Self-assembly of hydrogen-bonded networks of [Cu(HL)Cl](PF$_6$) (HL = N,N$'$-bis(2-pyridylmethyl)-1,3-diaminopropan-2-ol) into 1D chains: Formation of new submicrometer [Cu(HL)Cl](PF$_6$) rods

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Received 21 September 2007; revised 4 December 2007

A new mononuclear copper(II) complex [Cu(HL)Cl](PF$_6$) (I) having an N$_2$O-donor ligand (HL = N,N$'$-bis(2-pyridylmethyl)-1,3-diaminopropan-2-ol) has been synthesized and structurally characterized by X-ray crystallography. I shows a 1D chain in the packing structure through intermolecular O–H---Cl strong hydrogen bonding interaction (O–H---Cl, 1.99(4) Å and the angle (O–H---Cl) 163(4)°). The packing structure of I also shows π–π stacking [close contact 3.325 Å (a = 2-X,-Y,-Z)] of the large aromatic pyridine rings between adjacent chains. The 1D structure stabilized by this type of π–π stacking interaction between adjacent chains leads to a 2D supramolecular network. A submicrometer rod structure of [Cu(HL)Cl](PF$_6$) with a diameter of 580 nm and a length of several microns has been prepared by drop casting method from the methanolic solution of I. The morphology of submicrometer rod of I has been studied by SEM. The driving force for the growth of [Cu(HL)Cl](PF$_6$) rods is probably the strong intermolecular O–H---Cl hydrogen bonding interaction along the 1D chain and π–π stacking interaction between the adjacent chains.

IPC Code: Int. Cl.5 C07F1/08

Self-assembly through coordination and non-covalent interaction such as hydrogen bonds, aromatic π–π stacking, steric repulsion, and van der Walls forces leads to well-organized organic and inorganic supramolecular structures, which can be applied in areas such as selective clathration$^{1-3}$, molecular recognition$^{4-6}$ and catalysis$^{7-9}$. Coordination interactions between labile metal centers and multidentate organic ligand form the primary structure which can be further organized to supramolecular structures through weak noncovalent interactions$^{10-12}$. Therefore, the key steps in building supramolecular structures are to rationally design the ligand and to choose metal ions with suitable coordination geometry. Recent progress demonstrates that some supramolecules can also be applied as precursors or templates in the preparation of nanomaterials$^{13-16}$. Among the numerous supramolecules reported, it is very common to find counterions, small organic molecules, and solvated species in the void spaces of coordination polymers$^{17-20}$.

Over the past few years, studies have been conducted to obtain coordination complexes by using bis-pyridyl ligand with an endogenous μ-1,1 bridging alkoxo unit (N,N$'$-bis(2-pyridylmethyl)-1,3-diaminopropan-2-ol, HL)$^{21,22}$. The mononuclear and dinuclear Cu(II) complexes of this ligand have already been reported$^{22}$, along with structural and solution chemistry studies of copper(II) complexes. The kinetic studies on the hydrolysis of both activated and non-activated phosphodiester, promoted by a dinuclear copper(II) complex are also reported for these complexes. On the other hand, supramolecular chemistry involving any metal complex involving this ligand is a good candidate for pursuing, and surprisingly there is no report of such study. Herein we report the synthesis, X-ray crystal structure of a new mononuclear Cu(II) complex, [Cu(HL)Cl](PF$_6$) (I) (HL = N,N$'$-bis(2-pyridylmethyl)-1,3-diaminopropan-2-ol). The complex I shows 1D chain in the packing structure through intermolecular O–H---Cl--Cu strong hydrogen bonding interaction (O–H---Cl--Cu, 1.99(4) Å and the angle is 163(4)°). This type of H-bonding is rare in literature$^{23,24}$. The packing structure of I also shows the π–π stacking of the large aromatic pyridine rings between adjacent chains to...
form a 2D supramolecular network. The close contact is 3.325 Å \( (a = 2-X, Y, Z) \) between the two \( \pi \)-stacked intermolecular pyridine rings. Submicrometer rod structure of [Cu(HL)Cl](PF\(_6\)) with a diameter of 580 nm and a length of several microns is prepared. The morphology of submicrometer rod of I has been studied by scanning electron microscopy (SEM). The results reveal that the particular chain structure plays a significant role in the formation of submicrometer [Cu(HL)Cl](PF\(_6\)) rods.

