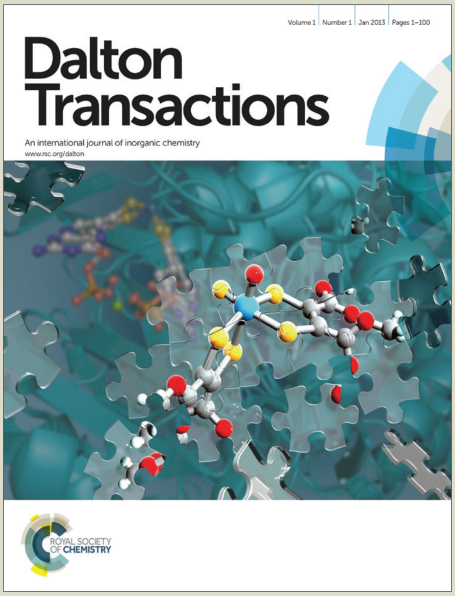
Dalton Transactions

Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/dalton

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE

Characterization of a meso-chiral isomer of a hexanuclear Cu(II) cage from racemization of L-alanine Schiff base

Chinnaiyan Mahalingam Rajesh and Manabendra Ray*

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

We are reporting structural characterization of two new hexanuclear cage $(H_3O)_2[Cu_3(\mu_3\text{-}OH)(\mu_3\text{-}NH_3)_{0.5}(L)_3]_2 \bullet 8H_2O$(**1**) and $(H_3O)_2[Cu_3(\mu_3\text{-}OH)(\mu_3\text{-}H_2O)_{0.5}(L)_3]_2 \bullet 8H_2O$(**1a**) where L^{2-} is the dianionic form of Schiff base of L-alanine and salicylaldehyde. The complex **1** has two C_3 symmetric hydroxo bridged trinuclear halves joined by an ammonia or water molecule at the center through H-bonding. Each of the trinuclear half is enantiopure but of opposite chirality to the other half, rendering the hexanuclear unit as a meso isomer. Temperature dependent magnetic measurement showed presence of ferromagnetic interactions among trinuclear Cu(II) units, a rare occurrence among trinuclear Cu(II) complexes. Characterization of the LiHL showed it to be enantiopure. Addition of base, monitored using optical rotation, showed that racemization occurs as a result of base addition. The racemization depends on base as well as temperature. Base or Cu(II) induced racemization of amino acid derivatives have been indicated in a number of cases in the past but structural characterization of the products or formation of this type of chiral hexanuclear architecture was never reported. Structures of the complex as well as the ligand have number of interesting H-bonding situation.

Introduction

Multinuclear cages, capsules of different size and shapes have been synthesized in view of their potential use as selective hosts for anion sensing, catalysis, selective recognition and separation of guest molecules.[1] Addition of chirality to the design, in principle, can extend their utility further towards chiral recognition. Incorporation of chirality through Schiff-base ligands is attractive due to their ease of synthesis and excellent metal binding property. However, very few attempts were made to incorporate chiral centre within a metalloorganic assembly or chiral host using such ligands.[1b,1d-e] Schiff-bases of salicylaldehyde and amino acids are well-studied area, mainly due to their use in understanding coordination chemistry[2d-e], bioinorganic active site model[2a-c], catalysis[2f-i] and biological[2j-n] activities. Salicylaldehyde owing to its structural similarity often substitute pyridoxal-5'-phosphate, the active form of vitamin B6, in model complexes. The simplest of this type of ligand, N-salicylidene glycinate, acting as a tridentate ligand binds readily with Co(II), Ni(II), Cu(II), Zn(II), and VO^{2+}.[2g-l, 3a-c] Most of the known complexes are mononuclear[2f-j] and binuclear or coordination polymers[3a-c] with the general formula $[M(L)]_n$, where M is dicationic transition metal ion and L is the N-salicylidene glycinate. Among hexanuclear Cu(II) complexes with Schiff base, we could find only three reports.[3d-f] All three are with achiral complex.

In this manuscript we are reporting isolation of a new hexanuclear Cu(II) cage starting with L-alanine derivative. The half of the hexanuclear complex has chirality that is opposite to the other half. This indicates that racemization took place during the reaction. The racemization of amino acid derivatives in solution due to base and/or metal ion has been studied in the past[2a, 2c, 4] but structural characterization of the products or formation of this type of chiral hexanuclear architecture was never reported.

Scheme 1

Scheme 1. The synthesis of the ligand and the hexanuclear Cu(II) complexes.

Results and Discussion

Ligand

Majority of the other reports utilizes in situ condensation of Schiff base without isolation.[3, 5] The ligand was synthesized by condensing salicylaldehyde and L-alanine in presence of one equivalent of LiOH. Base was used to deprotonate the zwitterion form of amino acid to free amine form. This is similar to the procedure reported by Heinart and Martell using KOH as base.[6] The ligand was isolated as monolithium salt (LiHL) with 82% yield. Analytical data and ESI-Mass support the formula (Experimental section).

Schiff-base of amino acids can have more than one tautomeric form (Scheme 1).[6] The FTIR showed a pair of strong vibration at 1648 and 1620 cm^{-1} indicating the formation of imine. Appearance of these two bands along with one at 1405 cm^{-1} indicates the tautomeric form in the solid state being type II (Scheme 1).[6] The molar conductance was found to be almost half of what is expected for 1:1 electrolyte suggesting significant association in solution.[7] In ^{1}H NMR spectra, the aromatic protons appeared between 6.77 and 7.30ppm. The appearance of imine hydrogen at 8.38 ppm and methyl protons at 1.54 ppm are as expected. Detailed assignments based on both position and integration has been provided in experimental section.

Crystallographic characterization of Schiff bases of amino acids is rare.[8] The LiHL was crystallized in the chiral space group of *C*2 in monoclinic crystal system. Although the structure did not show any significant disorder, the R-value was found to be high at 9% (Table 1). As a supportive measure, the powder diffraction of the sample and simulated from X-ray were compared and found to be consistent with each other (Figure S1). The asymmetric unit contains one molecule of the ligand and lithium (Figure 1). The bond N1-C4 at 1.289(7) Å is shorter due to its double bond nature. The hydrogen attached with N1 was located from difference Fourier map. Forcible attachment of this to oxygen leads to increase in R-value. Thus attachment of this hydrogen with N1 is justified. This support the tautomeric form II (Scheme 1) identified from FTIR spectra. Heinart and Martell proposed occurrence of this tautomeric form based on IR analysis.[6] The present structure supports that proposition. The only other closely related structure that we could find is a potassium salt of salicylidene-β-alaninate which unfortunately did not have the hydrogen refined.[8]

Table 1 is at the end of this document.

The structure is also notable because of coordination of lithium. Lithium ion is coordinated to carboxylate and phenolate oxygens and tetrahedral in geometry (Figure 1A). Carboxylates acting as bridges between lithium ions forms a zigzag chain network (Figure S2), a pattern which was seen earlier in lithium salt of glycine.[9] The coordination network formed because of lithium is two dimensional (2D) and each 2D layer has a hydrophilic core sandwiched between hydrophobic aromatic rings (Figure 1B-D). Partial retention of this network or coordination of lithium with the ligand in methanol perhaps reduced the conductance value substantially. The chirality at C2 was found to be *S* which is expected as it was synthesized from L-alanine (*S*-isomer). Specific rotation measured in methanol was found to be +109° (experimental section).

