CHAPTER-4(A)

Synthesis, Characterization and Structures of Binuclear Copper(II) and Polynuclear Cobalt(II), Nickel(II) and Cadmium(II) Complexes involving N_4-donor Pyrazolyl based ligand and dicyanamide as bridging ligand.

Abstract

Binuclear copper(II) complex [Cu(bdpab)(μ-$_{1,5}$dca)]$_2$(ClO_4)$_2$ and polynuclear complexes [M(bdpab)(μ-$_{1,5}$dca)]$_n$(ClO_4)$_n$ [M =Ni(II), Co(II) and Cd(II) and dca = dicyanamide anion {N(CN)$_2^-$}] were synthesized using pyrazolyl containing tetradentate N_4- coordinate ligand N,N-bis(3,5-dimethyl-1H-pyrazol-1-yl)methyl-N2-phenylethane-1,2-diamine (bdpab) and bridging ligand dca and characterized by spectral data and single crystal X-ray diffraction studies. Structural characterization by single crystal X-ray diffraction studies show copper complex is binuclear and two copper centers are bridged by two μ-$_{1,5}$dca ligands whereas Co(II) and Cd(II) complexes are polynuclear and two metal centers are bridged by one μ-$_{1,5}$dca ligand in zig-zag pattern and all metal centers have octahedral geometry.

4(A).1. Introduction

Bridging ligands which bind metal centres play an important role in the design and synthesis of polynuclear coordination complexes with multidimensional structures in presence of multidentate organic ligands. Pseudohalides are ambidentate ligand and can acts as bridging ligand and many pseudohalides such as azide (N_3^-), thiocyanate (SCN^-), selenocyanate($SeCN^-$) and isocyanate (NCO^-) have been used in the synthesis of multidimensional polynuclear compounds [1-13]. The versatile coordination modes of pseudohalides made the molecules very interesting due to their interesting structures and magnetic behaviors. An important characteristic of the large molecular ion such as dca is that dca, like azide, is a versatile ligand and it can display different coordination modes such as μ-$_{1,1,}$ μ-$_{1,3}$, μ-$_{1,5}$, μ-$_{1,1,5}$, μ-$_{1,3,5}$, μ-$_{1,3,5,5}$ and μ-$_{1,1,3,5,5}$ in the transition metal complexes [14,15]. Recently, dca has been used in the synthesis of polynuclear complexes of divalent metal ions with bi- or tridentate ligands and characterized with structures [15-24]. It has been observed that bidentate bridging mode μ-$_{1,5}$ is the common mode of coordination for most of the synthesized complexes. Pyrazolyl based chelating ligands form a variety of coordination complexes with a number of transition metal ions. Recently, we have synthesized and characterized transition metal complexes with di-valent metal ions using tetradentate N_4-coordinate ligands in presence of bridging pseudohalides like azide, thiocyanate and isocyanate but the synthesized complexes are mostly mono and binuclear complexes [25-29]. There is few reports on the dicyanamide bridged complexes with divalent metal ions and pyrazolyl based ligand [16]. In the chapter, we report on the coordination behaviour of N_4-coordinate pyrazolyl based ligand bdpab towards divalent metal ions such as Cu(II), Co(II), Ni(II) and Cd(II) in presence of bridging dca ligand. Structural data shows that copper(II) complex is binuclear and two copper centres are joined by two dca ligands whereas Co(II) and Cd(II) complexes are polynuclear and two metal centres are bridged by one dca ligand and all metal centres have octahedral geometry.

4(A).2. Experimental

4(A).2.1. Materials

The chemicals and solvents were analytical grade and purchased from commercial sources. $CuCO_3$, $NiCO_3$ and $CdCO_3$, paraformaldehyde, hydrazine hydrate, acetylacetone, (Loba, India) were reagent grade and used as received. *N*-(3,5-dimethyl-1H-pyrazole-1-yl)methanol [30] and N,N-bis(3,5-dimethyl-1H-pyrazol-1-yl)methyl-N2-phenylethane-1,2-

diamine(bdpab) [31] were synthesized as per the reported procedures. Metal perchlorate hexahydrate [M = Cu, Co, Ni and Cd] were prepared by reaction of metal carbonate with dilute $HClO_4$ acid and followed by slow evaporation over steam bath.

4(A).2.2. Synthesis of Ligand

N,N-bis(3,5-dimethyl-1H-pyrazol-1-yl)methyl-N2-phenylethane-1, 2-diamine (bdpab)

N,N-bis(3,5-dimethyl-1H- pyrazol-1-yl)-2-methy]-1,2-ethylenediamine (bdpab) was synthesized and characterized as per the published procedure [31]. Purity of the compound was checked by TLC.

Yield. 0.290 g (82%). Found C = 67.97, H = 8.05, N = 23.98%, Elemental analysis calc. for $C_{20}H_{28}N_6$: C = 68.15, H = 8.01, N = 23.84%. ^{1}H NMR (400 MHz, $CDCl_3$, 20 ^{o}C), δ/ppm: 2.240–2.326 (s, 12H, 4 -CH_3 of pz), 3.142–3.174 (t, J = 6.4 Hz, 2H, –NH–CH_2–CH_2 of ethylene), 3.376–3.392 (t, J = 6.4 Hz, 2H, –NH–CH_2–CH_2 of ethylene), 4.2 (s, 2H, N–CH_2–N), 4.921 (s, 2H, N–CH_2–N), 5.843 (s, 1H, pz ring), 5.853 (s, 1H, pz ring), 6.517 (d, 2H, J = 7.6 Hz, phenyl ring), 6.723 (t, 1H, J = 7.2 Hz, phenyl ring), 7.213–7.256 (m, 2H, phenyl ring).

4(A).2.3. Syntheses of Complexes

Caution! Metal complexes with perchlorate ion are potentially explosive and should be synthesized in small quantities and handled with care.

4(A).2.3.1. $[Cu(bdpab)(\mu\text{-}_{1,5}dca)]_2(ClO_4)_2$ (1)

A methanol solution (10ml) of copper perchlorate hexahydrate (0.057g, 0.25 mmol) was added to the methanol solution (10ml) of ligand bdpab (0.088 g, 0.25 mmol) and the light green color solution was stirred at room temperature for 10 min. A solution of dca (0.022 g, 0.25mmol) n methanol (10 ml) was added to the solution and the dark green solution was stirred for additional 4 hours. Filtered the solution and the filtrate was kept for slow evaporation at room temperature. Green crystals were obtained after five days, washed with methanol and dried at room temperature.

Yield. 0.112g (77%). Found C = 45.14, H = 4.72, N = 21.49%. Elemental analysis calc. for $C_{44}H_{56}Cu_2N_{18}Cl_2O_8$: C= 45.44, H = 4.82, N = 21.69%. IR(KBr pellet)cm^{-1}: ν(N-H), 3290s; νs (C≡N), 2182; νas(C≡N), 2241s; νs+νas(C≡N), 2308s; ν(C=C), 1600s; ν(C=C)+ν(C=N)/pz ring, 1554s, 1472s; ν(ClO_4^-), 1093br; δ(O-Cl-O), 623s. λ_{max}/nm (ε_{max}/ $mol^{-1}cm^{-1}$). 671(143), 362(1190). Λ_M ($\Omega^{-1}cm^2\,mol^{-1}$) = 120. μ_{eff} = 1.76 BM.

4(A).2.3.2. [Co(bdpab)(μ-1,5dca)]$_n$(ClO_4)$_n$ (2)

The compound was synthesized by following the same procedure as that of complex **1** except cobalt(II) perchlorate hexahydrate was used in the place of copper(II) perchlorate hexahydrate. Yield.0.102g (71%). Found C = 45.46, H = 4.78, N = 21.54%, Elemental analysis calc. for $C_{22}H_{28}CoN_9ClO_4$: C = 45.76, H = 4.86, N = 21.84%. IR (KBr pellet)cm^{-1}: ν(N-H), 3264s; νs(C≡N), 2208s, νas(C≡N), 2259s and νs+νas(C≡N), 2322s; ν(C=C), 1602s; ν(C=C)+ν(C=N)/pz ring,1555s, 1493s; ν(ClO_4^-), 1089br; δ(O-Cl-O),624s. λ_{max}/nm (ε_{max}/ $mol^{-1}cm^{-1}$). 495(41), 290(751). μ_{eff} = 3.90 BM.

4(A).2.3.3. [Ni(bdpab)(μ-$_{1,5}$ dca)]$_n$(ClO_4)$_n$ (3)

The compound was synthesized by following the same procedure as that of complex **1** except nickel(II) perchlorate hexahydrate was used in the place of copper(II) perchlorate hexahydrate. Yield. 0.102g(70%). Found C = 45.46, H = 4.58, N = 21.54%, Anal calc for $C_{22}H_{28}NiN_9ClO_4$: C = 45.89 H = 4.69, N = 21.90%. IR (KBr pellet) cm^{-1}: ν(N-H), 3267s; νs(C≡N), 2214s, νas(C≡N), 2266s and νs+νas(C≡N), 2323; ν(C=C), 1601s; ν(C=C)+ ν(C=N)/pz ring, 1556s, 1493 s; ν(ClO_4^-), 1092br ; δ(O-Cl-O), 622s. λ_{max}/nm (ε_{max}/$mol^{-1}cm^{-1}$). 574(35), 345(600). μ_{eff} = 2.79 BM.