**Materials and Methods**

All reagents and chemicals were purchased from Sigma and used without further purification. Solvents used for spectroscopic studies were purified and dried by standard procedures before use\(^25\). FT-IR spectrum was obtained on a Nicolet MAGNA-IR 750 spectrometer with samples prepared as KBr pellets. Elemental analysis was carried out in a 2400 Series-II CHN analyzer, Perkin-Elmer, USA. Absorption spectrum was studied on Shimadzu UV2100 UV-VIS recording spectrophotometer. For the SEM (scanning electron microscopy) study, a drop casting film was prepared on glass slide from the methanolic solution of the sample. After platinum coating, it was observed through a scanning electron microscope JEOL JEM 6700F.

**Synthesis of the ligand HL**

The compound was prepared by the procedure described previously\(^26\) after slight modification. To a solution of 0.9 g 1,3-diamino-2-propanol (10 mmol) in 50 mL ethanol, 2.14 g pyridine-2-carbaldehyde (20 mmol) was allowed to react for 8 h at room temperature. Then, 2 g of sodium borohydride was added in small portions while stirring over a period of 5 h. The solution was left overnight and warmed to boiling for 1 h. To the resulting solution, hydrochloric acid (3.0 mL, 12 \( M \)) was added and when the gas evolution had ceased, the solution was made alkaline with a NaOH solution (8 mL, 3 \( M \)). Precipitated sodium borate was filtered off and the volume of the filtrate was reduced by evaporation under reduced pressure. The remaining solution was extracted with CHCl\(_3\). The chloroform layer was dried over anhydrous MgSO\(_4\), filtered and evaporated to dryness. The solid was redissolved in 50 mL ethanol and then 8 mL concentrated hydrochloric acid was added. The white precipitate was filtered off and recrystallized from methanol. Yield: 5.8 g, 70%. The structure and purity was confirmed by NMR spectroscopy. \(^1\)H-NMR (in D\(_2\)O, \( \delta \)): \( \delta = 8.75 \) (d, 2H, pyrH), 8.40 (m, 2H, pyrH), 7.97 (d, 2H, pyrH), 7.90 (m, 2H, pyrH), 4.46 (m, 1H, CH\(_2\)-OH), 3.42 and 3.30 (m, 2H + 2H, CH\(_2\)-CH) and 3.29 (s, 4H, pyr–CH\(_2\)).

**Preparation of [Cu(HL)Cl](PF\(_6\)) (1)**

HL.4HCl (0.414 g, 0.10 mmol) dissolved in 5 mL of ethanol was neutralized with 4 equivalent of KOH (also dissolved in ethanol). A 10 mL of a methanolic solution of CuCl\(_2\).2H\(_2\)O (0.170 g, 0.10 mmol) was added to the mixture, followed by the addition of 0.163 g (0.1 mmol) of ammonium hexafluorophosphate. The whole mixture was stirred for 15 min at room temperature whereby a deep blue solution was formed. The resulting deep blue solution was refluxed for 2 h. After refluxing the solution, it was cooled to room temperature, and any precipitate appeared was filtered off. Finally the filtrate was layered with diethyl ether in a sealed test tube. Cobalt blue colored prismatic single crystals of 1 suitable for X-ray crystallography were obtained after a few days. (Yield: 75%, 38.6 mg). Anal. Calc. for C\(_{15}\)H\(_{20}\)CuCl\(_2\)N\(_4\)O\(_4\)F\(_6\): C, 34.89; H, 3.90; N, 10.85. Found: C, 34.79; H, 3.86; N, 10.81%. FT-IR (KBr phase) (cm\(^{-1}\)): 3280s, 3080m, 1610s, 1452s, 845vs, 560s (m, medium; s, strong; vs, very strong).

