Experimental

Chapter V
5.1 Introduction

The synthetic procedures of ligands and their metal complexes together with experimental details of different physicochemical measurements used to characterize ligands and model complexes of copper (I)/(II) are described in this chapter.

5.2 Syntheses

5.2.1 General

All the chemicals used in the preparation of ligands (L-1 to L-7) and metal complexes (Cu-1 to Cu-7, Cu-1A, Cu-1B, Cu-2A and Cu-2B) were of analytical grade. Lawsone (2-hydroxy-1,4-naphthoquinone), Menadione (2-methyl-1,4-naphthoquinone), Dicline (2,3 dichloro-1,4 naphthoquinone), 2,3 dibromo-1,4...
naphthoquinone, Hexafluoro phosphoric acid and Cupric perchlorate hexahydrate [Cu(ClO₄)₂.6H₂O] were obtained commercially from Sigma-Aldrich and used without further purification. AE grade cupric sulphate pentahydrate [CuSO₄.5H₂O] was obtained commercially from Qualigens fine chemicals. Tetrakis(acetonitrile) copper(I) hexafluorophosphate [Cu(CH₃CN)₄PF₆] was prepared as outlined in the literature[1]. Anhydrous sodium carbonate (Na₂CO₃), 30% hydrogen peroxide, conc. sulphuric acid (H₂SO₄), sodium hydroxide (NaOH), hydroxylamine hydrochloride (NH₂OH.HCl), anhydrous sodium acetate (CH₃COONa.), sodium dithionite (Na₂S₂O₄), potassium iodide (KI), potassium iodate (KIO₃), sodium nitrite (NaNO₂) obtained from Qualigens were of extra pure analytical grade. The solvents used for synthesis were of A.R. grade and were further purified according to the literature [2].

5.2.2 Syntheses of Ligands

(i) Lawsonemonoxime (LwOx), L-1

Lawsone (2-hydroxy-1,4-naphthoquinone), (0.871 g, 5 mmol) was dissolved in 10 ml of 2 N sodium hydroxide and was mixed with a solution of (0.521 g, 7.5 mmol) of hydroxylamine hydrochloride in 10 ml of distilled water. The mixture was maintained at 50–70 °C for 45 minutes in water bath. It was then allowed to cool in ice bath. On neutralization by 2N hydrochloric acid lawsonemonoxime precipitated as yellow crystals. The precipitate was filtered, washed with ice-cold water and dried under vacuum at room temperature. It was recrystallized from hot water containing trace of acetic acid. [dec. temp. 180 ± 1°C], {yield 95 %, %CHN [obs. (cal)] C= 59.08 (63.5), H= 4.123(3.72), N= 6.725 (7.40) }.

(ii) Phthiocolmonoxime (PhthOx), L-2

Phthiocol is a precursor for the synthesis of phthiocolmonoxime. Phthiocol was prepared by earlier reported procedure [3] and phthiocolmonoxime was prepared by reported procedure [4].

Step I: Menadione (3-methyl-1,4-naphthoquinone) (1.00 g, 5.81 mmol) was dissolved in 10ml of hot alcohol and the solution was cooled until it began to crystallize. A solution of anhydrous sodium carbonate (0.200 g, 2.41mmol) and 30% hydrogen peroxide (1ml)
in 5ml of water was added all at once. The solution was cooled in ice bath after an addition of about 100 ml of water. 3-methyl-1,4-naphthoquinone epoxide separates as colourless crystal. [m.p. 93.5-94.5 °C] (yield 89 %). 1 g of thoroughly dried epoxide was treated with conc. sulphuric acid (5ml). After 10 minutes the solution was cooled in ice and slowly diluted with excess water. Crude Phthiocoll (3-methyl-2-hydroxy-1,4-naphthoquinone) precipitates out and was purified by crystallization from methanol containing a little of conc. hydrochloric acid. [m. p. 176-179 °C], (yield 88 %).

Step II: Phthiocoll (0.861 g, 5 mmol) was dissolved in 10 ml 2 N sodium hydroxide solution and was mixed with a solution of (0.521 g, 7.5 mmol) hydroxylamine hydrochloride in 10 ml of distilled water. The clear red solution was maintained at 50 – 60 °C for half an hour in water bath. It was allowed to cool in ice bath. On neutralization of the solution using 2 N solution of hydrochloric acid, phthiocollmonoxime was precipitated as yellow crystals. The precipitate was filtered, washed with ice-cold water and dried under vacuum at room temperature. It was crystallized from ethanol containing trace of acetic acid. [dec. temp. 200 ± 1 °C], (yield 95 %, %CHN [obs. (cal)] C= 64.478 (65.02), H= 4.29(4.46), N= 6.65(6.89)].

