CHAPTER 2

Hexaaza copper macrocycles: the consequence of anion coordination
2.1 Introduction

The ligand rigidity, electron-donating properties of the nitrogen atoms constituting the polyaza network and their dispositions play significant role in determining the binding features of the macrocycles toward metal ions [1-6]. Polyazamacrocycles also provide the possibility for two or more alkylating moieties to be present in the same molecule and the distance between them can be modulated by varying the number of carbon atoms constituting the ring [6e]. Polyazamacrocyclic complexes show enhanced thermodynamic and kinetic stability as compared to non-cyclic chelating ligands [7-10]. Their diverse synthetic utility may be attributed to the cavity provided by the ring and exocyclic pendant groups. Their ability to encapsulate metal ions is governed mainly by the cavity size and ionic radii of the metal ions [11-13]. As the size of macrocyclic cavity increases, the ligand becomes more flexible making it more suitable to accommodate transition as well as heavy metal ions [4a].

The metal template procedure is generally preferred for the synthesis of polyazamacroyclic systems, as it often provides selective routes toward products that are not obtainable in the absence of metal ions. Template reactions involving formaldehyde and amines facilitate the synthesis of saturated polyaza multidentate macrocyclic complexes. Such processes are simple, inexpensive and high yielding ‘one pot reactions’. Metal template condensation has been employed in the preparation of various saturated polyazamacroyclic complexes containing N–CH2–N linkages [14-21]. The pendant-arms of the macrocycles may alter their stereochemistry and thermodynamic parameters [22-25]. However, the presence of rigid aromatic system gives particular coordination properties to the ligands defining distinct preorganized binding sites for the metal ions. Copper macrocycles are of considerable interest as low molecular weight models for biological copper-containing redox proteins [26].

In the present study complexes of Cu(II) containing different anions with 14-membered hexaaza macrocycle have been characterized by IR, electronic, EPR spectra, magnetic susceptibility and crystallographic data.
2.2 Experimental

2.2.1 Material and methods

Cu(OOCCCH\textsubscript{3})\textsubscript{2}.H\textsubscript{2}O, HClO\textsubscript{4} (Merck India), ethylenediamine, 1,2-diaminopropane (E. Merck), KPF\textsubscript{6}, KSCN (Acros), benzylamine and formaldehyde (S.D. Fine India) were used as received. Methanol and ethanol were distilled prior to use. Elemental analysis was done with a FLASH EA 1112 SERIES CHNS analyzer. IR spectra (4000-400 cm\textsuperscript{-1}) were recorded with a Spectrolab Interspec FT/IR–2020 spectrometer as KBr disc. The conductivity measurements were carried out with a CM–82T Elico conductivity bridge in acetonitrile. The electronic spectra were recorded with a Perkin Elmer Lambda–35 UV/vis spectrophotometer in CH\textsubscript{3}CN. Magnetic susceptibility measurements of powdered samples were performed at 25 °C by Faraday method with a Sherwood Scientific magnetic susceptibility balance, calibrated against Hg[Co(SCN)\textsubscript{4}]. EPR spectra were recorded in the solid state and in frozen CH\textsubscript{3}CN solution with a JEOL FE3X EPR spectrometer at X-band microwave frequency. Powder XRD pattern of all samples were recorded with a Bruker-Axs, D8 Avance diffractometer using Cu-K\textalpha X-radiation at 35 kV and 25 mA. Diffraction patterns were collected over 2\theta range of 5-50° at scan rate of 1 °/min.

Caution! Although our samples never exploded during handling, metal perchlorate complexes are potentially explosive and should be handled with care.

2.2.2 Synthesis of [CuL](ClO\textsubscript{4})\textsubscript{2} (1) [(L = 3,10-bisbenzyl-1,3,5,8,10,12-hexaaza-cyclotetradecane)]

To an ethanolic (50 mL) solution of Cu(OOCCCH\textsubscript{3})\textsubscript{2}.H\textsubscript{2}O (5 mM, 0.998 g) were slowly added ethylenediamine (10 mM, 0.669 mL), 40% formaldehyde (20 mM, 1.600 mL) and benzylamine (10 mM, 1.092 mL) with constant stirring. After refluxing this mixture for 48 h, the red–violet solution was cooled to room temperature and filtered to remove any insoluble solid. To this filtrate an excess of perchloric acid was added with continuous stirring which yielded pink coloured precipitate (Scheme 2.1). It was filtered and washed with ethanol and dried over P\textsubscript{2}O\textsubscript{5}. The complex was recrystallized from acetonitrile. Red crystals were obtained after 7 days. Yield: ~80% (2.58 g). M.p.: 255 °C. \( \Lambda _{m} \): 247 ohm\textsuperscript{-1} cm\textsuperscript{2} M\textsuperscript{-1}. Anal. Calc. for C\textsubscript{22}H\textsubscript{34}Cl\textsubscript{2}CuN\textsubscript{6}O\textsubscript{8} (1): C, 40.97; H, 5.31; N, 13.03. Found: C, 40.81; H, 5.41; N,
13.25%. IR (KBr, cm\(^{-1}\)): 3243, 3173, 2924, 2879, 1449, 1421, 1377, 1335, 1275, 1114, 1073, 997, 830, 896, 855, 750, 703, 624, 437.

2.2.3 Synthesis of \([\text{CuL}]\)\((\text{SCN})_2\) (2)

To a solution of \([\text{CuL}]\)(\text{ClO}_4)_2 (1) (1 mM, 0.645 g) in acetonitrile (20 mL) was added an excess of potassium thiocyanate and stirred for 1 h. It was filtered to remove solid KClO\(_4\) and the solvent was evaporated to dryness to give purple blue powder. It was dissolved in acetonitrile-DMF mixture with a few drops of water and left to stand at room temperature. Violet crystals thus obtained after 1 month were filtered and washed with ethanol. Yield: \(\sim 95\%\) (0.612 g). M.p.: 228 °C. \(\Lambda_m\): 254 ohm\(^{-1}\) cm\(^2\) M\(^{-1}\). Anal. Calc. for C\(_{24}\)H\(_{34}\)CuN\(_8\)S\(_2\) (2): C, 51.27; H, 6.10; N, 19.93. Found: C, 50.87; H, 5.99; N, 19.43. IR (KBr, cm\(^{-1}\)): 3194, 2897, 2868, 2049, 1459, 1418, 1269, 1188, 1147, 1060, 1012, 951, 856, 742, 698, 640, 592, 480, 418.

2.2.4 Synthesis of \([\text{CuL(CH}_3\text{CN})_2]\)(\text{PF}_6)_2(CH\(_3\)CN)_2 (3)

To an acetonitrile (20 mL) solution of \([\text{CuL}]\)(\text{ClO}_4)_2 (1) (1 mM, 0.645 g) was added an excess of potassium hexafluorophosphate and filtered to remove solid KClO\(_4\). The red filtrate was allowed to stand for a few days at 4 °C to give red crystals. Yield: \(\sim 94\%\) (0.606 g). M.p.: 297 °C. \(\Lambda_m\): 275 ohm\(^{-1}\) cm\(^2\) M\(^{-1}\). Anal. Calc. for C\(_{22}\)H\(_{34}\)CuF\(_{12}\)N\(_6\)P\(_2\) (3): C, 35.90; H, 4.66; N, 11.42. Found: C, 35.23; H, 4.68; N, 11.45%. IR (KBr, cm\(^{-1}\)): 3269, 3173, 2916, 2885, 2294, 2259, 1466, 1435, 1379, 1334, 1273, 1188, 1159, 1080, 1057, 999, 823, 738, 702, 638, 557, 445.

2.2.5 Synthesis of \([\text{CuL}^1]\)(\text{ClO}_4)_2 (4) ([L = 3,10-bisbenzyl-6,13-dimethyl-1,3,5,8,10,12-hexaazacyclotetradecane])

\([\text{CuL}^1]\)(\text{ClO}_4)_2 was synthesized by the procedure mentioned for 1 except that 1,2-diaminopropane was used instead of ethylenediamine. Red block shaped crystals were obtained from acetonitrile. Yield: \(\sim 50\%\) (1.68 g). M.p.: 240 °C. \(\Lambda_m\): 267 ohm\(^{-1}\) cm\(^2\) M\(^{-1}\). Anal. Calc. for C\(_{24}\)H\(_{38}\)Cl\(_2\)CuN\(_6\)O\(_8\) (4): C, 42.83; H, 5.69; N, 12.49. Found: C, 42.71; H, 5.60; N, 12.35%. IR (KBr, cm\(^{-1}\)): 3244, 3215, 3170, 2972, 2879, 1469, 1442, 1363, 1126, 1091, 979, 748, 702, 648, 621, 457.
Scheme 2.1 Synthesis of [CuL](ClO₄)₂ (1) and [CuL¹](ClO₄)₂ (4).

2.2.6 Synthesis of [CuL¹](PF₆)₂ (5)

To an acetonitrile (20 mL) solution of [CuL¹](ClO₄)₂ (4) (1 mmol, 0.673 g) was added an excess of potassium hexafluorophosphate and stirred for 10 min. It was filtered to remove solid KClO₄ and left to stand for few days which yielded red crystals. Yield: ~90% (0.68 g). M.p.: 222 ºC. Λₘ: 243 ohm–1 cm² M⁻¹. Anal. Calc. for C₂₄H₃₈CuN₆P₂F₁₂ (5): C, 37.73; H, 5.01; N, 11.00. Found: C, 38.00; H, 5.10; N, 11.05%. IR (KBr, cm⁻¹): 3265, 3170, 2971, 2889, 1456, 1370, 1282, 1190, 1105, 1052, 1003, 841, 744, 704, 560, 421.