4(A).2.3.4. [Cd(bdpab)(μ-$_{1,5}$dca)]$_n$(ClO_4)$_n$ (4)

The compound was synthesized by following the same procedure as that of complex **1** except cadmium (II) perchlorate hexahydrate was used in the place of copper (II) perchlorate hexahydrate

Yield. 0.120g (77%). Found C = 41.71, H = 4.34, N =19.80%, Elemental analysis calc. for $C_{22}H_{27}CdN_9ClO_4$: C = 41.91, H = 4.44, N = 20.00%, IR (KBr pellet) cm^{-1}: ν(N-H), 3270s; νs(C≡N), 2160s; νas(C≡N), 2236s and νs+νas(C≡N), 2317s; ν(C=C), 1601; ν(C=C)+ν(C=N)/pz ring, 1552,1490; ν(ClO_4^-) 1078br; δ(O-Cl-O),644s. λ_{max}/nm (ε_{max}/$mol^{-1}cm^{-1}$). 362(1190).

4(A).2.4. Physical Measurements

Room temperature magnetic susceptibilities of powder samples were measured using Guoy balance. The IR spectra were recorded on Bruker Alpha FT-IR spectrometer using KBr pellet. UV-Vis. spectra (900 - 190 nm) were recorded on a JASCO V-730 spectrophotometer in acetonitrile solution. The micro analysis (C, H and N) was carried out using a Perkin-Elmer IA 2400 series elemental analyzer. Solution conductivity were measured in acetonitrile solution using Equip-Tronics conductivity meter (model no. EQ-660A).

4(A).3. X-ray Crystallography

The X-ray single crystal data of compounds **1**, **2** and **4** were collected on Oxford X-CALIBUR-S diffractometer equipped with CCD detector. The details of crystallographic data collection and some important features of the structure refinements are given in [Table 4(A).1]. The intensities were collected with Mo Kα radiation (λ= 0.71073 Å) at 293 K for the compounds. The data interpretations were processed with CrysAlisPro, Agilent Technologies, Version 1.171.35.19 [32]. Absorption corrections were applied based on multi-scan method [33]. The structures were solved by direct methods and refined by the full-matrix least-square method based on F^2 technique using SHELXL-97 program package [34]. All calculations were carried out using WinGX system Ver-1.64 crystallographic software [35]. All non-hydrogen atoms were refined anisotropically. The position hydrogen atoms were fixed geometrically and were included on calculated positions.

4(A).4. Results and discussion

4(A).4.1. Syntheses

The compounds $[Cu(bdpab)(\mu\text{-}_{1,5}dca)]_2(ClO_4)_2$ and $[M(bdpab)(\mu\text{-}_{1,5}dca)]_n(ClO_4)_n$ [M = Co(II), Ni(II) and Cd(II)] were synthesized with high yield (>70%) by mixing methanol solution of metal perchlorate, the ligand bdpap and bridging ligand dca in 1:1:1 mole ratio according to [scheme- 4(A). 1].

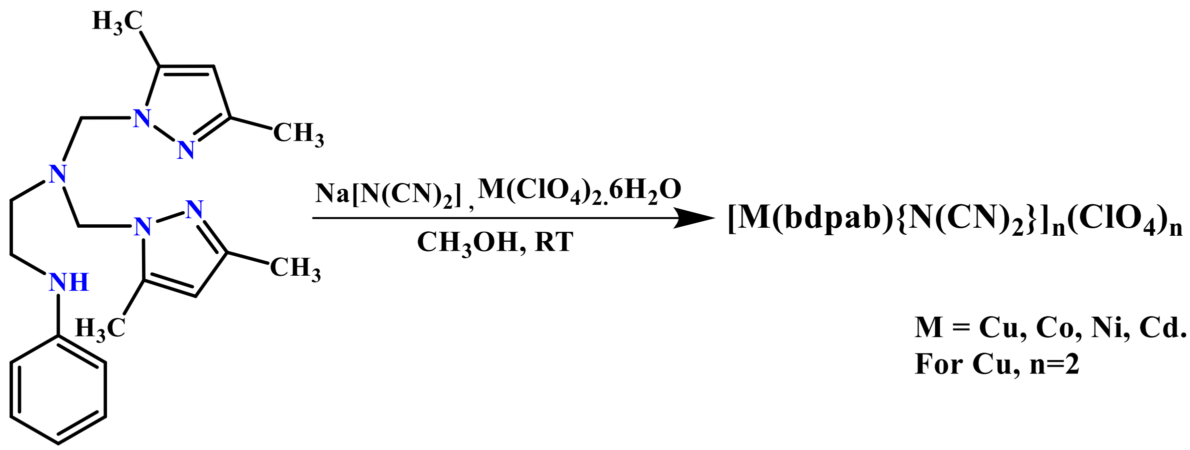
The complexes were characterized by microanalyses, spectral data and single crystal X-ray diffraction study. Molar conductivity data of copper(II) complex in CH_3CN (10^{-3}M) shows the compounds has 1:1 molar conductivity indicating it is ionic in nature. IR spectral data of all compounds exhibit one broad band at ~ 1100 cm^{-1} indicating the presence of ClO_4^-

Table: 4(A).1 Crystallographic data of complexes 1, 3 and 4

	[Cu(bdpab)(μ-$_{1,5}$ dca)]$_2$(ClO$_4$)$_2$	**[Co(bdpab)(μ-$_{1,5}$ dca)]$_n$(ClO$_4$)$_n$**	**[Cd(bdpab)(μ-$_{1,5}$ dca)]$_n$(ClO$_4$)$_n$**
Empirical formula	$C_{44}H_{54}Cl_2Cu_2N_{18}O_8$	$C_{22}H_{27}ClCoN_9O_4$	$C_{22}H_{27}CdClN_9O_4$
Formula weight	1161.03	575.90	629.37
Temperature/K	293	293	293
Crystal system	Triclinic	monoclinic	Monoclinic
Space group	P-1	P2$_1$/n	P 21/n
a/Å	9.0420(11)	16.1588(14)	8.9967
b/Å	16.7940(15)	8.7365(9)	29.256
c/Å	17.9173(13)	19.347(3)	10.1447
α/°	99.005(7)	90	90
β/°	90.932(8)	99.649(10)	91.274
γ/°	103.528(9)	90	90
Volume/Å^3	2608.7(4)	2692.7(5)	2669.5
Z	2	4	4
ρ_{calc}g/cm^3	1.478	1.4205	1.566
μ/mm^{-1}	0.987	0.782	0.964
F(000)	1200.0	1194.4	1276
Crystal size/mm^3	0.8 × 0.6 × 0.2	0.2 × 0.18 × 0.15	0.30 × 0.29 × 0.25

Radiation	MoKα (λ = 0.71073)	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)
Θ range for data collection/°	5.9 to 61	5.88 to 58.12	6.28 to 57.8
Index ranges	-11 ≤ h ≤ 11, -22 ≤ k ≤ 22, -23 ≤ l ≤ 23	-21 ≤ h ≤ 20, -11 ≤ k ≤ 10, -20 ≤ l ≤ 26	-10 ≤ h ≤ 10, -34 ≤ k ≤ 34, -12≤ l ≤ 12
Reflections collected	23637	13778	19057
Independent reflections	12022 [R_{int} = 0.0654, R_{sigma} = 0.1303]	6176 [R_{int} = 0.0523, R_{sigma} = 0.0733]	4698[R_{int} = 0.0465, R_{sigma} = 0.0539]
Data/restraints/parameters	12022/0/669	6176/0/338	4698/0/338
Goodness-of-fit on F^2	1.020	1.054	1.308
Final R indexes [I>=2σ (I)]	R_1 = 0.0769, wR_2 = 0.1860	R_1 = 0.0974, wR_2 = 0.2725	R_1 =0.0810, wR_2= 0.1398
Final R indexes [all data]	R_1 = 0.1628, wR_2 = 0.2413	R_1 = 0.1610, wR_2 = 0.3442	R_1=0.0910, wR_2 = 0.1439
Largest diff. peak/hole / e Å^{-3}	0.89/-0.50	1.51/-1.07	0.743/-2.508
CCDC number	1948076	1948110	1948111

ion outside the coordination sphere and this was confirmed by single crystal X-ray diffraction studies. All the complexes are soluble in acetonitrile, DMF but insoluble in methanol, ethanol and dichloromethane etc.



Scheme – 4(A).1. Syntheses of complexes.

4(A).4.2. Spectral Data

4(A).4.2.1. IR spectral Data

IR spectra of all the complexes exhibit one weak band in the region of 3260 cm^{-1} due to ν(N-H), a sharp intense band at ~ 1583 cm^{-1} assigned as ν(C=C) of phenyl ring, at ~ 1553 and ~ 1467 cm^{-1} due to vibration of ν(C=N) + ν(C=C) of the pyrazole ring of the ligand indicating the coordination of ligand with metal in the complexes. All the complexes exhibited series of strong bands in the region of 2160 to 2223 cm^{-1} - one strong band at less than 2215 cm^{-1} is due to νs(C≡N) and two strong bands in the range of 2236 – 2266 cm^{-1} and 2308-2323 cm^{-1} due to νas(C≡N) and νs+νas (C≡N), respectively of bridging dca ligand in the complexes[36,37]. All the complexes also exhibited one broad band at ~1090 cm^{-1} due to the ν_{asym}(Cl-O) and a weak band at ~624 cm^{-1} due to the δ(O-Cl-O), confirming the presence of the perchlorate ion outside the coordination sphere in the complexes.