(iii) Aminolawsone monoxime (NH₂-LwOx), L-3

3-aminolawsone is a precursor in the synthesis of aminolawsone oxime and 3-Nitrolawsone is a precursor in the synthesis of 3-aminolawsone. 3-nitrolawsone is prepared by earlier reported procedure [5] and details are given in infra article 5.2.2 (vii).

Step I: 3-Nitrolawsone (1.09575g, 5 mmol) was suspended in 11ml water and 3.6 ml of 10% NaOH was added. While stirring the above solution mixture 3.2g (20 mmol) of sodium dithionite (Na₂S₂O₄) was added. The temperature was raised to about 50°C and stirring was continued for 30 min. The reaction mixture was filtered and washed with ice cold water when black powder of 3-amino lawsonie was obtained. It was crystallized from ethanol to obtain reddish brown crystals. [M.P. 234-236°C] (yield 95% ).

Step II: 3-Aminolawsone (0.946g, 5mmol) and hydroxylamine hydrochloride (0.521g, 7.5mmol) were dissolved in 25ml of hot 2N NaOH solution and distilled water respectively. The mixture was warmed at 50-60°C for about 45 minutes on water bath.
and was set aside to cool. It was neutralized by 1:1 HCl to precipitate out 3-aminolawsone oxime. The precipitate was filtered, washed with ice cold water and dried under vacuum at room temperature. It was crystallized from ethanol to obtain reddish brown crystals. [M.P. 160°C] {yield 55%, %CHN [obs. (cal)] C= 57.87(58.82), H= 3.84 (3.95), N= 12.315(13.72)}.

(iv) Chloro Lawsone monoxide (Cl-LwOx), L-4

3-Chlorolawsone is a precursor in the synthesis of Chlorolawsone oxime and 3-Chlorolawsone is prepared from Diclone i.e. 2,3-Dichloro-1,4-naphthoquinone. Chlorolawsone oxime was prepared by using earlier reported procedure [4, 6]. Recrystallization of Diclone: Few grams of Diclone was dissolved in chloroform and warmed it for few minutes. Cooled in ice-bath. Few ml of diethyl ether added to obtain yellow coloured precipitate of diclone. Filtered and dried under vacuum.

Step-I: Diclone (5.676g, 25mmol) was moistened with 10ml methanol and warmed with 2M KOH solution (13ml). The mixture was warmed at 50-60°C for about 30 minutes. It was neutralized by 1:1 HCl to precipitate out 3-chlorolawsone. The yellow needles like precipitate was filtered, washed with ice cold water and dried under vacuum at room temperature. [M.P. 213°C](yield 76%).

Step II: Chlorolawsone (1.043g, 5mmol)was dissolved in 25ml 2N NaOH. Hydroxylamine hydrochloride (0.521g, 7.5mmol) dissolved in 25ml distilled water was added in it. The mixture was heated for 45 minutes at 50-60°C. Then cooled and acidified with 2N HCl to obtain yellow precipitate. The precipitate was filtered, washed with ice cold water and dried under vacuum at room temperature. [M.P. 188°C] {yield 82%, %CHN [obs. (cal)] C= 52.01(53.71), H= 3.037(2.70), N= 6.388 (6.26)}.

(v) Bromo Lawsone monoxide (Br-LwOx), L-5

3-Bromolawsone is a precursor in the synthesis of Bromolawsone oxime and 3-Bromolawsone is prepared from 2,3 Dibromo-1,4-naphthoquinone. Bromolawsone oxime was prepared by using earlier reported procedure [4, 6].

Step-I: 2,3-Dibromo-1,4- naphthoquinone (3.159g, 10mmol) was dissolved in 65ml methanol. KOH solution (15.5g KOH in 50 ml distilled water) was added in it. The
mixture was heated at 65-70°C for about 1 hour. The hot solution is filtered and cooled in ice bath. It was acidified by 1:1 HCl to precipitate out 3-bromolawson. The yellow needles like precipitate was filtered, washed with ice cold water and dried under vacuum at room temperature. [M.P. 198°C] (yield 70%).

