CHAPTER-6

Mononuclear mixed ligand complexes of Copper(II) and Cobalt(II) with Pyrazole based ligand: Syntheses, Characterizations, Structures and Bioactivities

Abstract

A series of mononuclear mixed ligand complexes of the type $[Co(CH_3COO)(dbdmp)]PF_6$ **(1)**, $[M(X)(dbdmp)]ClO_4$ **(2-7)** (X = trichloroacetate, benzoate and salicylate), $[Cu(ONO)(dbdmp)]ClO_4$ **(8)**, $[M(Y)(dbdmp)](ClO_4)_2$ **(9-10)** (Y = 3,5-dimethylpyrazole (pz)), $[Cu(NCCH_3)(dbdmp)](ClO_4)_2$ **(11)** and $[Cu(Cl)(dbdmp)]PF_6$ **(12)** where M = Cu(II) and Co(II) and dbdmp = *N,N*-diethyl-*N′,N′*-bis((3,5-dimethyl-*1H*-pyrazol-1-yl)methyl)ethane-1,2-diamine have been synthesized and characterized by IR, UV-Visible, magnetic, EPR and electrochemical properties. The crystal structures of eight copper(II) complexes **2, 2a, 4, 6, 8, 9, 11, 12** and three cobalt(II) complexes **1, 3** and **5** have been determined by single crystal X-ray diffraction studies. The structure of complex $[Co(CH_3COO)(dbdmp)]PF_6$ **(1)** has two $[Co(CH_3COO)(dbdmp)]^+$ cations and two PF_6^- anions in a unit cell and the coordination environment of both cobalt(II) centre is different. The complex $[Cu(Cl_3COO)(dbdmp)]ClO_4$ **(2)** has two geometrical isomers with distorted square pyramidal geometry and distorted trigonal bipyramidal geometry. The geometry of $[Cu(pz)(dbdmp)](ClO_4)_2$ is distorted square pyramidal and remaining complexes have distorted trigonal bipyramidal geometry. The solution phase EPR spectra (77 K) in acetonitrile solution of copper(II) complexes **2, 4, 6, 8, 9** and **12** exhibit axial spectra, characteristic of $d_{x^2-y^2}$ ground state. Redox studies of copper(II) complexes using glassy carbon electrode in acetonitrile solution show Cu(II) /Cu(I) couple with quasi reversible electron transfer versus Ag/Ag^+ reference electrode. Antimicrobial activity of all the synthesized complexes were investigated against two *Gram positive* and two *Gram negative* bacterial strains. Cytotoxic activity of complexes **4** and **6** against A549 cell was investigated.

6.1. Introduction

The nitrogen containing heterocyclic compounds play an important role in many biological systems as it is a component of metalloproteins [1]. The chemistry of carboxylate and pyrazole or imidazole containing ternary transition metal complexes has attracted a great deal of attention due to their variation in their structures, magnetism and also as potential models for a number of important biological molecules [3-10]. Ternary complexes of metal (II) containing N and O donor atom ligands have high stability [11]. Many factors such as nature of the carboxylic acids, steric factor of the additional ligand and stoichiometry determine the structure and properties of the complexes [12-14]. Recently, there has been considerable attention on aryl carboxylate containing copper complexes because of their bioactivity and antimicrobial activity [8]. Like copper, cobalt is also an important trace element in the biological system and involve in many bioactivities. Copper complexes play an important role in catalizing enzymatic activity. Benzoic acid is widely used as antimicrobial agents in foods and drugs and salicylic acid is also used as a fungicidal treatment [15]. Copper complexes of salicylic acid are potent SOD and they are known to more potential inflammatory drug [16]. There are few reports on copper(II) aryl carboxylate with monodentate nitrogen donor heterocycle such as imidazole, 2-aminopyridine etc [17-22]. But synthesis, characterization, structures and bioactivity of carboxylate containing copper(II) and cobalt(II) complexes with tetradentate N-containing ligand are relatively less [23]. Furthermore, alkyl and aryl carboxylates have different binding modes and form mono, di- and polynuclear complexes like pseudohalieds.

Nitrite ion is an ambidentate ligand and it can bind with divalent metal centre with different binding modes to form mono and dinuclear complexes. Copper(II)-nitrite complexes are model for the copper nitrite reductase (CuNIR) class of enzymes which are involved in the biological denitrification process [24-30]. There are few reports on copper(II)-nitrite complexes with pyrazole based ligands [30,31-33]. 3,5- dimethylpyrazole is a neutral ligand and can also form mono, di- and polynuclear complexes with transition metal ions [34-35].

In this chapter, we report on the synthesis, characterizations and structures of pyrazole containing copper(II) and cobalt(II) complexes of the type [Co(CH_3COO)(dbdmp)]PF_6 **(1)**, [M(X)(dbdmp)]ClO_4 **(2-7)** (X = trichloroacetate, benzoate and salicylate), [Cu(ONO)(dbdmp)]ClO_4 **(8),** [M(Y)(dbdmp)](ClO_4)$_2$ **(9-10)** (Y = 3,5-dimethylpyrazole (pz)) [Cu($NCCH_3$)(dbdmp)](ClO_4)$_2$ **(11)** and [Cu(Cl)(dbdmp)]PF_6 **(12)** where M = Cu(II) and Co(II) and dbdmp = *N,N*-diethyl-*N',N'*-bis((3,5-dimethyl-*1H*-pyrazol-1-yl)methyl)ethane-1,2-diamine. Antimicrobial activity of the all copper(II) and cobalt(II) complexes and cytotoxic activity of the complexes **4** and **6** have been investigated.

6.2. Experimental

6.2.1. Materials

The chemicals and solvents were of analytical grade and purchased from commercial sources. Trichloroacetic acid, salicylic acid, benzoic acid, $CuCl_2.2H_2O$, $Co(CH_3COO)_2.4H_2O$, $NaNO_2$ (SRL, India) were of reagent grade and used as received. $M(ClO_4)_2.6H_2O$ [M = Cu(II), Co(II)] were prepared by reaction of metal carbonate with dilute perchloric acid, followed by slow evaporation over steam bath.

6.2.2. Cell line and Culture

Human lung carcinoma (A549) cells were obtained from National Centre for Cell Science, Pune, India and were seeded (1x 10^5 cells / T25 flask) and cultured in DMEM containing 10% FBS and 1% antibiotic-antimycotic solution at 37°C with 5% in water jacketed CO_2 incubator (Thermo scientific, forma series II 3111, USA). Cells were sub-cultured every third day by trypsinization with TPVG solution. Reagents used herein were filtered through 0.22 µ filter (Millipore Biomedical Aids Pvt. Ltd, Pune) prior to their use for the experiment. A549 cells were maintained for a period of 24 h in absence or presence of complexes at a cell density of 5.0 x 10^3 cells/well in 96 well plates for MTT.

6.2.3. Cell Viability (MTT) Assay

A549 cells (7x10^3 cells/well) were maintained in 96-well culture plates (Tarson India Pvt. Ltd.) for 24 h with or without copper complexes **4** and **6** (25, 50, 125, 250, 500 µg/ml). Later, 10µl of 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl-tetrazolium bromide (MTT, 5 mg/ml) was added to the wells and plates were incubated at 37 °C for 4 h. Subsequently, the culture media were discarded and wells were washed with Phosphate Buffered Saline (PBS). The resultant formazan formed was dissolved in 150 µl of DMSO and absorbance was read at 540 nm in BIOTEK ELX800 Universal Microplate Reader (USA).

6.2.4. Statistical Analysis

Statistical evaluation of the data was done by one-way analysis of variance (ANOVA) followed by Dunnett's multiple comparison tests. The results were expressed as mean ± SEM using Graph Pad Prism version 6.0 for Windows, Graph Pad Software, San Diego, CA/USA.

6.2.5. Microbial Assay

The antimicrobial screening of synthesized Cu(II) and Co(II) complexes were carried out to check their effect on both the *Gram positive* (*Staphylococcus aureus* and *Bacillus subtilis*) and *Gram negative* (*Escherichia coli and Psedomonas aeruginosa*) bacteria. The stock solution of complexes was prepared in DMSO. Bacteria were grown in Luria broth medium and incubated at 37°C for 24 h followed by frequent subculturing to fresh medium and were used for inoculation. Melted Luria Agar poured in petriplates and after solidification, seven wells were made. To each well the test samples with different concentrations were added. The petriplates were incubated at 37°C for 24 h. Inhibition was recorded by measuring the diameter of the inhibitory zone after the period of incubation.

6.2.6. Syntheses of Complexes

6.2.6.1. [Co(CH_3COO)(dbdmp)]PF_6 (1)

A methanol solution (10 ml) of ligand dbdmp (0.166 g, 0.5 mmol) was added dropwise to a stirring $Co(CH_3COO)_2.4H_2O$ (0.125 g, 0.5 mmol) solution (10 ml) in the same solvent followed by the drop wise addition of a solution of NH_4PF_6 (0.082 g, 0.5 mmol) in water (1 ml) and stirring was continued for another 3 h. The pink coloured solution was filtered and kept for slow evaporation at room temperature. Pink coloured compound was obtained after few days. Yield. 0. 137 g (46 %). Found C = 40.57, H = 5.90, N = 13.96 %. Anal calc for $C_{20}H_{35}N_6O_2PF_6Co$: C = 40.34, H = 5.92, N = 14.11 %. IR (KBr pellet) cm^{-1}; ν(C = C) + ν (C = N)/pz ring, 1560 s, 1464 s; ν(COO^-) 1590 br, 1392 s; ν(PF_6^-), 848 br. UV-Vis spectra: λ_{max}/nm (ε_{max}/mol^{-1}cm^{-1}). 739 (16), 598 (63), 478 (97), 243 (3096). Λ_M ($\Omega^{-1}cm^2mol^{-1}$) = 124. μ_{eff} = 4.34 BM.

6.2.6.2. [M(Cl_3CCOO)(dbdmp)]ClO_4 [M = Cu(II), Co(II)]

A solution of ligand dbdmp (0.166 g, 0.5 mmol) in methanol (10 ml) was treated with M(ClO_4)$_2$.6H_2O (0.5 mmol) dissolved in methanol (10 ml). After 10 min, trichloroacetic acid (0.082 g, 0.5 mmol) in water (0.5 ml) was added and the resulting reaction mixture was stirred at room temperature for 4 h. The solution was filtered and kept for slow evaporation at room temperature. After 3 days, plate shaped crystals were obtained.

[Cu(Cl_3CCOO)(dbdmp)]ClO_4 (2) : Yield. 0.180 g (55 %). Found C = 36.65, H = 4.94, N = 12.69 %. Anal calc for $C_{20}H_{32}N_6Cl_4CuO_6$: C = 36.51, H = 4.90, N = 12.77 %. IR (KBr pellet) cm^{-1} (Green compound **2**); ν(COO^-), 1701 s, 1393 s; ν(C = C) + ν (C = N)/pz ring, 1556 s, 1468 s; ν_{asmy}(Cl–O), 1109 br; δ(O–Cl–O), 625 s. (Blue compound **2a**); ν(COO^-), 1694 s, 1396 s; ν(C = C) + ν (C = N)/pz ring, 1555 s, 1470 s; ν_{asmy}(Cl–O), 1098 br; δ(O–Cl–O), 624 s. UV-Vis spectra: λ_{max}/nm (ε_{max}/mol^{-1}cm^{-1}). 869 (111), 705 (122), 277 (1526), 218 (2080), 206 (2150). Λ_M (Ω^{-1}cm^{2}mol^{-1}) = 112. μ_{eff} = 1.70 BM.

[Co(Cl_3CCOO)(dbdmp)]ClO_4 (3) : Yield. 0.220 g (67 %). Found C = 36.75, H = 4.96, N = 12.89 %. Anal calc for $C_{20}H_{32}N_6Cl_4CoO_6$: C = 36.77, H = 4.94, N = 12.86 %. IR (KBr pellet) cm^{-1}; ν(COO^-), 1702 s, 1321 s; ν(C = C) + ν (C = N)/pz ring, 1552 s, 1468 s; ν_{asmy}(Cl–O), 1108 br; δ(O–Cl–O), 625 s. UV-Vis spectra: λ_{max}/nm (ε_{max}/mol^{-1}cm^{-1}). 744 (27), 582 (108), 490 (110), 245 (332). Λ_M (Ω^{-1}cm^{2}mol^{-1}) = 120. μ_{eff} = 4.46 BM.

6.2.6.3. [M(C_6H_5COO)(dbdmp)]ClO_4 [M = Cu(II), Co(II)]

A solution of ligand dbdmp (0.166 g, 0.5 mmol) in methanol was treated with M(ClO_4)$_2$.6H_2O (0.5 mmol) dissolved in methanol (10 ml). After 10 min benzoic acid (0.061 g, 0.5 mmol) in methanol (0.5 ml) was added and the resulting reaction mixture was stirred at room temperature for 4 h. The solution was filtered and kept for slow evaporation at room temperature. After 3 days, plate shaped crystals were obtained.

[Cu(C_6H_5COO)(dbdmp)]ClO_4 (4) : Yield. 0.195 g (64 %). Found C = 48.85, H = 6.09, N = 13.48 %. Anal calc for $C_{25}H_{37}N_6ClCuO_6$: C = 48.70, H = 6.05, N = 13.63 %. IR (KBr pellet) cm^{-1}; ν(COO^-), 1629 s, 1346 s; ν(C = C) + ν (C = N)/pz ring, 1555 s, 1466 m; ν_{asmy}(Cl–O), 1102 br; δ(O–Cl–O), 624 s. UV-Vis spectra: λ_{max}/nm (ε_{max}/mol^{-1}cm^{-1}). 842 (108), 683 (131), 297 (446), 221 (1344), 203 (2902). Λ_M (Ω^{-1}cm^{2}mol^{-1}) = 118. μ_{eff} = 1.76 BM.

$[Co(C_6H_5COO)(dbdmp)]ClO_4$ (5) : Yield. 0.240 g (78 %). Found C = 49.15, H = 6.10, N = 13.68 %. Anal calc for $C_{25}H_{37}N_6ClCoO_6$: C = 49.06, H = 6.09, N = 13.73 %. IR (KBr pellet) cm^{-1}; $\nu(COO^-)$, 1609 m, 1366 s; $\nu(C = C) + \nu$ (C = N)/pz ring, 1556 s, 1467 m; ν_{asmy}(Cl–O), 1102 br; δ(O–Cl–O), 624 s. UV-Vis spectra: λ_{max}/nm ($\varepsilon_{max}/mol^{-1}cm^{-1}$). 715 (22), 596 (96), 484 (105), 239 (3230). Λ_M ($\Omega^{-1}cm^2mol^{-1}$) = 120. μ_{eff} = 4.38 BM.

6.2.6.4. $[M(C_6H_4(OH)COO)(dbdmp)]ClO_4$ [M = Cu(II), Co(II)]

The complexes were prepared by following the same procedure as for complex **4** except salicylic acid was used in the place of benzoic acid. After 3 days, plate shape crystals were obtained.