4(A).4.2.2. Electronic Spectra and Magnetic Properties

Electronic spectral data of the complexes were recorded on CH_3CN solution (~10^{-3}M) and spectral band appearing below 400nm are due to intra-ligand charge transfer transition. All the complexes show d-d transition in the region of 671nm (complex **1**), 500nm (complex **2**) and 574 nm (complex **3**).

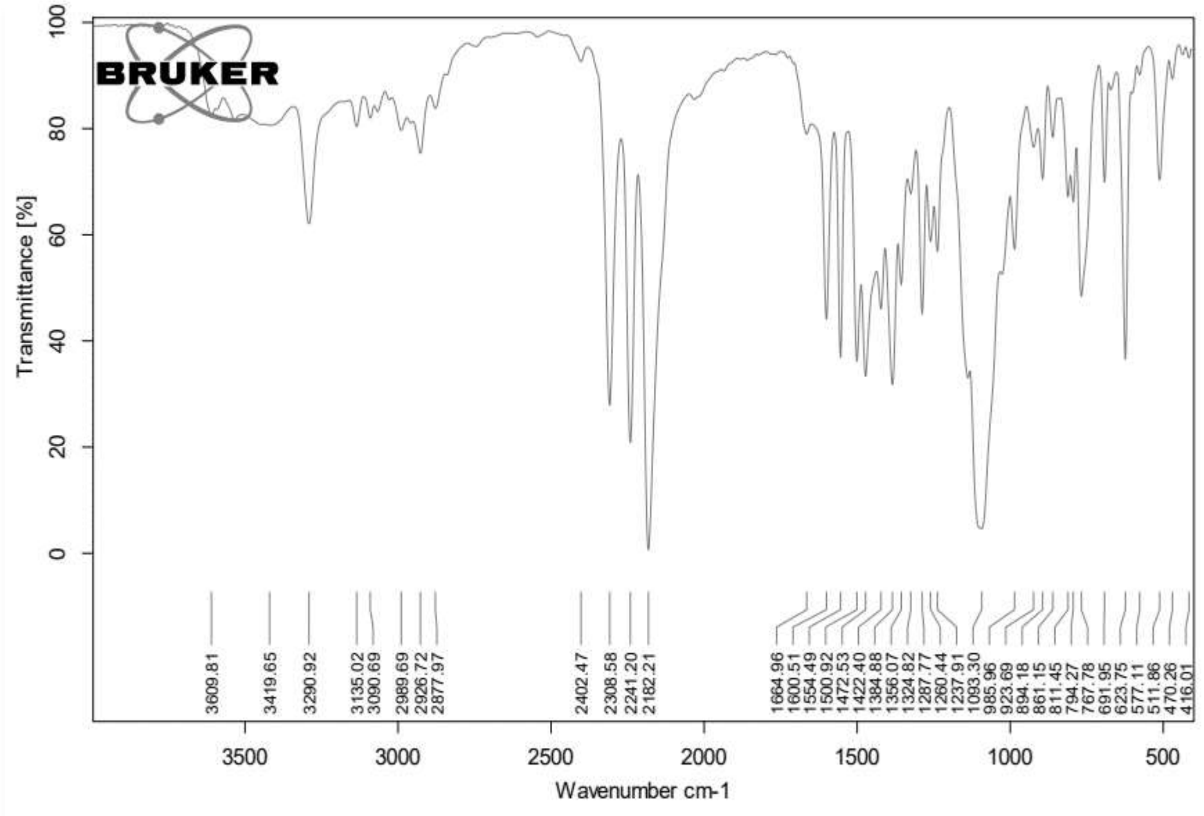


Figure. 4(A).1. IR spectrum of [Cu(bdpab)(μ-$_{1,5}$dca)]$_2$(ClO$_4$)$_2$

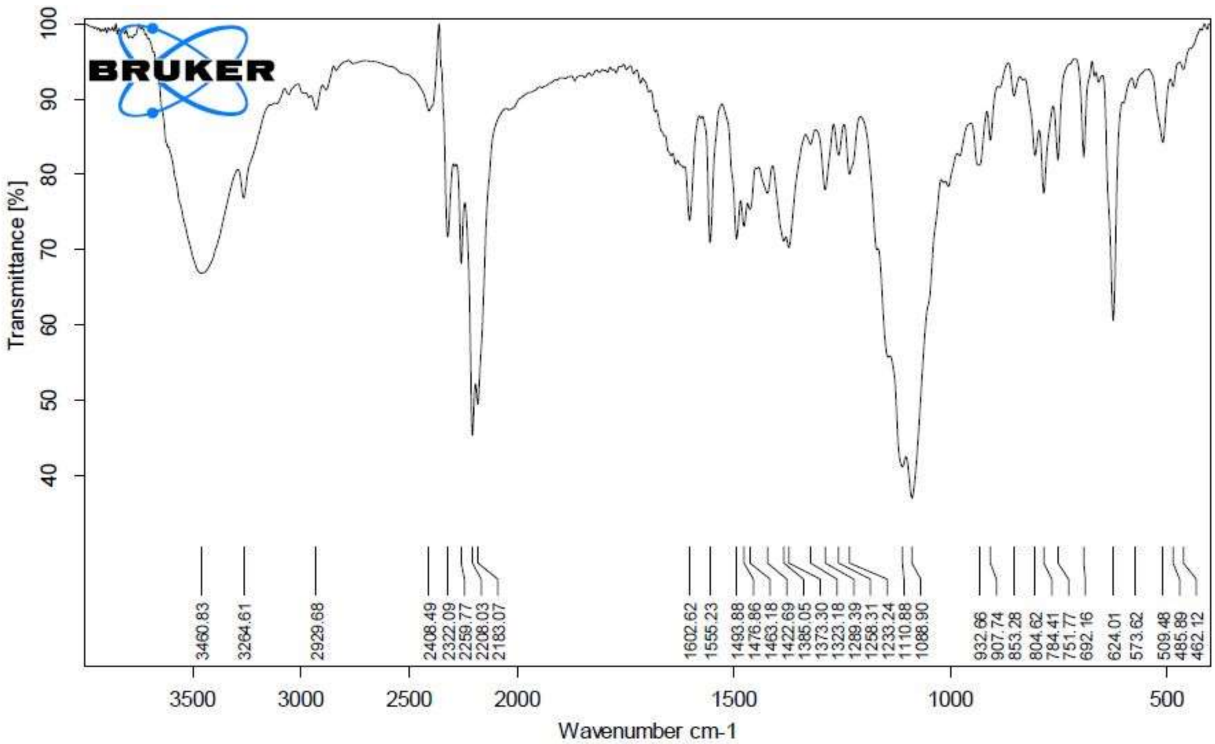


Figure. 4(A).2. IR spectrum of [Co(bdpab)(μ-1,5dca)]$_n$(ClO$_4$)$_n$

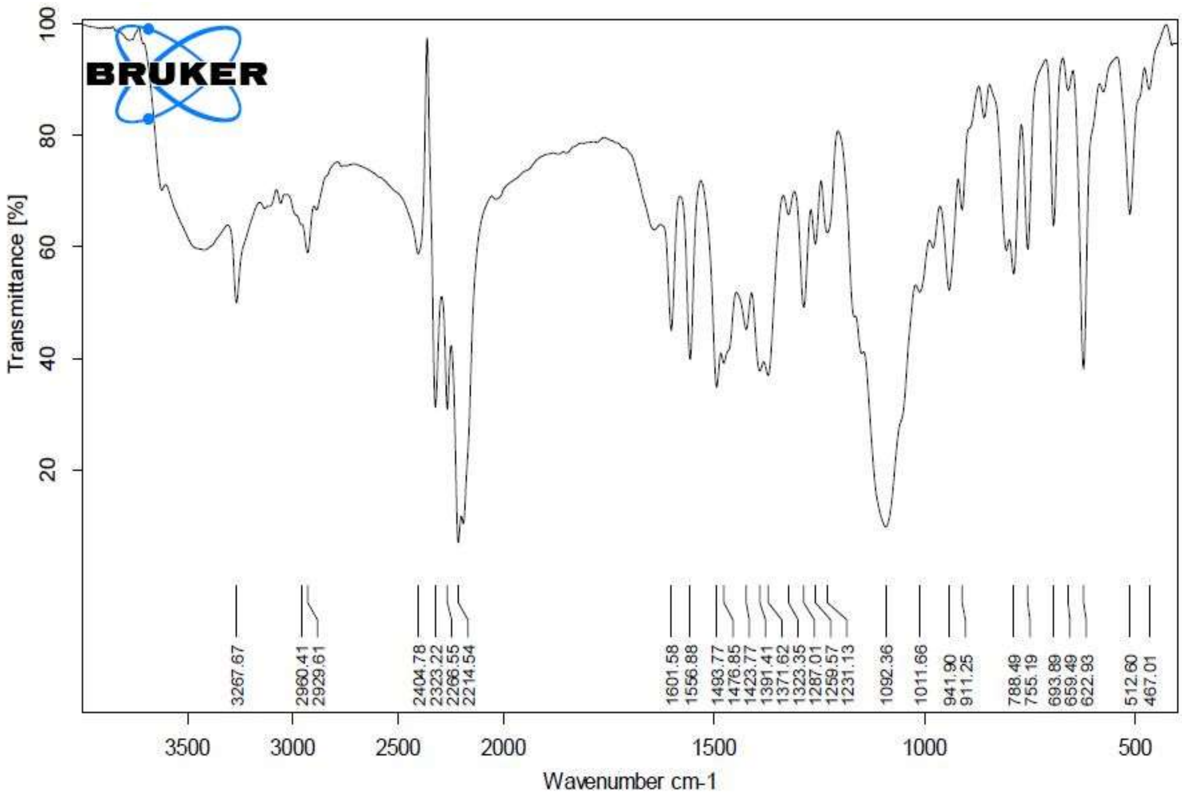


Figure. 4(A).3. IR spectrum of [Ni(bdpab)(μ-$_{1,5}$dca)]$_n$(ClO$_4$)$_n$

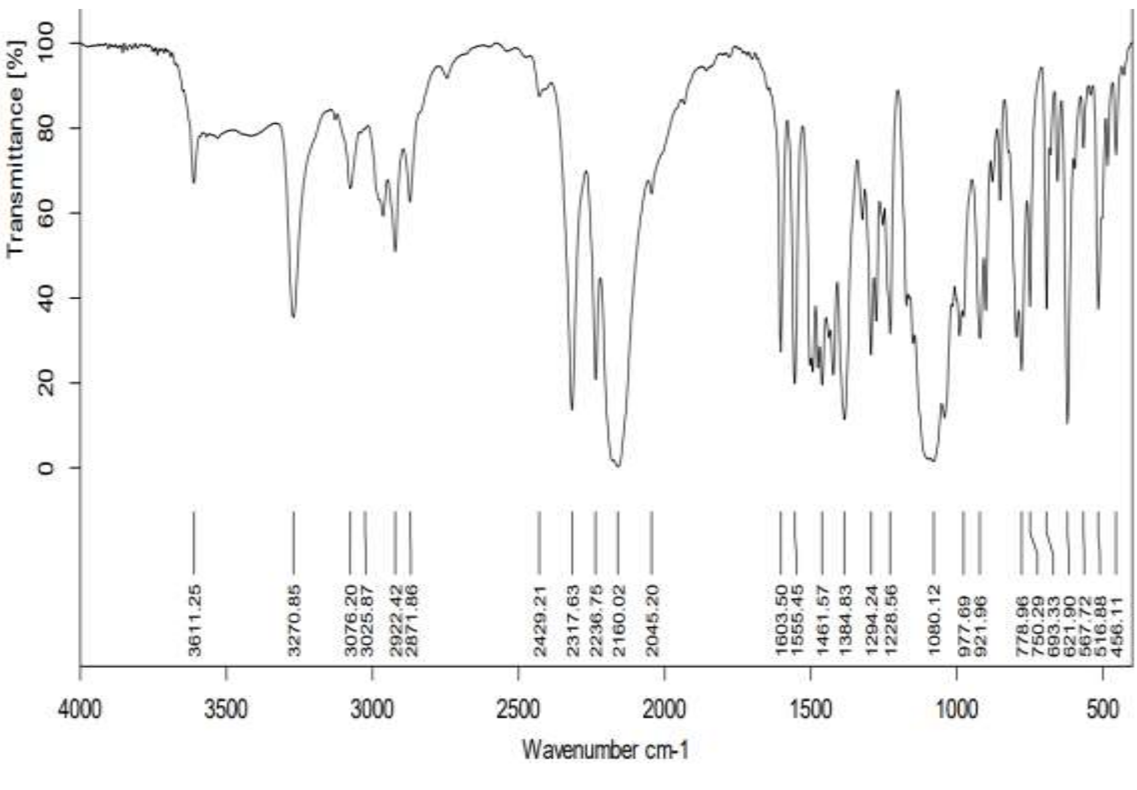


Figure. 4(A).4. IR spectrum of [Cd(bdpab)(μ-$_{1,5}$dca)]$_n$(ClO$_4$)$_n$

Powder sample magnetic susceptibility measurements at room temperature shows μ_{eff} is 1.80 BM for compound **1**, 3.90 BM for compound **2** and 2.80 BM for compound **3** indicating one, three and two electrons paramagnetism of the complexes **1**, **2** and **3** respectively. It is reported that dca bridged polynuclear Cu(II) complex show very weak or almost zero interaction due to very long Cu—Cu distance [16]. Since M-M distances are quite high (>6.0 Å) in the above complexes, variable temperature magnetic study of the complexes have not been carried out.

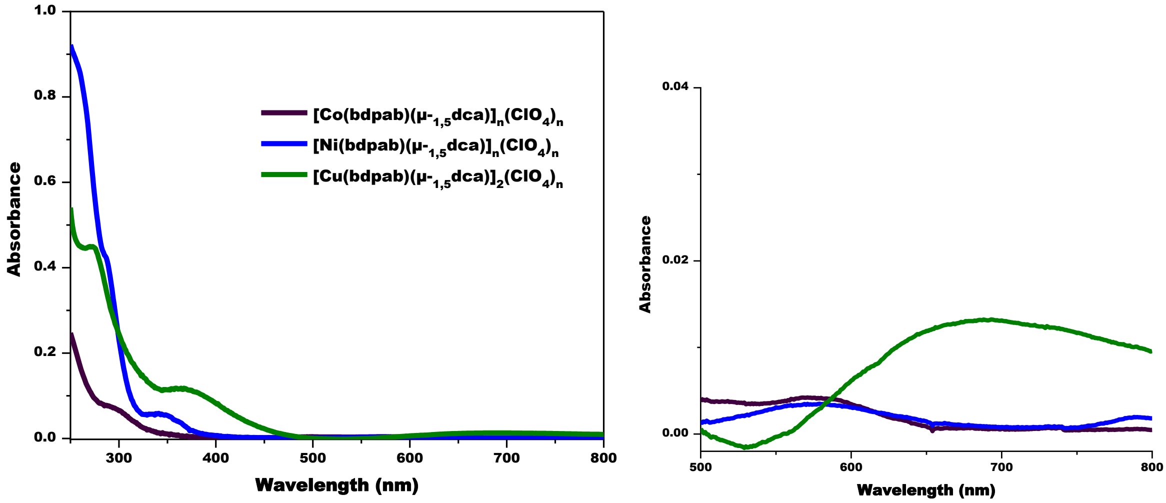


Figure. 4(A).5. Electronic spectra of the Cu(II), Co(II) and Ni(II) complexes.

4(A).4.3. Descriptions of crystal structures

4(A).4.3.1. Crystal structure of $[Cu(bdpab)(\mu\text{-}_{1,5}\,dca)]_2(ClO_4)_2$ (1)