Step II: Bromolawson (1.265g, 5mmol) was dissolved in 30ml 2N NaOH and hydroxylamine hydrochloride (0.521g, 7.5mmol) in 25ml distilled water was added in it. The mixture was heated for 1 hour at 60-70°C. Then cooled and acidified with 1:1 HCl to obtain yellow precipitate. The precipitate was filtered, washed with ice cold water and dried under vacuum at room temperature. [M.P. 208°C] {yield 96%, %CHN [obs. (cal)] C= 43.99(44.81), H= 2.549(2.25), N= 5.202(5.23)}.

(vi) Iodo Lawson monoxide (I-Lwox), L-6

3-Iodolawson is a precursor in the synthesis of Iodolawson oxide and 3-Iodolawson is prepared from Lawson. Iodolawson oxide was prepared by using earlier reported procedure [4, 7].

Step-I: Lawson (1.048g, 6mmol) was added in 40ml glacial acetic acid and heated till lawson dissolve completely. The solution of 0.41g potassium iodide(KI) and 0.535g potassium iodate (KIO₃) in 20ml distilled water was added in above solution of lawson. The deep red coloured solution is heated at 60-70°C for about 1 hour. The hot solution is filtered and cooled in ice bath. It was acidified by 1:1 H₂SO₄ to precipitate out 3-iodolawson. The precipitate (yellow needles) was filtered, washed with ice cold water and dried under vacuum at room temperature. [M.P. 180°C] (yield 70%).

Step II: Iodolawson (1.5g, 5mmol) was dissolved in 50ml 2N NaOH. Hydroxylamine hydrochloride (0.521g, 7.5mmol) in 25ml distilled water was added in it. The mixture was heated for 1 hour at 65-70°C. Then cooled in ice bath and 25ml ice cold water added in it. It was acidified with 1:1 H₂SO₄ to obtain yellow precipitate of Iodolawson oxide. The precipitate was filtered, washed with ice cold water and dried under vacuum at room temperature. [M.P. 155°C] (yield 87%, %CHN [obs. (cal)] C= 42.198(38.12), H= 3.095(1.92), N= 4.65(4.45)).
(vii) Nitrolawsone monoxime ($\text{NO}_2\text{-LwOx}$), L-7

3-Nitrolawsone is a precursor in the synthesis of Nitrolawsone oxime [5,8].

Step I: 2,3-Dichloro naphthoquinone (13.623g, 60 mmol) dissolved in 65ml methanol and sodium nitrite (2.76g, 0.2 mol) dissolved in 105ml water was mixed. The mixture was stirred at 80°C for 3 hours. The hot solution was filtered. The precipitate was collected, dissolved in warm water and then acidified with HCl. The mixture was cooled and obtained precipitate was filtered, washed with ice cold water to give light yellow crystals of 2-hydroxy, 3-Nitro, 1-4 naphthoquinone and dried under vacuum at room temperature. It was crystallized from chloroform [M.P. 158°C (yield 70%)].

Step II: 3-Nitrolawsone (1.096g, 5mmol) and hydroxylamine hydrochloride (0.521g, 7.5mmol) were dissolved in 10ml 10% NaOH and 10ml water respectively. The mixture was warmed at 50°C for about 45 minutes on water bath and was set aside to cool. It was neutralized by 1:1 HCl to precipitate out 3-nitrolawsone oxime. The precipitate was filtered, washed with ice cold water and dried under vacuum at room temperature. It was crystallized from ethanol to obtain yellowish crystals. [M.P. 188°C] (yield 69%, %CHN [obs. (cal)] C= 51.53 (51.29), H= 2.95(2.58), N= 9.542 (11.96)).

5.2.3 Synthesis of Cu(I) precursor complex [Cu(CH$_3$CN)$_4$].PF$_6$

Tetrakis(Acetonitrile) Copper(I) Hexafluorophosphate: Cuprous oxide, (Cu$_2$O), is the precursor in the synthesis of [Cu(CH$_3$CN)$_4$].PF$_6$.