2.2.7 X-ray crystal structure determination and refinements

Single crystals were obtained by slow evaporation of acetonitrile solution of 1, 4 and 5 at room temperature and that of 3 at 4 ºC. Crystals of 2 were grown by slow evaporation of a 1:1 mixture of acetonitrile and DMF and a few drops of water. X-ray data of 1 & 5 were collected using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) with “Bruker SMART APEX CCD diffractometer” at 100 K. The
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program SMART [27] was used for collecting frames of data, indexing reflections, and determining lattice parameters for 1 & 5. The data integration and reduction were processed with SAINT [27] software. An empirical absorption correction was applied to the collected reflections with SADABS [28] using XPREP [29]. X-ray data of 2, 3 & 4 were collected on Oxford Diffraction Gemini CCD equipped diffractometer at 298(2) K using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The strategy for the data collection was evaluated by the CrysAlisPro CCD software and collected by the standard ‘phi-omega scan’ techniques, scaled and reduced using CrysAlisPro RED software [30]. The linear absorption coefficients, scattering factors for the atoms and the anomalous dispersion corrections were taken from the International Tables for X-ray Crystallography [31]. The structures were solved by direct method using SHELXS-97 program [32] and were refined on \( F^2 \) by full-matrix least-square technique using the SHELXL-97 [32] program. Figures were drawn using ORTEP-3.2 [33], MERCURY-2.3 [34] and DIAMOND-3.0 [35]. The pertinent crystal data and refinement parameters for 1, 2 and 3 are compiled in Table 2.1 and for 4 and 5 in Table 2.8.

2.3 Results and Discussion

The Cu(II) complexes of hexaaza macrocycle have been synthesized in a one-pot condensation reaction involving copper acetate, ethylenediamine/1,2-diaminopropane, formaldehyde and benzyl amine (Scheme 2.1). The complexes are soluble in polar solvents such as MeCN, DMF and DMSO.

According to the Scheme 2.2, the reaction is initiated by the formation of an imine which is coordinated to a Cu(II) ion. The imine is attacked by alkylamine to yield a gem-diamine which subsequently condenses with a neighbouring imine group, producing a six-membered ring.
2.3.1 Structural description of \([\text{CuL}](\text{ClO}_4)_2\) (I)

The molecular structure and the atomic numbering scheme of the \(1\) is shown in Fig. 2.1a. Crystallographic data, selected bond lengths and bond angles are listed in Tables 2.1 & 2.2. It was crystallized in triclinic system with \(P\)-1 space group in a body-centered lattice. The unit cell parameters are \(a = 10.156(3) \ \text{Å}, b = 11.433(3) \ \text{Å}, c = 11.965(3) \ \text{Å}, \alpha = 86.679(5)^\circ, \beta = 75.765(4)^\circ \) and \(\gamma = 87.829(5)^\circ\). The asymmetric unit comprises of half the molecule and the other half was generated through a center of symmetry. Two independent molecules present in the asymmetric unit are structurally identical except for a slight variation in bond lengths and bond angles (Fig. 2.1b). Each copper atom sits on an inversion center. The crystallographic unit of \(1\) contains one \([\text{CuL}]^{2+}\) ion and two \(\text{ClO}_4^-\) ions. The coordination environment of the \(\text{Cu(II)}\) ion is \((4 + 2)\) containing four planar secondary amine nitrogen atoms \([\text{Cu}(1)–\text{N}(1) = 2.002(3) \ \text{Å}, \text{Cu}(1)–\text{N}(2) = 2.015(3) \ \text{Å}]\) and \((\text{Cu}(2)–\text{N}(4) = 1.994(3) \ \text{Å}, \text{Cu}(2)–\text{N}(5) = 2.019(3) \ \text{Å}]\) and two axially weakly coordinated perchlorate anions. The two
independent molecules in the asymmetric unit show slightly different Cu–O(perchlorate) interactions [Cu(1)–O(5) = 2.651(6) Å and Cu(2)–O(5) = 2.474(6) Å]. The overall coordination geometry around Cu(II) may, therefore be described as an elongated octahedron which is expected from the Jahn–Teller distortion.

Angles of C(12)–N(3)–C(15), C(12)–N(3)–C(16), C(15)–N(3)–C(16) are 116.6(2)°, 115.7(2)°, 117.8(2)° and C(4)–N(6)–C(1), C(4)–N(6)–C(5), C(1)–N(6)–C(5) are 115.2(2)°, 116.0(2)°, 113.1(2)° respectively, are larger than 109.47° indicating an $sp^2$-like hybridization of the tertiary nitrogen atoms [N(3) and N(6)]. Such observation has also been made in other polyaza macrocyclic or non-macrocyclic complexes containing uncoordinated tertiary amino groups [36-39]. The six-membered chelate rings involving C(1), C(4) and C(12), C(15) atoms adopt a chair conformation, whereas five-membered rings involving the C(2), C(3) and C(13), C(14) atoms assume a gauche conformation. The chelate angles N(1)–Cu(1)–N(2), N(1)–Cu(1)–N(2)#1 were 86.08(10)°, 93.92(10)° and N(4)–Cu(2)–N(5), N(4)–Cu(2)–N(5)#2 were 86.09(10)°, 93.91(10)° for six-membered and five-membered rings respectively. The Cu–N and Cu–O bond lengths are in the range similar to other Cu(II) complexes with cyclam-derived ligands where perchlorate ion is axially coordinated [40-44]. The trans-III configuration of N-donors enables the hexaaza ring to adopt least strained conformation, an eclipsed pair of gauche five-membered chelate rings and two chair six-membered rings. The torsion angle between the planes of benzene rings in two halves of first unit [Cu(1)] is 0.083° with a separation of 3.763 Å while for the second unit [Cu(2)], benzene rings are found to be parallel with a separation of 3.098 Å.

The bond angles in perchlorate ions at Cl(1) and Cl(4) are in the range 107.95(16)-110.96(15)° and 108.71(14)-110.48(15)° respectively, while bond distances vary from 1.429(2)-1.451(2) Å and 1.413(3)-1.446(3) Å respectively. The perchlorate ion indicates a lengthening of the Cl–O bond involving O(4) and O(5), which were weakly coordinated to the Cu atoms. The Cl(1)–O(5) and Cl(4)–O(4) bond lengths of 1.436(2) Å and 1.451(2) Å, are significantly longer than the mean of the other three Cl–O bonds [1.428(2) Å and 1.435(2) Å] of the two perchlorate ions. The Cu(1)–O(5)–Cl(1) and Cu(2)–O(4)–Cl(4) angles [122.3(3)° and 132.3(3)°] indicate significant tilting of the anions relative to the N(l), N(2), N(l)#1, N(2)#2 and
N(4), N(5), N(4)#2, N(5)#2 planes. The N(2)–H(2), N(5)–H(5), C(1)–H(1A) and C(15)–H(15A) protons were involved in intramolecular hydrogen bonding with O(8), O(3), O(2) and O(5) respectively. This interaction could possibly be responsible for tilting of the perchlorate ion [45].

The mononuclear units are held together by intermolecular hydrogen bonds involving the N(1)–H(1), N(4)–H(4) protons and O(1), O(6) respectively, to form an infinite two-dimensional polymeric array along \( a \)-axis (Fig. 2.2). The hydrogen bonding parameters are collected in Table 2.3. The 2D sheets are held together through C–H---O interactions (Fig. 2.3) between the methylene and phenyl C–H in one chain and O of perchlorate groups in adjacent chains. N–H---O, C–H---O hydrogen bonds and C–H---\( \pi \) interaction (Fig. 2.4) between the methylene H(3) and benzene ring leads to the formation of 3D supramolecular network (Figs. 2.5 & 2.6) contributing to molecular stability. The average Cu---Cu distance between the two adjacent chains is 8.511 Å.

![Fig. 2.1](image)

**Fig. 2.1** (a) Molecular structure (ORTEP diagram with 30% thermal ellipsoids) of one unit of 1, along with the atomic numbering scheme. (b) Structure of 1, displaying two independent units. Hydrogen atoms have been omitted for clarity.
Fig. 2.2 Depicting intermolecular hydrogen bonded 2D polymeric array along $a$-axis for 1. Hydrogen atoms except those involved in H-bonding have been omitted for clarity.

Fig. 2.3 Depicting C–H---O interaction between two adjacent layers along $a$-axis for 1. Hydrogen atoms except those involved in H–bonding have been omitted for clarity.

Fig. 2.4 Depicting C–H---$\pi$ interaction for 1. Hydrogen atoms except those involved in H–bonding have been omitted for clarity.
Fig. 2.5 Projection of spirally coiled 3D network along c-axis for 1. Hydrogen atoms have been omitted for clarity.

Fig. 2.6 Depiction of a polyhedral arrangement of macrocyclic units along a-axis for 1. Hydrogen atoms have been omitted for clarity.
Table 2.1 Crystallographic data and structure refinement parameters for 1, 2 and 3.