Figure1

Figure 1. (A) ORTEP diagram showing the LiHL with thermal ellipsoids set to 40% probability along with Lithium coordination, The atoms O1_ix, O2_xii and O2_ii were generated using symmetry operations (1-x, y, 1-z), (1-x , 1+y, 1-z) and (-1/2+x, ½+y, z) respectively. (B) 2D coordination network formed by LiHL. (C) and (D) space filling model of the coordination network along different axes. Selected bond distances (Å): N1-C4 1.289(7), N1-C2 1.511(8), O3-C6 1.296(8), C4-C5 1.409(9), C5-C6 1.418(9), C6-C7 1.419(9), C7-C8 1.379(8), C8-C9 1.431(11), C9-C10 1.336(11), C10-C5 1.427(8), Li1-O1 1.944(12), Li1-O2 1.922(12), Li1- O2 2.016(12), Li1-O3 1.949(13), Li1-Li1 3.153(15). H-bond d(D…..A) (Å): N1…O3 2.594(9).

Hexanuclear Cu(II) complex

The complex **1** was isolated from room temperature mixing of metal salt, ligand and base in the 1:2:2 ratios in methanol. Reaction is sensitive to reagent ratios and additives. Addition of NH$_4$Cl before isolation improves the yield by 5-10% and larger crystals. Only microcrystals were isolated without addition of NH$_4$Cl, which were unsuitable for X-ray structure. Changing the metal, ligand and base ratio to 1:1:1.33 resulted in microcrystals of **1a**. The **1a** is almost identical to **1** with respect to powder diffraction pattern and FTIR spectra (Figure S3-S4). Analysis on both supports identical formulation except that one ammonia molecule in **1** was replaced by water in **1a** (experimental section).

Another difference between the two is that while both **1** and crystals of **1a** are not optically active, bulk material of **1a** shows a specific rotation of +32° implying a mixture of both optically active and inactive form. Formulation for both the complexes support metal : ligand ratio of 1:1 in the complexes. These results indicate that (a) NH$_4$Cl worked as a crystal habit modifier and (b) extra set of ligand and/or base was required for complete racemization. The complex **1** has been further characterized using X-ray crystallography.

Figure 2

Figure 2. (A) ORTEP diagram of the asymmetric unit of **1** with thermal ellipsoids set to 40% probability. The atoms O5_i, O6_i, O7_i were generated using symmetry operations (x, y, -1+z), (x, y, -1+z), and (x, y, -1+z) respectively. (B) schematic presentation of the hexanuclear molecule. Selected bond distances (Å): Cu1-O3 1.918(3), Cu1-N1 1.921(4), Cu1-O2 1.933(3), Cu1-O4 1.968(2), Cu1-O3$_{axial}$ 2.490(3), N1-C4 1.277(5), O3-C6 1.341(5). H-bond d(D…A) (Å): N2-O3 3.017(4), O4-O5 2.714(11), O5-O6 2.811(6), O6-O1 2.731(9). Angles (deg): O3-Cu1-N1 94.20(13), N1-Cu1-O2 84.34(14), O2-Cu1-O4 94.13(16), O4-Cu1-O3 87.28(16), O3-Cu1-O2 178.54(14), N1-Cu1-O4 165.50(17), N1-Cu-O3$_{axial}$ 121.5(1), O4-Cu1-O3$_{axial}$ 72.9(2), Cu1-O4-Cu1 106.93(18). τ = 0.217.

The complex **1** was solved in achiral space group *R*-3 in the trigonal crystal system. The asymmetric unit contains one sixth of the molecule (Figure 2A). The molecule of **1** has two tricopper units face to face with an ammonia molecule at the centre (Figure 2B). Each tricopper unit consist of three five coordinated Cu(II) bound to a single terminal hydroxo bridge. Each Cu(II) is coordinated by one tridentate L^{2-}, hydroxo bridge and phenolate oxygen from the next Cu(II) in the axial position (Figure 2). The geometry at the Cu(II) is slightly distorted square pyramidal (τ 0.217).[10] The in-plane bond length ranges from 1.918(3) Å for phenolate to 1.968(2) Å for bridging hydroxide and considerably longer axial length of 2.490(3) Å for phenoxo bridge. The lengths and angles are comparable to other hydroxo-bridged trinuclear Cu(II) complexes.[11] The longer axial bond length due to Jahn-Teller effect, common for Cu(II).[12] The chirality of the ligands in tricopper units are identical but two tricopper half of a hexanuclear assembly have opposite chirality. Thus the hexanuclear assembly can be considered as a meso-isomer. Each of the trinuclear halves has a C_3 symmetric chiral cavity accommodating the central ammonia molecule (Figure 3A &B).

The structure has two notable H-bonding situations at N2 and O5. The N2 at the centre, assigned as ammonia, is within H-bonding distance of six equivalent phenolate oxygens (N2…O3 3.017(4) Å). Thus the H's on NH$_3$ is distributed over six equivalent sites. H's on N2 could not be located in the structure. The other position is around O5, which is within H-bonding distances of O4 (bridging hydroxide) and three O6 (Figure 3). The atom O6 is further H-bonded to carboxylate (O1) from neighboring unit. H's on O5 and O6 could not be attached. The charge balance on the $[Cu_3L_3OH]^-$ unit requires two cation. No other counter cation could be located in the lattice. We tentatively assigned the O5 as a hydronium ion as it within H-bonding distance of three O6 symmetrically. This assignment augurs well with the charge of the trinuclear half. Alternatively, it is possible that one proton/per trinuclear unit is disordered over O5 and three O6. The known examples of hydronium ion within crystals usually bind to three water with short H-bond distances ~2.5Å without any possibility of fourth H-bond on oxygen.[13] Thus a total four H-bond on O5 is difficult to explain. Thus it is not possible to pinpoint the location of the protons either on O5 or O6.

Figure 3

Figure 3. (A) ORTEP diagram of the trinuclear half of **1** with thermal ellipsoids set to 40% probability, (B) space filling model of the same showing the C_3 symmetric chiral cavity and (C) the cavity formed between two hydronium ion occupied by disordered water molecules. The atoms Cu1_i, Cu1_ii, Cu1_xv, O4_i, O5_xi, O6, O6_xvi, O6_xvii, O7 and O7_xii were generated using symmetry operations (1/3-x, 2/3-y, 2/3-z), (1/3+x-y, -1/3+x, 2/3-z), (-2/3+y, -1/3-x+y, 2/3-z), (1/3-x, 2/3-y, 2/3-z), (1/3-x, 2/3-y, 1.66667-z), (x, y, z), (-y, x-y, z), (-x+y, -x, z), (x, y, z) and (-x, -y, 2-z) respectively.

The lattice also contains a pocket, formed between six of the O6 from neighboring hexanuclear assembly (Figure 3). Electron density inside pocket was refined as oxygen atom (O7, water, 50% occupancy). Thermo gravimetric analysis (TGA) between 25-180 °C showed weight loss of 11.02% which could be accounted for one NH_3 and 10 H_2O molecules (calc. weight loss of 11.2 %)(Figure S5). Thus TGA support the assignment of O7 as water. However, large thermal ellipsoids and short O7-O7 distance indicate disorder at this position.