Step I: Cupric sulphate pentahydrate [CuSO$_4$.5H$_2$O] (1g) in 4ml distilled water, Glucose (0.3g) in 15ml water and NaOH (0.7g) in 3.5ml water were mixed and boiled for 10 minutes. The content cooled in ice bath, filtered and washed with cold water to obtain red coloured Cu$_2$O. Dried under vacuum. [yield 90%].

Step II: Cu$_2$O (4g) in 100ml Acetonitrile was stirred for 15 minutes under Nitrogen. In this solution 10ml of 60% HPF$_6$ was added dropwise. The reaction is exothermic and caused the solution to boil. After addition of HPF$_6$, the solution was stirred for 30 minutes at 50-60°C. The solution is filtered hot under N$_2$ atmosphere. Equal volume of diethyl ether is added to the filtrate and cooled to 0°C whereupon a white crystalline precipitate of [Cu(CH$_3$CN)$_4$].PF$_6$ was formed. The precipitate was filtered, washed with diethyl ether and dried under vacuum. (yield 60%).
5.2.4 Syntheses of complexes from Cu(I) as starting species

By using Cu(I) as starting species from precursor complex [Cu(CH₂CN)₄].PF₆ and L-1 to L-7 ligands, the complexes Cu-1 to Cu-7 were prepared respectively. The synthetic procedure for all complexes was same (except the chelating ligands) which is as below.

[Cu(CH₂CN)₄].PF₆ (0.3727g, 1mmol) was dissolved in 20ml anhydrous methanol. Triethyl orthoformate was added in traces as dehydrating agent and the mixture was deaerated by purging of N₂. 2 mmol of ligand e.g. L-1 was dissolved in 10ml of anhydrous methanol. Triethyl orthoformate was added in traces and deaerated by purging of N₂. The Cu(I) solution from addition funnel was slowly added to ligand solution with stirring under N₂ atmosphere. Coloured complex was precipitated out immediately. The pH of the solution was adjusted to 6-6.5 with 10% anhydrous sodium acetate in anhydrous methanol. The mixture was maintained at 50°C for 30 minutes. The precipitate was filtered under nitrogen, washed with diethyl ether and dried under vacuum.

5.2.5 Syntheses of complexes from Cu(II) as starting species

By using Cu(II) ion from, Cupric perchlorate hexahydrate [Cu(ClO₄)₂.6H₂O] and L-1, L-2 ligands, the complexes Cu-1A, Cu-1B, Cu-2A and Cu-2B were prepared.

(i) Cu-1A and Cu-1B: [Cu(ClO₄)₂.6H₂O] (0.371g, 1mmol) was dissolved in 6ml anhydrous acetonitrile and the mixture was deaerated by purging of N₂. The ligand (L-1) [0.378g, 2mmol] was dissolved in 25ml of anhydrous acetonitrile and deaerated by purging of N₂. The Cu(II) solution from addition funnel was slowly added to ligand solution in the flask. Immediately the complex precipitate appears. The content was divided into two parts.

Cu-1A: The one part is stirred for 30 minutes. Filtered the precipitate, washed with acetonitrile and dried under vacuum. The parrot green coloured Cu-1A complex was obtained, [yeild 85%].
Cu-1B: In another part 4-5 drops of pyridine was added to give pH of the solution upto 8. The mixture was stirred for 30 minutes. The precipitate was filtered, washed and dried under vacuum. The brown coloured Cu-1B complex was obtained, [yield 85%].

(ii) Cu-2A and Cu-2B: [Cu(ClO₄)₂.6H₂O] (0.371g, 1mmol) was dissolved in 10ml anhydrous methanol and the mixture was deaerated by purging of N₂. The ligand (L-2) [0.407g, 2mmol] was dissolved in 25ml of anhydrous methanol and deaerated by purging of N₂. The Cu(II) solution from addition funnel was slowly added to ligand solution in the flask. Immediately the complex was precipitated. The content was divided into two parts.

Cu-2A: The one part is stirred for 30minutes. Filtered the precipitate, washed with methanol and dried under vacuum. The brown coloured Cu-2A complex was obtained [yield 80%].

Cu-2B: In another part 4-5 drops of pyridine was added to give pH of the solution upto 8-8.5. The mixture was stirred for 30 minutes. The precipitate was filtered, washed and dried under vacuum. The brown coloured Cu-2B complex was obtained. [yield 80%].