The ORTEP diagram with atom numbering schemes of the complex **1** is shown in the [Fig. 4(A).6]. Details of crystallographic data collection are given in the Table 4(A).1 and the selected bond lengths and bond angles related to the metal coordination sphere for the structure is given in the Table 4(A).2 and 3. Structural data shows that copper compound is binuclear and two copper centres are bridged by two μ-1,5 dca ligands. Each copper centre has CuN_6 coordination environment with distorted octahedral geometry and each copper atom is coordinated by six nitrogen donor atoms four nitrogen atoms from the tetradentate N_4-

coordinate bdpab ligand and two positions were occupied by two nitrogen atoms of two bridging dca ligand.

The equatorial bond distances around Cu(1) centre Cu(1)-N(40) (2.392 Å), Cu(1)-N(43) (2.073 Å), Cu(1)-N(64)(1.926 Å) and Cu(1)-N(65) (2.767 Å) are not equal but the two axial bond distances Cu(1)-N(57) (1.985 Å) and Cu(1)-N(50) (1.972 Å) are nearly equal. The axial bond angle N(50)- Cu(1)-N(57) is not linear (103.38^{o}). The two copper atoms are joined by two µ-1,5 dca anions forming twelve membered ring in a chair form [Cu(1)-N(65)-C(66)-N(67)- C(68)-N(69)-Cu(2)-N(60)-C(61)-N(62)-C(63)-N(64)] and two Cu-NCNCN-Cu linkage is not linear due to sp2 hybridization of N(67) and N(62) atoms [bond angles C(61)-N(62)-C(63) (120^{0}) and C(68)-N(67)-C(66)(127.9^{0})]. The distances between Cu…Cu is 6.731 Å which is shorter than single µ-1,5 dca bridged polynuclear copper(II) compound with pyrazolyl containing N3-donor ligand [16]. Two phenyl groups are in anti-position in two copper centres. The unsymmetrical bond angles and bond lengths produce distortion in the molecule.