Microcrystals of **1a** were uneven in size, mostly too small for mounting in X-ray diffractometer. However, we were able to mount a relatively larger one (0.2 mm x 0.1 mm x 0.1 mm) and collected data. The diffraction spots were weak. The crystal space group, parameters and structure are nearly identical with that of **1** with the exception of water, instead of ammonia, at the centre (Table 1). This is supported by the elemental analysis. Thus, the crystal is of same meso isomer despite the bulk showing optical rotation. This indicates that the bulk contains both meso and chiral isomers. The relative ratio could not be determined. Interestingly, the solubility of **1** and **1a** differs significantly in MeOH. While **1a** is readily soluble in methanol, **1** takes ~18 hour to dissolve on standing. We attempted the separation of isomers using the difference in solubility. Unfortunately the optical rotation measurement, although differs for both fractions, implies that, complete separation using this method is not possible.

Racemization

The process of racemization of LiHL in presence of base was monitored using optical rotation at 589 nm over a time period of 12h (Figure S6). In methanol at room temperature (28°C), optical rotation of LiHL decreases gradually over 4h to about 40% of initial value and continue decreasing at a slower pace. The rate of decrease followed a first order behavior (Figure S7). The observed rate / mole was found to be 0.110 $min^{-1}M^{-1}$. This is slower (1/5) than the rate reported for Cu(4-NO_2sal-L-val)1.5H_2O in presence of base in ethanol at 50 °C, where $(4\text{-}NO_2\text{sal -L-val})^{2-}$ is the Schiff base of L-valine and 4-nitro-salicylaldehyde.[2c] Electron withdrawing nitro substitution on salicylaldehyde stabilizes the intermediate necessary for racemization, hence the rate is higher for nitro derivative. However, it is not a requirement for racemization to occur as is shown for non-substituted salicylaldehyde & amino acid esters.[2c] Thus the present result is consistent with the reported racemizations. The circular dichorism (CD) spectra of LiHL before addition of base, 20 min after and disappearance of it after 20h in methanol clearly shows that racemization indeed took place (Figure 4).

In water at room temperature, even without base addition, the optical rotation initially decreases faster up to 30min (40% decrease) but then remain constant for over 10 hour (Figure S6). In presence of 1 equivalent of base, it decreases to ~ 8% of initial value within 20 min and remain constant thereafter. From these observations, we infer that in presence of base, racemization occurs in both methanol and water. Racemization is much faster in water compared to methanol at room temperature.

In order to check the effect of temperature, the optical rotation of LiHL in presence of 1equivalent of base was measured at room temperature in methanol after stirring for 2h at 0°C, 28°C and 80°C before measurement to replicate the synthesis condition. The optical rotations were 0.313, 0.228 and 0 respectively. This means that racemization is faster at elevated temperature. Thus it is no wonder that complex **1a**, isolated from water in presence of base at room temperature is a mixture of isomers.

Figure 4

Figure 4. (a) UV-Vis spectrum of LiHL in MeOH (60.0 μM). (b) CD spectra of LiHL and LiHL with one equivalent LiOH•H_2O in MeOH at different time intervals (750.0 μM).

From these observations, we infer that in presence of base, racemization occurs in both methanol and water. Racemization is much faster in water compared to methanol at room temperature. This also means that at lower temperature, the racemization is quite slow. Thus we repeated the synthesis of complex 1a at ice cold condition (~5°C) and isolated the complex **1b**, which shows much higher specific rotation of 90° compared to **1a** (Scheme 1). The higher quantity of chiral isomer in complex **1b** became more evident from CD spectra of the copper (II) complexes (Figure 5). Out of three complex only complex **1b** showed spectrum with negative cotton effect, indicative of chirality in the sample. The reaction was attempted in methanol as well. However, in methanol, green amorphous solid precipitated immediately after reagents were added, perhaps due to lower solubility at low temperature, which shows specific rotation lower than **1b**. We suspect the purity of this solid. Hence the product from low temperature reaction in methanol has not been subjected to circular dichorism spectroscopy.

Figure 5

Figure 5. (a) UV-Vis spectrum of the complex **1** in MeOH (6.6 μM, /Cu_6 unit). (b) CD spectra of the complexes **1, 1a** and **1b** in MeOH, same concentration were maintained for all the complexes (43.0 μM, /Cu_6 unit).

Magnetic property

Temperature dependent magnetic studies on both **1** and **1a** were performed in the temperature range of 2-300 K at a fixed field of 1.0 T. The experimental data were corrected for underlying diamagnetism, calculated using Pascal's constants.[14] From room temperature χ_M x T for trinuclear unit gradually rises up to 14 K and then sharply decreases (Figure 6). This nature is consistent with ferromagnetic interaction within trinuclear unit but antiferromagnetic interaction between different trinuclear units.[15] Almost identical behaviour was observed for complex **1a** (Figure S8). Similar observation were made by Suh and coworkers for a hydroxo bridged trinuclear Cu(II) complex with a macrocyclic ligand.[15a]

The susceptibility data were further analyzed on the basis of the usual spin-Hamiltonian description for the electronic ground state by using the simulation package julX written by Eckhard Bill for exchange coupled systems of three s = ½ system.[16] The operator contained exchange Hamiltonian and Zeeman interaction. The zero-flied splitting option was not used. The ferromagnetic coupling constant *J* and Theta-Weiss constant in K for **1** was found from the fitted data and are 14 cm^{-1} and -0.6 K respectively. Same parameters for **1a** are 12 cm^{-1} and -0.6 K. The other parameters and plots for both are in supporting information (Figure S8-S9). Compared to this, complex reported by Suh and coworkers[15a] were J = 37.8 cm^{-1} and complex by Yan and coworkers[15b] were J = 7.83 cm^{-1}. Other than these two reported example and the complexes in this manuscript, rest of the reported trinuclear Cu(II) complexes shows anti-ferromagnetic behaviour.

Hatfield and others[17, 18] had shown that for a set of hydroxo-bridged complexes, coupling depends on the Cu-OH-Cu angle. The Cu-OH-Cu angle >97.5° promote antiferromagnetic coupling, whereas angle of < 97.5° promotes ferromagnetic coupling. In the present set of complexes, Cu-OH-Cu angle is ~106° and Cu-O(phenoxo)-Cu is 90.4°. Thus while one of the bridge support antiferromagnetic coupling, the other one promotes ferromagnetism leading to an overall ferromagnetic coupling. Compared to present set of complexes, the reported trinuclear hydroxo complexes have Cu-O(phenoxo)-Cu angles between 96 to 99° (reported Cu-OH-Cu angles lies between 100 to 107°).[11, 18] This shorter Cu-O(phenoxo)-Cu angle probably is the reason for overall ferromagnetism.

Figure 6

Figure 6. Plot of X_MT vs T in the range 2-300 K for **1.** The solid line is a best fit to the experimental data using the values given in the text.

Conclusions

The isolation and characterization of **1** and **1a** are significant for multiple reasons. First of all it shows that simplicity in Schiff base formation could be utilized for synthesizing large chiral multinuclear cages/assemblies. Even though handful of trinuclear hydroxo bridged Cu(II) complexes have been reported, none of them used chiral ligand[11f] or showed ferromagnetic interactions.

The structures of **1** and **1a** are unique in terms of H-bonding capability through both carboxylate and phenolate. Both of which contributed to the stabilization of protons as possible hydronium form within the lattice and the central ammonia in **1** or water in **1a**. The centre of the cage is especially notable as it is within H-bond distance (N2-O3, 3.017 Å) from six H-bond acceptors (phenolate) which resulted in a rather unique H-bonding situation for the central molecule, be it water (**1a**) or ammonia (**1**). Front to front organization of trinuclear units in to a hexanuclear capsular form in the solid state is another structural feature not seen before.