**X-ray crystallography**

Crystal data of 1 are summarised in Table 1. The diffraction experiment was carried out on a Bruker SMART CCD area-detector diffractometer at 150 K. No crystal decay was observed, so that no time-decay correction was needed. The collected frames were processed with the software SAINT\(^27\), and an empirical absorption correction was applied (SADABS)\(^28\) to the collected reflections. The calculations were performed using the Personal Structure Determination Package\(^29\) and the physical constants tabulated therein\(^30\). The structure was solved by direct methods (SHELX)\(^31\) and refined by full-matrix least-squares using all reflections and minimising the function \( \Sigma w(F_0^2 - kF_c^2)^2 \) (refinement on \( F^2 \)). The F atoms of the PF\(_6\) anion show an 87%-13% disorder. The six F atoms with occupancy factors
of 0.13 were refined with isotropic thermal parameters. The six F atoms with occupancy factors of 0.87, and all the other non-hydrogen atoms were refined with anisotropic thermal factors. Hydrogen atom H1, bonded to O, was refined with a fixed isotropic thermal parameter. All the other hydrogen atoms were placed in their ideal positions (C-H or N-H = 0.97 Å), with the thermal parameter $U_{1.10}$ times that of the atom to which they are attached, and not refined. The final Fourier map shows a maximum peak of 1.02(36) e Å$^{-3}$ at 0.11 Å from Cu.

**Results and Discussion**

**Description of the structure of [Cu(HL)Cl](PF$_6$)**

Complex 1 crystallizes in the monoclinic space group $P2_1/c$ (No. 14). The ORTEP diagram of the asymmetric unit is shown in Fig. 1 and the selected bond distances and bond angles are shown in Table 2. The copper atom in the [Cu(HL)Cl](PF$_6$) complex is found to have a coordination number of 5, with the hexafluorophosphate ion having no direct contact with the copper complex. The coordination geometry of copper atom in the solid state is described as being 47% ($\tau = 0.47$) along the pathway of distortion from perfect square-pyramidal to trigonal bipyramidal. The value of $\tau$ is defined as the difference between the two largest donor-metal-donor angles divided by 60, a value which is 0 for the ideal square pyramid and 1 for the trigonal bipyramid.

Although 17-electron Cu(II) complexes with four metal-donor bonds are common, five-coordinated Cu(II) complexes with 19-electrons are also not unusual. A five-coordinate metal complex can take an intermediate geometry between a regular square- and trigonal bipyramidal structure.
pyramidal and a regular trigonal bipyramid. The bond angles typical of square-pyramidal (2 × 160-170° and 4 × 95-100°) and trigonal-bipyramidal (1 × 180° and 3 × 120°) coordination can both, in a first approximation, describe the coordination geometry in [Cu(HL)Cl](PF₆). Based on the deviation from these two models, the coordination geometry of [Cu(HL)Cl](PF₆) is best described as a distorted square pyramid, with the four donor atoms (N₄) of the ligand on the equatorial plane, the chloro ligand being bound on a tilted apical position. The four nitrogen donor atoms (N1, N2, N3 and N4), are nearly coplanar, deviating by 0.236(2), -0.269(3), 0.273(3) and -0.240(2) Å, respectively, from their least-squares plane where the alcoholic O-H group remains uncoordinated. The Cu(II) center is lifted 0.402(1) Å above this least-squares plane toward the apical chloride ligand (Fig. 1). The distortion of the coordination sphere from a regular square pyramid can be described both bonding angles and bond distances in the molecule (Table 1). The Cl–Cu–N₄ (Cl–Cu–N1) and Cl–Cu–N₄(Cl–Cu–N4) angles are 94.59(7)° and 104.91(7)°, respectively, while Cl–Cu–N₃(N₄) (Cl–Cu–N2) and Cl–Cu–N₃(Cl–Cu–N3) angles are 112.66(8)° and 94.24(8)°, respectively. The large Cl–Cu–N₄ and Cl–Cu–N₃(N₄) angles can explain the distorted square pyramid geometry of 1. The Cu–N distances (Cu–N₄ and Cu–N₃(N₄)) in 1 are in the range from 1.981(2) to 2.062(2) Å. The N₃(N₄)–Cu and N₄–Cu bonds are usually found in the range between 1.94 and 2.06 Å and 1.98 and 2.06 Å, respectively, as they are in 1.