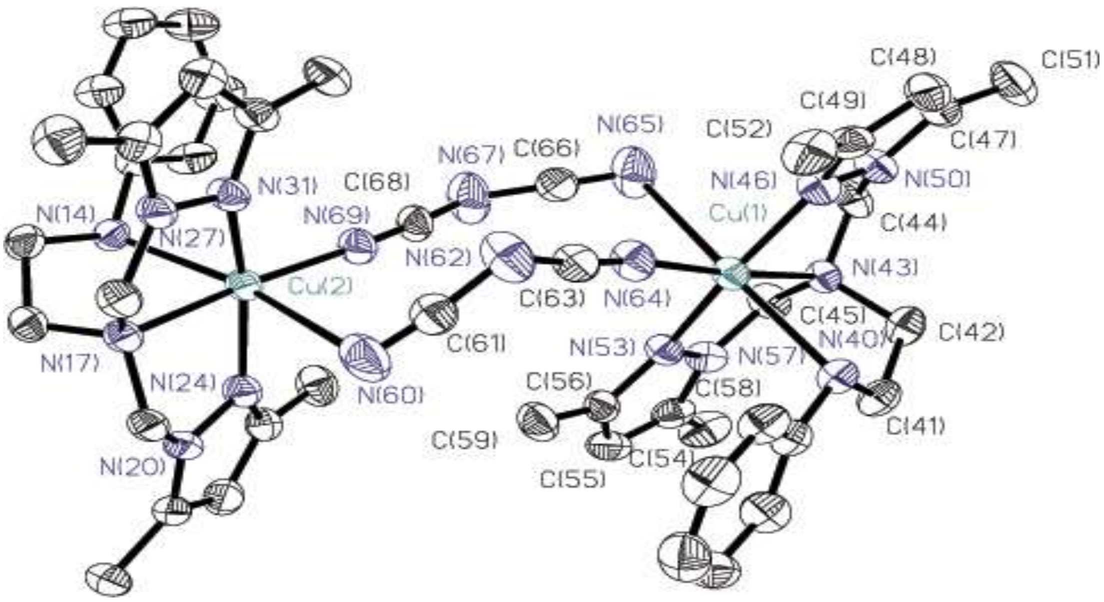
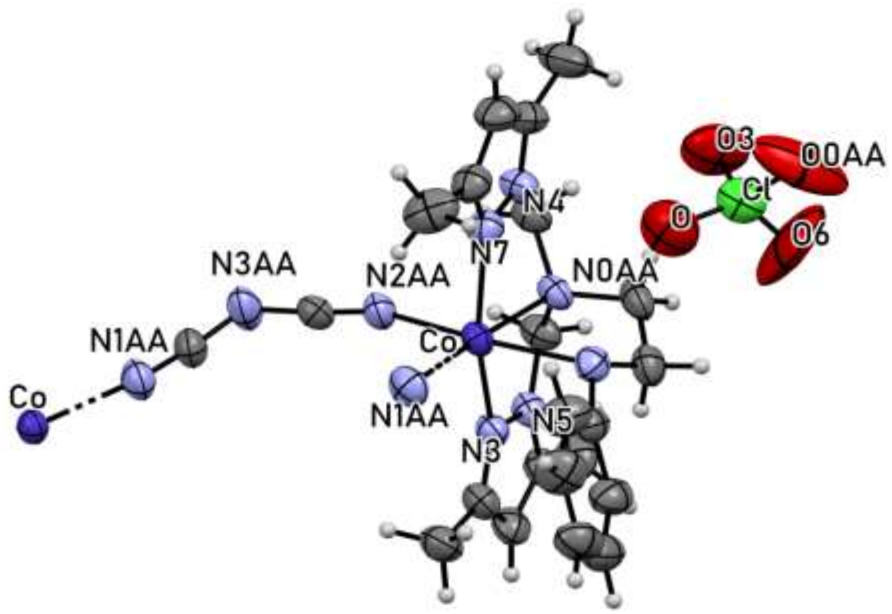


Figure. 4(A).6. ORTEP diagram of the [Cu(bdpab)(µ-$_{1,5}$ dca)]$_2$(ClO$_4$)$_2$ with atom numbering scheme. Perchlorate atoms and hydrogen atoms are omitted for clarity**.**

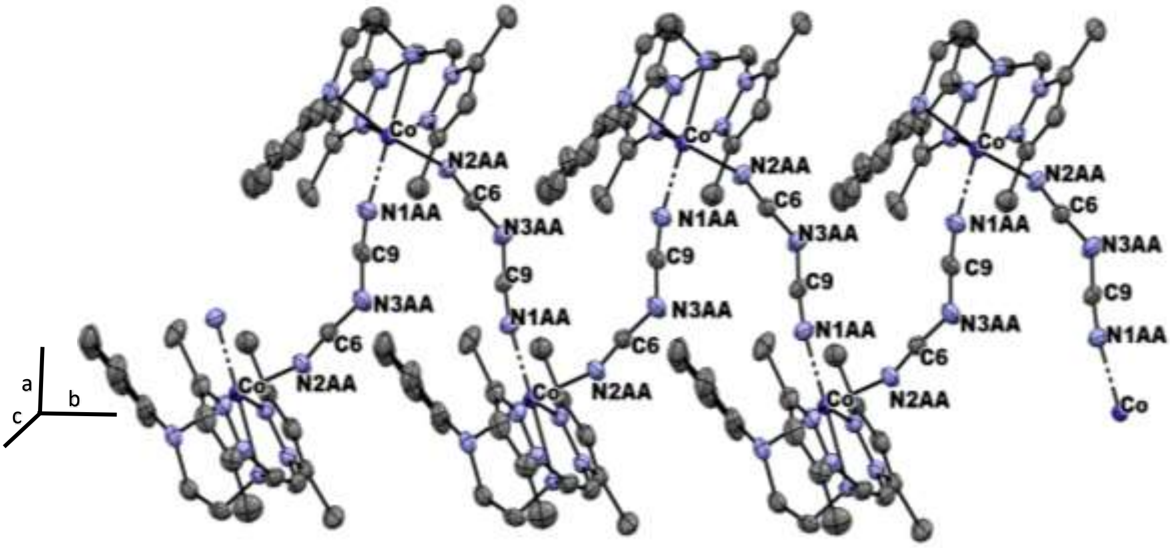
4(A).4.3.2. Crystal Structures of [Co(bdpab)(μ-$_{1,5}$dca)]$_n$(ClO_4)$_n$ and [Cd(bdpab)(μ-$_{1,5}$ dca)]$_n$(ClO_4)$_n$

The structures of both the complexes **2** and **4** are identical and ORTEP diagrams with atom numbering schemes of the complexes are shown in Fig 4(A).7 and Fig 4(A).8 respectively. In each complex, the metal atom has octahedral geometry and is bonded to the four nitrogen atoms of bdpab ligand with two nitrogen atoms from two bridging dca ligands. The bond M-NCNCN-M is not linear like copper(II) complex and the tetradentate ligand bdpab is acting as blocking ligand.

The asymmetric unit of complex **4** [Fig 4(A).8a] shows the equatorial positions of the complex is occupied by the N(1), N(6) atoms of the ligand bdpab and N(7) and N(9) atoms of two bridging dca co-ligand whereas the axial positions are occupied by N(3) and N(5) atom of the ligand bdpab. The cadmium center is distorted octahedral as the equatorial bond lengths Cd-N(1)(2.452 Å), Cd-N(6)(2.460Å), Cd-N(7)(2.213 Å) and Cd-N(9)(2.325 Å) are different from axial bond lengths Cd-N(3)(2.323 Å), Cd-N(5)(2.338 Å) and the axial bond angel N(6)-Cd-N(7) is not linear(163.40^0). Simillar distortions of equatorial and axial bond lengths were observed in cobalt complex **2**. The bond lengths of bridging $N(CN)_2^-$ between two cadmium centres are Cd(2)-N(22) (2.212 Å), N(11)-C(10) (1.133 Å), C(10)-N(9) (1.282 Å), N(9)-C(8) (1.295 Å), C(8)-N(7) (1.151Å), N(7)-Cd(1) (2.327Å) and the distance between the two cadmium centers Cd----Cd is 8.307Å [Fig 4(A).8b].



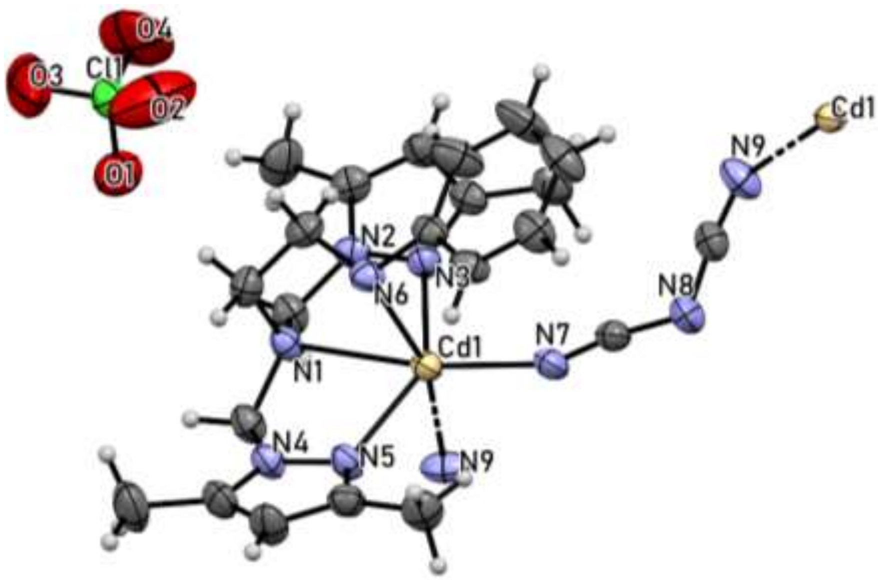
(a)