Apart from the structural aspect, observation of a meso-isomer showed that racemization of the amino acid took place. Racemization of amino acid derivatives in presence of base or Cu(II) have been reported.[2c,4] Based on the solution studies, either deprotonation at chiral carbon followed by rehydration or keto-enol tautomer form of has been cited as mechanism of such occurence.[2c] However, structural characterization of the products or formation of this type of hexanuclear architecture through racemization has not been reported.

Addition of 1eq LiOH to LiHL and resultant racemization studies showed that the extent of racemization depends on solvent, base as well as temperature. This explains the observation of optical rotation and CD spectrum in **1b**, synthesized at low temperature. The chiral excess in **1b** retains the possibiliy of isolation of enantiopure cage for chiral recognition in future.

This his work was supported by the Science & Engineering Research Board (SERB), New Delhi (Grant no. SR/S1/IC-69/2010). Circular dichorism, X-ray diffraction and SQUID measurement facilities were generously provided by DBT Programme Support funded by the Department of Biotechnology (Project No.BT/01/NE/PS/08), IIT Guwahati, CIF IIT Guwahati and Department of Physics, IIT Kanpur. We thank Prof. Siddartha Sankar Ghosh and Dr. Chandan Mukherjee of IIT Guwahati and Suman Kumar Burman of IIT Kanpur for helpful discussion. We thank Dr. Mohitosh Dey of IIT Guwahati, Mr Bireswar of IIT Kanpur for measurements. Analytical facilities used were provided by IIT Bombay, Guwahati biotech Park, IISc Bangalore.

Experimental

Materials and methods

Salicylaldehyde and L-alanine were purchased from Aldrich Chemical Co. and Sisco Research Laboratories Pvt. Ltd. (SRL), India, respectively and used as received. The IR spectra were recorded on Nicolet FT-IR spectrophotometer with KBr discs in the range 4000-400 cm^{-1}. UV-vis spectra were recorded on Perkin-Elmer Lambda 25 UV-vis spectrophotometer. ^{1}H NMR spectra were recorded using a Brucker 600 MHz instrument. Ionization mass (ESI-MS) spectra were recorded on Agilent 6500 Q-TOF LC/MS mass spectrometer. Solid-state magnetic susceptibility of the complexes at room temperature was recorded using Sherwood Scientific Magnetic balance MSB-1. Solution electrical conductivity measurements were made with a Eutech Instruments CON 5/TDS 5 Conductivity Meter calibrated with 0.01 N KCl solutions as calibrant. Optical rotation measurements were done using Rudolph Polarimeter. Elemental analyses were done using Thermo Finnigan FLASH EA 1112 and by EuroEA elemental analyzer instruments. X-Band EPR spectra were recorded at room temperature with a Jeol JES-FA series spectrometer. The spectra were calibrated with an internal manganese marker. Thermogravimetric analyses were performed with Mettler Toledo SDTA 851e and TA SDT Q600 instruments, with a heating rate of 5 ^{o}C per minute under N_2 atmosphere using 5-10 mg of sample per run. Powder X-Ray diffraction patterns were obtained using a MAKE Bruker, D2 phaser with Cu–Kα radiation (λ =1.5418 Å) equipped with an integrated PC and DIFFRAC. SUITE software. The diffraction patterns were collected over a 2θ range of 5–55° at a step scan rate of 0.02°. Variable temperature magnetic susceptibility data were collected by using a Quantum Design MPMS SQUID magnetometer over a temperature range of 2 to 300 K at a fixed field of 1T. CD spectra were recorded on a JASCO J-815 spectrophotometer.

LiHL. The amino acid, L-alanine (4.00 g, 0.045 mol) in 35 mL of MeOH was stirred for about 10-15 minutes to form white slurry. Partially grinded $LiOH•H_2O$ (1.88 g, 0.045 mol) was added to this slurry and stirred for about 30-40 minutes. The solution turned clear with few white undissolved particles. The reaction mixture was decanted to remove the undissolved particles. Drop wise addition of salicylaldehyde (5.50 g, 0.045 mol) to this solution, under stirring, produced a clear yellow solution. After about 15-20 minutes, a yellow precipitate started appearing. The reaction mixture was allowed to stir for another one and half hour, while the last 30 minutes the reaction mixture was heated on water bath at 50-55 °C. The precipitate was filtered through Büchner funnel. The solid was washed with ethanol followed by diethyl ether. Finally, it was dried in a vacuum desiccator. Yield 7.31 g (82%). Anal. Calcd. for $C_{10}H_{10}NO_3Li$: C, 60.31; H, 5.06; N, 7.03; found C, 60.35; H, 4.93; N, 7.30. ^{1}H NMR (600MHz, CD_3OD, ppm): 8.38 (imine, s, 1H), 7.30-7.27(Ph-H, m, 2H), 6.77(Ph-H, d, 1H, J = 8.8 Hz), 6.77(Ph-H, t, 1H, J = 7.8 Hz), 4.09 (C-H, q, 1H, J = 6.8 Hz), 1.54(CH_3, d, 3H, J = 6.8 Hz). ESI-MS ($[M+H]^+$): calcd 194.0817; found 194.0816. $[\alpha]_D^{25}$ = +109^{o} in MeOH, c = 1. UV/Vis (MeOH): λ_{max}, nm (ε, M^{-1} cm^{-1}): 216 (19000), 254 (9900), 277sh (5900), 316 (2900), 402 (2800). IR (KBr, cm^{-1}): 1648s, 1620s, 1525 s, 1405m, 1369m. Λ_M (ohm^{-1} cm^2 mol^{-1}): 50 in MeOH.

Single Crystals for X-ray diffraction were isolated by slow evaporation of the combined filtrate and washings collected in the above procedure. Crystals obtained were yellow plates. To confirm that the crystals isolated are of same composition with that of bulk, we have compared the powder diffraction data of the bulk precipitate with the simulated spectrum from the X-ray structure (Figure S1). Both this data and FTIR of both are identical.

$(H_3O)_2[Cu_6(\mu_3\text{-}OH)_2(L)_6(NH_3)]•8H_2O$ (1). LiHL (0.100 g, 0.502 mmol) and $LiOH.H_2O$ (0.021g, 0.502 mmol) were stirred in ~8mL of MeOH to give a clear yellow solution. To this, $Cu(ClO_4)_2.6H_2O$ (0.093g, 0.251mmol) in ~5mL of MeOH was added drop wise, which initially gave dull green coloured solution without any precipitation but the green color was considerably intensified at the end of addition. The reaction mixture was stirred for 1hr continuously, during which there was no precipitation. Ammonium chloride (0.014 g, 0.251 mmol) was added as solid and stirred continuously for another 1hr, during which there was no observable change in the reaction mixture. Equal volume of acetonitrile was added and kept in air. After 5-7 days most of the solvent was evaporated leaving small deep blue cubes along with green viscous solution. The crystals were washed first with minimum amount of ice cold water (0.5mL×2) and then with water: acetone (1:2) mixture. The isolated crystals were dried under vacuum and weighed. Yield 0.033 g (44%). Anal. Calcd. for $(H_3O)_2[Cu_6(\mu_3\text{-}OH)_2(L)_6(NH_3)]•8H_2O$: C, 40.91; H, 4.63; N, 5.57; found C, 40.74; H, 4.33; N, 5.35. UV/Vis (MeOH): λ_{max}, nm (ε, M^{-1} cm^{-1}, /Cu_6 unit): 221 (149000), 241 (155000), 268 (89000), 368 (36000), 651 (700). $[\alpha]_D^{25}$ = 0^{o} in MeOH, c = 0.1. IR (KBr, cm^{-1}): 3384(broad and weak), 1639(s), 1600(s), 1541(s), 1470(m), 1442(s), 1404(m), 1377, 1351, 1291(s), 1198 (s), 911, 799, 781, 770, 575 and 547. μ_{eff} (powder, 298K): 1.83 μ_B/Cu. Λ_M (ohm^{-1} cm^2 mol^{-1}): 58 in MeOH. EPR in DMF at 298K: g_{av} 2.151, A_{av} 90G. EPR in DMF at 77K: $g_{parallel}$ 2.303, $g_{perpendicular}$ 2.064, $A_{parallel}$ 196G.

