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

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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 (H₂O)₂[Co₃(μ₃-OH)(μ₃-NH₃)₆(L)₂]·8H₂O (I) and (H₂O)₂[Co₃(μ₃-OH)(μ₃-H₂O)₆(L)₂]·8H₂O (Ia) where L²⁻ is the dianionic form of Schiff base of L-alanine and salicylaldehyde. The complex 1 has two C₃ symmetric hydroxo bridged trinuclear halves joined by an ammonia or water molecule at the center through H-bonding. Each half 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. 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. Schiff-bases of salicylaldehyde and amino acids are well-studied area, mainly due to their use in understanding coordination chemistry, bioinorganic active site model, catalysis and biological 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 VO²⁺. Most of the known complexes are mononuclear with binuclear or coordination polymers with the general formula [M(L)]ₙ where M is dicatonic transition metal ion and L is the N-salicylidene glycinate. Among hexanuclear Cu(II) complexes with Schiff base, we could find only three reports. 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 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. The ligand was synthesized by condensing salicylaldehyde and L-alanine in presence of one equivalent of LiOH. Base was used to deprotonate the zwiterion form of amino acid to free amine form. This is similar to the procedure reported by Heinart and Martell using KOH as base. 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). 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). 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 7.30 ppm. 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 C2 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 salicyldieneβyalaninate which unfortunately did not have the hydrogen refined.\(^5\)

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).

Figure 1

Figure 1. (A) ORTEP diagram showing the LiHL with thermal ellipsoids set to 40% probability along with Lithium coordination. The atoms O1, O2, O2, O2, and O2 were generated using symmetry operations (1-x, y, -1-z), (1-x, 1-y, -z) and (-1/2+x, 1+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): N1yC4 1.289(7), N1yC2 1.511(8), O3yC6 1.296(8), C4yC5 1.409(9), C5yC6 1.418(9), C6-C7 1.419(9), C7-C8 1.379(8), C8-C9 1.431(11), C9-C10 1.336(11), C10-C15 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): N1y-C10 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 \(\text{NH}_4\text{Cl}\) before isolation improves the yield by 5-10% and larger crystals. Only microcrystals were isolated without addition of \(\text{NH}_4\text{Cl}\), which were unsuitable for X-ray structure. Changing the metal, ligand and base ratio to 1:1:1:3 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) \(\text{NH}_4\text{Cl}\) 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, O6, O7, O8 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 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): O3yCu1yO2 121.5(2), O3yCu1yO3 72.9(2), Cu1-O4-Cu1 106.93(18), t = 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 consists 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 (\(t = 0.217\)).\(^10\) 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
between two hydronium ion occupied by disordered water molecules. The distance indicates disorder at this position. 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. 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 C3 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, O7 and O7_xii were generated using symmetry operations (1/3yx, 2/3yy, 2/3yz), (1/3yx, -1/3+xy, 2/3-z), (1/3+xy, -1/3+y, 2/3-z), (1/3, 1/3+xy, 2/3-z), (1/3, 2/3-y, 1.66667-z), (x, y, z), (-x, y, -z), (-x, y-x+y, 2/3-z), (1/3, 2/3-y, 2/3-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). The 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 NH2 and 10 H2O 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-O6 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 change followed a first order behavior (Figure S7). The observed rate / mole was found to be 0.110 min⁻¹M⁻¹. This is slower (1/5) than the rate reported for Cu(4-NO2sal-L-val)1.5H2O in presence of base in ethanol at 50 °C, where (4-NO2sal -L-val)²⁻ is the Schiff base of L-valine and 4-nitro-salicylaldehyde. 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. Thus the present result is consistent with the reported racemizations. The circular dichroism (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 1 equivalent 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 the complex 1 in MeOH (6.6 µM), (b) CD spectra of LiHL and LiHL with one equivalent LiOH•H2O 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, 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, 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 \(T_{\text{做法}}\) 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.\(^{15b}\)

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 juliX written by Eckhard Bill for exchange coupled systems of three \(s = \frac{1}{2}\) system.\(^{16}\) The operator contained exchange Hamiltonian and Zeeman interaction. The zero-field splitting option was not used. The ferromagnetic coupling constant \(J_{1}\) 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\(^{15c}\) were \(J = 37.8\) cm\(^{-1}\) and complex by Yan and coworkers\(^{15d}\) 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 \(>97.5^\circ\) promotes antiferromagnetic coupling, whereas angle of \(<97.5^\circ\) promotes ferromagnetic coupling. In the present set of complexes, Cu-OH-Cu angle is \~106\(^\circ\) and Cu-O(phenoxy)-Cu is 90.4\(^\circ\). 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 hydroxy complexes have Cu-O(phenoxy)-Cu angles between 96 to 99\(^\circ\) (reported Cu-OH-Cu angles lies between 100 to 107\(^\circ\)).\(^{15c}\) This shorter Cu-O-phenoxy-Cu angle probably is the reason for overall ferromagnetism.