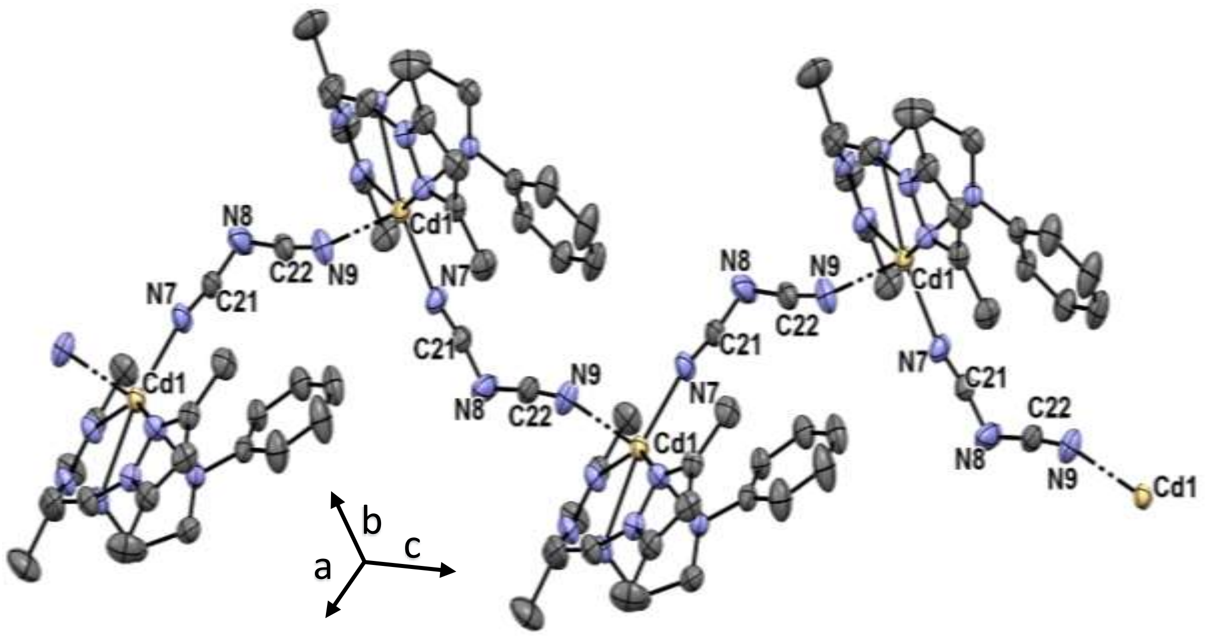
(b)

Figure. 4(A).7. (a). ORTEP diagram of the asymmetric unit of $[Co(bdpab)(\mu\text{-}_{1,5}dca)]_n(ClO_4)_n$ complex with atom numbering scheme. (**b).** ORTEP diagram of the polymeric unit of $[Co(bdpab)(\mu\text{-}1,5dca)]_n(ClO_4)_n$ complex with atom numbering scheme. Hydrogen atoms and perchlorate ions are omitted for clarity

Each asymmetric unit contains one non-coordinate ClO_4^- ion in the coordination sphere of both the complexes. Oxygen atoms of the ClO_4^- ion has short interaction with H-atom of the methyl group of 3,5-dimethy pyrazole, two short interaction with two oxygen atoms of ClO_4^- ion with two different pyrazole groups of the bdpab ligand and another one oxygen atom of ClO_4^- has short interaction with H atom of another methyl group of nearest pyrazole group



(a)



(b)

Figure. 4(A).8. (a). ORTEP diagram of the asymmetric unit of [Cd(bdpab)(μ-1,5 dca)]n(ClO4)n complex with atom numbering scheme. (**b).** ORTEP diagram of the polymeric unit of [Cd(bdpab)(μ-1,5dca)]n(ClO4)n complex with atom numbering scheme. Perchlorate and hydrogen atoms are omitted for clarity.

Table: 4(A).2 Bond lengths (A°) of complexes 1, 3 and 4.

[Cu(bdpab)(μ-$_{1,5}$dca)]$_2$(ClO$_4$)$_2$		**[Co(bdpab)(μ-$_{1,5}$dca)]$_n$(ClO$_4$)$_n$**		**[Cd(bdpab)(μ-$_{1,5}$dca)]$_n$(ClO$_4$)$_n$**	
Cu(1)-N(57)	2.790	Co-N(3)	2 .129	Cd(1)-N(7)	2.213(7)
Cu(1)-N(40)	2.392	Co-N(7)	2.117	Cd(1)-N(3)	2.323(6)
Cu(1)-N(64)	1.926	Co-N	2.252	Cd(1)-N(9)	2.325(7)
Cu(1)-N(43)	2.073	Co-N(0AA)	2.182	Cd(1)-N(5)	2.338(6)
Cu(1)-N(50)	1.972	Co-N(1AA)	2.031	Cd(1)- N(1)	2.452(6)
Cu(1)-N(65)	2.767	Co-N(2AA)	2.109	Cd(1)-N(6)	2.460(6)
Cu(2)-N(31)	1.986				
Cu(2)-N(17)	2.082				
Cu(2)-N(24)	1.985				
Cu(2)-N(69)	1.944				
Cu(2)-N(14)	2.372				
Cu(2)-N(60)	2.980				

Table : 4(A).3 Bond angles(º) of the complexes 1, 3 and 4.

$[Cu(bdpab)(\mu\text{-}_{1,5}dca)]_2(ClO_4)_2$		$[Co(bdpab)(\mu\text{-}_{1,5}dca)]_n(ClO_4)_n$		$[Cd(bdpab)(\mu\text{-}_{1,5}dca)]_n(ClO_4)_n$	
N(57)-Cu(1)-N(40)	88.63	N(7)-Co-N(3)	156.8	N(7)-Cd(1)-N(3)	103.9
N(57)-Cu(1)-N(43)	82.14	N-Co-N(3)	89.8	N(7)-Cd(1)-N(9)	97.4
N(64)-Cu(1)-N(57)	99.1	N-Co-N(7)	90.8	N(3)-Cd(1)-N(9)	95.4
N(64)-Cu(1)-N(40)	104.2	N(0AA)-Co-N(3)	78.86	N(7)-Cd(1)-N(5)	112.0
N(64)-Cu(1)-N(43)	174.4	N(0AA)-Co-N(7)	78.4	N(3)-Cd(1)- N(5)	143.9
N(64)-Cu(1)-N(50)	97.1	N(0AA)-Co-N	80.3	N(9)-Cd(1)-N(5)	84.0
N(43)-Cu(1)-N(40)	81.26	N(1AA)-Co-N(3)	99.1	N(7)-Cd(1)-N(1)	169.3
N(50)-Cu(1)-N(57)	162.2	N(1AA)-Co-N(7)	103.8	N(3)-Cd(1)-N(1)	71.9
N(50)-Cu(1)-N(40)	94.6	N(1AA)-Co-N(0AA)	177.1	N(9)-Cd(1)-N(1)	92.8
N(50)-Cu(1)-N(43)	81.1	N(2AA)-Co-N(3)	87.2	N(5)-Cd(1)-N(1)	72.1
N(31)-Cu(2)-N(17)	81.92	N(1AA)-Co-N	97.6	N(7)-Cd(1)-N(6)	97.1

N(31)-Cu(2)-N(24)	160.9	N(2AA)-Co-N(7)	88.9	N(3)-Cd(1)-N(6)	89.2
N(31)-Cu(2)-N(14)	90.78	N(2AA)-Co-N	171.8	N(9)-Cd(1)-N(6)	163.3
N(17)-Cu(2)-N(14)	81.54	N(2AA)-Co-N(0AA)	91.6	N(5)-Cd(1)-N(6)	83.0
N(24)-Cu(2)-N(17)	81.40	N(2AA)-Co-N(1AA)	90.4	N(1)-Cd(1)-N(6	73.4
N(24)-Cu(2)-N(14)	95.96	N(5)-N3-Co	110.7		
N(69)-Cu(2)-N(17)	175.0				
N(69)-Cu(2)-N(24)	96.9				
N(69)-Cu(2)-N(14)	103.33				

4(A).5. Conclusion

In this chapter, we have reported synthesis and characterization of four multinuclear complexes of Cu(II), Co(II), Cd(II) and Ni(II) of the type $[M(bdpab)(\mu\text{-}_{1,5}\ dca)]_n(ClO_4)_n$ [n =2 for Cu(II)] by the condensation of tetradentate N_4-coordinate ligand bdpab and metal perchlorate hexahydrate in presence of bridging co-ligand dca. Crystal structures of three complexes have been solved by the single crystal X-ray diffraction studies and it shows that copper(II) complex is binuclear with double $\mu\text{-}_{1,5}$ dca bridged between the two copper centres whereas Co(II) and Cd(II) complexes are polynuclear and two metal centres are bridged by one $\mu\text{-}_{1,5}$ dca ligand and all the metal atoms have octahedral geometry.

4(A).6. References

1. S. Mukherjee, P.S. Mukherjee. Dalton Trans. 42 (2013) 4019.
2. H. Yue-Qiao, Z. Ming-Hua, Z. Kun, H. Sheng, Z. Fu-Fang, M. Kurmoo. J. Am. Chem. Soc. 135 (2013) 7901.
3. S.S. Massoud, F.A. Mautner, R. Vicente, A.A. Gallo, E. Ducasse. Eur. J. Inorg. Chem. (2007) 1091.