5.2.6 Estimation of Cu

Estimation of metal ion from complex was done using Kjeldahl flask decomposition method [9]. 5 mg of complex was weighed and transferred to a Kjeldahl flask. It is then decomposed with 3 ml A. R. grade HCl and 1 ml A. R. HNO₃ (aqua regia). The solution is heated till complete decomposition occurs and then one or two drops of A. R. grade H₂SO₄ is added and again heated till white fumes are seen. The solution is cooled and diluted to a known amount by using deionised water and used for estimation of metal ion concentration by AAS.

5.2.7 Crystallization

Crystallization of 1, (Iodolawson) was carried out from methanol and ethanol under comparable conditions. A clear solution obtained after vigorous shaking of 1 in the specified solvent was allowed to evaporate by standing for 3-5 days at room temperature to give yellow-orange crystals. Crystallization of 1 from methanol gave
thin needle type crystals (Form I, Fig. 1A) as well as thick plates (Form II, Fig.1B) concomittantly, whereas crystallization from ethanol gave very thin and brittle plates (Form III, Fig. 1C). The amount of Form I crystals obtained from methanol was very less compared to the amount of Form II crystals, indicating the preference of 1 for crystallization as thick plates.

Fig. 1 Photomicrographs of crystals of 1, A) Form I crystals, B) Form II crystals and C) Form III crystals.

Crystallization of L-4, L-5 and L-6 ligands were carried out from acetonitrile under comparable conditions. A clear solution obtained after vigorous shaking of L-4, L-5 and L-6 in the specified solvent was allowed to evaporate by standing for 5-7 days at room temperature to give orange crystals of L-4, L-5 and L-6.

5.2.8 GOs Activity studies of complexes

The catalytic activity of model complexes were carried out as per procedure outlined in literature [10]. In a catalysis run, a Round bottom flask was charged with the Benzyl alcohol, NaOH in the molar ratio of 0.1 : 0.002 in CH3CN (2 ml) and to this mixture was added the copper complex (0.004 mmol). The reaction mixture was stirred in an O2 atmosphere for 30 h after which it was filtered and distilled out by applying vacuum. The distilled liquid mixture was diluted to the concentration of 1000 ppm and analyzed by HPLC.
5.3 Physico-chemical techniques

5.3.1 C, H, N Analyses

Carbon, hydrogen and nitrogen were determined using CHNS analyzer on FLASH EA 1112 series (Thermo Electron Corporation) at Department of Chemistry, University of Pune, Pune-411007. The sample size for analysis was ~ 3mg.

5.3.2 Atomic Absorption Spectroscopy

Estimation of metal ion in the complexes was done on Atomic Absorption Spectrophotometer using Perkin Elmer-3100 model at the Department of Geology, University of Pune, Pune-411007.

5.3.3 Thermal Analysis

(i) TG: Theromogravimetric analyses were performed on the laboratory-constructed instruments, details of which were reported elsewhere [11], consisting of a single pan balance (Tapson) of 0.01 mg accuracy, a quartz tube furnace, digital thermometer of 1°C accuracy upto 1200°C temperature controller (type 8D-IP automatic, Electroflow, England) and a cylindrical sample holder made up of corning glass. The following specifications of samples were used for dynamic TG studies.

<table>
<thead>
<tr>
<th>Sample size</th>
<th>20-30 mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle size</td>
<td>200-250 mesh (55 to 70 microns)</td>
</tr>
<tr>
<td>Rate of heating</td>
<td>3 to 5 °C/min</td>
</tr>
<tr>
<td>Temperature range of study</td>
<td>room temperature to 1000 °C</td>
</tr>
<tr>
<td>Thermocouple</td>
<td>chromel-alumel</td>
</tr>
<tr>
<td>Sample container</td>
<td>cylindrical quartz glass cup 6 mm (diameter), 20 mm (height)</td>
</tr>
<tr>
<td>Atmosphere</td>
<td>static air</td>
</tr>
</tbody>
</table>

The instrument was standardized for dynamic TG measurements in air using CaC$_2$O$_4$·H$_2$O compound [9].

(ii) DSC: The Iodolawsone, (I) crystal polymorphs were studied by Differential Scanning calorimeter on DSC-60, Shimatzu scientific instruments at Department of Chemistry, University of Pune, Pune-411007. Crystals (wt. 1 mg) were placed on an
aluminium pan (5 mm diameter) and were analyzed from low temperature (-120°C) to 400 °C using an empty pan as the reference. The heating rate was 5 °C/min and nitrogen gas was used for purging.