$(H_3O)_2[Cu_6(\mu_3\text{-}OH)_2(L)_6(H_2O)]•8H_2O$ (1a). LiHL (0.200 g, 1.00 mmol) was stirred and dissolved in ~4 mL of H_2O to give a clear yellow solution, to this $LiOH•H_2O$ (0.056 g, 1.33 mmol) as solid was added and dissolved, there was no any other change in the reaction mixture. A solution of $Cu(ClO_4)_2•6H_2O$ (0.371 g, 1.00 mmol) in ~2-3 mL of H_2O was stirred separately to which the above ligand solution was added in drops. It initially gave a light green solution, which on further addition gradually formed a pale bluish green precipitate (fluffy). Acetone was used as the wash solvent for complete transfer of ligand solution into the stirring reaction mixture. The reaction mixture was stirred for another 1hr continuously and then filtered through frit. The pale bluish green solid (0.145 g) was washed with water and acetone unless the washings were colorless, whereas the filtrate along with acetone (half the volume of filtrate) was kept in air. After 4-5 days most of the solvent was evaporated leaving very fine bluish crystalline solid (cubes under microscope) along with green viscous soln. The crystalline solid was washed with minimum volume of ice cold water (0.5 mL×3) and then with water: acetone mixture in the ratio (1:2). The isolated crystals were dried under vacuum and weighed. Yield 0.098 g (33%). Anal. Calcd. for $(H_3O)_2[Cu_6(\mu_3\text{-}OH)_2(L)_6].9H_2O$: C, 40.89; H, 4.57; N, 4.77; found C, 40.33; H, 4.34; N, 4.37. $[\alpha]_D^{25}$ = +32^{o} in MeOH, c = 0.1. UV/Vis (MeOH): λ_{max}, nm (ε, M^{-1} cm^{-1} /Cu_6 unit): 221 (143000), 241 (146000), 268 (86000), 367 (34000), 655 (670). IR (KBr, cm^{-1}): 3404 (broad and weak), 1639(s), 1600(s), 1541(s), 1470(m), 1443(s), 1403(m), 1380, 1352, 1291(s), 1198(s), 911, 799, 770, 577 and 547. μ_{eff} (powder, 298K): 1.83 μ_B/Cu. Λ_M (ohm^{-1} cm^2 mol^{-1}): 102 in MeOH. EPR in MeOH at 298K: g_{av} 2.153, A_{av} 83G. EPR in MeOH at 77K: $g_{parallel}$ 2.317, $g_{perpendicular}$ 2.072, $A_{parallel}$ 181G.

$(H_3O)_2[Cu_6(\mu_3\text{-}OH)_2(L)_6(NH_3)]•8H_2O$ (1b). LiHL (0.500 g, 2.512 mmol) and $LiOH•H_2O$ (0.140 g, 3.340 mmol) were stirred in ~5mL of H_2O at 5^{o}C to give a clear yellow solution, followed by formation of a pale yellow precipitate. To this, $Cu(ClO_4)_2•6H_2O$ (0.931 g, 2.512 mmol) in ~3mL of H_2O was added drop wise, to give a green solution with precipitation. The reaction mixture was stirred for 1hr continuously at 5^{o}C and then ammonium chloride (0.134 g, 2.512 mmol) in ~2mL of H_2O was added drop wise. Slight decrease in the intensity of green color of the solution was observed and the reaction mixture was further stirred for 1hr at 5°C. The reaction mixture was filtered and the filtrate was kept for slow evaporation. After 6-8 days most of the solvent was evaporated leaving fine deep blue crystalline solid along with green viscous solution. The crystals were isolated and washed first with minimum amount of ice cold water (0.5mL×2) and then with water: acetone (1:2) mixture. The isolated crystals were dried under vacuum and weighed. Yield 0.180 g (24%). The precipitate (0.060 g) obtained during the reaction was not characterized. Anal. Calcd. for $(H_3O)_2[Cu_6(\mu_3\text{-}OH)_2(L)_6(NH_3)]\bullet 8H_2O$: C, 40.91; H, 4.63; N, 5.57; found C, 40.73; H, 4.30; N, 5.76. UV/Vis (MeOH): λ_{max}, nm (ε, M^{-1} cm^{-1}, /Cu_6 unit): 223 (108000), 242 (152000), 268 (66600), 368 (26700), 650 (670). $[\alpha]_D^{25} = 90^o$ in MeOH, $c = 0.1$. IR (KBr, cm^{-1}): 3382(broad and weak), 1639(s), 1599(s), 1540(s), 1470(m), 1443(s), 1400(m), 1384, 1354, 1292(s), 1200 (s), 911, 799, 779, 676, 576 and 546. μ_{eff} (powder, 298K): 1.79μ_B/Cu. Λ_M (ohm^{-1} cm^2 mol^{-1}): 37 in MeOH.

References:

1. (a) Md. Akhtarul Alam, Munirathinam Nethaji and Dr.Manabendra Ray, *Angew. Chem. Int. Ed.,* 2003, **42**, 1940-1942. (b) Dennis H. Leung, Robert G. Bergman and Kenneth N. Raymond, *J. Am. Chem. Soc.,* 2007, **129**, 2746. (c) Jung Soo Seo, Dongmok Whang, Hyoyoung Lee, Sung Im Jun, Jinho Oh, Young Jin Jeon and Kimoon Kim, *Nature*, 2000, **404**, 982. (d) Eunsung Lee, Jaheon Kim, Jungseok Heo, Dongmok Whang and Kimoon Kim, *Angew. Chem. Int. Ed.*, 2001, **40**, 399. (e) J. M. Rivera, T. Martin and J. Rebek Jr., *Science*, 1998, **279**, 1021. (f) S. G kim, K. H. Kim, J. Jung, S. K. Shin and K. H. Ahn, *J. Am. Chem. Soc.*, 2002, **124**, 591. (g) Shohei Tashiro, Yasuyo Ogura, Sei Tsuboyama, Kaoru Tsuboyama and Mitsuhiko Shionoya, *Inorg. Chem.*, 2011, **50**, 4. (h) Y. Inokuma, M. Kawano and M. Fujita, *Nature Chem.*, 2011, **3**, 349. (i) S. C. Sahoo, M. Ray, *Chem. Eur. J.*, 2010, **16**, 5004.