<table>
<thead>
<tr>
<th>Complex</th>
<th><a href="ClO$_4$">CuL</a>$_2$ (1)</th>
<th><a href="SCN">CuL</a>$_2$ (2)</th>
<th><a href="CH$_3$CN">CuL</a>$_2$P(F$_2$)$_2$.2CH$_3$CN (3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C$<em>{22}$H$</em>{34}$Cl$_2$CuN$_6$O$_8$</td>
<td>C$<em>{24}$H$</em>{34}$CuN$_8$S$_2$</td>
<td>C$<em>{30}$H$</em>{46}$CuF$<em>{12}$N$</em>{10}$P$_2$</td>
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<tr>
<td>CCDC No.</td>
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<td>791739</td>
</tr>
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<td>900.25</td>
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<td>298(2)</td>
<td>298(2)</td>
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<td>0.71073</td>
<td>0.71073</td>
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<td>Rhombohedral</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P -1</td>
<td>R -3</td>
<td>P2(1)/c</td>
</tr>
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<td>10.156(3)</td>
<td>29.766(6)</td>
<td>12.5103(9)</td>
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<td>b (Å)</td>
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<td>29.766(6)</td>
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<td>c (Å)</td>
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<td>7.9265(11)</td>
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<td>90</td>
<td>90</td>
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<td>β (°)</td>
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<td>4133.6(5)</td>
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<td>2, 1.594</td>
<td>9, 1.382</td>
<td>4, 1.447</td>
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<td>Absorption coefficient (mm$^{-1}$)</td>
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<td>0.991</td>
<td>0.696</td>
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<tr>
<td>F(000)</td>
<td>670</td>
<td>2655</td>
<td>1852</td>
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<td>Crystal size (mm)</td>
<td>0.28 x 0.20 x 0.20</td>
<td>0.40 x 0.20 x 0.10</td>
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<td>Δ Range for data collection (°)</td>
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<td>2.74 - 24.99</td>
<td>1.61 to 25.00</td>
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<td>Limiting indices</td>
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<td>–27 ≤ h ≤ 27, –23 ≤ k ≤ 34, –9 ≤ l ≤ 9</td>
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<td>Reflections collected / unique</td>
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<td>0.9074 and 0.6926</td>
<td>0.8734 and 0.8453</td>
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<td>Refinement method</td>
<td>Full-matrix least-squares on $F^2$</td>
<td>Full-matrix least-squares on $F^2$</td>
<td>Full-matrix least-squares on $F^2$</td>
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<tr>
<td>Data / restraints / parameters</td>
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<td>2381 / 3 / 168</td>
<td>7278 / 2 / 516</td>
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<td>Goodness-of-fit on $F^2$</td>
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<td>1.039</td>
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<td>Final R indices [I &gt;2*sigma(I)]</td>
<td>$R_1 = 0.0473$, w$R_2 = 0.1331^{[a]}$</td>
<td>$R_1 = 0.0506$, w$R_2 = 0.1226^{[a]}$</td>
<td>$R_1 = 0.0699$, w$R_2 = 0.1953^{[a]}$</td>
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<td>R indices (all data)</td>
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<td>$R_1 = 0.0864$, w$R_2 = 0.2098$</td>
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<td>Largest diff. peak and hole (e Å$^{-3}$)</td>
<td>1.141 and -0.812</td>
<td>0.573 and -0.360</td>
<td>1.021 and -0.426</td>
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<td>Completeness to θ = 25.00 (%)</td>
<td>98.5</td>
<td>99.9</td>
<td>100.0</td>
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</table>

$^{[a]} R_1 = \frac{\sum|F_o| - |F_c|}{\sum|F_o|}; wR_2 = \left[ \sum[w(|F_o|^2 - |F_c|^2)^2]/\sum[w(|F_o|^2)^2] \right]^{1/2}; w = 1/[\sigma^2(|F_o|^2 + (x p)^2)]; where p = [(|F_o|^2 + 2|F_c|^2)/3; x = 0.0605.$
Table 2.2 Selected bond lengths [Å] and bond angles [°] for [CuL](ClO₄)₂ (1).

<table>
<thead>
<tr>
<th>Bond lengths</th>
<th>Bond angles</th>
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<td>N(1)–Cu(1)</td>
<td>C(1)–N(6)–C(5) 113.1(2)</td>
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<td>N(2)–Cu(1)</td>
<td>C(13)–N(1)–Cu(1) 107.79(18)</td>
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<td>N(4)–Cu(2)</td>
<td>C(12)–N(1)–Cu(1) 115.54(18)</td>
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<td>N(5)–Cu(2)</td>
<td>C(14)–N(2)–C(15) 112.6(2)</td>
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<tr>
<td>Cu(1)–O(5)</td>
<td>C(14)–N(2)–C(1) 107.30(17)</td>
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<tr>
<td>Cu(2)–O(5)</td>
<td>C(15)–N(2)–Cu(1) 114.81(19)</td>
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<td>O(5)–Cl(1)</td>
<td>N(1)–Cu(1)–N(2)#1 93.92(10)</td>
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<td>O(6)–Cl(1)</td>
<td>N(1)–Cu(1)–N(2) 86.08(10)</td>
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<td>O(7)–Cl(1)</td>
<td>N(4)–Cu(2)–N(5)#2 93.91(10)</td>
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<td>O(8)–Cl(1)</td>
<td>N(4)–Cu(2)–N(5) 86.09(10)</td>
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<td>O(1)–Cl(4)</td>
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<td>O(5)–Cu(1)–N(2)#1 83.44(8)</td>
</tr>
<tr>
<td>Bond angles</td>
<td>O(4)–Cu(2)–N(4) 84.14(9)</td>
</tr>
</tbody>
</table>

Symmetry transformations used to generate equivalent atoms: #1 –x+1, –y+1, –z+1 #2 –x+1, –y, –z.

Table 2.3 Intramolecular and intermolecular hydrogen bonds of the N–H---O and C–H---O type in [CuL](ClO₄)₂ (1).

<table>
<thead>
<tr>
<th>D–H---A</th>
<th>d(D---A) (Å)</th>
<th>d(H---A) (Å)</th>
<th>(D–H---A) (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intramolecular</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N(2)–H(2)---O(8)</td>
<td>2.994(4)</td>
<td>2.17(3)</td>
<td>161(3)</td>
</tr>
<tr>
<td>N(5)–H(5)---O(3)</td>
<td>3.106(3)</td>
<td>2.37(3)</td>
<td>158(3)</td>
</tr>
<tr>
<td>C(1)–H(1A)---O(2)</td>
<td>3.506(4)</td>
<td>2.58(3)</td>
<td>156(4)</td>
</tr>
<tr>
<td>C(15)–H(15A)---O(5)</td>
<td>3.219(4)</td>
<td>2.55(4)</td>
<td>125(4)</td>
</tr>
<tr>
<td>Intermolecular</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N(1)–H(1)---O(1)</td>
<td>2.977(3)</td>
<td>2.23(3)</td>
<td>147(3)</td>
</tr>
<tr>
<td>N(4)–H(4)---O(6)</td>
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<td>2.21(3)</td>
<td>145(3)</td>
</tr>
<tr>
<td>C(1)–H(1B)---O(7)</td>
<td>3.204(5)</td>
<td>2.41(5)</td>
<td>136(4)</td>
</tr>
<tr>
<td>C(9)–H(9)---O(8)</td>
<td>3.244(5)</td>
<td>2.60(4)</td>
<td>126(5)</td>
</tr>
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<td>3.395(4)</td>
<td>2.55(4)</td>
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</tr>
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<td>2.43(4)</td>
<td>153(4)</td>
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<td>C(22)–H(22)---O(8)</td>
<td>3.158(5)</td>
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<td>126(5)</td>
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</table>
2.3.2 Structural description of [CuL](SCN)$_2$ (2)

The molecular structure of 2 along with the atomic numbering scheme is shown in Fig. 2.7. Crystallographic data, selected bond lengths and bond angles are given in Tables 2.1 & 2.4. It was crystallized in rhombohedral crystal system with R–3 space group. The unit cell contains nine macrocyclic units (Fig. 2.8) with cell parameters: $a = 29.766(6)$ Å, $b = 29.766(6)$ Å, $c = 7.9265(11)$ Å. The asymmetric unit is made up of half molecule; the other half of the molecule is generated through a center of symmetry. The crystallographic unit of 2 consists of one [CuL]$^{2+}$ ion and two thiocyanate anions in isothiocyanate binding mode. The thiocyanate ion is known to form both thiocyanato (M–SCN) and isothiocyanato (M–NCS) complexes, depending on the nature of metal ion [46]. Pearson [47] suggested that S in SCN$^-$ is soft base and will obviously prefer to coordinate with soft acids whereas N in SCN$^-$ is hard and prefer to coordinates with hard acids. The copper atom is in axially distorted octahedral (N$_4$+N$_2$) environment with four secondary amine nitrogen atoms occupying the equatorial plane, similar to 1 and, two isothiocyanate groups at the axial positions. The $trans$ bond angles of 180.0°, N(1)–Cu(1)–N(1)#1 and N(2)–Cu(1)–N(2)#1 in equatorial plane show that the Cu(II) ion is located in a square plane without any axial displacement.

