Anion-driven conformation control of aryl linked salicylaldoximes

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ESI for paper

X-ray Crystal Structure of L^1.tol

Colourless block shaped crystals of a toluene solvate of L^1 suitable for X-ray diffraction were grown by the slow evaporation of toluene containing the oxime ligand and the crystal structure was determined (Figure S1). The asymmetric unit consists of one half of the complex with the other half generated by inversion, confirming the successful synthesis of the ligand.

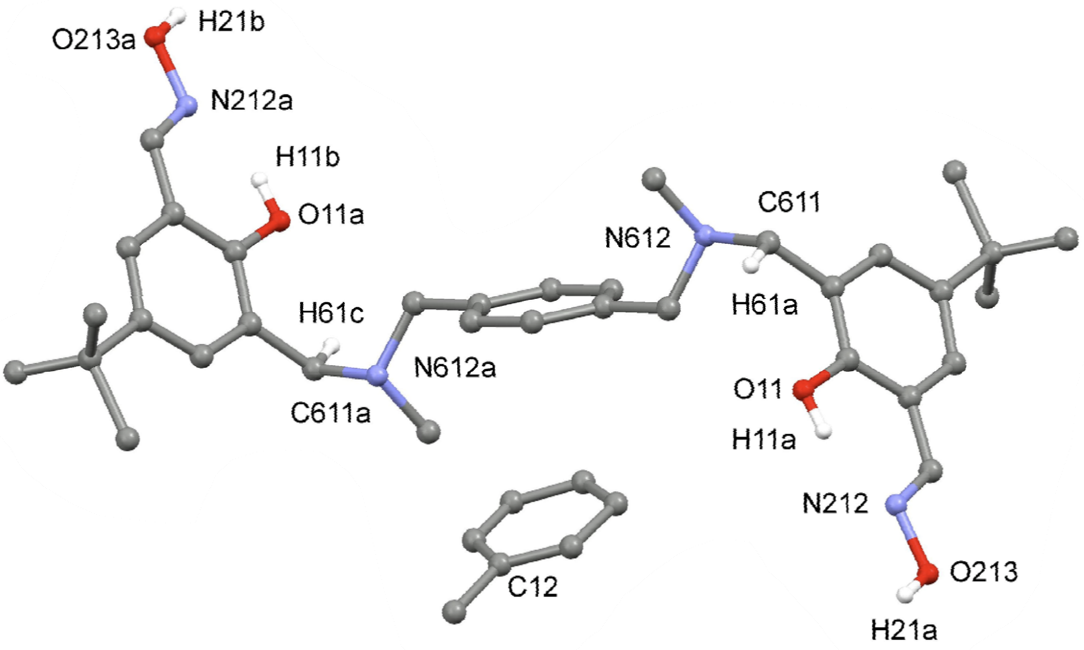

Figure S1 Perspective view of L^1 with included toluene solvent molecule showing the adopted labelling scheme (hydrogen atoms have been omitted for clarity and the disordered *t*-butyl groups and disordered methyl group of the toluene are not shown).

The salicylaldoxime groups at each end of the molecule are orientated in opposite directions. This orientation allows a repeating inter and intramolecular hydrogen bonding network to form throughout the crystal lattice. The intermolecular interactions form between the oxime hydrogen H21a and the tertiary nitrogen atom N612 from adjacent L^1 molecules. The intramolecular interactions occur between the phenolic hydrogen H11a and the oxime nitrogen N212 and between the alkyl hydrogen H61a and the phenolic oxygen O11 (refer to Table S1 for H-bond lengths and angles).