Within the metal-ligand fragment, the four adjacent bond angles about the Cu center are unevenly distributed from the ideal 90°. While the N₄(1)–Cu–N₃(N₄)(2) and N₄(4)–Cu–N₃(N₄)(3) bond angles (each of which is within a five-membered ring) are 83.59(10)° and 80.59(10)°, respectively, the six-membered chelate-ring-contained N₃(N₄)(2)–Cu–N₃(N₄)(3) which is only 87.95(10)°, and the N₄(1)–Cu–N₄(4) of the open sector is 102.36(9)°. Although the angles are unevenly distributed, none of the angles is unusual related to the chelate rings found in other complexes of Cu(II).

In square-pyramidal complexes with an apical Cu–Cl bond, the Cu–Cl distances observed are in the range 2.39–2.63 Å, depending on the nature of the basal ligands. In the present molecule, a Cu–Cl distance of 2.443(1) Å is found. This is similar to the Cu–Cl distances known for other complexes containing monoanionic basal NNNO ligand donor sets derived from bidentate ligands, where apical Cu–Cl distances have been found with the values of 2.5096, 2.558, 2.605, and 2.546 Å (mean = 2.555 Å). The same Cu–Cl distance (2.556 Å) was found in a dinuclear complex containing a basal monoanionic NNNO ligand donor set while in a complex containing a basal monoanionic dithiaoxime (S₉N₂) ligand, Cu–Cl distance is 2.3931 Å. With a neutral basal (NNNO) ligand, the apical Cu–Cl distance was found to be shorter (2.474 Å), as compared to the Cu–Cl distances in Cu(II) complexes containing monoanionic basal (NNNO) ligands. With a dianionic (N₉O₂) ligand, a longer Cu–Cl distance of 2.630 Å was observed in the axial site.

The concept of non-covalent interaction such as hydrogen bonds, aromatic π–π stacking, steric repulsion, and van der Waals forces, existing as significant secondary interactions, and occasionally assuming the dominant interaction in molecular solids is now well established. Figure 2 shows the molecular packing of 1 in which the molecules in the crystal are held together by intermolecular O–H---Cl hydrogen bonding interactions to form a 1D chain. Intermolecular hydrogen bonding occurs between O–H1---Cl along crystallographic 0-axis (Fig. 2) as evident by the O–H1---Cl distance 1.99(4) Å (having O–H1---Cl angle 163(4)°) being shorter than the corresponding van der Waals separation. The packing diagram of 1 is shown in Fig. 2, which also shows the π–π stacking of the large aromatic pyridine rings between adjacent chains. The close contact is 3.325 Å (a = 2-X, -Y, -Z) between the two intermolecular pyridine rings in the π–π stacking interaction. It is clearly seen that [Cu(HL)Cl]⁺ species are interlinked by strong intermolecular hydrogen bonding interactions (O–H1---Cl) to form a 1D chain structure, which is further stabilized by π–π stacking interaction between adjacent chains to form a 2D network.