2. (a) David E. Metzler, Miyoshi Ikawa and Esmond E. Snell, *J. Am. Chem. Soc.*, 1953, **76**, 648. (b) D. L. Leussing and Kyu Sun Bai, Anal. Chem., 1968, **40**, 575. (c) G. N. Weinstein, M. J. O'connor and R. H. Holm, *Inorg. Chem.,* 1970, **9**, 2104. (d) Loys J. Nunez and Gunther L. Eichhorn, *J. Am. Chem. Soc.*, 1962, **84**, 901. (e) Havva Demirelli and Fitnat Koseoglu, *J. Solution Chem.*, 2005, **34**, 561. (f) Yu. N. Belokon, V. I. Maleeva, I. L. Mal'favno, T. F. Savel'eva, N. S. Ikonikov, A. G. Bulychev, D. L. Usanov, D. A. Kataev and M. North, *Russ.Chem.Bull., Int.Ed.,* 2006, **55**, 821. (g) Chang-Ying Chu, Der-Ren Hwang, Sheng-Kai Wang and Biing-Jiun Uang, *Chem. Commun.*, 2001, 980. (h) Ryuji Ando, Hashira Inden, Miho Sugino, Hiroyuki Ono, Daisuke Sakaeda, Takeyoshi Yagyu and Masunobu Maeda, *Inorg. Chim. Acta*, 2004, **357**, 1337. (i) Shalin kumar, Durga Nath Dhar, P N Saxena, *J. Sci. Ind. Res.*, 2009, **68**, 181. (j) Zahid H. Chohan, M. Arif and M. Sarfraz, *Appl. Organometal. Chem.,* 2007, **21,** 294. (k) R. C. Das, M. K. Mishra, S. K. Mohanty, *Acta Chim. Hung.*, 1983, **112**, 377. (l) Laijin Tian, Junlian Tian, Tantuan Li, Guizhi Li, Siwei Bi, Enqing Gao and Shuxiang Liu, Huaxue Shiji, 1996, **18**, 114.
3. (a) Chuan-Gao Zhu, *Synth. React. Inorg., Met.-Org., Nano-Met. Chem.*, 2013, **43**, 886. (b) Yu-Guang Li, Da-Hua Shi, Hai-Liang Zhu, Hong Yan, Seik Weng Ng, *Inorg. Chim. Acta*, 2007, **360**, 2881. (c) Zhijun Zhang, Xi Li, Chenggang Wang, Chaocan Zhang, Peng Liu, Tingting Fang, Yan Xiong and Wenjing Xu, *Dalton Trans.*, 2012, **41**, 1252. (d) Shyamapada Shit, Madhusudan Nandy, Georgina Margaret Rosair, Mohamed Salah El Fallah, Joan Ribas, Eugenio Garribba, Samiran Mitra, *Polyhedron*, 2013, **52**, 963. (e) Pritha Talukder, Shyamapada Shit, Ashok Sasmal, Stuart R. Batten, Boujemaa Moubaraki, Keith S. Murray, Samiran Mitra, *Polyhedron*, 2011, **30**, 1767. (f) Yanhua Lan, Ghenadie Novitchi, Rodolphe Clérac, Jin-Kui Tang, N T Madhu, Ian J Hewitt, Christopher E Anson, Sally Brooker, Annie K Powell, *Dalton Trans.*, 2009, 1721.
4. (a) Joanne Olivard, David E. Metzler and Esmond E. Snell, *J. Biol. Chem.*, 1952, **199**, 669. (b) Yu. N. Belokon', I. E. Zel'tzer, V. I. Bakhmutov, M. B. Saporovskaya, M. *G.* Ryzhov, A. I. Yanovsky, Yu. T. Struchkov and V. M. Belikov, *J. Am. Chem. Soc.*, 1983, **105**, 2010. (c) Ming-Daw Tsai, Herschel J. R. Weintraub, Stephen R. Byrn, Ching-jer Chang and Heinz G. Floss, *Biochemistry*, 1978, **17**, 3183.
5. Angel Garcia-Raso, Juan J. Fiol, Adela Lo´pez-Zafra, Ignasi Mata, Enrique Espinosa and Elies Molins, Polyhedron, 2000, 19, 673.
6. Heinert and Arthur Martell, J. Am. Chem. Soc., 1962, 84, 3257.
7. Molar conductance (ohm^{-1} cm^2 mol^{-1}) range for 1:1 electrolyte in MeOH: 80-115.W. J. Geary, *Coord. Chem. Rev.* 1971, *7*, 81.
8. Xu-Sheng Gao, Yong-Min Wan, Qin Zhou, Yuan-Xiang Shi, Jin-Tang Wang, Acta Crystallogr., Sect. E, 2007, 63, m1417.
9. Gerhard Miiller, Gerd-Michael Maier and Martin Lutz, Inorg. Chim. Acta, 1994, 218, 121.
10. The amount of distortion was calculated from the structural data where the value of τ should be 0 for perfect square-pyramidal geometry and 1 for perfect trigonal bipyramidal structure; A. W. Addision, T. N. Rao, J. Reedijk, J. van Rijn and G. C. Verschoor, *J. Chem. Soc., Dalton Trans.,* 1984, 1349.
11. Hydroxo-bridged Cu(II)trinuclear complexes: (a) He-Dong Bian, Jing-Yuan Xu, Wen Gu, Shi-Ping Yan, Peng Cheng, Dai-Zheng Liao and Zong-Hui Jianga, *Polyhedron* , 2003, **22**, 2927. (b) B. Sarkar, M. Sinha Ray, M. G. B. Drew, A. Figuerola, C. Diaz and A. Ghosh, *Polyhedron*, 2006, **25**, 3084. (c) P. Mukherjee, M. G. B. Drew, M. Estrader, C. Diaz and A. Ghosh, *Inorg. Chim. Acta* , 2008, **361**, 161. (d) B. L. Guennic, S. Petit, G. Chastanet, G. Pilet, D. Luneau, N. Ben Amor and V. Robert, *Inorg. Chem.*, 2008, **47**, 572. (e) C. Biswas, M. G. B. Drew, A. Figuerola, S. Gómez-Coca, E. Ruiz, V. Tangoulis and A. Ghosh, *Inorg. Chim. Acta* , 2010, **363**, 846. (f) Yuan-Bo Cai, Lei Liang, Jing Zhang, Hao-Ling Sunc and Jun-Long Zhang, *Dalton Trans.*, 2013, **42**, 5390.
12. (a) B. J. Hathaway, in *Comprehensive Coordination Chemistry*, G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon Press, London, 1987, vol. 5, p. 533 (b) A. W. Addison and E. Sinn, *Inorg. Chem.*, 1983, **22**, 1225 (c) M. Bonamico, G. Dessy, A. Mugnoli, A.Vaeiago and L. Zambonelli, *Acta Crystallogr.*, 1965, **19**, 886 (d) Y. Agus, R. Louis and R. Weiss, *J. Am. Chem. Soc.*, 1979, **101**, 3381.
13. Chris Knight, Gregory A. Voth, Acc. Chem. Res., 2012, **45**, 101.
14. (a) A. Earnshaw, *Introduction to Magnetochemistry*, Academic Press, London, 1968. (b) C. J. OConnor, *Prog. Inorg. Chem.*, 1982, *29*, 203.
15. (a) M. Paik Suh, M. Young Han, J. Ho Lee, K. Sik Min and C. Hyeon, *J. Am. Chem. Soc* 1998, **120**, 3819 (b) He- Dong Bian, Jing-Yuan Xu, Wen Gu, Shi-Ping Yan, Peng Cheng, Dai-Zheng Liao, Zong-Hui Jiang, *polyhedron*, 2003, **22**, 2927.
16. The program package JulX was used for spin-Hamiltonian simulations and fittings of the data by a full-matrix diagonalization approach (E. Bill, unpublished results).
17. W. E. Hatfield, in, Magneto-Structural Correlations in Exchange Coupled Systems, ed. R. D. Willett, D. Gatteschi and O. Kahn, NATO-ASI Series, Reidel, Dordrecht, 1985, p. 555, and references therein.
18. M. Fondo, N. Ocampo, A. M. Garc´ıa-Deibe, M. Corbella, M. R. Bermejoc and J. Sanmart´ın, *Dalton Trans.*, 2005, 3785.