Specifications:

<table>
<thead>
<tr>
<th>Specification</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Principle Heat</td>
<td>Flux Type</td>
</tr>
<tr>
<td>Temperature Range</td>
<td>-150 to 600°C</td>
</tr>
<tr>
<td>Heat Flow Range</td>
<td>± 40mW</td>
</tr>
<tr>
<td>Program Rate</td>
<td>5 K/min</td>
</tr>
<tr>
<td>Hold Time</td>
<td>0-999 min, hour</td>
</tr>
<tr>
<td>Cooling Time</td>
<td>About 6 min from 600°C to 40°C with Liq. N₂</td>
</tr>
<tr>
<td>Noise Level</td>
<td>1μW</td>
</tr>
<tr>
<td>Atmosphere</td>
<td>Inert gas (N₂)</td>
</tr>
</tbody>
</table>

5.3.4 IR Spectroscopy

Infrared spectra of ligands and their copper complexes were recorded as KBr pellets on FTIR-8400 Shimadzu infrared spectrophotometer at Department of Chemistry, University of Pune, Pune-411007.

5.3.5 Electron Paramagnetic Resonance Spectroscopy

Low-temperature X-band measurements on frozen solutions of ligands and metal complexes were carried out on a Bruker ESP 300E spectrometer (Bruker ER035M and a microwave frequency counter HP5352B and an Oxford Instruments ESR 910 helium flow cryostat with an ITC 503 temperature controller) at Max-Planck-Institut für Bioanorganische Chemie, Stiftstrabe 34-36, Mülheim an der Ruhr, Germany. The temperature stability was 0.2 K.

The X-band powder and frozen glass EPR spectra of ligands and complexes were recorded on Varian E-4 EPR spectrometer employing 100 kHz field modulation using tetracyanoethylene radical (TCNE) as the g-marker at Indian Instiutute of Technology, Powai, Mumbai.
The X-band EPR spectra of Iodolawsone crystal polymorphs were recorded on BRÜKER EMX EPR spectrometer at NCL, Pune-7 operating at X-band (9.5 GHz) and 100 kHz field-modulation.

Spin concentrations of L-4, L-5 and L-6 ligands were determined by comparing areas of the EPR signals of these compounds with that of a known concentration of DPPH at the same instrumental parameters (receiver gain, modulation frequency, etc.).

5.3.6 Variable Temperature Magnetic Susceptibility Measurements (SQUID)

Magnetic susceptibilities of the copper complexes were recorded on a SQUID magnetometer (MPMS, Quantum Design) at in the temperature range 2–290 K with an applied field of 1 T.

The data were automatically calibrated by the machine parameters (calibrated with Gd\(_2\)(SO\(_4\))\(_3\) salt) on polycrystalline samples. The experimental molar magnetic susceptibilities were corrected for the underlying diamagnetic susceptibility using Pascal constants. Effective magnetic moments were calculated by the equation,

\[ \mu_{\text{eff}} = 2.828 \times \sqrt{\chi_M^{\text{corr}} T} \]

where \( \chi_M^{\text{corr}} \) is the molar susceptibility corrected for diamagnetism of constituted atoms. Diamagnetic contributions were estimated for each compound by using Pascal’s constants [12, 13].

5.3.7 Cyclic Voltammetry

Cyclic voltammograms (CV) were recorded on a CHI 1200A Electrochemical analyser (CH instruments, Inc, USA) at Department of Chemistry, University of Pune, Pune-411007. The three-electrode cell includes a working electrode as a platinum inlay or glassy carbon referenced with an Ag/AgCl electrode, a platinum wire as an auxiliary electrode. The setup parameters can be varied in the range as below.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Init E (V)</td>
<td>-2.4 - +2.4</td>
</tr>
<tr>
<td>High E (V)</td>
<td>-2.4 - +2.4</td>
</tr>
<tr>
<td>Low E (V)</td>
<td>-2.4 - +2.4</td>
</tr>
<tr>
<td>Limit P/N</td>
<td>Positive or Negative</td>
</tr>
</tbody>
</table>
Scan Rate (V/s)  1e-6 - 10  
Sweep Segments  1 - 1000000 (each segments is half cycle)  
Sample Interval (V)  0.001 - 0.064  
Quiet Time (sec)  0 - 100000  
Sensitivity (A/V)  1e-10 - 0.01  

The solvent used in CV studies viz. dimethyl sulphoxide was purified according to the procedure cited in the literature [2]. 0.1 M Tetraethyl ammonium perchlorate (TEAP) was used as a supporting electrolyte. Complex concentrations used were 0.1 mM. Purified nitrogen atmosphere was maintained in the cell during CV run.