The large Cu(1)–N(4) bond length of 2.528(3) Å in $trans$ configuration, are similar to those found for weakly coordinated axial SCN$^-$ in hexa-coordinate (4+2) copper complexes such as $trans$-[Cu(Me$_2$en)$_2$(NCS)$_2$] [48], $trans$-[Cu(amepy)$_2$(NCS)$_2$] and [Cu($\alpha$-L)(NCS)$_2$] [48-50]. The thiocyanate groups show small distortions [N(4)–(C12)–S(2) = 177.74(4)°] from linearity which is quite common [51]. The Cu(1)–N(4)–C(12) angles related to the thiocyanate anion is 119.9(6)° which indicates that the Cu(1)–N(4) linkage is slightly bent off the perpendicular to the CuN$_4$ plane by 0.08-2.42°. The overall geometry of Cu(II) may, therefore, be described as an elongated octahedron similar to 1. The planes of two thiocyanate group are parallel to each other with a separation of 2.167 Å while that of two benzene rings are also parallel with a gap of 4.895 Å. Similar to 1, angles C(7)–N(3)–C(8), C(8)–N(3)–C(9) and C(9)–N(3)–C(7) are in the range 114.8(3)-115.7(3)° and are larger than the ideal tetrahedral angle. The six-membered chelate rings involving the C(8) and C(9) atoms adopt a chair conformation, whereas five-membered rings involving the C(10) and C(11) atoms assume a gauche conformation.
Fig. 2.7 Molecular structure (Ortep diagram with 50% thermal ellipsoids) of 2, along with the atomic numbering scheme. Hydrogen atoms have been omitted for clarity.

Fig. 2.8 Unit cell diagram of 2 displaying nine units in one cell. Hydrogen atoms have been omitted for clarity. Cu (red) atoms are shown as small spheres of arbitrary radii.

Fig. 2.9 Depicting intermolecular hydrogen bonded 1D polymeric array along a-axis in 2. Hydrogen atoms except those involved in H–bonding have been omitted for clarity. Cu (red), S (yellow) and H (grey) atoms are shown as small spheres of arbitrary radii.
Chapter 2

The chelate angles N(1)–Cu(1)–N(2), N(1)–Cu(1)–N(2)#1 were 94.14(11)°, 85.86(11)° for six- and five-membered rings respectively. There is extensive intramolecular hydrogen bonding involving N(4) of the thiocyanate ions. Analysis of the crystal packing reveals that mononuclear units are held together by intermolecular hydrogen bonds involving N(2)–H(2A) and S(2) to form an infinite one-dimensional polymeric chain along the \( b \)-axis (Fig. 2.9). The 1D chains are held together through C–H---π interaction (Fig. 2.10) between the methylene H(8B) and benzene ring. The average Cu---Cu distance between the two adjacent chains is 7.927 Å. Extensive intermolecular hydrogen bonds involving the C–H---π and N–H---S interactions lead to the formation of a 3D supramolecular architecture (Fig. 2.11). The hydrogen bonding parameters are given in Table 2.5.

Table 2.4 Selected bond lengths [Å] and bond angles [°] for \([\text{CuL}](\text{SCN})_2\) (2).

<table>
<thead>
<tr>
<th>Bond lengths</th>
<th>Bond angles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(1)–N(1)</td>
<td>2.035(3)</td>
</tr>
<tr>
<td>Cu(1)–N(2)</td>
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<td>S(2)–C(12)</td>
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<td>C(12)–N(4)</td>
<td>1.192(5)</td>
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<td>Cu(1)–N(4)</td>
<td>2.528(3)</td>
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<tr>
<td>N(2)–Cu(1)–N(2)#1</td>
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<td>N(1)–Cu(1)–N(1)#1</td>
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<tr>
<td>N(2)–Cu(1)–N(1)</td>
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</tr>
<tr>
<td>N(2)#1–Cu(1)–N(1)</td>
<td>85.86(11)</td>
</tr>
<tr>
<td>C(11)–N(1)–C(9)</td>
<td>113.6(3)</td>
</tr>
<tr>
<td>C(11)–N(1)–Cu(1)</td>
<td>106.05(19)</td>
</tr>
<tr>
<td>C(8)–N(3)–C(9)</td>
<td>115.1(3)</td>
</tr>
<tr>
<td>C(8)–N(3)–C(7)</td>
<td>114.8(3)</td>
</tr>
<tr>
<td>C(9)–N(3)–C(7)</td>
<td>115.7(3)</td>
</tr>
<tr>
<td>N(4)–C(12)–S(2)</td>
<td>177.7(4)</td>
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<tr>
<td>N(1)–Cu(1)–N(4)</td>
<td>89.93(12)</td>
</tr>
<tr>
<td>N(1)–Cu(1)–N(4)#1</td>
<td>90.07(12)</td>
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<tr>
<td>N(1)–Cu(1)–N(4)</td>
<td>90.07(12)</td>
</tr>
<tr>
<td>N(2)–Cu(1)–N(4)</td>
<td>87.59(13)</td>
</tr>
<tr>
<td>N(2)–Cu(1)–N(4)#1</td>
<td>92.40(13)</td>
</tr>
</tbody>
</table>

Symmetry transformations used to generate equivalent atoms: #1 \(-x+1, -y, -z+1\).
Fig. 2.10 Depicting C–H---π interaction in 2. Hydrogen atoms except those involved in H–bonding have been omitted for clarity. Cu (red) and H (grey) atoms are shown as small spheres of arbitrary radii.

Fig. 2.11 Projection of layered 3D network of 2 along c-axis. Hydrogen atoms have been omitted for clarity. Cu (red) atoms are shown as small spheres of arbitrary radii.
Table 2.5 Intramolecular and intermolecular hydrogen bonds of the N–H---N, N–H---S and C–H---N type in [CuL](SCN)$_2$ (2).

<table>
<thead>
<tr>
<th></th>
<th>(d(D---A)) (Å)</th>
<th>(d(H---A)) (Å)</th>
<th>((D--H---A)) (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intramolecular</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N(1)–H(1A)---N(4)</td>
<td>3.243(4)</td>
<td>2.797(5)</td>
<td>114.05(5)</td>
</tr>
<tr>
<td>N(2)–H(2A)---N(4)</td>
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<td>2.705(6)</td>
<td>114.39(5)</td>
</tr>
<tr>
<td>C(7)–H(7B)---N(1)</td>
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<td>2.757(3)</td>
<td>99.63(2)</td>
</tr>
<tr>
<td>C(7)–H(7B)---N(2)</td>
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<td>2.896(3)</td>
<td>88.41(3)</td>
</tr>
<tr>
<td>C(1)–H(1)---N(3)</td>
<td>2.975(4)</td>
<td>2.740(3)</td>
<td>95.35(7)</td>
</tr>
<tr>
<td>C(9)–H(9A)---N(4)</td>
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<td>2.771(3)</td>
<td>120.60(2)</td>
</tr>
<tr>
<td>C(8)–H(8B)---N(4)</td>
<td>3.358(5)</td>
<td>2.720(4)</td>
<td>123.85(2)</td>
</tr>
<tr>
<td>Intermolecular</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N(2)–H(2A)---S(2)</td>
<td>3.615(3)</td>
<td>2.882(9)</td>
<td>143.43(2)</td>
</tr>
</tbody>
</table>

2.3.3 Structural description of [CuL(CH$_3$CN)$_2$](PF$_6$)$_2$.2CH$_3$CN (3)

The molecular structure of 3 along with the atomic numbering scheme is shown in Fig. 2.12. Crystallographic data, selected bond lengths and bond angles are given in Tables 2.1 & 2.6. It was crystallized in the space group \(P2(1)/c\) of the monoclinic system in a cell of dimensions \(a = 12.5103(9)\) Å, \(b = 16.0648(11)\) Å, \(c = 20.8753(15)\) Å, \(\beta = 99.8510(10)^\circ\). The unit cell is shown in Fig. 2.13. The crystal structure contains a monomeric [CuL(CH$_3$CN)$_2$]$^{2+}$ cation, two hexafluorophosphate anions and two lattice acetonitrile molecules. The Cu(1) atom is (N$_4$ + N$_2$) coordinated in a distorted elongated octahedron with four secondary amine nitrogen atoms [Cu(1)–N(1) = 2.006(4) Å, Cu(1)–N(2) = 2.002(3) Å, Cu(1)–N(3) = 2.011(3) Å and Cu(1)–N(4) = 2.010(3) Å] occupying the equatorial plane in a square planar arrangement and two nitrogen atoms from two acetonitrile molecules at the axial position [Cu(1)–N(9) = 2.432(4) Å and Cu(1)–N(7) = 2.747(4) Å]. The two \(trans\) bond angles in equatorial plane N(1)–Cu(1)–N(3) and N(2)–Cu(1)–N(4) are 176.23(15)° and 177.18(15)° respectively and deviate from 180° unlike the \(trans\) N–Cu–N angles (180°) in 1 & 2. It shows that the Cu(II) ion is slightly out of equatorial plane with some axial displacement. The copper ion is 0.057 Å above the basal plane constituted via N(1), N(2), N(3), N(4) atoms, towards the N(9) of CH$_3$CN indicating different coordinating strength of CH$_3$CN which is also evident from different Cu(1)–N$_{NCMe}$ bond lengths. The two coordinated CH$_3$CN are located at \(trans\) positions to each other and are not exactly at the axial sites of Cu(II) as evident from the bond lengths.
angle (N(7)–Cu(1)–N(9) = 178.93°). Although, in most transition metal complexes of acetonitrile the coordination is approximately linear, it deviates slightly from linearity by 0.76-0.95°.

Fig. 2.12 Molecular structure (ORTEP diagram with 50% thermal ellipsoids) of 3, along with the atomic numbering scheme. Hydrogen atoms have been omitted for clarity.