Notes and references

Department of Chemistry, Indian Institute of Technology Guwahati, Guwahati - 781039, Assam, India. Fax: +91 3612 690762; Tel: +91 3612 582310; E-mail: manabray@iitg.ernet.in

† Electronic Supplementary Information (ESI) available: X-ray, Uv-vis, IR, TGA, EPR and Magnetic plots (Figure S1 to S16) . See DOI: 10.1039/b000000x/

Table of content entry:

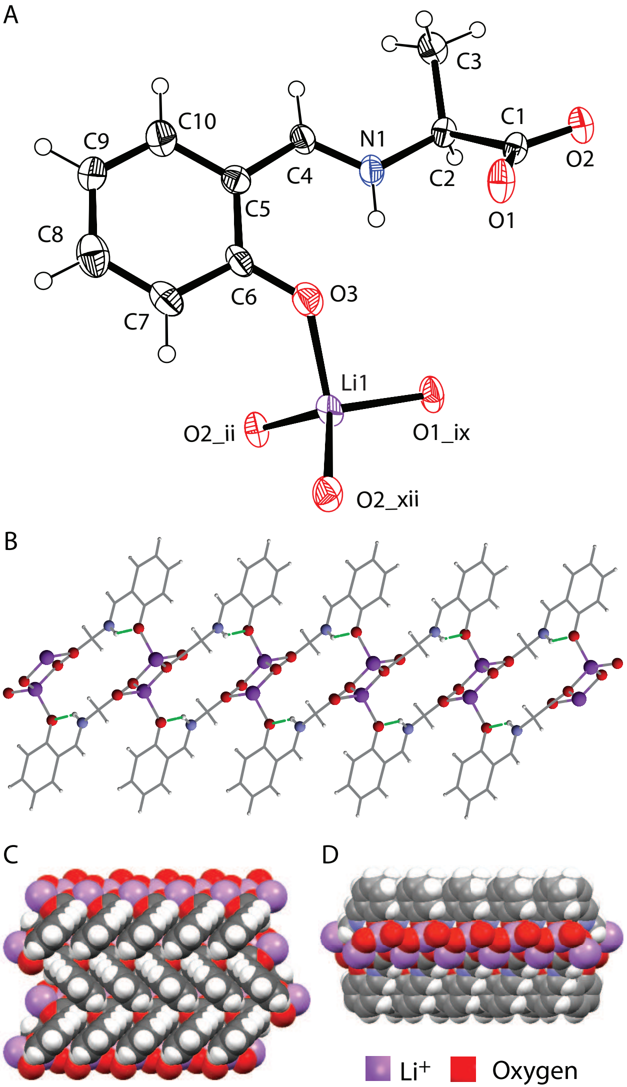
Revising well studied Schiff base racemization led to isolation of new chiral architecture exhibiting relatively rare ferromagnetic property.

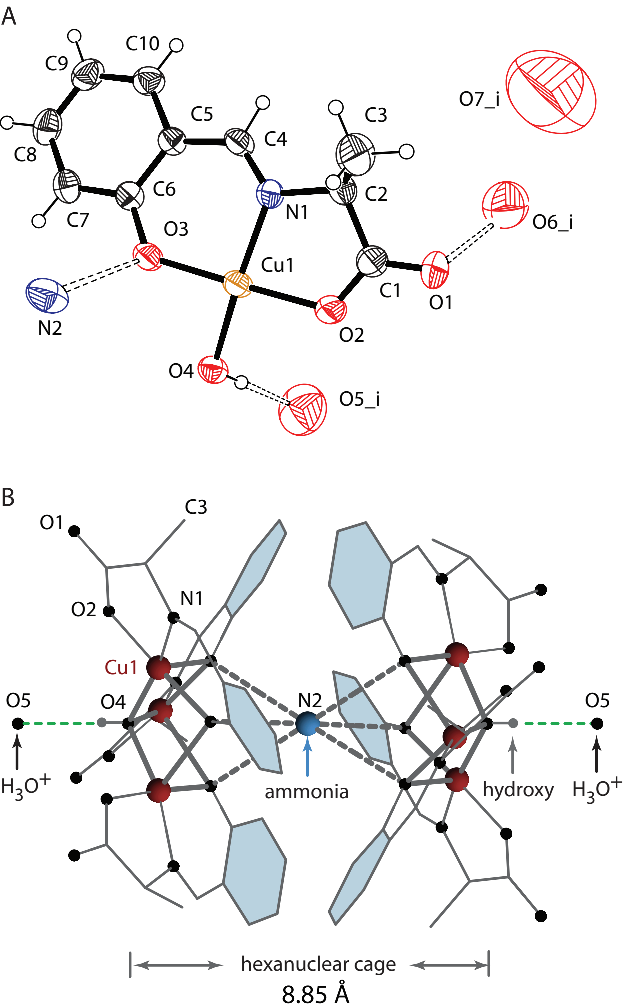
Table Of Content Figure

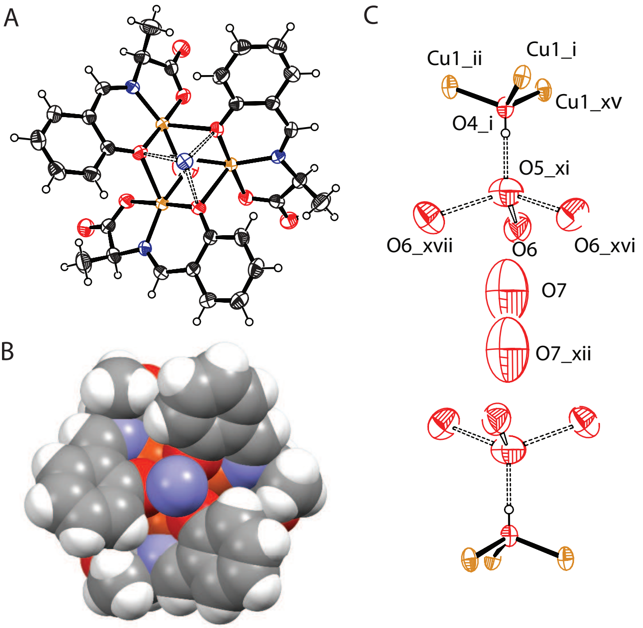
Table 1. Crystal data for the Cu(II) complexes[a] and LiHL[a]