Figure 6

**Figure 6.** Plot of \(X_{\text{做法}}\) 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\(^{11}\) 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 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.\(^{20,21}\) Based on the solution studies, either deprotonation at chiral carbon followed by rehydration or keto-enol tautomer form of has been cited as a mechanism of such occurrence.\(^{21}\) However, structural characterization of the products or formation of this type of hexanuclear architecture through racemization has not been reported.

Although one eq 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 possibility 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/1/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 400-4000 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
LiHL. The amino acid, L-alanine (4.0 g, 0.045 mol) in 35 mL of MeOH was stirred for about 10-15 minutes to form white slurry. Partially ground LiOH•H₂O (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 C₁₀H₁₁O₆ (19000), 254 (9900), 277sh (5900), 316 (2900), 402 (2800). IR (KBr, cm⁻¹): 3370, 3280 (NH₃), 2934, 2876, 1600(s), 1541(s), 1470(m), 1443(s), 1403(m), 1380, 1352, 1291(s), 1198 (s), 1198, 781, 770, 577 and 547. µ[eff] (powder, 298K): 1.83 µµ/Cu. Λ₉ (ohm² cm⁻¹ mol⁻¹): 58 in MeOH. EPR in DMF at 298K: gᵥ= 2.151, Λᵥ. EPR in DMF at 77K: Λᵥ= 2.303, g[perpendicular] 2.064, A[perpendicular] 196G.

(H₂O)₃[Cu₂(µ₂-OH)₂(L)(H₂O)]·8H₂O (1a). LiHL (0.200 g, 1.00 mmol) was stirred and dissolved in ~4 mL of H₂O to give a clear yellow solution, to this LiOH•H₂O (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 CuClO₄·6H₂O (0.371 g, 1.00 mmol) in ~2-3 mL of H₂O was stirred separately to which anhydrous LiOH was stirred separately to which H₂O to give a clear yellow solution, to this LiOH•H₂O (0.056 g, 1.33 mmol) as solid was added and dissolved, there was no any other change in the 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 (1:2) mixture. The isolated crystals were dried under vacuum and weighed. Yield 0.098 g (33%). Anal. Calcd. for (H₂O)₃[Cu₂(µ₂-OH)₂(L)(H₂O)]·8H₂O: C, 40.89; H, 4.57; N, 4.77; found C, 40.33; H, 4.34; N, 4.37. µ[eff] = +32 in MeOH, c = 0.1. UV/Vis (MeOH): λₘαx nm (ε, M⁻¹ cm⁻¹): 216 (19000), 254 (9900), 277 (5900), 316 (2900), 402 (2800). IR (KBr, cm⁻¹): 1648s, 1620s, 1525 s, 1405m, 1369m. Λ₉ (ohm² cm⁻¹ mol⁻¹): 30 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.

(H₂O)₃[Cu₂(µ₂-OH)₂(L)(NH₃)]·8H₂O (1b). LiHL (0.100 g, 0.502 mmol) and LiOH•H₂O (0.021g, 0.502 mmol) were stirred in ~8 mL of MeOH to give a clear yellow solution. To this, CuClO₄·6H₂O (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 (H₂O)₃[Cu₂(µ₂-OH)₂(L)(NH₃)]·8H₂O: C, 40.91; H, 4.63; N, 5.57; found C, 40.74; H, 4.33; N, 5.35. UV/Vis (MeOH): λₘαx nm (ε, M⁻¹ cm⁻¹): 211 (149000), 241 (155000), 268 (89000), 368 (36000), 651 (700). µ[eff] (powder, 298K): 1.83 µµ/Cu. Λ₉ (ohm² cm⁻¹ mol⁻¹): 58 in MeOH. EPR in DMF at 298K: gᵥ= 2.151, Λᵥ. EPR in DMF at 77K: Λᵥ= 2.317, g[perpendicular] 2.072, A[perpendicular] 181G.
ammonium chloride (0.134 g, 2.512 mmol) in ~2 mL of H_{2}O 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 1 hr at 5°C. The reaction mixture was filtered and the filtrate was kept for slow evaporation. After 6-8 days most of the solvot 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 (0.5 mL × 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_{2}O)_{2}Cu[(µ-OH)(L)_{2}(NH_{3})]•8H_{2}O: C, 40.91; H, 4.63; N, 5.57; found C, 40.73; H, 4.30; N, 5.76. UV/Vis (MeOH): \(\varepsilon_{\text{max}}\) nm (e, M⁻¹ 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. \(\mu_{\text{eff}}\) (powder, 298K): 1.79 μμB/Cu. \(\Lambda_{\text{M}}\) (ohm⁻¹ cm⁻² mol⁻¹): 37 in MeOH.