Fig. 2.13 Unit cell diagram of 3. Hydrogen atoms have been omitted for clarity. Cu (red), P (orange) and F (yellow) atoms are shown as small spheres of arbitrary radii.
The bond angles $N(1)$–$Cu(1)$–$N(9)$, $N(4)$–$Cu(1)$–$N(9)$, $N(2)$–$Cu(1)$–$N(9)$, and $N(3)$–$Cu(1)$–$N(9)$ are 89.96(15)$^\circ$, 89.59(15)$^\circ$, 93.22(15)$^\circ$ and 93.77(15)$^\circ$ respectively, suggest that the $Cu(1)$–$N(7)$ and $Cu(1)$–$N(9)$ linkages are slightly bent off the perpendicular to the $N(1)$–$Cu(1)$–$N(4)$ plane by 0.04–0.40$^\circ$ while 3.23–3.77$^\circ$ to the $N(2)$–$Cu(1)$–$N(3)$ plane. The torsion angle between the planes of the two benzene rings is 23.32$^\circ$ which is possibly due to intramolecular hydrogen bonding while the angle between the two acetonitrile planes is 37.14$^\circ$.

Acetonitrile can coordinate as $\eta^1$–$\text{NCCH}_3$ (end-on) although back-bonding may also occur [52]. The different C–N bond distances [C(23)–N(9) = 1.120(5) Å and C(27)–N(7) = 1.118(7) Å] indicate that CH$_3$CN(9) is strongly and CH$_3$CN(7) is weakly coordinated. These distances depend on the degree of $\pi$–back-bonding between the metal and the CH$_3$CN. Angles subtended at N(5) and N(6) are larger than the ideal tetrahedral angle (109.47$^\circ$) similar to 1 & 2. The six- and five-membered rings assume chair and gauche conformation, respectively. The chelate angles $N(1)$–$Cu(1)$–$N(4)$, $N(2)$–$Cu(1)$–$N(3)$ were 94.03(14)$^\circ$, 92.96(13)$^\circ$ and $N(1)$–$Cu(1)$–$N(2)$, $N(3)$–$Cu(1)$–$N(4)$ were 86.26(14)$^\circ$, 86.57(13)$^\circ$ for six-membered and five-membered rings respectively.

The P–F bond length ranges from 1.454(5)$^\circ$ to 1.571(5)$^\circ$ with an average of 1.528(5)$^\circ$. The mononuclear units are held together by extensive intermolecular hydrogen bonds involving the C–H---F and N–H---F interactions that lead to the formation of a 3D supramolecular architecture (Figs. 2.14 & 2.15). The [CuL(CH$_3$CN)$_2$]$^{2+}$ cation is linked through intramolecular N–H---F hydrogen bond with uncoordinated PF$_6$ $^-$ anions and N–H---N NCMe through two lattice acetonitrile molecules (Fig. 2.16), which are further linked by C–H---F hydrogen bonds. Pertinent structural parameters of the hydrogen-bonded contacts are collected in Table 2.7. Some F atoms are part of bifurcated and trifurcated hydrogen bonding (Fig. 2.14) arrangements. In the crystal packing four PF$_6$ $^-$ anions and two lattice CH$_3$CN were arranged in a square manner by H---F bonding forming a 2D network (Fig. 2.17).

During solving the crystal structure, it was suggested that some F atoms were disordered and multiple splitting was suggested for single F atoms. The fluorine
atoms of PF₆⁻ counter ions have a high thermal parameter since data was collected at room temperature. We tried refining those atoms in two positions with reduced occupancy but there was no decrease in $R$ value and, therefore, we consider that our original refinement is the best.

Fig. 2.14 Spider-like arrangement in chains for 3. Adjacent chains are oriented in opposite direction. Hydrogen atoms have been omitted for clarity. Cu (red) atoms are shown as small spheres of arbitrary radii.
Fig. 2.15 Polyhedral arrangement for 3. Hydrogen atoms have been omitted for clarity.

Fig. 2.16 Intramolecular hydrogen bonding in 3. Hydrogen atoms except those involved in H–bonding have been omitted for clarity. Cu (red), P (orange), F (yellow), C (black), N (blue) and H (grey) atoms are shown as small spheres of arbitrary radii.
Fig. 2.17 Solvent-anion interaction for 3. Arrangement of PF$_6^-$ and solvent molecules due to F---H bonding in the unit cell. Hydrogen atoms have been omitted for clarity.
Table 2.6 Selected bond lengths [Å] and bond angles [°] for [CuL(CH₃CN)₂](PF₆)₂.2CH₃CN (3).

<table>
<thead>
<tr>
<th>Bond lengths</th>
<th>Bond angles</th>
</tr>
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<tbody>
<tr>
<td>Cu(1)–N(1)</td>
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</tr>
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<tr>
<td>Cu(1)–N(3)</td>
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<tr>
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</tr>
<tr>
<td>Cu(1)–N(7)</td>
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Table 2.7 Hydrogen bonds of the N–H---F and N–H---N type between the macrocycle and PF$_6$ and CH$_3$CN in [CuL(CH$_3$CN)$_2$](PF$_6$)$_2$.2CH$_3$CN (3).

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<th>$d$(H---A) (Å)</th>
<th>($D$–H---$A$) (°)</th>
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<td><strong>Intramolecular</strong></td>
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<td>2.760(5)</td>
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<td>2.757(4)</td>
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<td>N(1)–H(1N)---N(10)</td>
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<td>2.301(2)</td>
<td>154.27(6)</td>
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<tr>
<td>N(2)–H(2N)---F(10)</td>
<td>3.210(2)</td>
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<td>152.83(3)</td>
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<td>N(2)–H(2N)---F(7)</td>
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<td>2.795(2)</td>
<td>141.93(3)</td>
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<td>N(3)–H(3N)---N(8)</td>
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<td>2.269(2)</td>
<td>146.84(2)</td>
</tr>
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<td>3.316(4)</td>
<td>2.594(4)</td>
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<td>C(2)–H(2)---F(4)</td>
<td>3.516(5)</td>
<td>2.624(4)</td>
<td>160.59(5)</td>
</tr>
<tr>
<td>C(7)–H(7A)---F(5)</td>
<td>3.203(3)</td>
<td>2.693(2)</td>
<td>113.25(3)</td>
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<td>C(7)–H(7B)---F(5)</td>
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</tr>
<tr>
<td>C(11)–H(11B)---F(4)</td>
<td>3.302(5)</td>
<td>2.572(5)</td>
<td>132.09(5)</td>
</tr>
<tr>
<td>C(13)–H(13A)---F(2)</td>
<td>3.362(3)</td>
<td>2.605(2)</td>
<td>135.21(2)</td>
</tr>
<tr>
<td>C(18)–H(18)---F(7)</td>
<td>3.467(3)</td>
<td>2.583(2)</td>
<td>159.22(2)</td>
</tr>
<tr>
<td>C(19)–H(19)---F(6)</td>
<td>3.502(6)</td>
<td>2.702(6)</td>
<td>144.61(6)</td>
</tr>
<tr>
<td>C(24)–H(24C)---F(5)</td>
<td>3.371(3)</td>
<td>2.780(3)</td>
<td>120.44(5)</td>
</tr>
<tr>
<td>C(26)–H(26A)---F(2)</td>
<td>3.347(3)</td>
<td>2.516(2)</td>
<td>144.86(3)</td>
</tr>
<tr>
<td>C(26)–H(26B)---F(9)</td>
<td>3.281(5)</td>
<td>2.665(4)</td>
<td>123.28(5)</td>
</tr>
<tr>
<td>C(26)–H(26C)---F(8)</td>
<td>3.499(3)</td>
<td>2.765(3)</td>
<td>133.76(4)</td>
</tr>
<tr>
<td>C(26)–H(26C)---F(12)</td>
<td>3.570(4)</td>
<td>2.638(5)</td>
<td>163.62(4)</td>
</tr>
<tr>
<td>C(28)–H(28B)---F(4)</td>
<td>3.540(3)</td>
<td>2.404(2)</td>
<td>156.83(2)</td>
</tr>
<tr>
<td>C(30)–H(30A)---F(11)</td>
<td>3.373(9)</td>
<td>2.637(7)</td>
<td>133.71(7)</td>
</tr>
<tr>
<td>C(30)–H(30C)---F(1)</td>
<td>3.665(5)</td>
<td>2.729(3)</td>
<td>165.25(5)</td>
</tr>
<tr>
<td>C(30)–H(30C)---F(6)</td>
<td>3.374(6)</td>
<td>2.799(5)</td>
<td>119.27(5)</td>
</tr>
</tbody>
</table>
2.3.4 Crystal structure description of \([\text{CuL}_1^1](\text{ClO}_4)_2\) (4)

The ORTEP drawing of 4 and atom labeling scheme is illustrated in Fig. 2.18. Crystallographic data, selected bond lengths and bond angles are collected in Tables 2.8 & 2.9. It was crystallized in monoclinic crystal system with \(P2(1)/c\) space group in a body-centered lattice. The crystallographic asymmetric unit of 4 contains one \([\text{CuL}_1^1]^{2+}\) cation and two perchlorate anions (Fig. 2.18). The molecule is highly symmetrical, with the Cu(II) ion on a crystallographic inversion center (Fig 2.19). The Cu(II) ion is octahedral (4 + 2) coordinated with four secondary amine nitrogen atoms of the macrocyclic ring \([\text{Cu}(1)–\text{N}(1) = 1.994(2) \, \text{Å} \text{ and } \text{Cu}(1)–\text{N}(2) = 2.0079(19) \, \text{Å}]\) occupying the equatorial plane in an essentially square-planar arrangement and two weakly held perchlorate ions at the axial position \([\text{Cu}(1)–\text{O}(1) = 2.585(6) \, \text{Å}].\) The two cross bond angles \(\text{N}(1)#1–\text{Cu}(1)–\text{N}(1)\) and \(\text{N}(2)–\text{Cu}(1)–\text{N}(2)#1\) are 180º. The axial Cu–O linkages are slightly bent off the perpendicular to the CuN\(_4\) planes by 2.0–4.0º similar to 1.

