1**·(*P*)-$C_2H_4Cl_2$ and



(a)

(b)

**Fig. 4** View of the two-dimensional layered structures of (a) **1** and (b) **2** along the *c*-axis; only the $H_2O$ and the $CH_2$ group H-atoms involved in the non-covalent interactions (dashed lines) are shown.



(a) (b)

**Fig. 5** Projections of the crystal lattices of (a) **1**·(*P*)-$C_2H_4Cl_2$ and (b) **2**·(*M*)-$C_2H_4Cl_2$ onto the *ac*-plane.

**2**·(*M*)-$C_2H_4Cl_2$, respectively. These C–H···O interactions act as bridges between the parallel layers of the complex molecules and a three-dimensional network, with the polar alignment of both host and guest molecules, is formed.

Self-assembly *via* intermolecular non-covalent interactions is one of the powerful tools for designing and synthesising polar crystals as well as enantioselective chiral host frameworks. The spatial disposition of the functional groups participating in the intermolecular non-covalent interactions is expected to control the alignment of the host and guest molecules as well as spontaneous resolution of chiral guest compounds. The structures of **1**·(*P*)-$C_2H_4Cl_2$ and **2**·(*M*)-$C_2H_4Cl_2$ reveal this functional group directed alignment of molecules and selective trapping of guest molecules. The self-assembly of the host molecules (**1** and **2**) occurs through the O–H···O interactions and the guest molecules (1,2-dichloroethane) are held *via* the C–H···O interactions. In both intermolecular interactions, ligand nitro group O-atoms act as the acceptors. The positions and orientations of the nitro groups on the enantiomeric ligands in **1** and **2** are befitting for a perfectly polar alignment of the host molecules and for enantioselective confinement of the chiral rotamers of 1,2-dichloroethane in a polar order.

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## Notes and references

‡ Synthesis of $HL^1$: a methanol solution (30 ml) of 5-nitrosalicylaldehyde (1.67 g, 10 mmol) was added to a methanol solution (30 ml) of (*R*)-α-methylbenzylamine (1.21 g, 10 mmol) and stirred at room temperature for ½ h. To the resulting yellow solution, 0.74 g (20 mmol) of $NaBH_4$ was added and the mixture was stirred for another ½ h until a colourless solution was obtained. The reaction mixture was evaporated to dryness on a rotary evaporator, followed by addition of 100 ml of water. The solid suspended in water was extracted with (2 × 30 ml) $CH_2Cl_2$. The $CH_2Cl_2$ extracts were dried over anhydrous $Na_2SO_4$ and then evaporated to dryness. The compound ($HL^1$) was obtained in the form of light yellow solid (1.96 g, yield 72%, m.p. 91–93 °C). $HL^2$ was prepared in similar yield by following the same procedure as described above using (*S*)-α-methylbenzylamine instead of (*R*)-α-methylbenzylamine. The elemental analysis data and the $^1H$ NMR spectra (in $CDCl_3$) of the compounds are consistent with the expected molecular formula and structures.

Synthesis of **1**: a methanol solution (10 ml) of $CuCl_2·2H_2O$ (89 mg, 0.5 mmol) was added to a methanol solution (20 ml) of $HL^1$ (272 mg, 1 mmol) and $LiOH·H_2O$ (42 mg, 1 mmol). The mixture was stirred at room temperature for 1 h. The green solid separated was collected by filtration, washed with methanol and dried in vacuum. Yield, 230 mg (74%). Complex **2** was synthesized in similar yield and isolated as a green solid by following the same procedure as described for **1** using $HL^2$ instead of $HL^1$.

§ *Crystal data*: for **1**·$C_2H_4Cl_2$: $CuC_{32}H_{36}N_4O_7Cl_2$, $M$ = 723.09, monoclinic, space group $C2$, $a$ = 20.2834(12), $b$ = 8.1769(5), $c$ = 12.8799(7) Å, $\beta$ = 128.6480(10)°, $V$ = 1667.94(17) $Å^3$, $T$ = 293(2) K, $Z$ = 2, 3842 independent reflections, 3572 reflections with $I > 2\sigma(I)$, 215 parameters, $R_1$ = 0.0411 and $wR_2$ = 0.1035 [$I > 2\sigma(I)$], $R_1$ = 0.0443 and $wR_2$ = 0.1056 (all data), goodness-of-fit on $F^2$ = 1.068, Flack parameter = −0.01(1), largest peak 0.647 e $Å^3$. For **2**·$C_2H_4Cl_2$: $CuC_{32}H_{36}N_4O_7Cl_2$, $M$ = 723.09, monoclinic, space group $C2$, $a$ = 20.1329(17), $b$ = 8.0328(6), $c$ = 12.7987(13) Å, $\beta$ = 128.290(2)°, $V$ = 1624.6(2) $Å^3$, $T$ = 293(2) K, $Z$ = 2, 3815 independent reflections, 3661 reflections with $I > 2\sigma(I)$, 215 parameters, $R_1$ = 0.0433 and $wR_2$ = 0.1063 [$I > 2\sigma(I)$], $R_1$ = 0.0451 and $wR_2$ = 0.1076 (all data), goodness-of-fit on $F^2$ = 1.053, Flack parameter = −0.01(1), largest peak 1.187 e $Å^3$. Data were collected on a Bruker-Nonius SMART APEX CCD single crystal diffractometer using Mo Kα radiation ($\lambda$ = 0.71073 Å) and $\omega$-scans. An absorption correction was applied to each data set with the help of the SADABS[10] program. The structures were solved by direct methods and refined by least-squares methods on $F^2$ with all reflections (SHELX-97[11]). CCDC 263054–263055. See http://www.rsc.org/suppdata/cc/b5/b501642h/ for crystallographic data in CIF or other electronic format.

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