$[Cu(C_6H_4(OH)COO)(dbdmp)]ClO_4$ (6) : Yield. 0.230 g (74 %). Found C = 47.55, H = 5.92, N = 13.15%. Anal calc for $C_{25}H_{37}N_6ClCuO_7$: C = 47.47, H = 5.90, N = 13.28 %. IR (KBr pellet) cm^{-1}; ν(OH), 3243 s; $\nu(COO^-)$, 1602 br, 1395 s; ν(C = C) + ν (C = N)/pz ring, 1556 s, 1448 s; ν_{asmy}(Cl–O), 1105 br; δ(O–Cl–O), 624 s. UV-Vis spectra: λ_{max}/nm ($\varepsilon_{max}/mol^{-1}cm^{-1}$). 880 (166), 685 (104), 298 (959), 220 (2762), 208 (4582). Λ_M ($\Omega^{-1}cm^2mol^{-1}$) = 120. μ_{eff} = 1.72 BM.

$[Co(C_6H_4(OH)COO)(dbdmp)]ClO_4$ (7): Yield. 0.210 g (67 %). Found C = 47.95, H = 5.99, N = 13.28 %. Anal calc for $C_{25}H_{37}N_6ClCoO_7$: C = 47.81, H = 5.94, N = 13.38 %. IR (KBr pellet) cm^{-1}; ν(OH), 3227 m; $\nu(COO^-)$, 1623 s, 1366 s; ν(C = C) + ν(C = N)/pz ring, 1553 s, 1486 s; ν_{asmy}(Cl–O), 1156 br; δ(O–Cl–O), 626 s. UV-Vis spectra: λ_{max}/nm ($\varepsilon_{max}/mol^{-1}cm^{-1}$). 674 (33), 591 (73), 521 (110), 479 (103), 307 (2950), 242 (3522). Λ_M ($\Omega^{-1}cm^2 mol^{-1}$) = 118. μ_{eff} = 4.36 BM.

6.2.6.5. $[Cu(ONO)(dbdmp)]ClO_4$ (8)

To a stirring solution of $Cu(ClO_4)_2.6H_2O$ (0.183 g, 0.5 mmol) in methanol (10 ml), ligand dbdmp (0.166 g, 0.5 mmol) in methanol was added slowly. After 10 min $NaNO_2$ (0.04 g, 0.5 mmol) in water (0.5 ml) was added and the green coloured solution was stirred for 4 h. The reaction mixture was filtered and kept for slow evaporation at room temperature. After 3 days, plate shape light green coloured crystals were obtained. Yield. 0.220 g (81 %). Found C = 39.65 , H = 5.94, N = 18.19 %. Anal calc for $C_{18}H_{32}N_7ClCuO_6$: C = 39.93, H = 5.96, N = 18.11 %. IR

(KBr pellet) cm^{-1}; ν(C = C) + ν (C = N)/pz ring, 1554 s, 1495 s; ν_s(N–O), 1255 m; ν_{asmy}(N–O), 1185 m; ν_{asmy}(Cl–O), 1113 br; δ(O–Cl–O), 624 s. UV-Vis spectra: λ_{max}/nm (ε_{max}/$mol^{-1}cm^{-1}$). 676 (115), 291 (966), 204 (3598). Λ_M ($\Omega^{-1}cm^2$ mol^{-1}) = 120. μ_{eff} = 1.76 BM.

6.2.6.6. [M(pz)(dbdmp)]$(ClO_4)_2$ [M = Cu(II), Co(II)]

This type of complexes was prepared by following the same procedure as for complex **4** except 3,5-dimethylpyrazole was used in the place of benzoic acid. After 3 days, plate shape crystals were obtained.

[Cu(pz)(dbdmp)]$(ClO_4)_2$ (9) : Yield. 0.205 g (60 %). Found C = 39.85, H = 5.84, N = 16.23 %. Anal calc for $C_{23}H_{40}N_8Cl_2CuO_8$: C = 39.97, H = 5.83, N = 16.21 %. IR (KBr pellet) cm^{-1}; ν(NH), 3202 m; ν(C = C) + ν (C = N)/pz ring, 1559 s, 1467 s; ν_{asmy}(Cl–O), 1088 br; δ(O–Cl–O), 624 s. UV-Vis spectra: λ_{max}/nm (ε_{max}/$mol^{-1}cm^{-1}$). 674(132), 288(1425), 220(2412), 202(2586). Λ_M ($\Omega^{-1}cm^2mol^{-1}$) = 198. μ_{eff} = 1.74 BM.

[Co(pz)(dbdmp)]$(ClO_4)_2$ (10) : Yield. 0.200 g (58 %). Found C = 40.35, H = 5.84, N = 16.40 %. Anal calc for $C_{23}H_{40}N_8Cl_2CoO_8$: C = 40.24, H = 5.87, N = 16.32 %. IR (KBr pellet) cm^{-1}; ν(NH), 3202; ν(C = C) + ν (C = N)/pz ring, 1555 s, 1470 s; ν_{asmy}(Cl–O), 1146 br; δ(O–Cl–O), 626 s. UV-Vis spectra: λ_{max}/nm (ε_{max}/$mol^{-1}cm^{-1}$). 663 (41), 527 (227), 475 (126), 302 (1992), 244 (3642), 219 (3350). Λ_M ($\Omega^{-1}cm^2mol^{-1}$) = 210. μ_{eff} = 4.37 BM.

6.2.6.7. [Cu($NCCH_3$)(dbdmp)]$(ClO_4)_2$ (11)

To a stirring solution of $Cu(ClO_4)_2.6H_2O$ (0.183 g, 0.5 mmol) in methanol (10 ml), ligand dbdmp (0.166 g, 0.5 mmol) in methanol was added slowly and the green coloured solution was stirred for 4 h. The reaction mixture was filtered and kept for slow evaporation at room temperature. After 4 days, light green coloured microcrystalline compound was obtained which was recrystallized from acetonitrile and plate shaped green crystals were obtained. Yield. 0.150 g (48 %). Found C = 37.69, H = 5.57, N = 15.29 %. Anal calc for $C_{20}H_{35}N_7Cl_2CuO_8$: C = 37.77, H = 5.55, N = 15.42 %. IR (KBr pellet) cm^{-1}; ν(CN), 2254 m; ν(C = C) + ν (C = N)/pz ring, 1554 s, 1483 s; ν_{asmy}(Cl–O), 1043 br; δ(O–Cl–O), 627 s. UV-Vis spectra: λ_{max}/nm (ε_{max}/$mol^{-1}cm^{-1}$). 871 (149), 680 (99), 290 (598), 204 (2384). Λ_M ($\Omega^{-1}cm^2mol^{-1}$) = 220. μ_{eff} = 1.78 BM.

6.2.6.8. [Cu(Cl)(dbdmp)]PF_6 (12)

To a stirring solution of $CuCl_2.2H_2O$ (0.085 g, 0.5 mmol) in methanol (10 ml), ligand dbdmp (0.166 g, 0.5 mmol) in methanol was added slowly. After 10 min, NH_4PF_6 (0.082 g, 0.5 mmol) in water (0.5 ml) was added and the green coloured solution was stirred for 4 h. The reaction mixture was filtered and kept for slow evaporation at room temperature. After 3 days, needle shape light green coloured crystals were obtained. Yield. 0.160 g (56 %). Found C = 37.45, H = 5.62, N = 14.69 %. Anal calc for $C_{18}H_{32}N_6PCuF_6$: C = 37.50, H = 5.60, N = 14.58 %. IR (KBr pellet) cm^{-1}; ν(C = C) + ν (C = N)/pz ring, 1554 s, 1470 s; ν(PF_6^-), 840 s. UV-Vis spectra: λ_{max}/nm (ε_{max}/$mol^{-1}cm^{-1}$). 1000 (140), 743 (98), 291 (2500). Λ_M ($\Omega^{-1}cm^2mol^{-1}$) = 120. μ_{eff} = 1.76 BM.

6.2.7. Physical Measurements

The IR spectra were recorded on a Perkin-Elmer FT-IR spectrometer RX1 spectrum using KBr pellets. The micro analyses (C, H and N) were carried out using a Perkin-Elmer IA 2400 series elemental analyzer. UV-Vis spectra (1200 - 190 nm) of copper(II) complexes were recorded on a JASCO V630 in CH_3CN solution. UV-Vis spectra (900 - 190 nm) of cobalt(II) complexes were recorded on a Perkin-Elmer spectrophotometer model Lambda 35 in CH_3CN solution. Solution conductivity were measured in CH_3CN solution using Equip-Tronics conductivity meter (model no. EQ-660A). Room temperature magnetic susceptibilities of powder samples were measured using a Faraday magnetic balance equipped with a Metler UMX 5 balance, OMEGA temperature controller with a field strength of 0.8 Tesla using Hg[Co$(SCN)_4$] as the reference. Cyclic voltammetry studies were carried out using a CH instrument model 600C. The cell consisted of three electrodes: Glassy carbon electrode, Pt-wire as counter electrode and Ag/Ag^+ as reference electrode. Tetra n-butyl ammonium hexafluorophosphate (0.1 M) was used as supporting electrolyte. EPR measurements were performed on a Bruker EMX EPR spectrometer at X-band frequency (9.46 GHz) at liquid nitrogen temperature (77 K).

6.3. X-ray Crystallography

Crystals of suitable size of complexes were obtained by slow evaporation of methanol solution. The details of data collection and some important features of the refinement for the compounds **1-6**, **8**, **9, 11** and **12** are given in Table 6.1-6.4 and selected bond lengths and angles are given in Table 6.5-6.6. Single crystal X-ray diffraction intensity data of the complexes **1-6**, **8**, **9** and **11** were collected on Oxford X-CALIBUR-S CCD diffractometer with Cu-K_α radiation (λ = 1.54184 Å) or Mo-K_α radiation (λ = 0.71731 Å). For complex **4**, the data was collected with Mo-K_α radiation (λ = 0.71731 Å) at 293 K. The data interpretation was processed with CrysAlisPro, Agilent Technologies,Version 1.171.35.19 [36]. For complex **12,** data were collected on a Bruker SMART APEX diffractometer equipped with CCD area detector using Mo-K_α radiation (λ = 0.71731 Å) at 110 K. The data interpretation was processed with SAINT software [37]. Empirical absorption correction was applied with SADABS software programs [38]. The structures were solved by direct methods and refined by the full-matrix least-square technique on F^2 using the programs SHELXS-97 and SHELXL-97 [39] respectively. All calculations were carried out using WinGX system Ver-1.64 [40]. All hydrogen atoms were located from difference Fourier map and treated as riding. All non hydrogen atoms were refined with anisotropic displacement coefficients.

6.4. Results and Discussion

6.4.1. Syntheses of Complexes

The copper(II) and cobalt(II) complexes **1-11** were isolated as hexaflurophosphate/perchlorate salt by treating the metal acetate / perchorate [M = Cu(II), Co(II)], ligand dbdmp, X^- [where X = CH_3COO^-, CCl_3COO^-, $PhCOO^-$, $Ph(OH)COO^-$ and NO_2^-] or Y [Y = 3,5-dimethylpyrazole (pz) / acetonitrile(MeCN)] with appropriate molar ratio in methanol solvent according to the scheme 6.1. In the case of complex $[Cu(CH_3CN)(dbdmp)](ClO_4)_2$, acetonitrile was coordinated to the copper centre during recrystallization of microcrystalline green powder which was obtained by reacting ligand dbdmp with copper perchlorate in methanol. There was no change of composition when the reactions were carried out with excess carboxylic acids or nitrite or pyrazole or by using different solvents. Complex $[Cu(Cl)(dbdmp)]PF_6$ **(12)** was obtained by treating ligand dbdmp with $CuCl_2.2H_2O$ in the presence of NH_4PF_6.

Table.6.1. Crystal parameters of complexes **1**, **2** and **2a**.

	$[Co(CH_3COO)(dbdmp)]PF_6$ **(1)**	**$[Cu(Cl_3CCOO)(dbdmp)]ClO_4$** **(2)**	**$[Cu(Cl_3CCOO)(dbdmp)]ClO_4$** **(2a)**
Empirical formula	$C_{40}H_{32}Cl_4CuN_6O_6$	$C_{20}H_{32}Cl_4CuN_6O_6$	$C_{20}H_{32}Cl_4CuN_6O_6$
Formula weight	1190.88	657.86	657.86
Temperature (K)	110(2)	293(2)	150(2)
Wavelength (Å)	0.71073	1.54184	1.54184
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/c$	*P-1*	*P-1*
a (Å)	21.4526(7)	8.5732(7)	10.3441(5)
b (Å)	8.6364(2)	9.9817(4)	12.5644(6)
c (Å)	27.7785(10)	16.4382(10)	12.8796(7)
α (°)	90.00	99.116(4)	111.976(5)
β (°)	91.355(3)	94.703(6)	109.545(5)
γ (°)	90.00	96.259(5)	91.962(4)
Volume (Å^3)	5145.2(3)	1373.57(15)	1438.31(13)
Z	4	2	2

Density (g/cm^3)	1.537	1.591	1.485
Absorption coefficient (mm^{-1})	0.803	5.112	1.519
F(000)	2472	678	678
θ range for data collection (°)	3.17 to 29.16	4.52 to 70.40	3.86 to 70.37
Index ranges	$-28 \le h \le 28$, $-11 \le k \le 11$, $-37 \le l \le 37$	$-10 \le h \le 10$, $-6 \le k \le 11$, $-20 \le l \le 18$	$-12 \le h \le 12$, $-15 \le k \le 14$, $-25 \le l \le 12$
Reflections collected	56669	8341	9033
Independent reflections	12436 [R(int) =0.1557]	5177 [R(int) =0.0506]	5518 [R(int) = 0.0285]
Max. and min. transmission	0.897 and 0.725	1.000 and 0.30622	0.505 and 0.401
Data / restraints / parameters	12436 / 0 / 649	5177 / 0 / 334	5518 / 0 / 334
Goodness-of-fit on F^2	1.114	1.136	1.048
Final R indices [I>2sigma(I)]	$R1$ = 0.1128, w$R2$ = 0.1456	$R1$ = 0.0832, w$R2$ = 0.2029	$R1$ = 0.0482, w$R2$ = 0.1349
R indices (all data)	$R1$ = 0.2675, w$R2$ = 0.2936	$R1$ = 0.1110, w$R2$ = 0.2453	$R1$= 0.0536, wR2 = 0.1407
Largest diff. Peak and hole (eA^{-3})	1.636 and -2.182	1.187 and -1.797	0.986 and -0.471
CCDC	1056563	1053838	1053839

Table.6.2. Crystal parameters of complexes **3**, **4** and **5.**

	[Co(Cl_3CCOO)(dbdmp)]ClO_4 (3)	**[Cu(C_6H_5COO)(dbdmp)]ClO_4 (4)**	**[Co(C_6H_5COO)(dbdmp)]ClO_4 (5)**
Empirical formula	$C_{20}H_{32}Cl_4CoN_6O_6$	$C_{25}H_{37}ClCuN_6O_6$	$C_{25}H_{37}ClCoN_6O_6$
Formula weight	653.25	616.61	611.99
Temperature (K)	110(2)	293(2)	150(2)
Wavelength (Å)	0.71073	0.71073	1.54184
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	*P-1*	$P2_1/c$	$P2_1/c$
a (Å)	8.4930(3)	12.8992(4)	12.9779(5)
b (Å)	9.9535(3)	16.2123(4)	16.1035(7)
c (Å)	16.7225(5)	13.9924(5)	13.8944(6)
α (°)	98.501(3)	90.00	90.00
β (°)	94.424(3)	108.143(4)	107.334(4)
γ (°)	95.823(2)	90.00	90.00
Volume (Å^3)	1384.78(8)	2780.69(15)	2771.9(2)
Z	2	4	4
Density (g/cm^3)	1.567	1.473	1.467