Angles subtended at N(3) are in the range 114.9(2)–115.7(2)º indicating an \(sp^2\)-like hybridization of N(3). The six-membered chelate rings involving C(8) and C(9) atoms adopt a chair conformation, whereas five-membered rings involving the C(10) and C(11) atoms assume a gauche conformation. The chelate angles \(\text{N}(1)–\text{Cu}(1)–\text{N}(2)\) and \(\text{N}(1)#1–\text{Cu}(1)–\text{N}(2)\) are 94.18(8)º and 85.82(8)º for six-membered and five-membered rings, respectively. The two methyl substituents are located in opposite hemispheres, resulting in a high crystallographic symmetry. The Cu(1)–N(1)–C(10) angle (109.03(4)º) is larger than the Cu(1)–N(2)–C(11) angle (107.84(4)º) and the C(11)–N(2)–C(9) angle (113.35(3)º) is also larger than the C(10)–N(1)–C(8) angle (111.80(2)º). This may be due to the steric repulsion caused by the C-methyl group next to the N(2) atom. The torsion angle between benzene rings in two halves is 180.0º indicating parallel arrangement with a separation of 4.877 Å.

The bond angles in perchlorate ion at Cl(2) are in the range 108.23(13)-111.26(16)º while bond distances vary from 1.403(2)-1.431(2) Å. The perchlorate ion indicates a lengthening of the Cl–O bonds involving O(1), which are weakly coordinated to the Cu atom \([\text{Cu}(1)–\text{O}(5) = 2.585(2) \, \text{Å}].\)
Table 2.8 Crystallographic data of \([\text{CuL}^1](\text{ClO}_4)_2\) and \([\text{CuL}^1](\text{PF}_6)_2\).

<table>
<thead>
<tr>
<th>Complex</th>
<th>(<a href="%5Ctext%7BClO%7D_4">\text{CuL}^1</a>_2) (4)</th>
<th>(<a href="%5Ctext%7BPF%7D_6">\text{CuL}^1</a>_2) (5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>(\text{C}<em>{24}\text{H}</em>{38}\text{Cl}_2\text{CuN}_6\text{O}_8)</td>
<td>(\text{C}<em>{24}\text{H}</em>{38}\text{CuF}_{12}\text{N}_6\text{P}_2)</td>
</tr>
<tr>
<td>CCDC No.</td>
<td>791740</td>
<td>791741</td>
</tr>
<tr>
<td>Formula weight</td>
<td>673.04</td>
<td>764.08</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>298(2) K</td>
<td>100(2)</td>
</tr>
<tr>
<td>Wavelength (Å)</td>
<td>0.71073</td>
<td>0.71073</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>(\text{P2}(1)/c)</td>
<td>(\text{P2}(1)/n)</td>
</tr>
<tr>
<td>(a) (Å)</td>
<td>10.9177(12)</td>
<td>11.377(2)</td>
</tr>
<tr>
<td>(b) (Å)</td>
<td>13.1138(14)</td>
<td>8.3013(16)</td>
</tr>
<tr>
<td>(c) (Å)</td>
<td>10.7709(12)</td>
<td>18.455(3)</td>
</tr>
<tr>
<td>(\alpha) (°)</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>(\beta) (°)</td>
<td>102.144(2)</td>
<td>114.596(8)</td>
</tr>
<tr>
<td>(\gamma) (°)</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>Volume (Å³)</td>
<td>1507.6(3)</td>
<td>1584.8(5)</td>
</tr>
<tr>
<td>(Z), (\rho) (g cm⁻³)</td>
<td>2, 1.483</td>
<td>2, 1.601</td>
</tr>
<tr>
<td>Absorption coefficient (mm⁻¹)</td>
<td>0.957</td>
<td>0.888</td>
</tr>
<tr>
<td>(F(000))</td>
<td>702</td>
<td>782</td>
</tr>
<tr>
<td>Crystal size (mm)</td>
<td>0.20 x 0.10 x 0.10</td>
<td>0.30 x 0.25 x 0.20</td>
</tr>
<tr>
<td>(\theta) Range for data collection (°)</td>
<td>1.91 - 25.00 °</td>
<td>2.41 to 25.00</td>
</tr>
<tr>
<td>Limiting indices</td>
<td>(-12 \leq h \leq 12, -15 \leq k \leq -13 \leq h \leq 13, -9 \leq k \leq 9, -15, -12 \leq l \leq 12)</td>
<td>(21 \leq l \leq 20)</td>
</tr>
</tbody>
</table>
| Reflections collected / unique | 14181 / 2651 | \([R_{\text{int}} = 0.0337]\)
| Max. and min. transmission | 0.9104 and 0.8317 | 0.8424 and 0.7776 |
| Refinement method | Full-matrix least-squares on \(F^2\) | Full-matrix least-squares on \(F^2\) |
| Data / restraints / parameters | 2651 / 3 / 195 | 2773 / 0 / 206 |
| Goodness-of-fit on \(F^2\) | 0.989 | 0.719 |
| Final R indices \([I > 2\sigma(I)]\) | \(R_1 = 0.0352, wR_2 = 0.0526, wR_2 = 0.1350^{[a]}\) | \(R_1 = 0.0390, wR_2 = 0.0912\) |
| R indices (all data) | \(R_1 = 0.0352, wR_2 = 0.0912\) | \(R_1 = 0.0644, wR_2 = 0.1596\) |
| Largest diff. peak and hole (e Å⁻³) | 0.260 and \(-0.181\) | 0.726 and \(-0.717\) |
| Completeness to \(\theta = 25.00\) (%) | 100.0 | 99.5 |

\(^{[a]} R_1 = \frac{\sum(|F_o| - |F_c|)^2}{\sum|F_o|}; wR_2 = \frac{\sum[w(|F_o|^2 - |F_c|^2)^2]}{\sum[w(|F_o|^2)^2]^{1/2}}; w = 1/[\sigma^2|F_o|^2 + (x p)^2] \); where \(p = [|F_o|^2 + 2|F_c|^2]/3\); \(x = 0.0605\).
Fig. 2.18 ORTEP view of the molecular structure (showing 50% thermal ellipsoids) of 4, along with the atomic numbering scheme. Hydrogen atoms have been omitted for clarity.

Fig. 2.19 Unit cell diagram of 4. Cu (red) atoms are shown as small spheres of arbitrary radii.
The mononuclear units are hydrogen bonded via a N–H---F involving H1A(N1) and O(3) of perchlorate ion forming an infinite two-dimensional polymeric array along the $a$-axis (Fig. 2.20). The hydrogen bonding parameters are given in Table 2.10. The 2D arrays are further held together through C–H---O interactions (Fig. 2.21) involving the methylene and phenyl C–H in one sheet and oxygen of perchlorate ions in adjacent sheets forming 3D supramolecular network (Fig. 2.22).

Fig. 2.20 Depicting intermolecular hydrogen bonded 2D polymeric array along $a$-axis for 4. Hydrogen atoms except those involved in H–bonding have been omitted for clarity. Cu (red) and H (white) atoms are shown as small spheres of arbitrary radii.
Fig. 2.21 Depicting C–H—O interaction between adjacent layers along c-axis for 4. Hydrogen atoms except those involved in H–bonding have been omitted for clarity. Cu (red) and H (grey) atoms are shown as small spheres of arbitrary radii.

Fig. 2.22 Projection of hydrogen bonded 3D network of 4. Cu (red) atoms are shown as small spheres of arbitrary radii.
Table 2.9 Bond lengths [Å] and angles [°] for 4.

<table>
<thead>
<tr>
<th>Bond lengths</th>
<th>Bond angles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(1)–N(1) 1.994(2)</td>
<td>O(1)–Cu(1)–N(1) 83.56</td>
</tr>
<tr>
<td>Cu(1)–N(2) 2.0079(19)</td>
<td>O(1)–Cu(1)–N(1)#1 96.44</td>
</tr>
<tr>
<td>Cu(1)–O(1) 2.5854(2)</td>
<td>O(1)–Cu(1)–N(2) 91.96</td>
</tr>
<tr>
<td>Cl(2)–O(2) 1.403(2)</td>
<td>O(1)–Cu(1)–N(2)#1 88.04</td>
</tr>
<tr>
<td>Cl(2)–O(4) 1.428(2)</td>
<td>O(1)–Cu(1)–O(1)#1 180.00</td>
</tr>
<tr>
<td>Cl(2)–O(3) 1.431(2)</td>
<td>C(9)–N(3)–C(8) 115.7(2)</td>
</tr>
<tr>
<td>Cl(2)–O(1) 1.431(2)</td>
<td>C(9)–N(3)–C(7) 115.9(2)</td>
</tr>
<tr>
<td>N(1)–C(10) 1.481(3)</td>
<td>C(8)–N(3)–C(7) 114.9(2)</td>
</tr>
<tr>
<td>N(2)–C(11) 1.489(3)</td>
<td>O(2)–Cl(2)–O(4) 111.26(16)</td>
</tr>
<tr>
<td>C(11)–C(12) 1.516(4)</td>
<td>O(2)–Cl(2)–O(3) 108.79(13)</td>
</tr>
<tr>
<td></td>
<td>O(4)–Cl(2)–O(3) 108.91(14)</td>
</tr>
</tbody>
</table>

Symmetry transformations used to generate equivalent atoms: #1 –x+1, –y, –z.

Table 2.10 Hydrogen bonds of the N–H---O and C–H---O type between the macrocycle and ClO$_4^-$ in 4.