5.3.8 Single Crystal X-ray Crystallography

Single crystal X-ray diffraction studies were conducted on selected good quality single crystals of Iodolawsone 1, L-4, L-5 and L-6 ligands using Leica polarizing microscope and mounted on glass fibers with epoxy cement. The X-ray data were collected on a Brüker-AXS Smart Apex CCD diffractometer at 297(2) K with graphite-monochromatized (Mo K\text{\scriptsize a} = 0.71073 Å) radiation. The X-ray generator was operated at 50 kV and 30 mA. The intensity measurements were monitored by the SMART program (version 5.63, Brüker AXS Inc., Madison, Wisconsin, USA, 1997). Data reduction was performed with the SAINT software (version 6.45, Brüker AXS Inc., Madison, Wisconsin, USA, 2003). All the data were corrected for Lorentz and polarization effects. A semi-empirical absorption correction based on symmetry equivalent reflections was applied by using the SADABs program, G.M. Sheldrick, SADABs (version 2.10, Brüker AXS Inc., Madison, Wisconsin, USA, 2003). Lattice parameters were determined from the least squares analysis of all reflections. The structure was solved by direct method and refined by full matrix least squares, based on F², using the SHELXTL software package (G.M. Sheldrick, SHELXTL 6.14, Program for the structure solution and refinement, Brüker AXS Inc., Madison. Wisconsin, USA, 2000). All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms in all the structures were located from a difference Fourier map, and their positional coordinates and isotropic thermal parameters were refined, except for H-atom of the hydroxyl group of Form I crystal of I which was included in the refinement
as per the riding model option in SHELXL. Molecular and packing diagrams were generated using ORTEP-32 and Mercury-2.1. Geometrical calculations were performed using SHELXTL (Brüker, 2003) and PLATON.

H-atoms bonded to water molecule in chloro L-4, bromo L-5 and iodo L-6 ligands as well as hydroxyl groups in iodo L-6 ligands were located from a difference Fourier map, and their positional coordinates and isotropic thermal parameters were refined.

5.3.9 Hot Stage Microscopy (HSM) Studies

Needles of Form I crystals of 1 when heated on a hot stage polarizing microscope showed some changes on the surface of the crystals and subsequently became brighter ~160 °C which finally melted at ~175 °C (Fig. 2). Determination of the unit cell parameters of one such needle picked up just before melting (Fig. 2E) confirmed it to be the Form II crystal of 1. Form II and Form III crystals of 1 when heated on a hot stage microscope did not show any physical change till their melting. Unit cell parameters determined close to their melting were the same as that of the original crystal.

![Fig. 2 A to E) Photomicrographs of Form I crystals of 1 during hot stage microscopy at different temperatures, F) Needle selected for unit cell determination is marked in E.](image)

5.3.10 High Performance Liquid Chromatography

The amount of Benzyl alcohol converted into Benzaldehyde by using model complexes as a catalyst was analysed by HPLC (Shimadzu Prominence UFLC, Shimadzu Corporation) with UV-Visible detector (Model SPD-20A) at Department of Chemistry, University of Pune, Pune-411007. The column used was Luna 5u 618(2) 100A of make Phenomenex. For each HPLC run following details are used.
Mobile phase: A: Water, B: Acetonitrile
Injection Volume: 5µL
Gradient: 5% B to 95% B in 8 min, hold for 1.5 min, 9.51 to 12 min 5% B. The LC programme is as below.

<table>
<thead>
<tr>
<th>Time</th>
<th>Action</th>
<th>Action</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>B Conc.</td>
<td>5</td>
</tr>
<tr>
<td>8.00</td>
<td>B Conc.</td>
<td>95</td>
</tr>
<tr>
<td>9.51</td>
<td>B Conc.</td>
<td>95</td>
</tr>
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<td>10.01</td>
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References


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