Absorption coefficient (mm^{-1})	1.052	0.932	6.172
F(000)	674	1292	1284
θ range for data collection (°)	3.7180 to 29.1046	3.14 to 25.00	3.5540 to 73.1470
Index ranges	$-11 \le h \le 11$,	$-14 \le h \le 15$,	$-15 \le h \le 16$,
	$-13 \le k \le 13$,	$-19 \le k \le 19$,	$-18 \le k \le 20$,
	$-22 \le l \le 22$	$-15 \le l \le 16$	$-16 \le l \le 17$
Reflections collected	29424	13019	16527
Independent reflections	5637 [R(int) = 0.0383]	4900 [R(int) = 0.0244]	5689 [R(int) =0.0597]
Max. and min. transmission	0.881 and 0.838	0.846 and 0.800	0.421 and 0.303
Data / restraints / parameters	5637 / 0 / 346	4900 / 0 / 352	5689 / 0 / 352
Goodness-of-fit on F^2	1.078	1.103	1.076
Final R indices [I>2sigma(I)]	$R1$ = 0.0427, w$R2$ = 0.0570	$R1$ = 0.0391, w$R2$ = 0.1123	$R1$ = 0.0527, w$R2$ = 0.0643
R indices (all data)	$R1$= 0.1153, w$R2$ = 0.1214	$R1$= 0.1277, w$R2$ = 0.1313	$R1$ = 0.1358, w$R2$ = 0.1446
Largest diff. Peak and hole (eA^{-3})	1.147 and -1.021	2.553 and -0.892	0.506 and -0.465
CCDC	1056562	1053840	1053837

Table.6.3. Crystal parameters of complexes **6**, **8** and **9.**

	$[Cu(C_6H_4(OH)COO)(dbdmp)]ClO_4$(6)	**$[Cu(ONO)(dbdmp)](ClO_4)_2$(8)**	**$[Cu(pz)(dbdmp)](ClO_4)_2$ (9)**
Empirical formula	$C_{25}H_{37}ClCuN_6O_7$	$C_{18}H_{32}ClCuN_7O_6$	$C_{23}H_{40}Cl_2CuN_8O_8$
Formula weight	632.60	541.51	691.07
Temperature (K)	150(2)	150(2)	150(2)
Wavelength (Å)	0.71073	1.54184	1.54184
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$P2_1/c$	*P-1*
a (Å)	12.8440(17)	8.54060(10)	8.8100(4)
b (Å)	16.104(2)	19.2835(2)	11.5069(6)
c (Å)	14.067(2)	14.3158(10)	15.5607(7)
α (°)	90.00	90.00	94.076(4)
β (°)	106.745(15)	92.7750(10)	99.892(4)
γ (°)	90.00	90.00	98.196(4)
Volume (Å^3)	2786.2(7)	2354.94(4)	1530.75(13)
Z	4	4	2
Density (g/cm^3)	1.508	1.527	1.499

Absorption coefficient (mm^{-1})	0.935	2.783	3.117
F(000)	1324	1132	722
θ range for data collection (°)	3.24 to 29.09	3.8090 to 72.1970	3.88 to 70.12
Index ranges	$-16 \leq h \leq 17$,	$-10 \leq h \leq 10$,	$-10 \leq h \leq 5$,
	$-21 \leq k \leq 22$,	$-23 \leq k \leq 23$,	$-13 \leq k \leq 14$,
	$-18 \leq l \leq 19$	$-16 \leq l \leq 17$	$-18 \leq l \leq 18$
Reflections collected	16120	23485	9748
Independent reflections	7464 [R(int) = 0.0691]	4652 [R(int) = 0.0303]	5814 [R(int) = 0.0318]
Max. and min. transmission	0.886 and 0.817	0.693 and 0.636	0.599 and 0.688
Data / restraints / parameters	7464 / 0 / 371	4625 / 0 / 298	5814 / 0 / 383
Goodness-of-fit on F^2	1.045	1.051	1.050
Final R indices [*I*>2sigma(*I*)]	*R1* = 0.0765, w*R2* = 0.1252	*R1* = 0.0391, w*R2* = 0.1123	*R1* = 0.0826, w*R2* = 0.0922
R indices (all data)	*R1* = 0.1678, w*R2* = 0.1888	*R1*= 0.0410, w*R2* = 0.1140	*R1* = 0.2182, w*R2* = 0.2281
Largest diff. Peak and hole (eA^{-3})	2.635 and -0.495	0.704 and -0.545	2.788 and -2.156
CCDC	1056564	1053793	1053795

Table.6.4. Crystal parameters of complexes **11**and **12**.

	[Cu(NCCH$_3$)(dbdmp)](ClO$_4$)$_2$ (11)	**[Cu(Cl)(dbdmp)]PF$_6$ (12)**
Empirical formula	$C_{20}H_{35}Cl_2CuN_7O_8$	$C_{18}H_{32}ClCuN_6F_6P$
Formula weight	635.99	576.46
Temperature (K)	150(10)	110(2)
Wavelength (Å)	1.54184	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$
a (Å)	19.0838(9)	8.4536(13)
b (Å)	8.4089(3)	13.855(2)
c (Å)	19.0408(9)	21.235(3)
α (°)	90.00	90.00
β (°)	117.301(6)	96.151(2)
γ (°)	90.00	90.00
Volume (Å^3)	2715.2(2)	2472.7(6)
Z	4	4

Density (g/cm^3)	1.556	1.548
Absorption coefficient (mm^{-1})	3.449	1.120
F(000)	1324	1188
θ range for data collection (°)	4.42 to 72.14	1.76 to 28.31
Index ranges	$-23 \le h \le 23$,	$-11 \le h \le 11$,
	$-9 \le k \le 10$,	$-13 \le k \le 18$,
	$-22 \le l \le 23$	$-20 \le l \le 28$
Reflections collected	13287	14383
Independent reflections	5367 [R(int) = 0.0702]	5677 [R(int) = 0.0287]
Max. and min. transmission	0.661and 0.498	0.9672 and 0.7828
Data / restraints / parameters	5367 / 0 / 345	5677 / 0 / 410
Goodness-of-fit on F^2	1.054	1.212
Final R indices [I>2sigma(I)]	*R1* = 0.0795, w*R2* = 0.0817	*R1* = 0.0520, w*R2* = 0.1110
R indices (all data)	*R1*= 0.2206, wR2 = 0.2243	*R1*= 0.0572, w*R2* = 0.1133
Largest diff. Peak and hole (eA^{-3})	1.307 and -1.153	0.559 and -0.394
CCDC	1053794	872100

Table.6.5. Bond Lengths of the complexes.

Bond Lengths (Å)							
[Co(CH$_3$COO)(dbdmp)]PF$_6$ (1)				**[Cu(Cl$_3$CCOO)(dbdmp)]ClO$_4$ (2)**		**[Cu(Cl$_3$CCOO)(dbdmp)]ClO$_4$ (2a)**	
Co(1)-O(1)	2.019(4)	Co(2)-O(3)	2.036(5)	Cu(1)-O(1)	1.920(4)	Cu(1)-O(5)	1.942(2)
Co(1)-N(1)	2.064(5)	Co(2)-O(4)	2.393(5)	Cu(1)-N(1)	2.117(5)	Cu(1)-N(1)	2.014(3)
Co(1)-N(3)	2.334(5)	Co(2)-N(7)	2.075(5)	Cu(1)-N(3)	2.050(5)	Cu(1)-N(3)	2.078(3)
Co(1)-N(5)	2.096(5)	Co(2)-N(9)	2.339(5)	Cu(1)-N(5)	2.052(6)	Cu(1)-N(5)	2.225(3)
Co(1)-N(6)	2.165(5)	Co(2)-N(11)	2.092(5)	Cu(1)-N(6)	2.122(5)	Cu(1)-N(6)	2.062(2)
		Co(2)-N(12)	2.154(7)				
[Co(Cl$_3$CCOO)(dbdmp)]ClO$_4$ (3)		**[Cu(C$_6$H$_5$COO)(dbdmp)]ClO$_4$ (4)**		**[Co(C$_6$H$_5$COO)(dbdmp)]ClO$_4$ (5)**		**[Cu(C$_6$H$_4$(OH)COO)(dbdmp)]ClO$_4$ (6)**	
Co(1)-O(1)	1.9754(18)	Cu(1)-O(5)	1.901(3)	Cu(1)-O(1)	2.002(2)	Cu(1)-O(5)	1.906(3)
Co(1)-N(1)	2.040(2)	Cu(1)-N(1)	2.079(3)	Cu(1)-N(1)	2.074(3)	Cu(1)-N(1)	2.073(4)

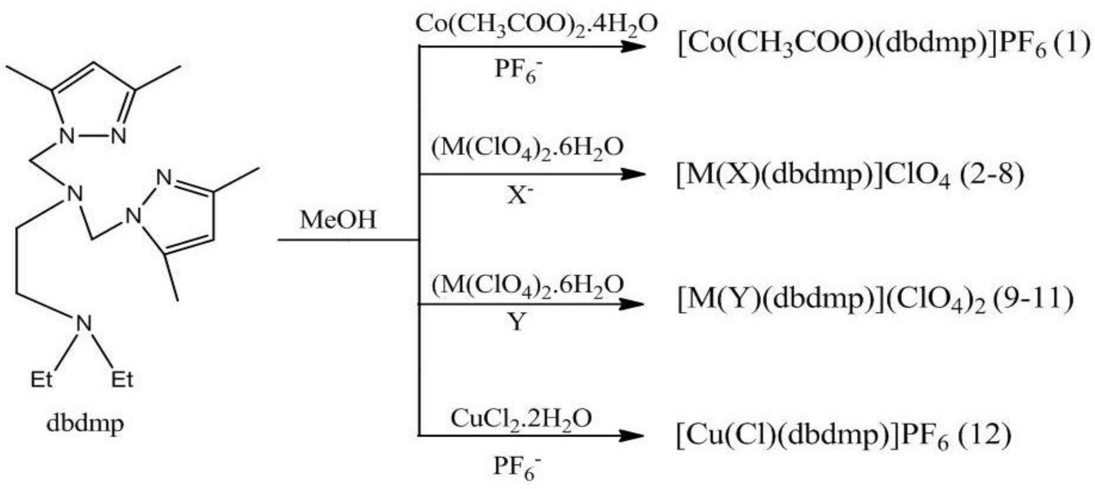
Co(1)-N(3)	2.244(2)	Cu(1)-N(3)	2.068(3)	Cu(1)-N(3)	2.272(3)	Cu(1)-N(3)	2.056(4)
Co(1)-N(5)	2.032(2)	Cu(1)-N(5)	2.088(3)	Cu(1)-N(5)	2.090(3)	Cu(1)-N(5)	2.068(5)
Co(1)-N(6)	2.130(2)	Cu(1)-N(6)	2.168(3)	Cu(1)-N(6)	2.140(2)	Cu(1)-N(6)	2.175(4)
[Cu(ONO)(dbdmp)]ClO$_4$(8)		**[Cu(pz)(dbdmp)](ClO$_4$)$_2$ (9)**		**[Cu(NCCH$_3$)(dbdmp)](ClO$_4$)$_2$ (11)**		**[Cu(Cl)(dbdmp)]PF$_6$ (12)**	
Cu(1)-O(5)	1.9277(17)	Cu(1)-N(7)	1.964(3)	Cu(1)-N(7)	1.964(3)	Cu(1)-Cl(1)	2.2474(9)
Cu(1)-N(1)	2.0751(19)	Cu(1)-N(1)	2.013(3)	Cu(1)-N(1)	2.013(3)	Cu(1)-N(1)	2.090(3)
Cu(1)-N(3)	2.0501(17)	Cu(1)-N(3)	2.030(3)	Cu(1)-N(3)	2.030(3)	Cu(1)-N(3)	2.073(2)
Cu(1)-N(5)	2.1210(19)	Cu(1)-N(5)	2.111(3)	Cu(1)-N(5)	2.111(3)	Cu(1)-N(5)	2.143(3)
Cu(1)-N(6)	2.1098(18)	Cu(1)-N(6)	2.076(3)	Cu(1)-N(6)	2.076(3)	Cu(1)-N(6)	2.104(2)
O(5)-N(7)	1.298(3)						
O(6)-N(7)	1.224(3)						

Table.6.6. Bond Angles (°) of the complexes.

Bond Angles (°)					
[Co(CH_3COO)(dbdmp)]PF_6 (1)				**[Cu(Cl_3CCOO)(dbdmp)]ClO_4 (2)**	
O(1)-Co(1)-N(1)	108.05(18)	O(3)-Co(2)-N(7)	106.6(2)	O(1)-Cu(1)-N(1)	104.8(2)
O(1)-Co(1)-N(3)	173.98(16)	O(3)-Co(2)-N(11)	103.1(2)	O(1)-Cu(1)-N(3)	172.54(19)
N(1)-Co(1)-N(3)	75.70(17)	N(7)-Co(2)-N(11)	138.0(2)	N(1)-Cu(1)-N(3)	81.0(2)
O(1)-Co(1)-N(5)	102.84(18)	O(3)-Co(2)-N(12)	95.4(2)	O(1)-Cu(1)-N(5)	101.2(2)
N(1)-Co(1)-N(5)	135.04(19)	N(7)-Co(2)-N(12)	105.5(3)	N(1)-Cu(1)-N(5)	113.2(2)
N(3)-Co(1)-N(5)	76.75(18)	N(11)-Co(2)-N(12)	100.6(3)	N(3)-Cu(1)-N(5)	80.2(2)
O(1)-Co(1)-N(6)	94.16(17)	O(3)-Co(2)-N(9)	175.7(2)	O(1)-Cu(1)-N(6)	88.9(2)
N(1)-Co(1)-N(6)	106.32(17)	O(4)-Co(2)-N(12)	154.1(2)	N(1)-Cu(1)-N(6)	107.0(2)
N(3)-Co(1)-N(6)	80.15(17)	O(4)-Co(2)-N(9)	125.1(2)	N(3)-Cu(1)-N(6)	84.9(2)
N(5)-Co(1)-N(6)	103.08(18)	N(9)-Co(2)-N(12)	80.6(2)	N(5)-Cu(1)-N(6)	134.0(2)
[Cu(Cl_3CCOO)(dbdmp)]ClO_4 (2a)		**[Co(Cl_3CCOO)(dbdmp)]ClO_4 (3)**		**[Cu(benz)(dbdmp)]ClO_4 (4)**	
O(5)-Cu(1)-N(1)	98.66(10)	O(1)-Co(1)-N(1)	106.09(8)	O(5)-Cu(1)-N(1)	98.88(12)
O(5)-Cu(1)-N(3)	177.90(9)	O(1)-Co(1)-N(3)	172.40(7)	O(5)-Cu(1)-N(3)	178.26(12)
N(1)-Cu(1)-N(3)	80.16(10)	N(1)-Co(1)-N(3)	76.85(8)	N(1)-Cu(1)-N(3)	81.82(12)