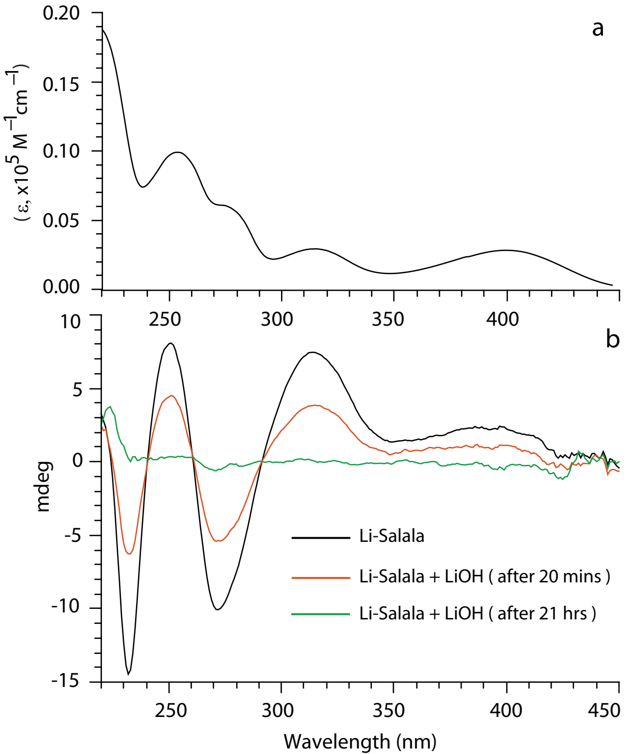
Compounds	**1**	**1a**	LiHL
Empirical formula	$C_{60}H_{77}Cu_6N_7O_{29}$	$C_{30}H_{38}Cu_3N_3O_{15}$	$C_{10}H_{10}LiNO_3$
M	1741.56	871.27	199.13
Crystal system	Trigonal	Trigonal	Monoclinic
Space group	R -3	R -3	C 2
a/ Å	16.4342(9)	16.3913(7)	14.561(5)
b/ Å	16.4342(9)	16.3913(7)	5.1031(14)
c/ Å	22.5159(15)	23.2922(12)	14.153(5)
$\beta/^{o}$	90	90	114.57(4)
V / Å^3	5266.4(8)	5419.6(6)	956.4(6)
Z	3	6	4
ρ/ g cm^{-3}	1.627	1.583	1.383
μ/ mm^{-1}	1.873	1.821	0.101
Flack parameter	-	-	-1(4)
Reflections collected	4611	8704	3500
Independent reflections	3043	3142	2449
Goodness of fit	1.054	1.016	0.989
R_{int}	0.0252	0.0377	0.0806
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0522 wR2 = 0.1393	R1 = 0.0564 wR2 = 0.1480	R1 = 0.0906 wR2 = 0.1109
R indices (all data)	R1 = 0.0844 wR2 = 0.1604	R1 = 0.0867 wR2 = 0.1664	R1 = 0.1910 wR2 = 0.1534

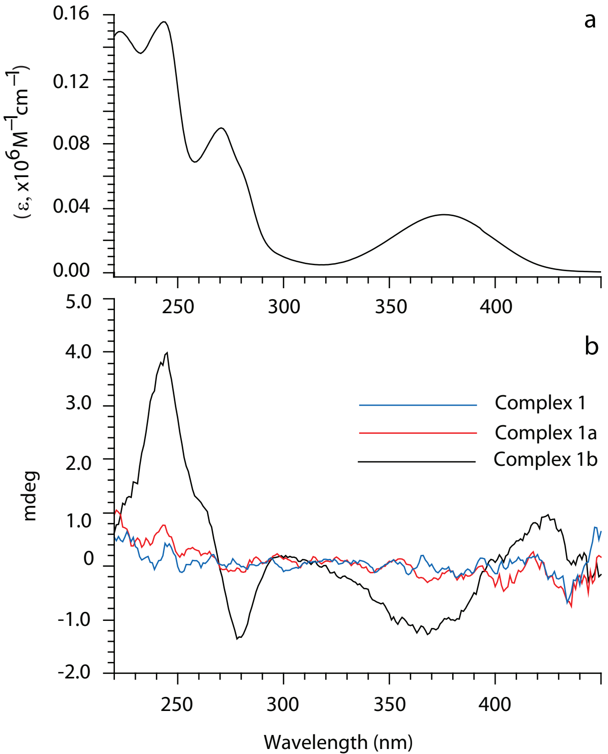
[a] Refinement method: full-matrix least-squares on F^2

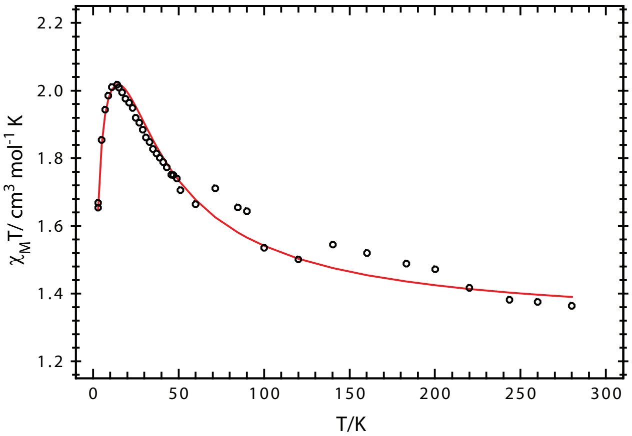

A
C3
C10
C9
C1
C4
N1
O2
C2
C5
O1
C8
O3
C6
C7
Li1
O2_ii
O1_ix
O2_xii
B
C
D
Li+
Oxygen

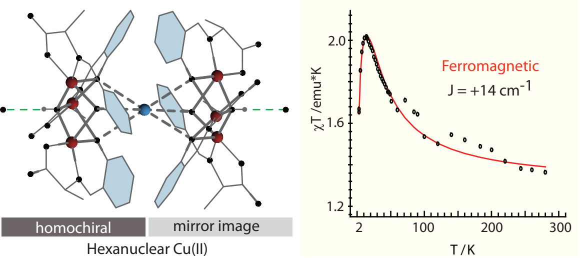

A
C9
C10
C5
C4
C3
O7_i
C8
C6
N1
C2
O6_i
C7
O3
Cu1
C1
O1
N2
O2
O4
O5_i
B
O1
C3
O2
N1
Cu1
O5
O4
N2
O5
H_3O^+
ammonia
hydroxy
H_3O^+
hexanuclear cage
8.85 Å


A
B
C
Cu1_ii
Cu1_i
Cu1_xv
O4_i
O5_xi
O6_xvii
O6
O6_xvi
O7
O7_xii


a
(ε, x10^5 M^-1cm^-1)
0.20
0.15
0.10
0.05
0.00
250
300
350
400
b
mdeg
10
5
0
-5
-10
-15
Li-Salala
Li-Salala + LiOH (after 20 mins)
Li-Salala + LiOH (after 21 hrs)
250
300
350
400
450
Wavelength (nm)


a
0.16
0.12
0.08
0.04
0.00
(ε, x10^{6}M^{-1}cm^{-1})
250
300
350
400
b
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
mdeg
Complex 1
Complex 1a
Complex 1b
250
300
350
400
Wavelength (nm)


$\chi_M T$/ cm^3 mol^{-1} K
T/K
2.2
2.0
1.8
1.6
1.4
1.2
0
50
100
150
200
250
300


homochiral
mirror image
Hexanuclear Cu(II)
2.0
1.6
1.2
χT /emu*K
2
100
200
300
T / K
Ferromagnetic
J = +14 cm^{-1}