4 V. Tangoulis, D. Pangoulish, C.P. Raptopoulou, C. Dendrinou-Samara. Dalton Trans. (2008) 1752.

5 M.A.M. Abu-Youssef, A. Escuer, F.A. Mautner, L. Ohrstrom. Dalton Trans. (2008) 3553.

6. B. Machura, A. Switlicka, J. Mrozinski, B. Kalinska, R. Kruszynski. Polyhedron 52 (2013) 1276.
7. A.A. Khandar, V.T. Yilmaz, F. Costantino, S. Gumus, S.A. Hosseini-Yazdi, G.Mahmoudi. Inorg. Chim. Acta 394 (2013) 36.
8. P. Dhal, M. Nandy, D. Sadhukhan, E. Zangrando, G. Pilet, C.J. Gomez-Garciad, S. Mitra. Dalton Trans. 42 (2013) 14545.
9. A. D. Khalaji, M. Weil, H. Hadadzadeh, M. Daryanavard. Inorg. Chim. Acta 362 (2009) 4837.

10 S. Das, K. Bhar, S. Chattopadhyay, P. Mitra, V.J. Smith, L.J. Barbour, B.K. Ghosh. Polyhedron 38 (2012) 26.

11 M. H. Sadhu, A. Solanki, T. Kundu, V. Hingu, B. Ganguli, S. B. Kumar. Polyhedron 133 (2017) 8.

12 J. Carranza, J. Sletten, F. Lloret, M. Julve. J. Mol. Struct. 890 (2008) 31.

13 S. Sasmal, S. Sarkar, N. Aliaga-Alcalde, S. Mohanta. Inorg. Chem. 50 (2011) 5687.

14 S.R. Batten, K.S. Murray. Coord. Chem. Rev. 246 (2003) 103.

15 S. Biswas, C. J. Gomez-García, J. M. Clemente-Juan, S. Benmansour, A. Ghosh. Inorg. Chem. 53 (2014) 2441.

16 S. S. Massoud, M. M. Lemieux, L. L. Quan, R. Vicente, J. H. Albering, F. A. Mautner. Inorg. Chim. Acta 388 (2012) 71.

17 F. A. Mautner, J. H. Albering, M. Mikuriya, S. S. Massoud. Inorg. Chem. Commun. 13 (2010) 796.

18 F.A. Mautner, M. Mikuriya, H. Ishida, H. Sakiyama, F. R. Louka, J.W. Humphrey. S. S. Massoud. Inorg. Chim. Acta 362 (2009) 4073.

19 P. Talukder, S. Shit, A. Sasmal, S. R. Batten, B. Moubaraki, K. S. Murray, S. Mitra. Polyhedron 30 (2011) 1767.

20. D. Mal, C. Adhiary, E. Rentschler, Y. Miyashita, K. I. Okamoto, S. Koner. Polyhedron 26 (2007) 736.

21. G. A. van Albada, M. G. van der Horst, S. J. Teat, P. Gamez, O. Roubeau, I. Mutikainen, U. Turpeinen, J. Reedijk. Polyhedron 28 (2009) 1541.

22 K. S. Banu, S. Mondal, A. Guha, S. Das, T. Chattopadhyay, E. Suresh, E. Zangrando, D. Das. Polyhedron 30 (2011) 163.

23. M. Fondo, A. M. García-Deibe, N. Ocampo, R. Vicente, J. Sanmartín, C. Sañudo. Inorg. Chim. Acta 373 (2011) 73.

24. K. Bhar, S. Chattopadhyay, S. Khan, B. K. Kumar, T. K. Maji, J. Ribas, B. K. Ghosh, Inorg. Chim. Acta 370 (2011) 492.

25. A. Solanki, M. Monfort , S. B. Kumar. J. Mol. Struct. 1050 (2013) 197.

26. M. H. Sadhu, S. B. Kumar. Polyhedron 123 (2017) 419.

27. M. H. Sadhu, C. Mathoniere, Y. P. Patil, S. B. Kumar. Polyhedron 122 (2017) 210.

28. M. H. Sadhu, A. Solanki, S. B. Kumar. Polyhedron 100 (2015) 206.

29 M. Zala, S. B. Kumar, E. Suresh, J. Ribas. Transit. Met. Chem. 35 (2010) 757.

30. W.L. Driessen. Recl. Trav. Chim. PaysBas. 101 (1982) 441.

31 M. H. Sadhu, S. B. Kumar, J. K. Saint, S. S. Purani, T. R. Khanna. Inorg. Chim. Acta 466 (2017) 219.

32 Agilent, CrysAlis PRO. Agilent Technologies UK Ltd, Yarnton, England (2011).

33 G.M. Sheldrick, SAINT, 5.1 ed. Siemens Industrial Automation Inc., Madison, WI (1995).

34 G.M. Sheldrick, SHELXL-97: Program for Crystal Structure Refinement, University of Gottingen, Gottingen (1997).

35 L.J. Farrugia, J. Appl. Cryst. 32 (1999) 837.

36. K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds. Part B. Applications in coordination, Organometallic, and Bioinorganic Chemistry, 5th ed., Wiley, New York (1997) 116.

37. H. Kohler, A. Kolbe, G. Lux, Z. Anorg. Allg. Chem. 428 (1977) 103.

CHAPTER-4(B)

Synthesis and Structural Characerization of polymeric Cu(II) complex involing N_2O donor Schiff base ligand and dicyanamide as bridging ligand

Abstract

One new polymeric copper(II) complex $\{[Cu(L2)\{N(CN)_2\}](CH_3CN)\}_n$, where HL2 = {((2- (phenyl amino)ethyl)imino)methyl}phenol and dca = dicyanamide, $\{N(CN)_2^-\}$, has been synthesized and characterized. Single crystal X-ray diffraction studies of the complex shows the complex $\{[Cu(L2)\{N(CN)_2\}](CH_3CN)\}_n$ has 1D polymeric chain, each copper centre has distorted square pyramidal geometry and two copper(II) centres are joined by two nitrile groups of one dicyanamide ligand.

4(B).1. Introduction

Transition metal complexes with tridentate N_2O donor Schiff base ligand have been an interesting area of research in inorganic chemistry. There are many reports on mono- and multinuclear complexes with tridentate N_2O donor Schiff base ligand {((2- (phenylamino) ethyl)imino)methyl}phenol (HL2) e.g. mononuclear complexes of Al(III), Ni(II), Co(III), Zn(II) and dinuclear double end-on azide bridged complex with Cu(II) and polynuclear halide bridged complexes with $CuCl_2$ and $MnCl_2$ salt [1-6]. Like azide, dicyanamide is a large pseudohalide and can acts as monodentate as well as bridging ligand and form mononuclear and polynuclear complexes, respectively. As we are interested in the synthesis and structural characterization of coordination polymer of divalent metal ions using bridging ligand dca in presence of multidentate organic chelating ligand, we have synthesized and characterized few multinuclear coordination complexes with divalent metal ions using blocking organic ligand N, N-bis(3,5–dimethyl-1H–pyrazol–1-yl)methyl-N2–phenylethane-1,2-diamine(bdpab) in presence of bridging ligand dca [7].

Here, we report on the synthesis, characterization with structure of polymeric Cu(II)) complex with the Schiff base ligand {((2- (phenylamino)ethyl)imino)methyl}phenol (HL2) in presence of bridging ligand dca. Structural data shows $\{[Cu(L2)\{N(CN)_2\}](CH_3CN)\}_n$ has polymeric 1D chain structure and each copper centre has distorted square pyramidal geometry and two copper centres are linked by two nitrile groups of the dca.

4(B).2. Experimental

4(B).2.1. Materials

The chemical and solvents were of analytical grade and purchased from commercial source. Salicyldehyde, N, N-diethyl ethylene-diamine (Aldrich) and sodium dicyanamide (Aldrich) were reagent grade and used as received. Copper perchlorate hexahydrate were prepared by the reaction of copper carbonates with dilute $HClO_4$ acid and followed by evaporation of the solution on steam bath.

Caution! Metal complexes with perchlorate ion are potentially explosive and should be synthesized in small quantities and handled with care.

4(B).2.2. Synthesis of Complex

Synthesis of $\{[Cu(L2)\{N(CN)_2\}](CH_3CN)\}_n$

A methanol solution (10ml) of copper(II) perchlorate hexahydrate (0.057g, 0.25 mmol) was added to the methanol solution (10ml) of ligand (HL2) (0.066 g, 0.25 mmol) and the light green color solution was stirred at room temperature for 10 min. A solution of dca (0.022 g, 0.25 mmol) in methanol (10 ml) was added to the solution and the dark green solution was stirred for additional 4 hr. Green solid compound was isolated after slow evaporation of the solution at room temperature. Square shape green crystals were obtained on recrystallization of compound in acetonitrile after five days, washed with methanol and dried at room temperature.

Yield. 0.085g (83%). Found C = 55.92, H = 4.53, N = 20.24 %. Elemental analysis calc. for $C_{19}H_{18}N_6OCu$: C= 55.68, H = 4.40, N = 20.51%. IR (KBr pellet)cm^{-1}: ν(N-H),3089; ν(N-H), 3089; νs(C≡N), 2181, νas(C≡N), 2251 and νs+νas(C≡N), 2307. λ_{max}/nm (ε_{max}/mol^{-1}cm^{-1}). 620(35), 368(280), 314(312), 272(688), 228(1285). Λ_M (Ω^{-1}cm^{2}mol^{-1}) = 10. μeff = 1.76 BM.