O(5)-Cu(1)-N(5)	97.97(10)	O(1)-Co(1)-N(5)	106.60(8)	O(5)-Cu(1)-N(5)	101.16(12)
N(1)-Cu(1)-N(5)	96.64(11)	N(1)-Co(1)-N(5)	115.41(9)	N(1)-Cu(1)-N(5)	128.25(12)
N(3)-Cu(1)-N(5)	80.48(10)	N(3)-Co(1)-N(5)	77.80(8)	N(3)-Cu(1)-N(5)	79.56(12)
O(5)-Cu(1)-N(6)	96.48(9)	O(1)-Co(1)-N(6)	91.24(8)	O(5)-Cu(1)-N(6)	93.87(11)
N(1)-Cu(1)-N(6)	149.19(11)	N(1)-Co(1)-N(6)	124.57(9)	N(1)-Cu(1)-N(6)	122.46(12)
N(3)-Cu(1)-N(6)	85.36(10)	N(3)-Co(1)-N(6)	81.42(8)	N(3)-Cu(1)-N(6)	84.41(11)
N(5)-Cu(1)-N(6)	107.65(10)	N(5)-Co(1)-N(6)	108.61(8)	N(5)-Cu(1)-N(6)	103.18(12)
[Co(benz)(dbdmp)]ClO$_4$ (6)		**[Cu(C$_6$H$_4$(OH)COO)(dbdmp)]ClO$_4$ (7)**		**[Cu(ONO)(dbdmp)]ClO$_4$ (8)**	
O(1)-Co(1)-N(1)	107.70(10)	O(5)-Cu(1)-N(1)	100.04(14)	O(5)-Cu(1)-N(1)	100.15(7)
O(1)-Co(1)-N(3)	175.43(9)	O(5)-Cu(1)-N(3)	179.13(16)	O(5)-Cu(1)-N(3)	176.90(7)
N(1)-Co(1)-N(3)	75.12(10)	N(1)-Cu(1)-N(3)	79.47(15)	N(1)-Cu(1)-N(3)	80.19(7)
O(1)-Co(1)-N(5)	103.45(10)	O(5)-Cu(1)-N(5)	98.67(15)	O(5)-Cu(1)-N(5)	102.87(7)
N(1)-Co(1)-N(5)	124.94(10)	N(1)-Cu(1)-N(5)	128.64(15)	N(1)-Cu(1)-N(5)	116.13(7)
N(3)-Co(1)-N(5)	77.25(10)	N(3)-Cu(1)-N(5)	82.19(16)	N(3)-Cu(1)-N(5)	79.64(7)
O(1)-Co(1)-N(6)	95.11(9)	O(5)-Cu(1)-N(6)	94.60(13)	O(5)-Cu(1)-N(6)	91.81(7)
N(1)-Co(1)-N(6)	103.60(10)	N(1)-Cu(1)-N(6)	103.04(15)	N(1)-Cu(1)-N(6)	130.45(7)
N(3)-Co(1)-N(6)	80.64(9)	N(3)-Cu(1)-N(6)	84.83(14)	N(3)-Cu(1)-N(6)	85.67(7)

N(5)-Co(1)-N(6)	117.59(10)	N(5)-Cu(1)-N(6)	122.53(14)	N(5)-Cu(1)-N(6)	107.41(7)
				O(5)-N(7)-O(6)	112.5(2)
[Cu(pz)(dbdmp)](ClO_4)$_2$ (9)		**[Cu(CH_3CN)(dbdmp)](ClO_4)$_2$ (11)**		**[Cu(Cl)(dbdmp)]PF_6 (12)**	
N(7)-Cu(1)-N(1)	93.49(18)	N(7)-Cu(1)-N(1)	98.37(13)	Cl(1)-Cu(1)-N(1)	100.44(7)
N(7)-Cu(1)-N(3)	162.85(17)	N(7)-Cu(1)-N(3)	179.04(12)	Cl(1)-Cu(1)-N(3)	178.60(7)
N(1)-Cu(1)-N(3)	81.86(17)	N(1)-Cu(1)-N(3)	81.11(12)	N(1)-Cu(1)-N(3)	79.22(9)
N(7)-Cu(1)-N(5)	94.58(17)	N(7)-Cu(1)-N(5)	99.99(12)	Cl(1)-Cu(1)-N(5)	100.13(7)
N(1)-Cu(1)-N(5)	150.33(17)	N(1)-Cu(1)-N(5)	109.89(12)	N(1)-Cu(1)-N(5)	112.70(10)
N(3)-Cu(1)-N(5)	82.07(16)	N(3)-Cu(1)-N(5)	80.96(12)	N(3)-Cu(1)-N(5)	78.79(9)
N(7)-Cu(1)-N(6)	112.92(16)	N(7)-Cu(1)-N(6)	94.10(12)	Cl(1)-Cu(1)-N(6)	96.02(7)
N(1)-Cu(1)-N(6)	105.50(17)	N(1)-Cu(1)-N(6)	137.43(12)	N(1)-Cu(1)-N(6)	130.88(10)
N(3)-Cu(1)-N(6)	84.22(16)	N(3)-Cu(1)-N(6)	85.76(12)	N(3)-Cu(1)-N(6)	85.20(9)
N(5)-Cu(1)-N(6)	97.49(16)	N(5)-Cu(1)-N(6)	107.69(11)	N(5)-Cu(1)-N(6)	109.34(9)



M = Cu(II), Co(II)
X = Cl_3CCOO, C_6H_5COO, $C_6H_4(OH)COO$, NO_2, etc
Y = pz, MeCN

Scheme.6.1. Syntheses of complexexes.

We are unable to isolate the solid product of $[Cu(dbdmp)(CH_3COO)]PF_6$ by reacting copper acetate, ligand dbdmp and ammonium hexafluorophosphate in 1:1:1 or 1:1:2 mole ratio and it is always obtained as gummy material. All complexes are reproducible and stable at room temperature. The complex **2** was isolated with two different colours – green **(2)** and blue **(2a)** and these are due to different geometry of the compounds. Complexes were characterized by different spectroscopic and analytical tools. All the complexes gave satisfactory microanalysis results, confirming their composition. Molar conductivity measurements in acetonitrile solution (~10^{-3} M) show that complexes **1-8** and **12** are 1:1 electrolytes (Λ_M = ~ 115 $cm^2\,mol^{-1}$) and complexes **9-11** are 1:2 electrolytes (Λ_M = ~ 200 $cm^2\,mol^{-1}$) which indicate the presence of counter anions in the molecules and there was no change in molar conductivity even after 2 h, indicating no dissociation of the complexes in the solution [41]. Further the presence of counter anion was confirmed by IR and single crystal X-ray diffraction studies. Diffraction quality crystals of the complexes were obtained by slow evaporation of the solution. All compounds are soluble in all common organic solvents like acetonitrile, methanol, ethanol, acetone etc.

6.4.2. Descriptions of Crystal Structures

6.4.2.1. [Co(CH_3COO)(dbdmp)]PF_6 (1)

An ORTEP view with atom numbering scheme of cobalt(II) complex **1** is shown in Fig.6.1**.** Complex **1** crystallizes in monoclinic crystal system with *P2₁/c* space group which consists of two crystallographically independent [Co(CH_3COO)(dbdmp)]$^+$ cations and two PF_6^- anions in the asymmetric unit. The coordination environment and geometry around both the cobalt centres are different. One cationic part is penta coordinated with distorted trigonal bipyramidal geometry which is revealed by trigonality index (τ = 0.65) [42] wheres another cationic part is hexa coordinated with distorted octahedral geometry. The trigonal bipyraidal coordination around Co(1) centre is completed by four nitrogen atoms [N(1), N(3), N(5) and N(6)] of ligand dbdmp and one oxygen atom O(1) of the acetate ion. The equatorial plane of five coordinated complex is occupied by N(1) and N(5) atoms of pyrazole ring and N(6) of tertiary amine and axial plane is occupied by N(3) of tertiary amine and O(1) of acetate ion. The equatorial Co(1)-N bond lengths vary in the range of 2.019(4)-2.165(5) Å and axial bond distances Co(1)-N(3) and Co(1)-O(1) distances are 2.334(5) and 2.019(4) Å, respectively. The equatorial bond angles are in the range of 103.08(18)° to 135.04(19)° but the axial bond angle O(1)-Co(1)-N(3) is 173.98(16)°.

The octahedral Co(2) centre is completed by four nitrogen atoms [N(7), N(9), N(11) and N(12)] of ligand dbdmp and two oxygen atoms [O(3) and O(4)] of acetate ion. The basal plane is made by N(9) and N(12) of two tertiary amines' nitrogen atoms and O(3) and O(4) of acetate ion and the bond distances of Co(2)-N(9), Co(2)-N(12), Co(2)-O(3) and Co(2)-O(3) are 2.330(5) Å, 2.154(7) Å, 2.036(5) Å and 2.393(5) Å, respectively. The equatorial bond angles O(3)-Co(2)-N(9) and O(4)-Co(2)-N(12) are vary from 175.7(2)° and 154.1(2)°, respectively. The axial plane is occupied by N(7) and N(11) of two pyrazole rings and the bond distances of Co(2)-N(7) and Co(2)-N(11) are 2.075(5) Å and 2.092(5) Å, respectively. The axial bond N(7)-Co(2)-N(11) is distorted (138.0(2)°).

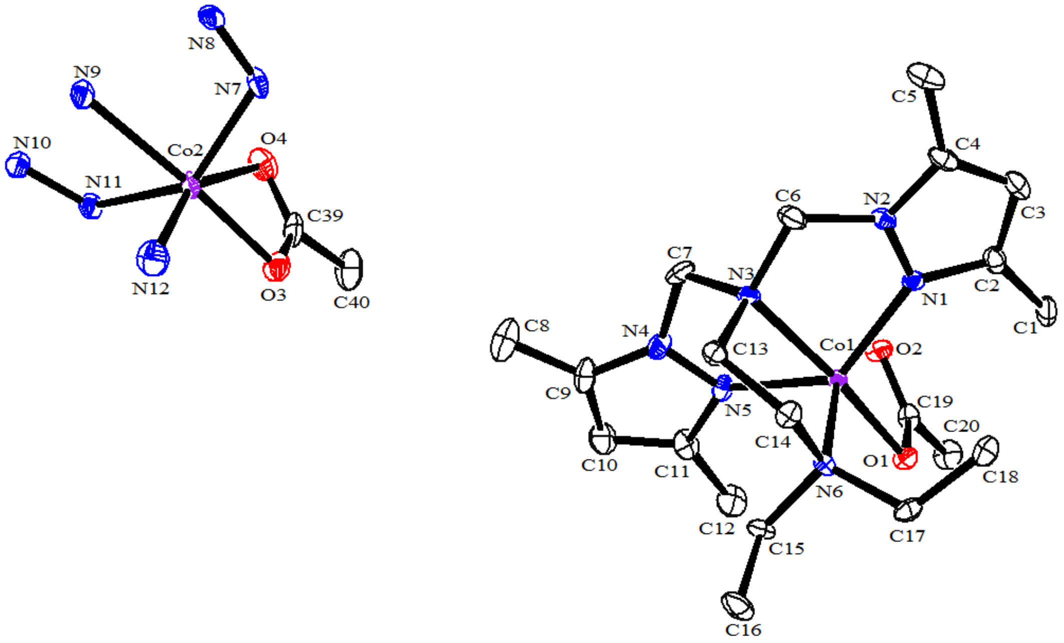
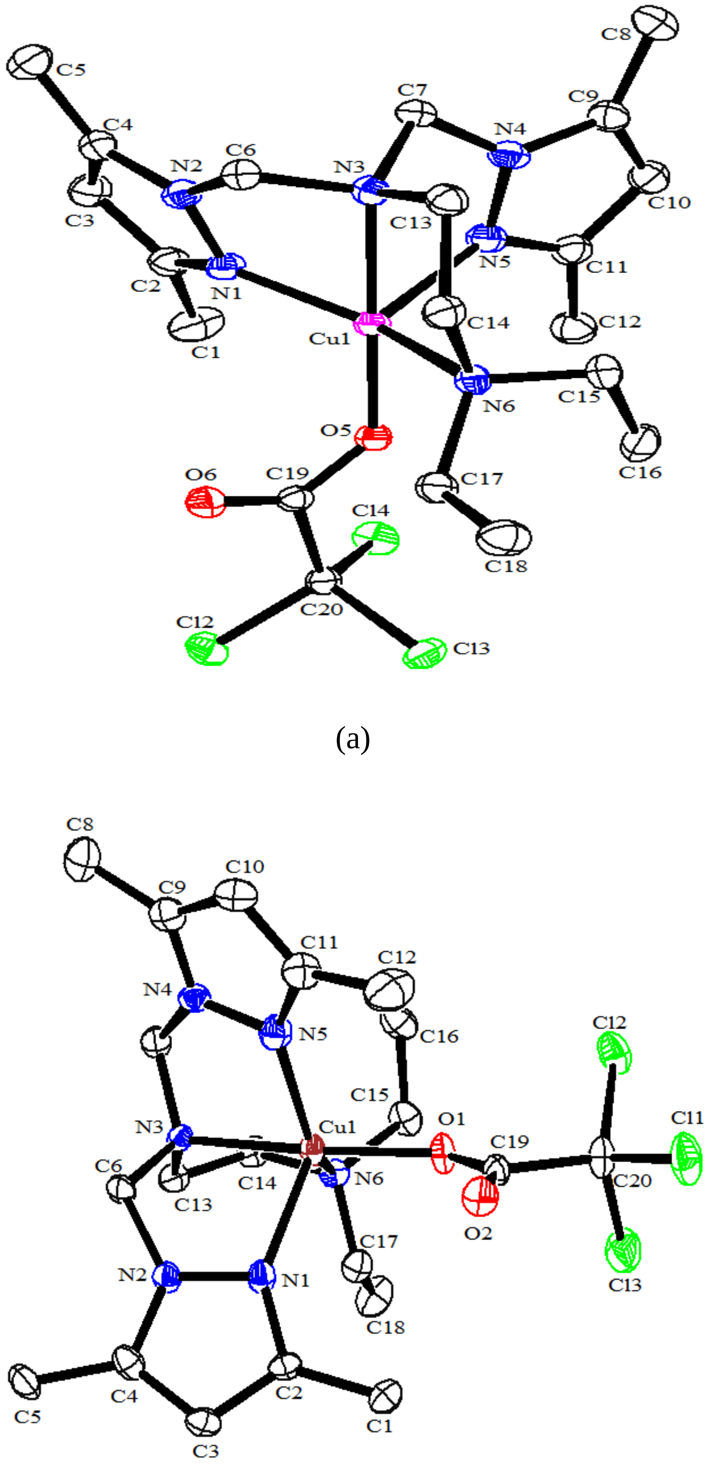


Fig.6.1. ORTEP diagram depicting the cationic parts of the complex **1** with atom numbering scheme (30% probability factor for the thermal ellipsoids; C atoms of second cationic part and H atoms are omitted for clarity).

6.4.2.2. [M(X)(dbdmp)]ClO_4 (2-7) [M = Cu(II), Co(II) and X = trichloroacetate, benzoate and salicylate] and [Cu(ONO)(dbdmp)]ClO_4 (8).