Electronic spectra

The UV-vis spectra (Fig. 3) of the complex 1 in methanol has absorption maximum at 654 nm. For pentacoordinated Cu(II) complexes, this spectral feature is typical for Cu(II) complexes with square-pyramidal geometry, which generally exhibits a band in the 550-660 nm range (dₓz, dᵧz → dₓᵧz). The slightly higher λ max value indicates that the geometry is distorted from the usual square-pyramidal geometry. The spectral data are consistent with the
degree of distortion from the square-pyramidal geometry found in the X-ray structural analysis. In addition the solution spectrum of complex \( \text{1} \) shows the high energy band at 256 nm due to the \( \pi \rightarrow \pi^* \) ligand transition.

Scanning electron microscopy (SEM) study

For the SEM study, a drop casting film was prepared on glass side from the methanolic solution of the sample. After platinum coating, it was characterized by SEM. The morphology of the submicrometer rod of \([\text{Cu(HL)Cl]}(\text{PF}_6)\) was observed in SEM with a diameter of 580 nm and a length of several microns (presented in Fig. 4). On the basis of the experimental results, a mechanism was put forward to explain the formation of the \([\text{Cu(HL)Cl]}(\text{PF}_6)\) rods, which is most probably facilitated by the reorientation of the 1D chain structure of \( \text{1} \). The driving force for the growth of \([\text{Cu(HL)Cl]}(\text{PF}_6)\) rods is probably the strong intermolecular O–H1---Cl (1.99(4) Å, O–H1---Cl angle 163°) interaction along 1D chain and \( \pi-\pi \) stacking [close contact of 3.325 Å \((a = 2-X,-Y,-Z)\)] interaction between adjacent chains. The known weak interactions acting as a template in the preparation of 1D nanomaterial are hydrogen bond interactions, as evidenced by the several recent reports such as hydrogen bonding\(^{14,47-49}\) for the formation of linear

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structures derived from cyclic polypeptides\textsuperscript{47}, for the synthesis of nanotubes originated from organic calyx[4] hydroquinone\textsuperscript{14}, and for the formation of cobalt oxide nanotubes from 1D Co(III) complexes\textsuperscript{48}. On the other hand, the effect of large steric inhibition of phenanthroline was also observed in the formation of silver nanorods\textsuperscript{50}, whereas in our approach, both the intermolecular O–H\textsubscript{1}---Cl hydrogen bonding and \pi--\pi stacking interactions and the templating effect of the chain structure play a significant role in the formation of the [Cu(HL)Cl](PF\textsubscript{6})\textsubscript{2} rods.

Conclusions

A new mononuclear copper(II) complex [Cu(HL)Cl](PF\textsubscript{6}) (1) having N\textsubscript{4}O-donor ligand (HL) has been synthesized and structurally characterized by X-ray crystallography. 1 shows 1D chain in the packing structure through intermolecular O–H---Cl hydrogen bonding interaction (O–H---Cl–Cu, 1.99(4) Å and the angle 163(4)°). This type of H-bonding is rare in literature. 1 in the packing structure also shows the \pi--\pi stacking of the large aromatic pyridine rings between adjacent chains. The close contact is 3.325 Å (a = 2-X, -Y, -Z) between the two intermolecular pyridine rings in the \pi--\pi stacking interaction. 1D chain structure is further stabilized by this type of \pi--\pi stacking interaction between adjacent chains to form a 2D supramolecular network. Submicrometer rod structure of [Cu(HL)Cl](PF\textsubscript{6}) with a diameter of 580 nm and a length of several microns has been prepared by drop casting method from the methanolic solution of 1 and the morphology of submicrometer rod of 1 has been studied by SEM. The driving force for the growth of [Cu(HL)Cl](PF\textsubscript{6}) rods is probably the strong intermolecular O–H1---Cl hydrogen bonding interaction along 1D chain and \pi--\pi stacking between adjacent chains.

Supplementary Data

Crystallographic data file for complex 1 has been deposited in the Cambridge Crystallographic Data Centre (CCDC), with deposition number 637296. This data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgement

K D acknowledges the Council of Scientific and Industrial Research, New Delhi, India, for financial support.

References