References:


12. 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).


Notes and references

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† 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 1. Crystal data for the Cu(II) complexes and LiHL

<table>
<thead>
<tr>
<th>Compounds</th>
<th>I</th>
<th>Ia</th>
<th>LiHL</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Empirical formula</strong></td>
<td>C_60H_77Cu_6N_7O_29</td>
<td>C_30H_38Cu_3N_3O_15</td>
<td>C_{30}H_{10}LiNO_3</td>
</tr>
<tr>
<td><strong>M</strong></td>
<td>1741.56</td>
<td>871.27</td>
<td>199.13</td>
</tr>
<tr>
<td><strong>Crystal system</strong></td>
<td>Trigonal</td>
<td>Trigonal</td>
<td>Monoclinic</td>
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<td><strong>Space group</strong></td>
<td>R -3</td>
<td>R -3</td>
<td>C 2</td>
</tr>
<tr>
<td><strong>α/Å</strong></td>
<td>16.4342(9)</td>
<td>16.3913(7)</td>
<td>14.361(5)</td>
</tr>
<tr>
<td><strong>β/Å</strong></td>
<td>16.4342(9)</td>
<td>16.3913(7)</td>
<td>14.361(5)</td>
</tr>
<tr>
<td><strong>γ/Å</strong></td>
<td>22.5159(15)</td>
<td>23.2922(12)</td>
<td>14.153(5)</td>
</tr>
<tr>
<td><strong>β/°</strong></td>
<td>90</td>
<td>90</td>
<td>114.57(4)</td>
</tr>
<tr>
<td><strong>V/Å³</strong></td>
<td>5266.4(8)</td>
<td>5419.6(6)</td>
<td>956.4(6)</td>
</tr>
<tr>
<td><strong>Z</strong></td>
<td>3</td>
<td>6</td>
<td>4</td>
</tr>
<tr>
<td><strong>ρ/ g cm⁻³</strong></td>
<td>1.627</td>
<td>1.583</td>
<td>1.383</td>
</tr>
<tr>
<td><strong>μ/ mm⁻¹</strong></td>
<td>1.873</td>
<td>1.821</td>
<td>0.101</td>
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<tr>
<td><strong>Flack parameter</strong></td>
<td>-</td>
<td>-</td>
<td>-1(4)</td>
</tr>
<tr>
<td><strong>Reflections collected</strong></td>
<td>4611</td>
<td>8704</td>
<td>3500</td>
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<tr>
<td><strong>Independent reflections</strong></td>
<td>3043</td>
<td>3142</td>
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<tr>
<td><strong>Goodness of fit</strong></td>
<td>1.054</td>
<td>1.016</td>
<td>0.989</td>
</tr>
<tr>
<td><strong>R_int</strong></td>
<td>0.0252</td>
<td>0.0377</td>
<td>0.0806</td>
</tr>
<tr>
<td><strong>Final R indices [I &gt; 2σ(I)]</strong></td>
<td>R1 = 0.0522</td>
<td>R1 = 0.0564</td>
<td>R1 = 0.0906</td>
</tr>
<tr>
<td><strong>R indices (all data)</strong></td>
<td>R1 = 0.0844</td>
<td>R1 = 0.0867</td>
<td>R1 = 0.1910</td>
</tr>
</tbody>
</table>

*Refinement method: full-matrix least-squares on F²*
Li-Salala

Li-Salala + LiOH (after 20 mins)

Li-Salala + LiOH (after 21 hrs)
Hexanuclear Cu(II) T /K

\[ J = +14 \text{ cm}^{-1} \]

\[ \chi_T / \text{emu*K} \]

Ferromagnetic homochiral mirror image