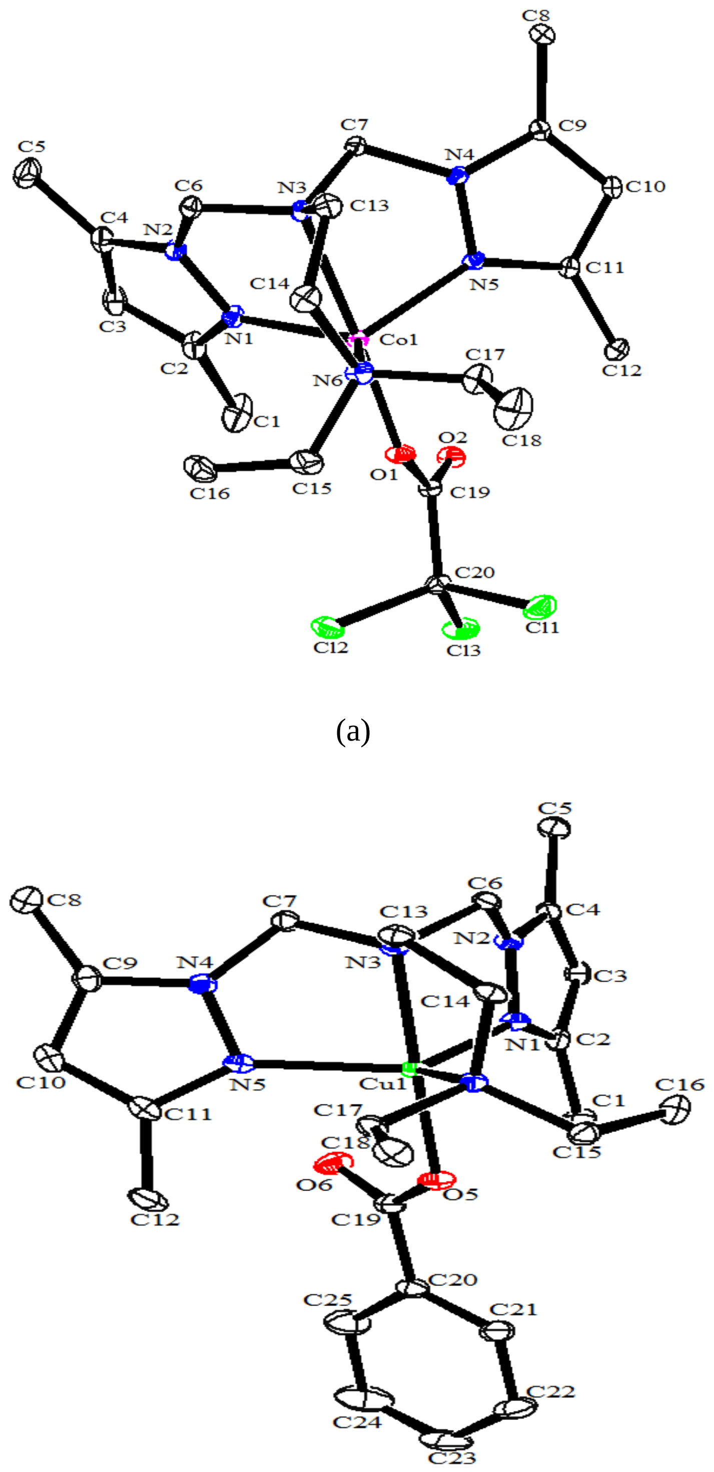
The X-ray quality crystals of the complexes **2, 3, 4, 5, 6** and **8** were obtained from the slow evaporation of methanol solution at room temperature. The ORTEP diagrams of complexes are shown in Fig.6.2-6.5. Complexes **2** and **3** crystallize in triclinic crystal system with *P-1* space group, complexes **4, 5** and **8** crystallize in monoclinic crystal system with $P2_1/c$ space group whereas complex **6** crystalizes in monoclinic crystal system with $P2_1/n$ space group. All the compounds are isostructural, penta coordinated and having MN_4O coordination environment. For all synthesized compounds, ligand dbdmp act as a tetradentate ligand. In their crystal structures, the M cations are coordinated by one oxygen atom of the trichloroacetate / benzoate / salicylate / nitrite group and four nitrogen atoms of the ligand dbdmp with slightly distorted trigonal bipyramidal geometry and the τ values are in the range of 0.6 to 0.9. The basal plane is made by two pyrazole rings' nitrogen atom N(1), N(5)



(a)

(b)

Fig.6.2. ORTEP diagram depicting the cationic part of the complexes **2** (a) and **2a** (b) with atom numbering scheme (30% probability factor for the thermal ellipsoids; H atoms are omitted for clarity).



(a)

(b)

Fig.6.3. ORTEP diagram depicting the cationic part of the complexes **3** (a) and **4** (b) with atom numbering scheme (30% probability factor for the thermal ellipsoids; H atoms are omitted for clarity).

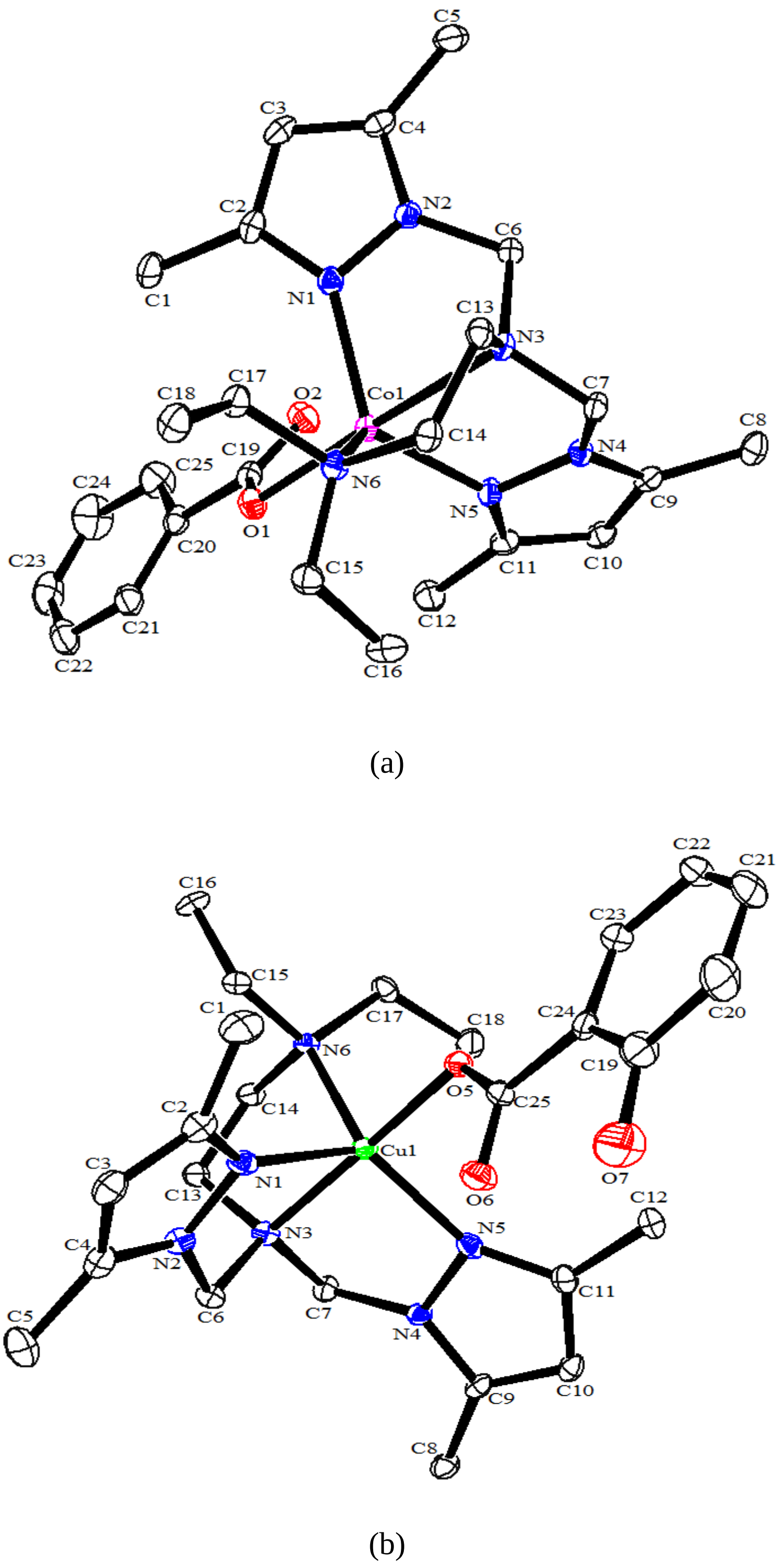


Fig.6.4. ORTEP diagram depicting the cationic part of the complexes **5** (a) and **6** (b) with atom numbering scheme (30% probability factor for the thermal ellipsoids; H atoms are omitted for clarity).

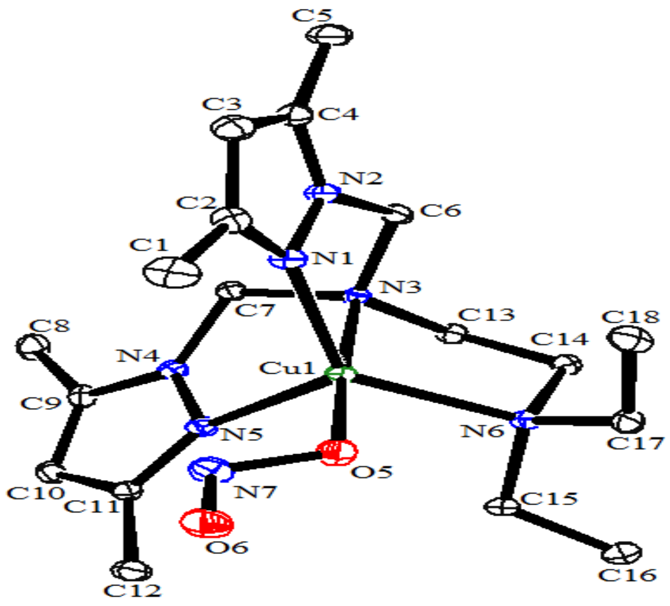


Fig.6.5. ORTEP diagram depicting the cationic part of the complex **8** with atom numbering scheme (30% probability factor for the thermal ellipsoids; H atoms are omitted for clarity).

and one tertiary amine's nitrogen atom N(6) while apical position is occupied by tertiary amine nitrogen N(3) and one oxygen atom O(5) from corresponding acetate / trichloroacetate / benzoate / salicylate group.

In the case of complex **2**, we observed two types of crystals which are different in colour, one is blue (**2a**) and another one is green **(2)**. The τ value for **2** and **2a** are 0.64 and 0.48 respectively. So the complex **2a** is more distorted from ideal trigonal bipyramidal geometry and its geometry is in between square pyramidal and trigonal bipyramidal. The M-N distances of complexes in basal plane fall in the range 2.014(3)-2.175(4) Å whereas apical Cu-N bond lengths are in the range of 2.050(5) Å-2.272(3) Å. The Cu-O bond length varies in the range 1.901(3) Å-2.002(2) Å which is comparable with reported carboxylate containing complexes [22]. The metal – oxygen distances increase from complex in the order **4** (1.901(3) Å) < **6** (1.906(3) Å) < **2** (1.920(4) Å) < **2a** (1.942(2) Å) < **3** (1.9754(18) Å) < **5** (2.002(2) Å).

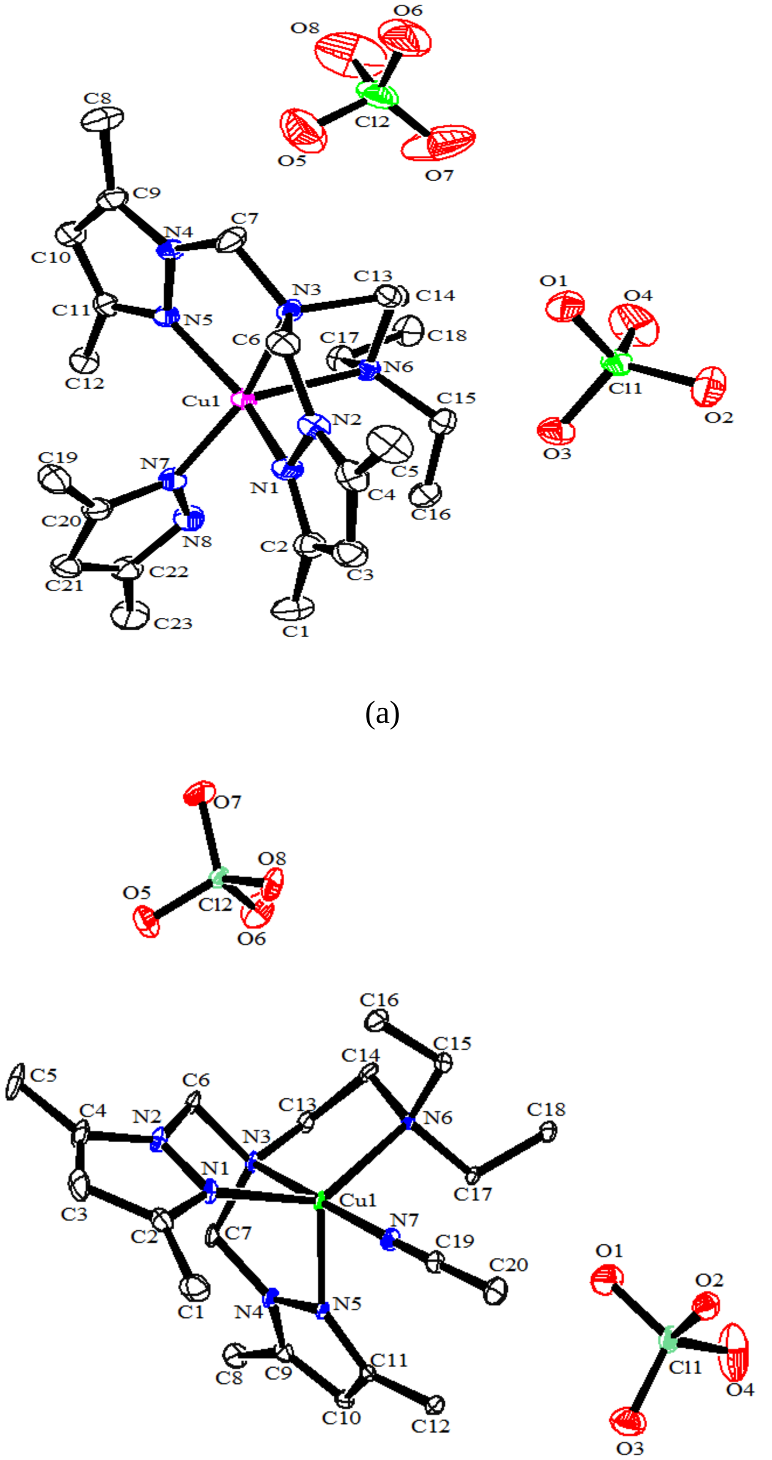
The Cu(1)-O(5) distance in complex **8** is 1.9277(17) Å which is comparable to reported Cu-O distance of O-bounded copper(II)-nitrite complexes [30-33].

6.4.2.3. [Cu(pz)(dbdmp)]$(ClO_4)_2$ (9) and [Cu(CH_3CN)(dbdmp)]$(ClO_4)_2$ (11)

The X-ray quality crystals of complexes **9** and **11** were obtained from the slow evaporation of methanol and acetonitrile solution at room temperature, respectively. The ORTEP diagram of complexes **9** and **11** are shown in Fig.6.6**.** Complex **9** crystallize in triclinic crystal system with *P-1* space group whereas complex **11** crystallizes in monoclinic crystal system with $P2_1/c$ space group. Both the complexes are penta coordinated with CuN_5 coordination environment. Four nitrogen atoms of tetradentate ligand dbdmp and one nitrogen atom of 3,5-dimethylpyrazole ring completes the coordination environment around copper centre in complex **9**. The geometry around copper centre can be best describe as distorted square pyramidal [τ = 0.21]. The equatorial plane is occupied by N(1), N(5) and N(7) of three pyrazole groups and N(3) of tertiary amine nitrogen whereas N(6) of another tertiary amine nitrogen occupied the apical position of the square pyramid geometry.