<table>
<thead>
<tr>
<th>D–H---A</th>
<th>d(D---A) (Å)</th>
<th>d(H---F) (Å)</th>
<th>(D–H---A) (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intramolecular</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N(2)–H(2A)---O(4)</td>
<td>3.130(12)</td>
<td>2.280</td>
<td>164</td>
</tr>
<tr>
<td>C(7)–H(7B)---O(4)</td>
<td>3.495(11)</td>
<td>2.570</td>
<td>159</td>
</tr>
<tr>
<td>Intermolecular</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N(1)–H(1A)---O(3)</td>
<td>3.074(12)</td>
<td>2.274</td>
<td>152.22</td>
</tr>
<tr>
<td>C(3)–H(3)---O(3)</td>
<td>3.586(15)</td>
<td>2.678</td>
<td>165.67</td>
</tr>
<tr>
<td>C(7)–H(7A)---O(4)</td>
<td>3.430(11)</td>
<td>2.535</td>
<td>153.35</td>
</tr>
<tr>
<td>C(8)–H(8A)---O(2)</td>
<td>3.229(11)</td>
<td>2.608</td>
<td>122.09</td>
</tr>
</tbody>
</table>
2.3.5 Structural description of $[\text{CuL}^1](\text{PF}_6)_2$ (5)

The molecular structure of 5 and the atomic numbering scheme is shown in Fig. 2.23. Crystallographic data, selected bond lengths and bond angles are given in Tables 2.8 & 2.11. It was crystallized in the space group $P2(1)/n$ of the monoclinic system. The crystal structure of 5 contains a monomeric $[\text{CuL}^1]^2^+$ cation and two hexafluorophosphate anions (Fig. 2.23). The Cu atom is (N$_4$ + F$_2$) coordinated with four secondary amine nitrogen atoms (Cu–N(1) = 2.008(3) Å and Cu–N(2) = 2.000(3) Å) occupying the equatorial plane in square-planar fashion and two weakly coordinated hexafluorophosphate anions at the axial position (Cu–F(1) = 2.539(4) Å). The $trans$ bond angles in equatorial plane [N(1)#1–Cu–N(1) and N(2)#1–Cu–N(2)] are 180°. The bond angles N(1)–Cu–F(1), N(1)#1–Cu–F(1), N(2)–Cu–F(1), and N(2)#1–Cu–F(1) are 85.73(15)°, 94.27(15)°, 86.73(15)° and 93.27(15)° respectively, suggest that the Cu–F(1) linkages are slightly bent off the perpendicular to the CuN$_4$ plane.

The geometry of the tertiary nitrogen atom N(3) is normal; average C–N distances (1.452(2) Å) and C–N–C angles are in the range 113.5(3)-115.4(3)°. The six-membered chelate rings adopt chair conformation, whereas five-membered rings assume gauche conformation. The chelate angles N(1)–Cu–N(2) and N(1)–Cu–N(2)#1 are 94.01(13)° and 85.99(13)° for six-membered and five-membered rings, respectively. The benzene rings are positioned completely parallel to each other (dihedral angle of 0.0°) with interplanar separation of 7.241(4) Å. The PF$_6^-$ groups appear as distorted octahedra. The P–F distances vary from 1.570(3) to 1.609(3) Å, in the normal range. The F–P–F angles range from 88.7(2)-91.9(2)° for adjacent (cis position) fluorines and 178.4(2)-179.4(17)° for opposite (trans position) fluorines.

These apparent distortions and large thermal parameters are commonly observed in hexafluorophosphates. The mononuclear units are held together by intermolecular hydrogen bonds involving the N–H--F which gives 1D polymeric chain (Fig. 2.24) propagating along $a$-axis. The 1D chains are held together through C–H--F interaction (Fig. 2.25) between the methylene H(7B) and benzene ring (Fig. 2.26). Intermolecular hydrogen bonds involving the C–H--F, N–H--F and C–H--π interactions lead to the formation of a 3D supramolecular architecture (Fig. 2.27). Pertinent structural parameters of the hydrogen-bonded contacts are collected in Table 2.12.
Fig. 2.23 ORTEP diagram (with 50% thermal ellipsoids) of 5 along with the atomic numbering scheme. Hydrogen atoms have been omitted for clarity.

Fig. 2.24 Depicting intermolecular (N–H---F) hydrogen bonded 1D polymeric chain along $a$-axis for 5. Hydrogen atoms except those involved in H–bonding have been omitted for clarity. Cu (red) atoms are shown as small spheres of arbitrary radii.

Fig. 2.25 Depicting C–H---$\pi$ interaction in 5. Hydrogen atoms except those involved in H–bonding have been omitted for clarity. Cu (red) and H (grey) atoms are shown as small spheres of arbitrary radii.
Fig. 2.26 Depicting C–H---F interaction in 5. Hydrogen atoms except those involved in H–bonding have been omitted for clarity. Cu (red) atoms are shown as small spheres of arbitrary radii.

Fig. 2.27 Projection of 3D network of 5 as a result of C–H---F, N–H---F and C–H---π interactions. Hydrogen atoms have been omitted for clarity. Cu (red) atoms are shown as small spheres of arbitrary radii.
Table 2.11 Bond lengths [Å] and angles [°] for 5.

<table>
<thead>
<tr>
<th>Bond lengths</th>
<th>Bond angles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu–N(1) 2.008(3)</td>
<td>N(2)–Cu–N(1) 94.01(13)</td>
</tr>
<tr>
<td>Cu–N(2) 2.000(3)</td>
<td>F(5)–P(1)–F(2) 178.4(2)</td>
</tr>
<tr>
<td>P(1)–F(5) 1.592(3)</td>
<td>F(6)–P(1)–F(3) 178.4(2)</td>
</tr>
<tr>
<td>P(1)–F(6) 1.570(3)</td>
<td>F(1)–P(1)–F(4) 179.48(17)</td>
</tr>
<tr>
<td>P(1)–F(2) 1.575(3)</td>
<td>F(6)–P(1)–F(2) 91.9(2)</td>
</tr>
<tr>
<td>P(1)–F(1) 1.609(3)</td>
<td>F(5)–P(1)–F(6) 89.7(2)</td>
</tr>
<tr>
<td>P(1)–F(3) 1.602(3)</td>
<td>F(5)–P(1)–F(1) 90.98(18)</td>
</tr>
<tr>
<td>P(1)–F(4) 1.604(3)</td>
<td>F(6)–P(1)–F(1) 90.20(17)</td>
</tr>
<tr>
<td>N(1)–C(11) 1.488(5)</td>
<td>F(2)–P(1)–F(1) 89.39(17)</td>
</tr>
<tr>
<td>N(1)–C(12) 1.489(5)</td>
<td>F(5)–P(1)–F(3) 88.7(2)</td>
</tr>
<tr>
<td>N(2)–C(9) 1.492(5)</td>
<td>F(2)–P(1)–F(3) 89.69(18)</td>
</tr>
<tr>
<td>N(2)–C(8) 1.493(5)</td>
<td>F(6)–P(1)–F(4) 89.95(18)</td>
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<tr>
<td>N(3)–C(11) 1.438(5)</td>
<td>F(5)–P(1)–F(4) 89.52(18)</td>
</tr>
<tr>
<td>N(3)–C(8) 1.442(5)</td>
<td>F(6)–P(1)–F(4) 89.39(17)</td>
</tr>
<tr>
<td>N(3)–C(7) 1.479(6)</td>
<td>F(2)–P(1)–F(4) 90.11(17)</td>
</tr>
<tr>
<td>C(9)–C(10) 1.503(7)</td>
<td>F(3)–P(1)–F(4) 90.25(16)</td>
</tr>
<tr>
<td>C(11)–N(3)–C(8) 113.5(3)</td>
<td></td>
</tr>
</tbody>
</table>

Symmetry transformations used to generate equivalent atoms: #1 –x+2, –y, –z.

Table 2.12 Hydrogen bonds of the N–H---F and C–H---F type between the macrocycle and PF₆⁻ in 5.

<table>
<thead>
<tr>
<th>D–H---A</th>
<th>d(D---A) (Å)</th>
<th>d(H---F) (Å)</th>
<th>(D–H---A) (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(2)–H(2A)---F(3)</td>
<td>3.048</td>
<td>2.24</td>
<td>155</td>
</tr>
<tr>
<td>N(1)–H(1A)---F(5)</td>
<td>3.031(12)</td>
<td>2.315</td>
<td>139.86</td>
</tr>
<tr>
<td>C(4)–H(4)---F(2)</td>
<td>3.542(15)</td>
<td>2.610</td>
<td>166.41</td>
</tr>
<tr>
<td>C(7)–H(7A)---F(6)</td>
<td>3.399(11)</td>
<td>2.692</td>
<td>128.54</td>
</tr>
<tr>
<td>C(12)–H(12B)---F(4)</td>
<td>3.393(11)</td>
<td>2.520</td>
<td>146.88</td>
</tr>
</tbody>
</table>
2.3.6 IR Spectral studies

IR spectra of 1-5 (Fig. 2.28) show characteristic absorption bands of the polyaza macrocycle in the region 3269-3194 cm\(^{-1}\), indicating the presence of NH group in the complexes. Several weak bands in the range 3050-2800 cm\(^{-1}\) assignable to C–H stretching vibration are routinely observed. It is apparent from the IR spectrum of complex 1 & 4, that there is considerable broadening and splitting in the 1100 cm\(^{-1}\) region (\(\nu_3\)-antisymmetric stretching) with two peaks (1111 and 1074 cm\(^{-1}\)) assigned to perchlorate ions [53]. This splitting clearly explains the presence of coordinated perchlorate ion [54,55] which is further supported by \(\nu_2\)-symmetric stretching at 999 cm\(^{-1}\) [56]. A peak at 621 cm\(^{-1}\) (\(\nu_4\)-antisymmetric bending) belongs to perchlorate bending vibration.