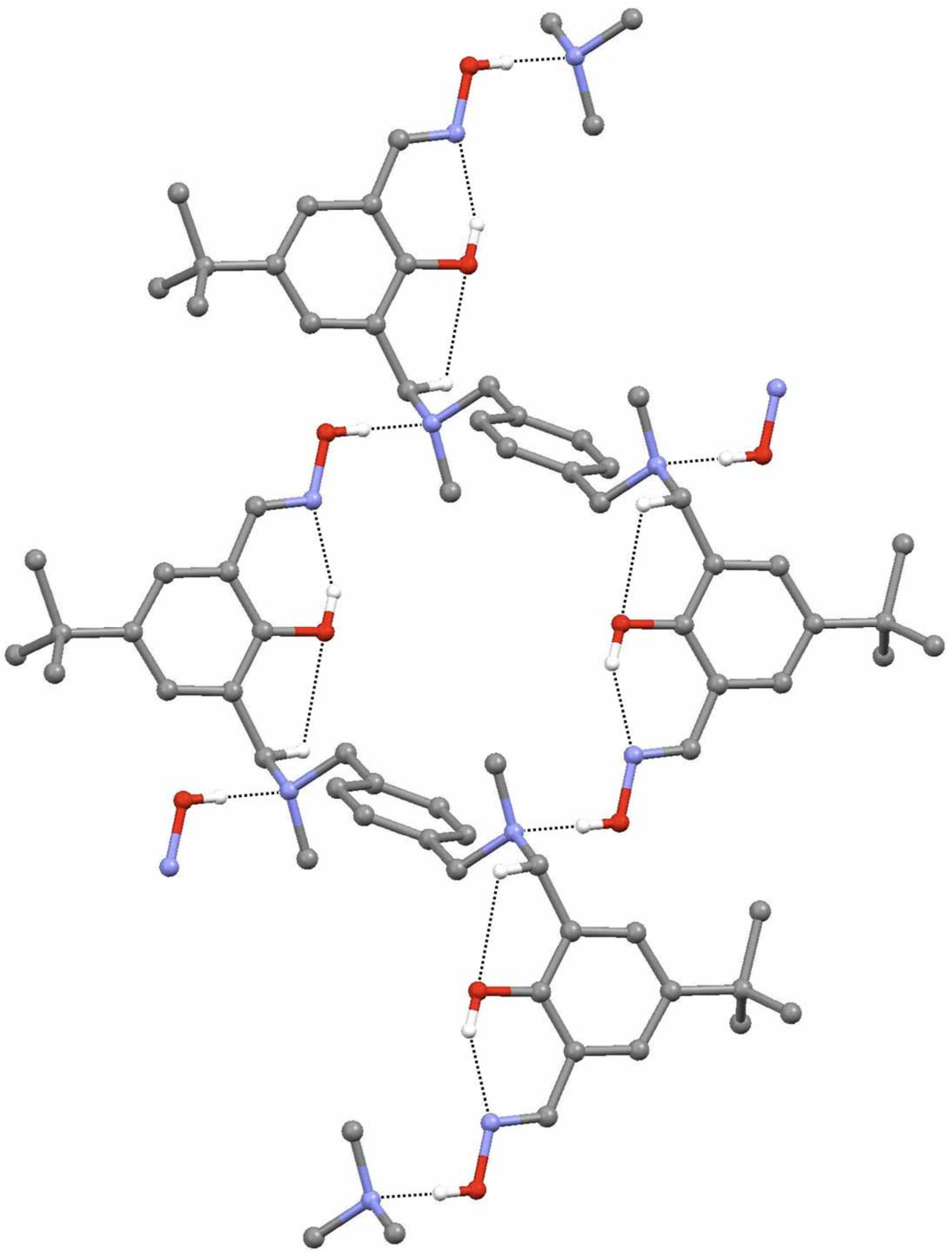

Figure S2 Perspective view of L^1 showing the extended intra and intermolecular H-bonding network (hydrogen atoms and the solvent toluene molecule not involved in H-bonding have been omitted for clarity).

Table S1 Selected intra and inter H-bond distances for L^1.

Atoms	H-bond distances (Å)	D-H-A angles (°)
O11-H11a … N212	1.905(3)	149.1
C611-H61a … O11	2.442(1)	106.0
O213-H21a … N612b	1.936(1)	162.5

Within L^1 molecule, the tertiary butyl groups were found to be positionally disordered over two sites (0.67:0.33).