The Cu(1)-N bond lengths of equatorial plane fall in the range 1.988(5) Å - 2.106(4) Å and axial Cu(1)-N(6) bond distance is 2.254(4) Å. The equatorial bond angles N(7)-Cu(1)-N(3) and N(1)-Cu(1)-N(5) are 162.85(17)° and 150.33(17)°, respectively. The Cu(1)-N(7) distance of 3,5-dimetylpyarazole is comparable with reported parazole containing complexes [43-44]. This is the first complex with ligand dbdmp which has distorted square pyramidal geometry. All complexes synthesized previously with this ligand have distorted trigonal bipyramidal geometry.

In the case of complex **11**, four nitrogen atoms of ligand and one nitrogen atom of acetonitrile completes the penta coordination. The geometry of copper centre can be described as distorted trigonal bipyramidal as τ value is 0.69. The equatorial plane is made by N(1), N(5) and N(6) of ligand dbdmp and axial plane is made by N(3) of tertiary amine nitrogen of ligand dbdmp and N(7) from coordinated acetonitrile molecule. The equatorial bond distance Cu(1)-N(1), Cu(1)-N(5) and Cu(1)-N(6) are 2.013(3) Å, 2.111(3) Å and 2.076(3) Å, respectively whereas axial bond lengths Cu(1)-N(3) and Cu(1)-N(7) are 2.030(3) Å and 1.964(3) Å, respectively. The equatorial bond angles fall in the range of 107.69(11)-137.43(12)° and axial bond angle N(7)-Cu(1)-N(3) is linear (179.04(12)°).



(a)

(b)

Fig.6.6. ORTEP diagram depicting the cationic part of the complexes **9** (a) and **11** (b) with atom numbering scheme (30% probability factor for the thermal ellipsoids; H atoms are omitted for clarity).

6.4.2.4. [Cu(Cl)(dbdmp)]PF_6 (12)

An ORTEP view of the coordination environment around the cationic part of complex **1** and atom-labeling scheme is shown in the Fig.6.7**.** The structure shows that the Cl$^-$ ion and tetradentate ligand dbdmp is bonded to copper(II) ion. The ligand is tetradentate, utilized all its potential donor sites - a tertiary nitrogen atom attached with two ethyl group N(6), another tertiary nitrogen atom N(3), attached with two pyrazole rings via methylene carbon and two pyrazole nitrogen atoms N(1) and N(5) for complex formation.

Copper atom has five coordination with trigonal bipyramydal geometry being bonded to three nitrogen atoms - one tertiary nitrogen atom N(6), two pyrazole nitrogen atoms N(1) and N(5) in the trigonal plane and tertiary nitrogen atom N(3) and Cl(1) atom are in the axial position. The coordination geometry around the copper is best described as distorted trigonal bipyramidal which is revealed by the magnitude of the trigonality index τ (0.795).The Cu(1)-N bond distance in trigonal plane are in the range of 2.090(3) Å-2.143(3) Å and bond angles are in the range of 109.34(9)°-130.88(10)°. The two Cu(1)-N bond lengths in axial plane are 2.073(2) Å and 2.2474(9) Å respectively.

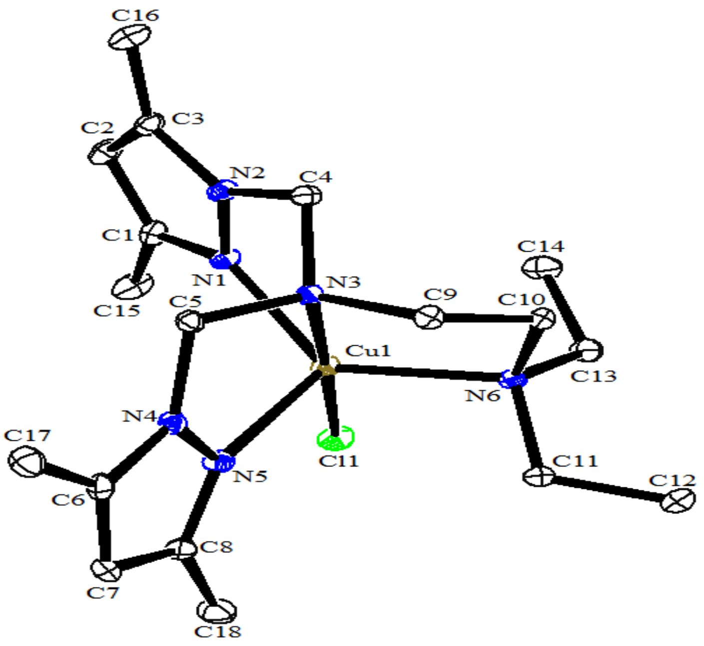


Fig.6.7. ORTEP diagram depicting the cationic part of the complex **12** with atom numbering scheme (30% probability factor for the thermal ellipsoids).

6.4.3. IR spectra

The IR spectra of the complexes were assigned in comparison of the spectra of the ligand. All the complexes show two intense bands at ~ 1550 and ~ 1460 cm^{-1} and these two bands are also present in the ligand indicating the coordination of ligand dbdmp in the metal coordination sphere. For complexes **1** and **12**, a broad band is observed at ~ 844 cm^{-1} which is attributed to the stretching vibration of PF_6^- anion. The IR spectra of complexes **2-11** exhibited two bands: one broad band at ~ 1100 cm^{-1} due to ν_{assy}(Cl-O) and a weak band at ~ 624 cm^{-1} due to δ(O-Cl-O), confirming the presence of perchlorate ion outside the coordination sphere in the complexes. For complexes **2** and **3**, a strong absorption band in the region of ~1702 cm^{-1} indicates the presence of $\nu_{assym}(COO^-)$ and a band appears at 1393 cm^{-1} (for **2** and **2a**) and 1321 cm^{-1}(for **3**) due to symmetric stretching vibration of monodentate carboxylate group and the band of carboxylate group appeared at high frequency due to presence of neighouring trichloro group [45]. In the complexes **4** and **5**, the asymmetric stretching vibration of benzoate ion appear at 1629 and 1609 cm^{-1}, respectively and symmetric stretching vibration appear at 1346 and 1366 cm^{-1}. For complexes **6** and **7**, the coordination occurs by the acidic COOH group of the salicylic acid and the phenolic OH group of salicylic acid does not participate in the coordination with metal ions and the salicylic acid acts as monodentate ligand. The monodentate coordination behaviour of salicyclic acid with metal ions is reported in the literature [46]. A broad band of ν(OH) appeared at 3242 and 3227 cm^{-1} in the complexes **6** and **7.** In the complex **8**, the identification of the vibrations of the ν(N-O) is complicated due to domination of the pyrazolyl ligand. The band at 1255 cm^{-1} is assigned to the ν_s(N-O) of nitrite whereas the corresponding ν_{ass}(N-O) is identified with the band at 1185 cm^{-1} [47-48]. These are consistent with nitrito (Cu-O) rather than the nitro (Cu-N) coordination of the NO_2 ligands [46]. The absence of δ(O-N-O) mode at approximately 840-890 cm^{-1} suggests that the nitrito ligands are monodentate, consistent with the X-ray crystal structure (Fig.6.5). In the IR spectra of complexes **9** and **10**, a sharp band appeared at 3202 and 3396 cm^{-1} which indicates the presence of ν(NH) of pyrazole ring confirms that 3,5-dimethylpyrazole act as a neutral ligand in this complex. In the complex **11**, a sharp band at 2253 cm^{-1} indicates the presence of ν(CN) in the complex which confirms that CH_3CN is coordinated to the metal centre.

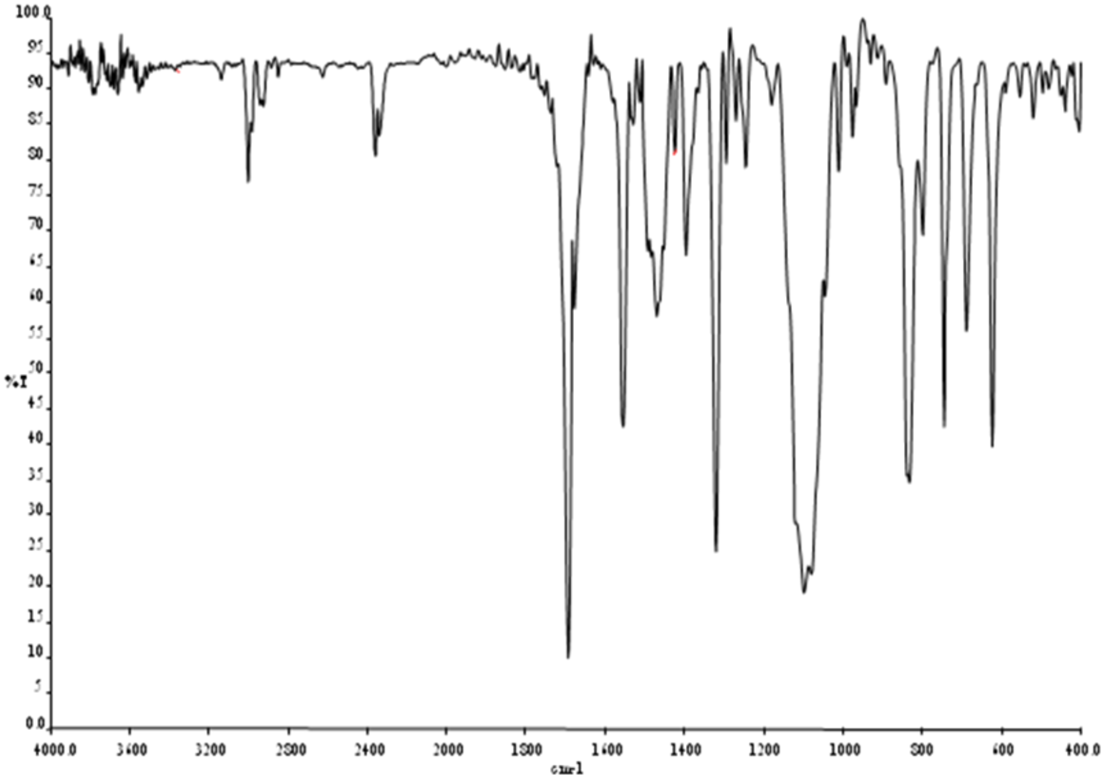


Fig.6.8. IR spectrum of [Cu(Cl_3CCOO)(dbdmp)]ClO_4 (2a)

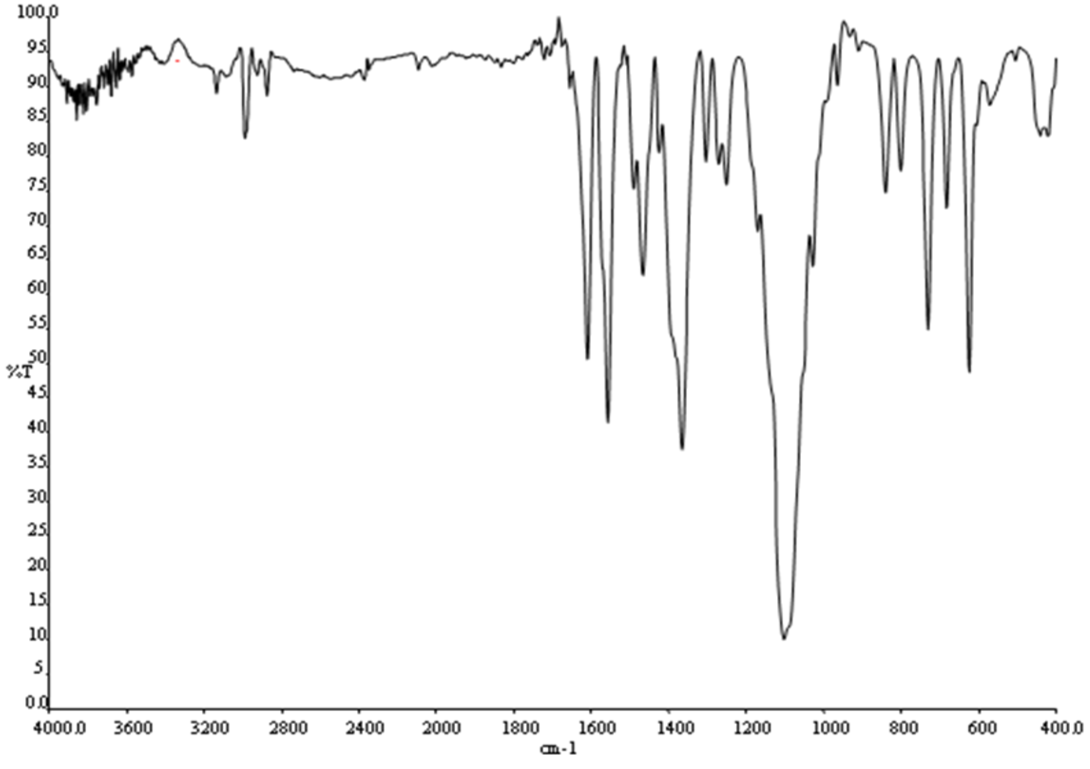


Fig.6.9. IR spectrum of [Co(C_6H_5COO)(dbdmp)]ClO_4 (**5**).

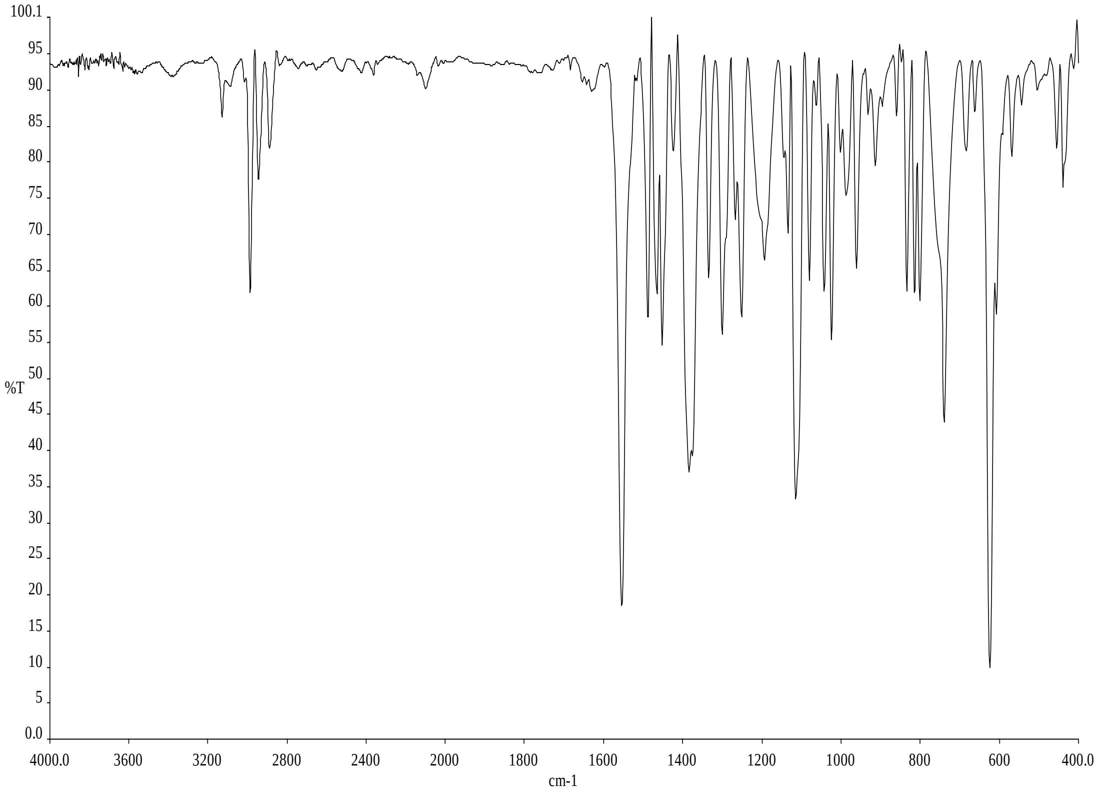


Fig.6.10. IR spectrum of [Cu(ONO)(dbdmp)]ClO_4 (**8**).