The \(\nu(CN)\) stretching frequency of the thiocyanate group can be used for characterization of the coordination mode to the metal ion [57-60]. The \(\nu(CN)\) of thiocyanate is lower in N–bonded (near 2050 cm\(^{-1}\)) than S–bonded complexes (near 2100 cm\(^{-1}\)). The \(\nu(CN)\) observed at 2050 cm\(^{-1}\) in 2 suggests that the pseudo-halide is coordinated to copper through the nitrogen atom (terminal N–bonded) [59,61,62].

The spectrum of 3 displays broad and intense bands at 845 and 555 cm\(^{-1}\) corresponding to \(\nu_3(F_{2u})\) IR-active modes of the PF\(_6^-\) anions [58]. It showed two bands at 2341 and 2313 cm\(^{-1}\) due to the asymmetric and symmetric \(\nu(C≡N)\) of the coordinated acetonitrile [63]. A band at 2250 cm\(^{-1}\) is indicative of uncoordinated lattice acetonitrile [64]. When IR spectrum of 3 was taken after drying at 80 °C for 30 min, acetonitrile bands disappeared indicating the loss of acetonitrile molecules.

The spectrum of 5 displays broad and intense bands at 845, 735 and 555 cm\(^{-1}\) consistent with the characteristic \(\nu_3(F_{2u})\), \(\nu_1(A_{1g})\) and \(\nu_4(F_{1u})\) IR-active modes of the weakly coordinated hexafluorophosphate counter ion [65,66]. The spectrum of 5 shows very broad \(\nu_3\) band and medium intensity infrared-forbidden bands (\(\nu_1\)). These results indicate some distortion of the anions below \(O_h\) symmetry possibly due to weak anion-cation interaction [67].
2.3.7 Electronic spectra and magnetic moment

The electronic spectra of 1-5 were measured in acetonitrile solution. They exhibit very intense bands in the 250-275 nm region assignable to $\pi\rightarrow\pi^*$ intraligand charge-transfer. The appearance of a single broad $d-d$ band in the visible spectrum of square-planar or tetragonally distorted octahedral complexes containing neutral macrocyclic diimine ligands is common [68,69]. The spectra display one broad $d-d$ band at $\lambda_{\text{max}}$ 497, 532, 498, 505 and 506 nm for 1, 2, 3, 4 and 5 respectively,
contributed from the CuN$_4$ square-planar coordination which indicates that the M–X
[where X= ClO$_4^-$, SCN$^-$, NCCH$_3$ and PF$_6^-$ ] bonds are entirely dissociated [70].
Similar behaviour has also been reported by Kang et al. [71,72]. This can be
adequately explained as a $d$-$d$ transition of Cu(II) ion in the complex with $D_{4h}$
symmetry [73,74].

Tetragonal distortions involving elongation of the axial bonds that remove the
degeneracy are very common, especially with $\sigma$–bonding ligands such as
1,2-diamines [75]. This fact suggests that in tetragonally distorted octahedral Cu(II)
complexes involving unidentate ligands, the axially coordinated groups are weakly
bonded and not positioned by lattice packing factors. This is indicative of a reduction
in coordination number of the complex forming a square-plane with CuN$_4$
chromophore after solvation. The molar conductance of perchlorate, thiocyanate and
hexafluorophosphate salts of Cu(II) complexes measured in acetonitrile solution falls
in the range 243-275 ohm$^{-1}$ cm$^2$ M$^{-1}$ corresponding to a 1:2 electrolyte [76]. The
contradiction between the crystal structure of Cu(II) complex and the conductivity
data indicate that the counter-ions are coordinated to the Cu(II) ion in solid state and
are labile in solution. Room-temperature solid phase magnetic susceptibility
measurement of 1-5 shows one-electron paramagnetism with $\mu_{\text{eff}} = 1.81$-1.90 BM
which is greater than spin only value (1.73 BM); the behaviour is expected for the
discrete and magnetically non-coupled mononuclear copper(II) center (3d$^9$, $S = 1/2$)
with orbital contribution [77].

2.3.8 EPR studies

The X-band EPR spectra of polycrystalline powder of 1-4 were recorded at
room temperature and in frozen acetonitrile-toluene (1:1) mixture (Fig. 2.29). The
powder spectra at RT were typical of axial-type Cu(II) complexes with two $g$ values,
and $g_{||} > g_{\perp} > 2.03$, (Table 2.13) suggesting a $d_{x^2}$-$y^2$ ground state which is consistent
with a tetragonally distorted octahedral stereochemistry [78]. The broadening of the
spectrum of 2 and 3 is probably due to spin relaxation. The absence of any half field
signal suggests the presence of only one transition metal ion. The $g_{||}$<2.3 indicates a
considerable covalent character [65,66]. The smaller $g_{||}$ value indicates increased
delocalization of the unpaired electron away from the metal nucleus. It has been often
interpreted in terms of increased covalency in the metal-ligand bond [79,80]. The calculated G value \[\frac{(g_{\|}-2.0023)}{(g_{\perp}-2.0023)}\] > 4 (Table 2.13) suggest that the extent of interaction between Cu(II) centres is negligible indicating an essentially mononuclear structure [81].

The frozen solution spectra of the complexes are axial with \(g_{\|} > g_{\perp} > 2.0\) and G = 3.6-4.1 and, confirm the square based geometry as observed in the X-ray crystal structures of 1-4. Frozen spectrum of 1 is well resolved with a quartet hyperfine structure (Cu, \(I = 3/2\)) while those of 2, 3 and 4 are partially resolved. A square-based CuN4 chromophore is expected to show \(g_{\|}\) value of 2.200 and \(A_{\|}\) value of 180-220 G. The nuclear hyperfine coupling for 2, 3 and 4 is observed in the \(g_{\|}\) signal with three of the four components clearly resolved, the last one being obscured by the \(g_{\perp}\) component. Accordingly, the orbital ground state of the Cu(II) would be basically \(d_{x^2-y^2}\) and the polyhedra could be statistically distorted [82].

![EPR spectra of 1-4 at RT and LNT.](image)

Fig. 2.29 EPR spectra of 1-4 at RT and LNT.
Fig. 2.30 Simulated and experimental PXRD pattern of 1-5.
Table 2.13 EPR parameters of the complexes 1-4.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Temperature</th>
<th>g_∥</th>
<th>g_⊥</th>
<th>g_iso</th>
<th>G</th>
<th>A_∥</th>
</tr>
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<tr>
<td><a href="ClO_4">CuL</a>_2 (1)</td>
<td>RT</td>
<td>2.180</td>
<td>2.043</td>
<td>2.088</td>
<td>4.366</td>
<td>......</td>
</tr>
<tr>
<td></td>
<td>LNT</td>
<td>2.095</td>
<td>2.025</td>
<td>2.048</td>
<td>4.083</td>
<td>96</td>
</tr>
<tr>
<td><a href="SCN">CuL</a>_2 (2)</td>
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<td>2.177</td>
<td>2.045</td>
<td>2.089</td>
<td>4.091</td>
<td>......</td>
</tr>
<tr>
<td></td>
<td>LNT</td>
<td>2.067</td>
<td>2.019</td>
<td>2.035</td>
<td>3.874</td>
<td>170.6</td>
</tr>
<tr>
<td><a href="PF_6">CuL(CH_3CN)_2</a>·2CH_3CN (3)</td>
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<td>2.225</td>
<td>2.056</td>
<td>2.112</td>
<td>4.147</td>
<td>......</td>
</tr>
<tr>
<td></td>
<td>LNT</td>
<td>2.176</td>
<td>2.050</td>
<td>2.092</td>
<td>3.64</td>
<td>214</td>
</tr>
<tr>
<td><a href="ClO_4">CuL'</a>_2 (4)</td>
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<td>2.051</td>
<td>2.084</td>
<td>3.032</td>
<td>......</td>
</tr>
<tr>
<td></td>
<td>LNT</td>
<td>2.172</td>
<td>2.065</td>
<td>2.100</td>
<td>2.706</td>
<td>162</td>
</tr>
</tbody>
</table>

2.3.9 PXRD studies

The phase purity of all the Cu(II) complexes was confirmed by PXRD. The experimental PXRD patterns of 1-5 (except that of 3) are consistent with the simulated ones, as determined from the single-crystal X-ray diffraction data (Fig. 2.30). The peak positions are in agreement with each other. Difference in intensities and peak position between the PXRD patterns of the two sets of compound 3 is due to the loss of solvent molecules during grinding. Intensity of the experimental XRD patterns is weak due to the preferred orientation of the powder samples and the instrumental limitations.

2.4 Conclusion

Cu(II) complexes have been synthesized by one-pot template reaction. It is believed that in the solid state, the geometry of Cu(II) is distorted octahedral most probably due to crystal packing effects whereas in solution, it exists as square-planar. Further, oxygen from perchlorate ions, fluorine from hexafluorophosphate ions and nitrogen from thiocyanate ions and acetonitrile are weakly coordinated to Cu(II) maintaining an octahedral geometry in the solid state. The molar conductivity determined in acetonitrile solution indicated that axially bonded groups are entirely dissociated in solution.
References