Crystal data for L^1

Formula $C_{34}H_{46}N_4O_4$ $2(C_7H_8)$,
M_r = 759.02, colourless block, 0.20 × 0.20 × 0.05 mm, monoclinic, ***P21/n***, a = 10.8782(2) Å, b = 8.8537(2) Å, c =

22.8729(16) Å, α = 90.000°, β = 92.114(7)°, γ = 90.000°, U = 2201.44(17) Å^3, Z = 2, μ = 0.569 mm^{-1}, $F(000)$ = 820, T = 140(2) K. A total of 31069 reflections were collected in the range 6.7° < 2θ < 66.6°. The 3846 independent reflections [R(int) = 0.041] were used after absorption correction (T_{min} = 0.435, T_{max} = 1.000). Refinement of 286 parameters converged to R_1 = 0.0611 [for 2406 reflections having $I > 2\sigma(I)$], wR_2 = 0.2127 and goodness-of-fit of 1.14 (for all 3846 F^2 data). Peak/hole 0.26/-0.31 e Å^{-3}.

Counter anion interactions with complexes

$[\mathrm{ClO_4}\subset\mathrm{Cu_2L^1_2}](\mathrm{ClO_4})_3$ (3)

The counter perchlorate anions are involved in a myriad of hydrogen bonds with the complex (see figure S3 below). One of the perchlorate anions (Cl2 O21 O22 O23 O24) is positioned slightly differently than the other two counter anions as it sits along side two neighboring complexes near the oxime functionalities. It makes two interactions with a polarised CH_2 hydrogen (connected to 3° N amine atom) H61f between its oxygen atoms O21 and O24 and an interaction with H63eb, which is another polarised CH_2 hydrogen (next to a N atom) but from an adjacent complex. This is in comparison to 1 which forms a variety of intermolecular H-bonds between adjacent complexes. Another perchlorate counter anion (Cl3 O31 O32 O33 O34) is similar in respects to having interactions with two CH_2 hydrogen's H64b and H64c with its O33 and O34 oxygen's. Whereas the last perchlorate counter anion (Cl4 O41 O42 O43 O44) makes weak H-bonds between oxygen O43 and a CH_2 hydrogen H64a and a methyl hydrogen H64f, while O41 has weak interactions with a CH_2 hydrogen H64d and a close contact with an aromatic hydrogen H54a.

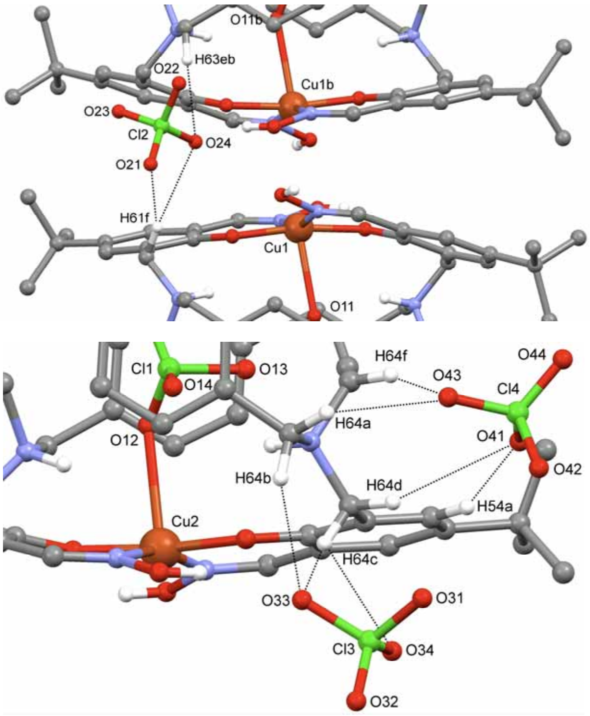

Figure S3 Partial perspective views of the counter perchlorate anions showing the H-bonds created with **3** (Hydrogen atoms not involved in H-bonding have been omitted for clarity).

Table S2 Selected H-bond distances and angles for the counter ClO_4^- anions of **3**.

Atoms	H-bond distances (Å)	D–H–A angles (°)
C611-H61f … O21	2.5694(2)	152.0
C611-H61f … O24	2.5755(2)	152.4
C634b-H63eb … O24	2.5174(3)	173.5
C641-H64c … O34	2.6861(2)	119.3
C641-H64c … O33	2.5801(2)	139.6
C644-H64b … O33	2.5098(2)	157.8
C644-H64a … O43	2.4216(2)	148.0
C643-H64f … O43	2.5426(1)	146.0
C641-H64d … O41	2.7636(3)	148.5
C54-H54a … O41	2.6847(3)	151.8