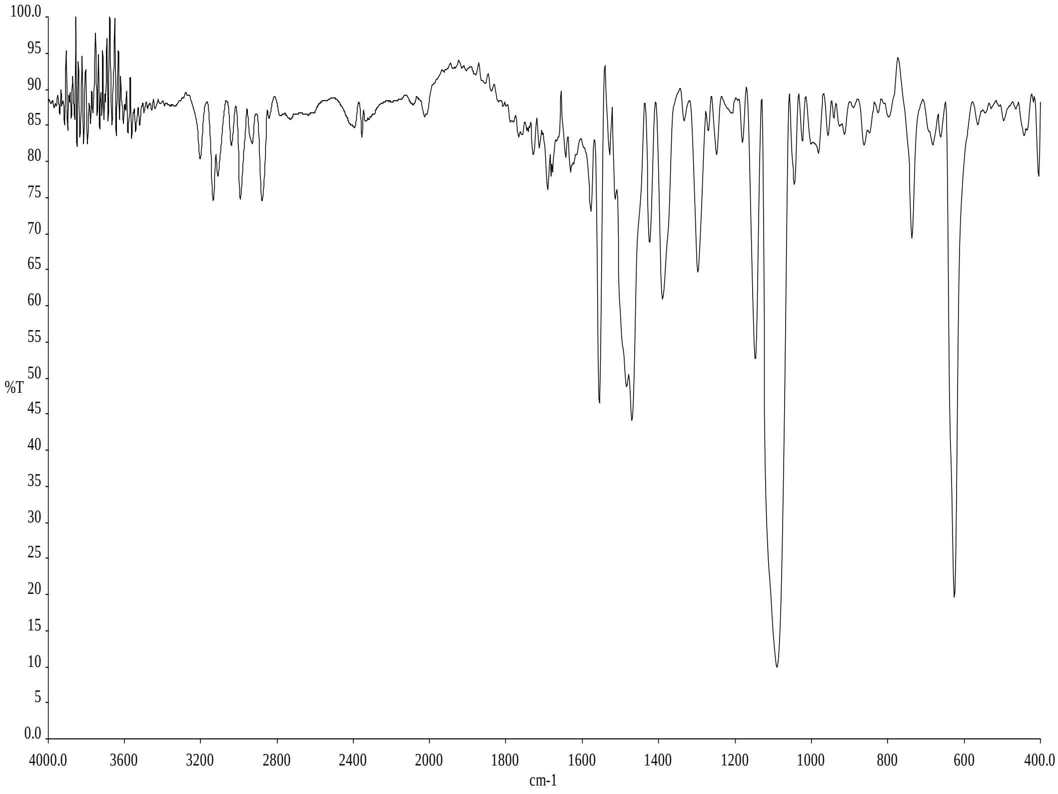


Fig.6.11. IR spectrum of [Cu(pz)(dbdmp)]$(ClO_4)_2$ (**9**).

6.4.4. Electronic Spectral Studies

The UV-Visible spectra of the complexes **1-12** were recorded in CH_3CN (10^{-3} M) in the range of 200-1000 nm. The high intensity bands appeared at < 400 nm (~245 nm) are due to intraligand n-π^* / π-π^* transition. For copper (II) complexes **2**, **4, 6, 8, 11** and **12**, there are two absorption bands: one broad band observed at λ > 800 nm due to d_{xy},, $d_{x}{}^{2}$-$_{y}{}^{2}$ $\rightarrow dz^2$ and a weak transition due to d_{xy}, $d_{yz} \rightarrow d_z{}^2$ at higher energy region λ < 750 nm. This type of spectral feature is typical for Cu(II) complexes with trigonal bipyramidal geometry [49-54]. Complex **9** show a band at 674 nm due to d_{xz}, $d_{yz} \rightarrow$ $d_{x}{}^{2}$-$_{y}{}^{2}$ transition. Generally, square pyramidal or distorted square pyramidal Cu(II) complexes show spectral band in the region of 550 - 660 nm due to d_{xz}, $d_{yz} \rightarrow$ $d_{x}{}^{2}$-$_{y}{}^{2}$ transition. Absence of spectral band in this region in the copper (II) complexes **2**, **4, 6, 8, 11** and **12** also support the geometry around copper(II) centre is trigonal bipyramid. For cobalt(II) complexes, the three absorption bands appeared at >700, ~590, ~490 nm for complexes **1**, **3, 5, 7** and **10** are due to d-d transition or ligand field transitions. This type of transitions are generally observed for TBP high spin cobalt(II) complexes [55].

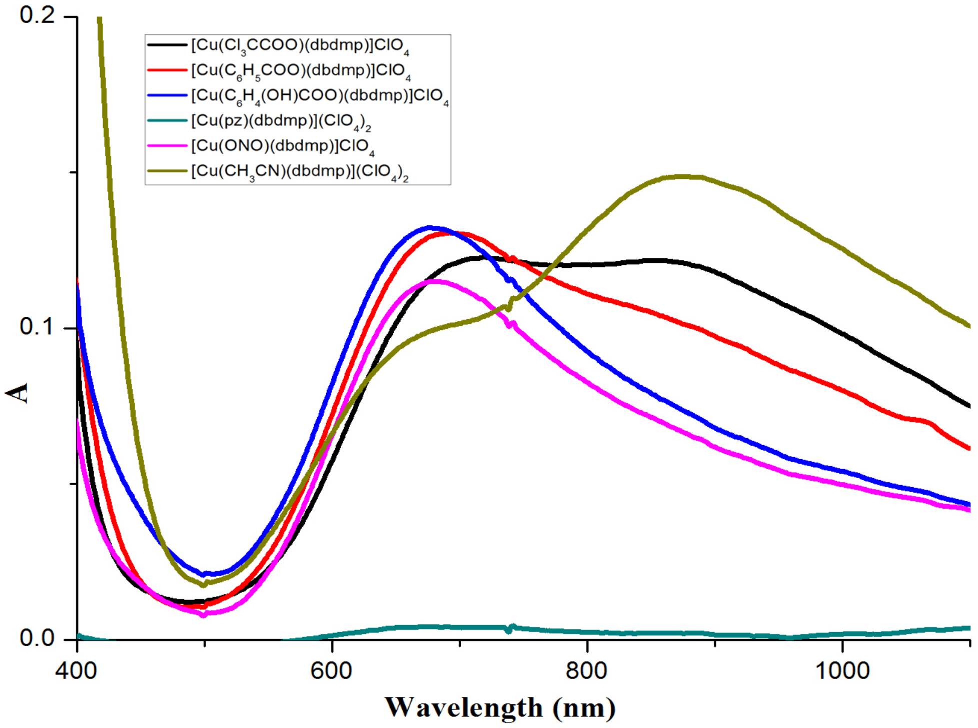


Fig.6.12. Electronic specta of copper(II) complexes.

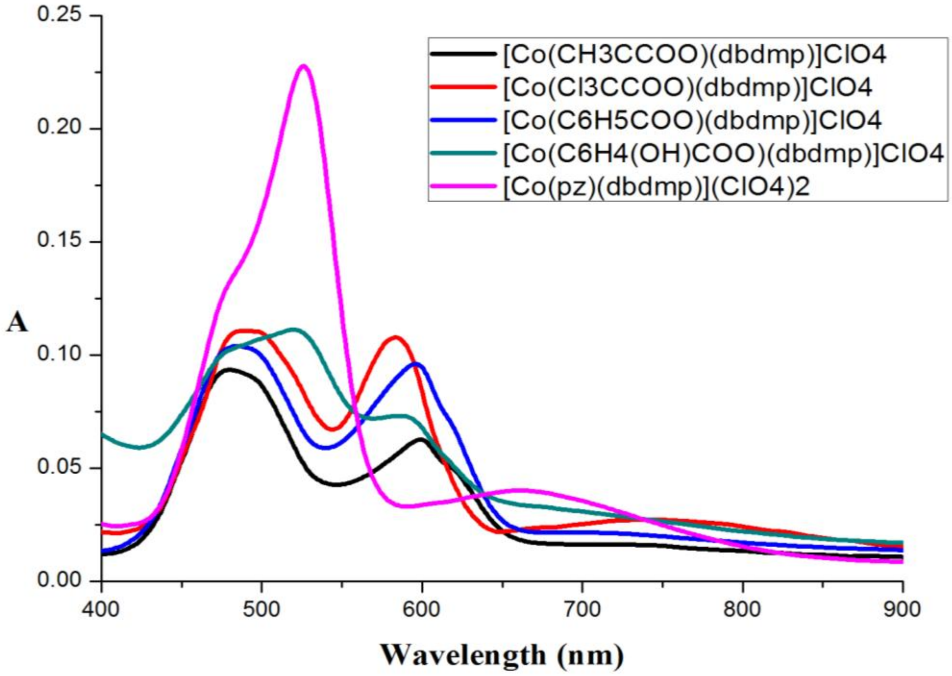


Fig.6.13. Electronic specta of cobalt(II) complexes.

6.4.5. EPR and Cyclic Voltammetry Study

The X-band EPR spectrum of copper(II) complexes **2**, **4**, **6, 8, 9** and **12** were recorded in CH_3CN solution at liquid nitrogen temperature (77 K) and exhibited a typical four line splitting pattern with well resolved hyperfine peaks. This is due to interaction of the unpaired electron with the nuclear spin of the copper nucleous (^{63,65}Cu: I = 3/2). The g_{II} values of the complexes are ~2.226 and $g_{\perp}$ values are ~2.077. The observed feature $g_{II} > g_{\perp} > 2$ and is diagnostic of a pseudotetragonal site for copper(II) and these values indicate that the ground states of Cu(II) is predominantly $d_{x^2-y^2}$.

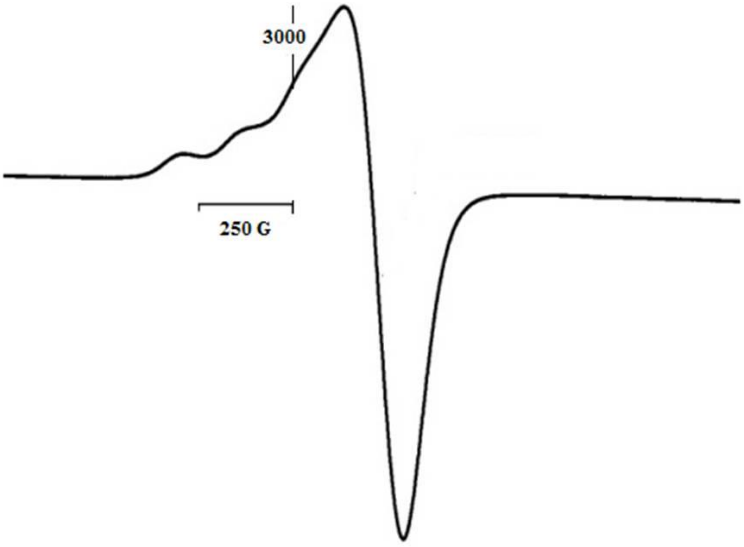


Fig.6.14. X-Band EPR spectrum of complex **4** in CH_3CN at 77 K.

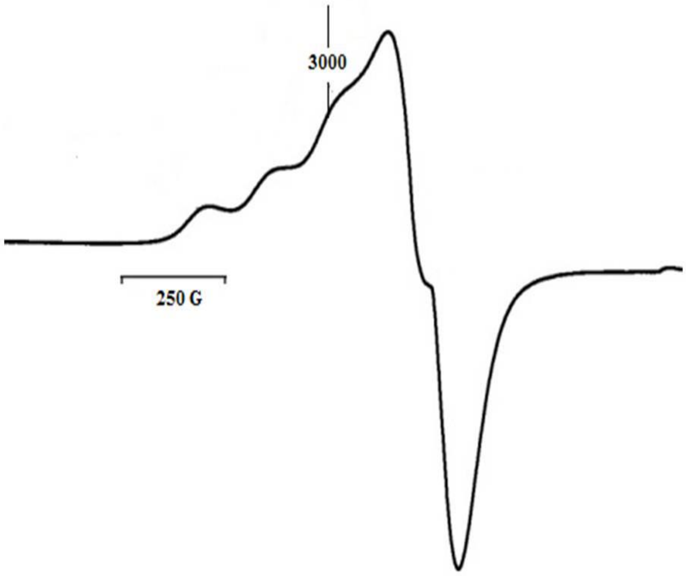


Fig.6.15. X-Band EPR spectrum of complex **6** in CH_3CN at 77 K.

The electrochemcial behavior of the copper (II) complexes **2**, **4**, **6**, **8**, **9** and **12** have been examined by cyclic voltammetry using glassy carbon electrode as working electrode in CH_3CN solution (~ 10^{-3} M) and n-Bu_4NPF_6 (0.1M) as supporting electrolyte in the potential range 1.0 to -1.5 V versus Ag/Ag^+ reference electrode. The electrochemical data of the complexes are given in the Table 7. In the positive range, from 0 to 1.5V, the oxidation process due to ligand was observed at 0.600V and no oxidation potential due to metal center was observed in the complexes in this range.

The cyclic voltammograms of all the complexes was recorded at 100 mVs^{-1} towards cathodic zone 0 to -1.0 V, show a reduction potential E_{pc} in the potential range -0.4 to -0.6V and the corresponding anodic potential -0.03 to -0.2 V. The couple is associated with Cu(II)/Cu(I) reduction. The ΔEp values of the complexes is more than 300 mV except complex **9** indicating quasi reversible electron transfer process. The quasi reversible reduction process was increasing in the order **4** > **2** > **6** > **12** > **8** and this is due to electron withdrawin property of the co-liand attached with the molecule. In complex **9**, the pyrazole is a neutral co-ligand and has no electron withdrawing property and therefore the reduction potential as well as ΔE_p (176 mV) is less compare to other complexes.

Table.6.7. Summary of the electrochemical and EPR data of the complexes

Compounds	Cu(II)/Cu(I)			EPR data	
	E_{pc}(V)	E_{pa}(V)	ΔE_p(mV)	g_{II}	$g_{\perp}$
(2)	-0.465	-0.020	424	2.226	2.077
(4)	-0.610	-0.033	577	2.223	2.082
(6)	-0.460	-0.080	380	2.230	2.075
(8)	-0.470	-0.170	300	2.227	2.092
(9)	-0.138	0.038	176	2.225	2.074
(12)	-0.541	-0.190	351	2.229	2.088

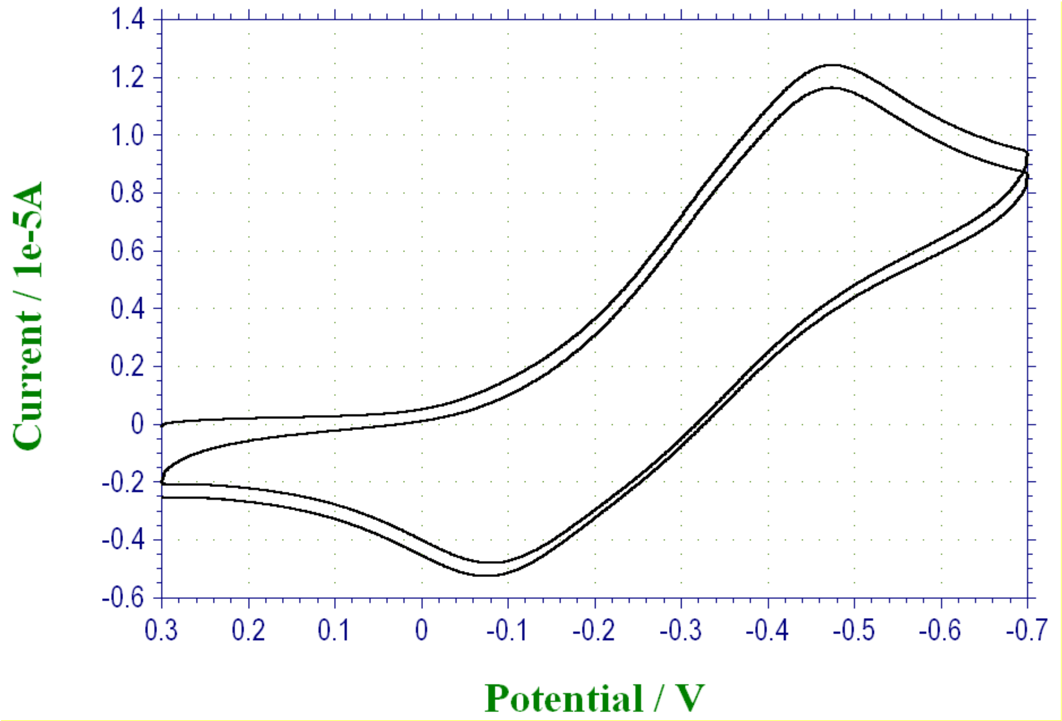


Fig.6.16. Cyclic voltammogram of complex **6** at 100 mVs^{-1} using glassy carbon electrode in CH_3CN contained1 mM complex and 0.1M n-Bu_4NPF_6.

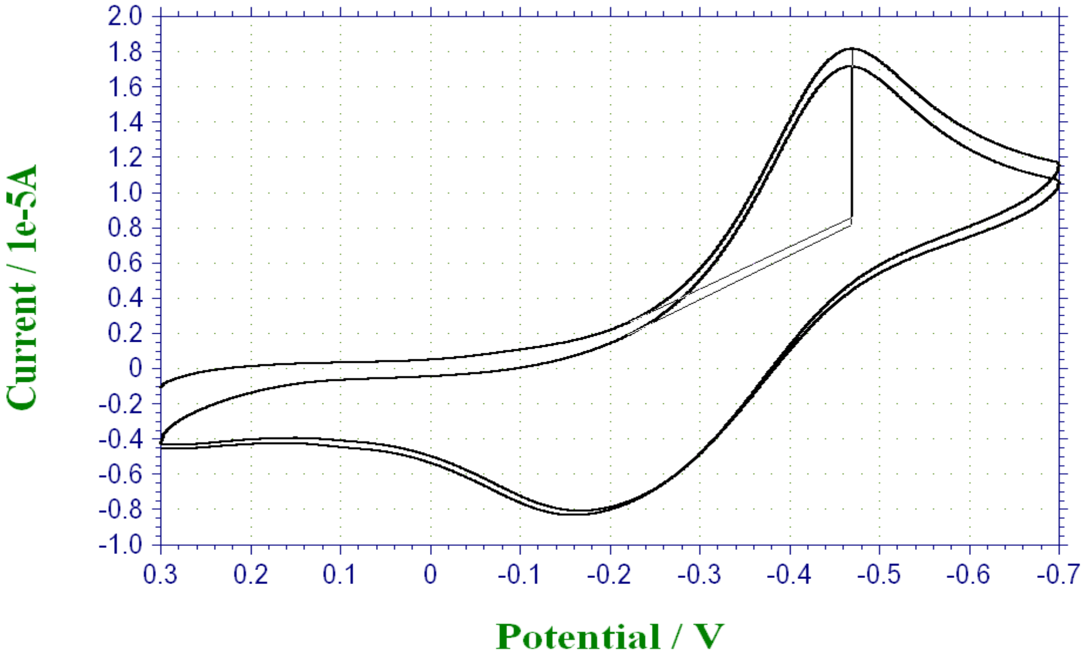


Fig.6.17. Cyclic voltammogram of complex **8** at 100 mVs^{-1} using glassy carbon electrode in CH_3CN contained1 mM complex and 0.1M n-Bu_4NPF_6.

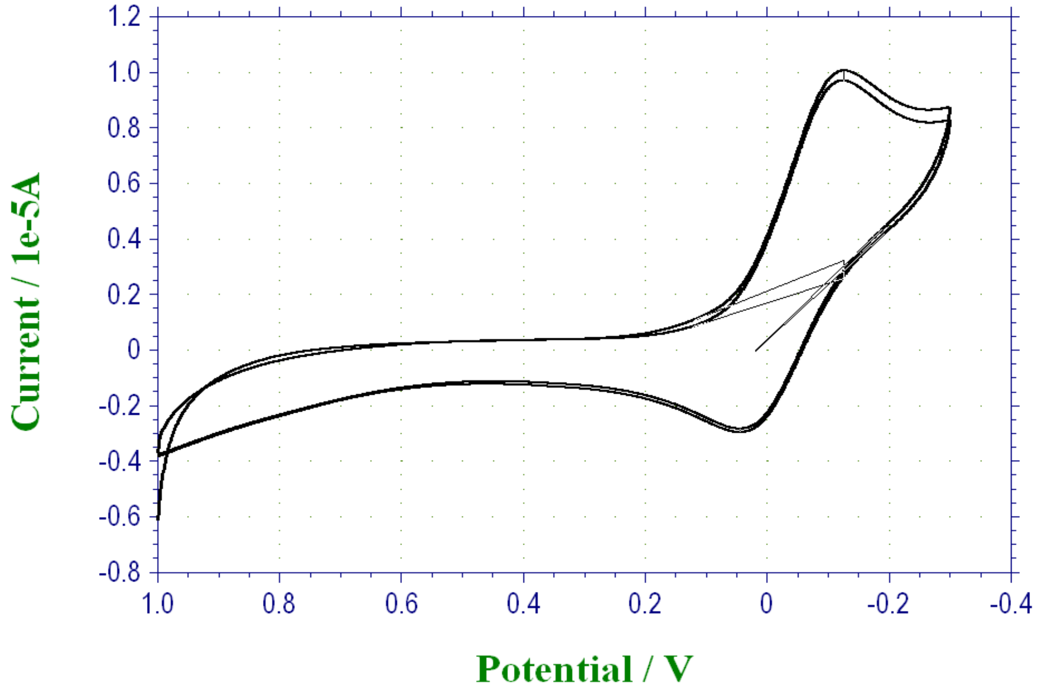


Fig.6.18. Cyclic voltammogram of complex **9** at 100 mVs^{-1} using glassy carbon electrode in CH_3CN contained1 mM complex and 0.1M n-Bu_4NPF_6.

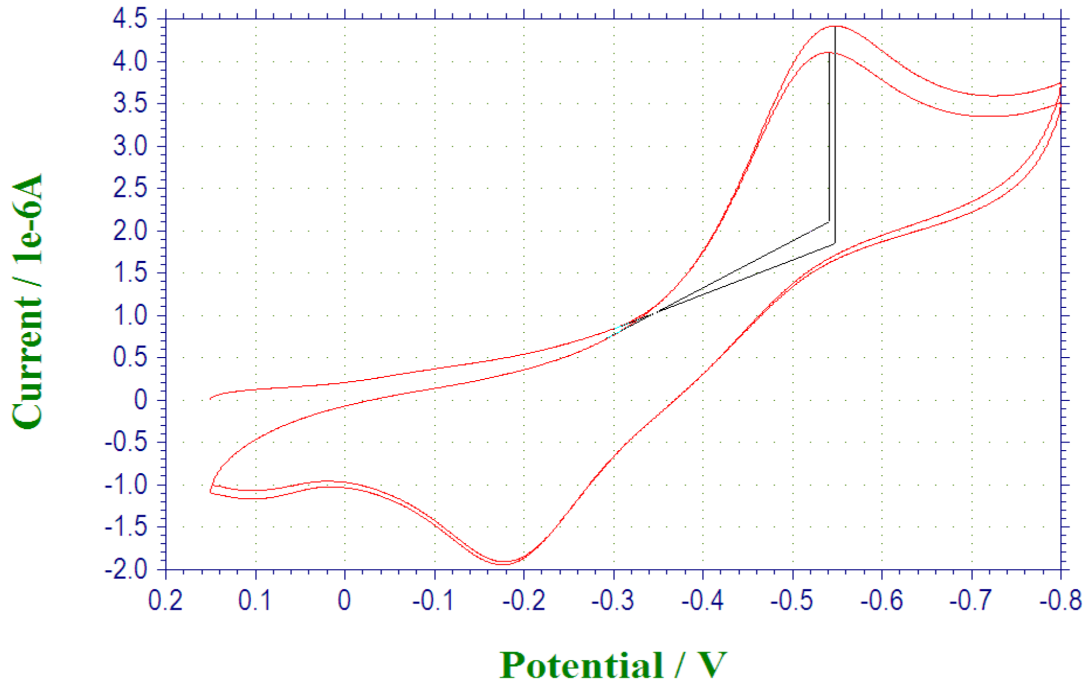


Fig.6.19. Cyclic voltammogram of complex **12** at 100 mVs^{-1} using glassy carbon electrode in CH_3CN contained1 mM complex and 0.1M n-Bu_4NPF_6.

6.4.6. Magnetic Studies

The room temperature magnetic moment of the copper(II) complexes **2, 4, 6, 8, 9, 11** and **12** show μ_{eff} ~ 1.78 BM indicating one electron paramagnetism and this is typical for all copper(II) complexes. Room temperature magnetic moment of the powder cobalt(II) complexes **1, 3, 5, 7** and **10** are in the range of 4.32-4.42 BM. due to three unpaired electrons in the high spin cobalt(II) ion. Magnetic moment for cobalt(II) complexes with tripodal ligand fall in the range of 4.4-4.7 BM [56].

6.4.7. Antimicrobial Activity

The synthesized copper(II) and cobalt(II) complexes were screened for antibacterial activity against *Gram positive* (*Staphylococcus aureus* and *Bacillus subtilis*) and *Gram negative* (*Escherichia coli and Psedomonas aeruginosa*) bacteria using disk diffusion method. The MIC (minimum inhibitory concentration) values of the complexes are summarized in the Table 8**.** The copper(II) complexes show considerable activity whereas cobalt (II) complexes show moderate activity against bacterial strain tested. The result indicates that at 400 µg/ml concentration, copper(II) complexes are active against *Grams positive* and *Gram negative* bacteria. Complexes **6** and **9** are more active among all the synthesized complexes against both the *Gram positive* bacteria. Complex **6** is more active against *S. aureus* and complexes **6** and **9** are active against *B. Subtilis* (*Gram positive*) bacteria at the concentration of 200 µg/ml. Complex **2** is more active against *Pseudomonas aeruginosa* (*Gram negative*) becteria. Cobalt(II) complex **1** is active against both the gram negative bacteria at 400 µg/ml concentration. The ligand dbdmp and cobalt(II) complexes show inhibition at higher concentration. From the antimicrobial studies, it can be concluded that metallation is essential for inhibition activity and all the complexes have higher activity than the organic ligand dbdmp.

Table.6.8. MIC values of the complexes.

Compound	MIC value in µM			
	S. aureus	***B. Subtilis***	***E. coli***	***P. aeruginosa***
(1)	>400	>400	400	400
(2)	400	400	400	200
(3)	400	>400	400	>400
(4)	400	400	400	400
(5)	>400	>400	>400	>400
(6)	200	200	400	400
(7)	>400	>400	400	>400
(8)	>400	>400	>400	400
(9)	400	200	200	400
(10)	>400	400	400	>400
(11)	400	400	>400	400
(12)	400	400	400	400

6.4.8. Cytotoxicity Assay of Copper(II) Complexes.

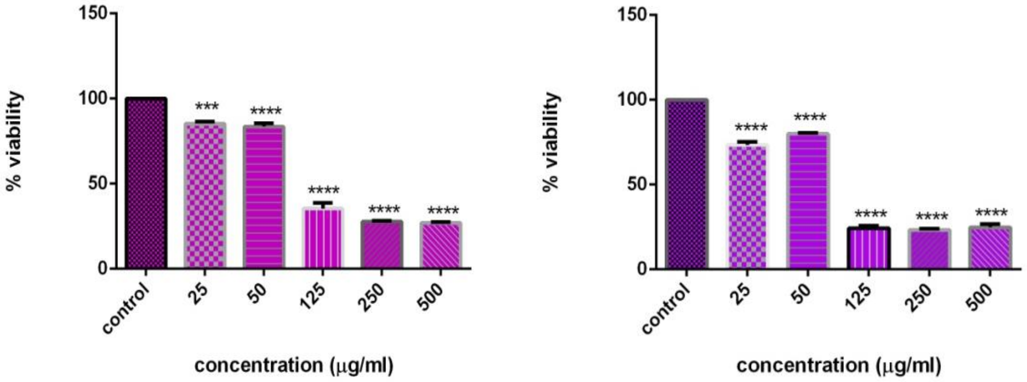


Fig.6.20. Effect of Complexes **4** and **6** exposed to A549 cells on cell viability. Data expressed as mean ± S.E.M. for n=3. ***P<0.001 & ****P<0.0001.

The cytotoxic activity of copper(II) complexes **4** and **6** were investigated against A549 lung carcinoma cancer cells. In the present study copper(II) complexes **4** and **6** showed a dose dependent cytotoxic activity and at 125 µM concentration both the complexes show maximum toxicity. The IC_{50} value for the complexes **4** and **6** are 94 and 84 µM respectively. Encouraging results of cytotoxicity assay warrants a profound investigation to establish the mechanism of cytotoxicity of copper(II) complexes **4** and **6** against A549 cells.

6.5. Conclusion

Mononuclear mixed ligand complexes of copper(II) and cobalt (II) with tetradentate ligand dbdmp in the presence of alkyl and aryl carboxylate / nitrite / 3,5-dimethylpyrazole (pz) / chloride have been synthesized characterized. Moleculer structure of ten complexes were solved by single crystal X-ray diffraction studies and showed that complex **1** has two different geometries (distorted trigonal bipyramidal and distorted octahedral geometry), complex **2** has distrorted square pyramidal geometry and remaining complexes have penta coordination with distorted trigonal bipyramidal geometry. The EPR spectra of complexes **4, 6, 8, 9** and **12** in frozen acetonitrile solution show axial spectra with $g_{II} > g_{\perp}$ indicating $d_{x^2-y^2}$ is the ground state of the complexes. The redox property of copper(II) complexes show that Cu(II)/Cu(II) reduction with quasi revercible electron transfer process. The results of antibacterial studies against *Gram positive* and *Gram negative* bacterial strain showed that complexes **6** and **9** are most active among all the synthesized complexes. The MTT assay of complexes **4** and **6** revealed that both the complexes have dose dependant cytotoxic activity on A549 cells with the IC_{50} values of 94 and 84 µM, respectively.

6.6. References:

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