4(B).2.3. Physical Measurements

The FT-IR spectra were recorded on a Bruker Alpha spectrometer using KBr pellets. The micro analyses (C, H and N) were carried out using a Thermo finnigan Flash EA 1112 series elemental analyzer. UV-Vis spectra (850 - 190 nm) of the ligand and complexes were recorded on a JASCO V730 in CH_3CN solution (1 x 10^{-3} M). X-band EPR measurements were performed on a JES-FA200 EPR spectrometer in DMSO at liquid nitrogen temperature (77 K). Solution conductivity were measured in acetonitrile solution using Equip-Tronics conductivity meter (model no. EQ660 A). Room temperature magnetic susceptibilities of powder samples were measured using Guoy balance.

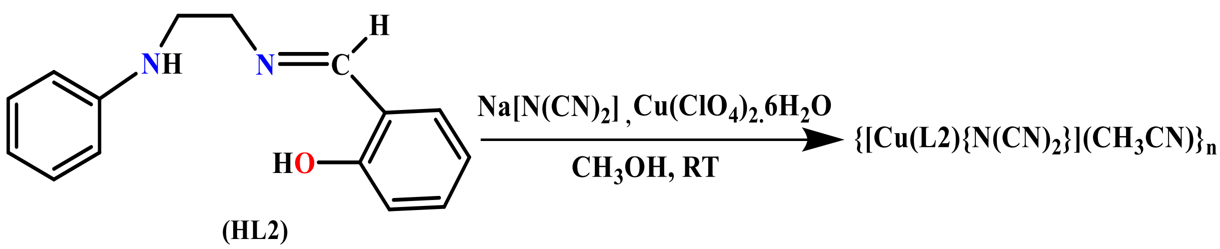
4(B).3. X-ray Crystallography

X-ray single crystal data was collected using an Xtlab Synergy Rigaku Oxford diffraction with HyPix – 3000 detector and graphite monochromator Mo Kα radiation (= 0.71073 A^o) at 293K. The data collection range was from 2.990 to 49.452^0. CrysAlisPro, Xtlab Synergy Rigaku oxford diffraction Version 171.39 was used to process the data interpretations [8,9]. The multi-scan method was used to apply absorption corrections[10]. The structure was solved by direct methods and refined by the full-matrix least-square method based on F^2 technique using SHELXL-97 program package [11]. WinGX system Ver-1.64 crystallographic software used for calculations [12]. All non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms were added to their geometrically ideal position. For generating molecular graphics used ORTEP3 Windows program software [13].

4(B).4. Results and discussion

4(B).4.1. Synthesis

The complex was synthesized by stirring the copper perchlorate hexahydrate, ligand HL2 and bridging ligand dca in 1:1:1 mole ratio at room temperature in methanol [scheme 4(B).1]. There was no change of molecular structure of the complex when excess mole ratio of dca used in the synthesis. Diffraction quality crystal of the complex was obtained during recrystallization by slow evaporation of acetonitrile solution of the complex. The molecular composition of the complex was determined by the IR, molar conductivity measurement and single crystal diffraction studies. Molar conductivity measurement in acetonitrile indicates the complex is nonelectrolyte. Single crystal X-ray diffraction studies showed that the Cu(II) complex is polynuclear and each copper(II) centre has square pyramidal geometry. The complex is soluble in acetonitrile, DMF, DMSO, but insoluble in common organic solvents such as methanol, dichloromethane, etc.



Scheme 4(B). 1. Synthesis of complex

Table 4(B).1 Crystal parameters of Cu(II) complex

	$\{[Cu(L2)\{N(CN)_2\}](CH_3CN)\}_n$
Empirical formula	$C_{38}H_{36}Cu_2N_{12}O_2$
Formula weight	820.87
Temperature/K	300.00
Crystal system	Triclinic
Space group	P-1
a/Å	11.865(10)
b/Å	12.045(6)
c/Å	13.788(12)
α/°	90.411(19)
β/°	98.73(4)
γ/°	98.49(2)
Volume/$Å^3$	1925(3)
Z	2
$\rho_{calc}g/cm^3$	1.416
μ/mm^{-1}	1.155
F(000)	846.0
Crystal size/mm^3	0.3 × 0.2 × 0.2
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.99 to 49.452
Index ranges	$-12\leq h\leq 12$, $-12\leq k\leq 13$, $-14 \leq l \leq 15$
Reflections collected	7119
Independent reflections	4256 [R_{int} = 0.0864, R_{sigma} = 0.1612]
Data/restraints/parameters	4256/0/471
Goodness-of-fit on F^2	1.128
Final R indexes [I>=2σ (I)]	R_1 = 0.1243, wR_2 = 0.3162
Final R indexes [all data]	R_1 = 0.1921, wR_2 = 0.3545
Largest diff. peak/hole / e $Å^{-3}$	2.75/-0.83
CCDC number	2167123

4(B).4.2. Spectral Data

4(B).4.2.1. IR spectral data

The IR spectrum of the complex was assigned with respect to IR spectrum of the free ligand HL2 in order to determine the coordination of ligand to the metal centres. One strong absorption bands exhibited at 1637 cm^{-1} in the complex but the band is shifted to higher wave numbers in the range of 5-10 cm^{-1} in the complex in comparison to ligand which may be attributed to the coordination of the imine nitrogen atom to the copper centre in the complex. There are three bands - one strong and two weak bands appeared in the region of 2181–2307 cm^{-1} due to ν(C=N) of the dca in the complex. One strong band exhibited at 2181 cm^{-1} is due to νs(C≡N) and two weak bands - one appeared at 2250 cm^{-1} due to νas(C≡N) and another appeared at 2307 cm^{-1} due to νs+νas(C≡N) of bridging dca ligand in the complex [14,15].

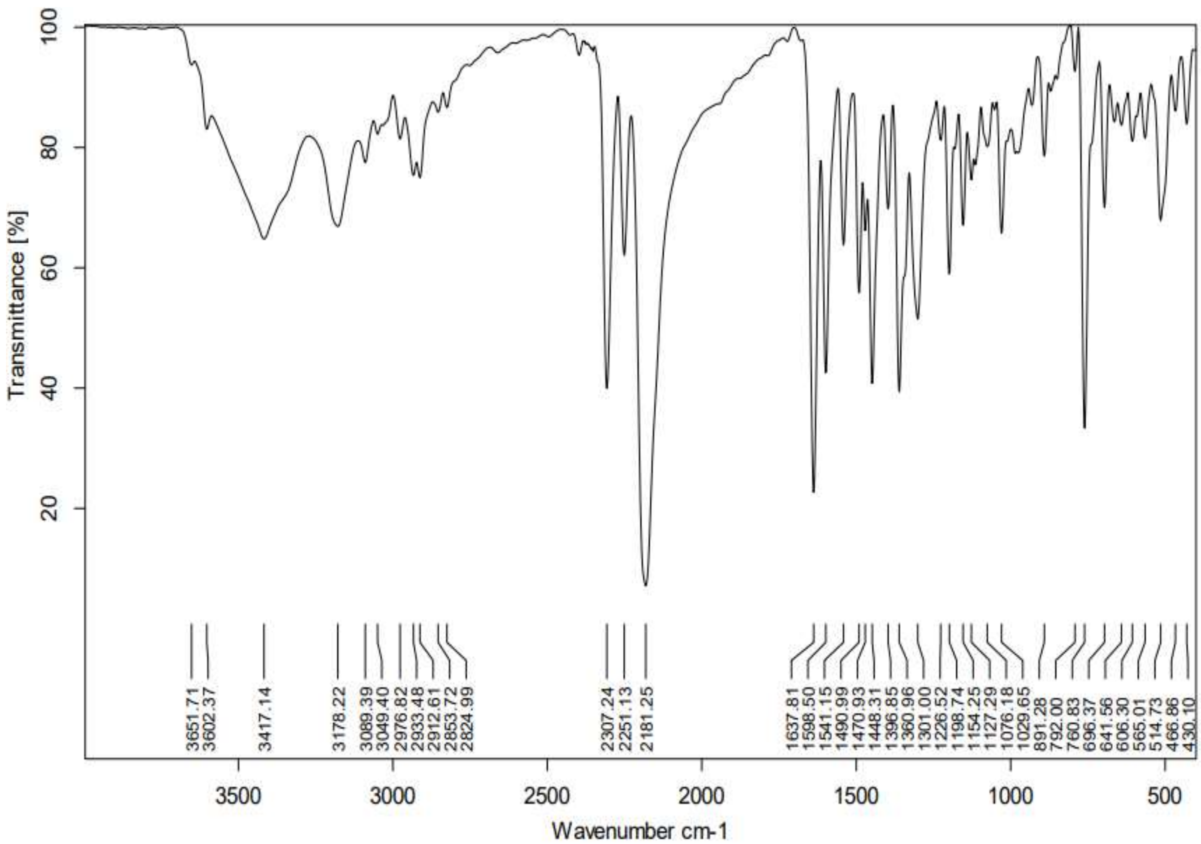


Figure 4(B).1. IR spectrum of $\{[Cu(L2)\{N(CN)_2\}](CH_3CN)\}_n$

4(B).4.2.2. EPR spectral data

The X-band EPR spectrum of the complex is drawn in frozen acetonitrile solution at 77 K and exhibited four line splitting pattern due to interaction of the unpaired electron of copper(II) complex with d^9 configuration (S=1/2) with the nuclear spin of the copper nucleus ($^{63,65}Cu$, I = 3/2). The g_{II} and $g_{\perp}$ values of the complex is 2.276 and 2.064, respectively and $g_{II} > g_{\perp} > 2.0023$ indicates the $d_{x^2-y^2}$ is the ground state.

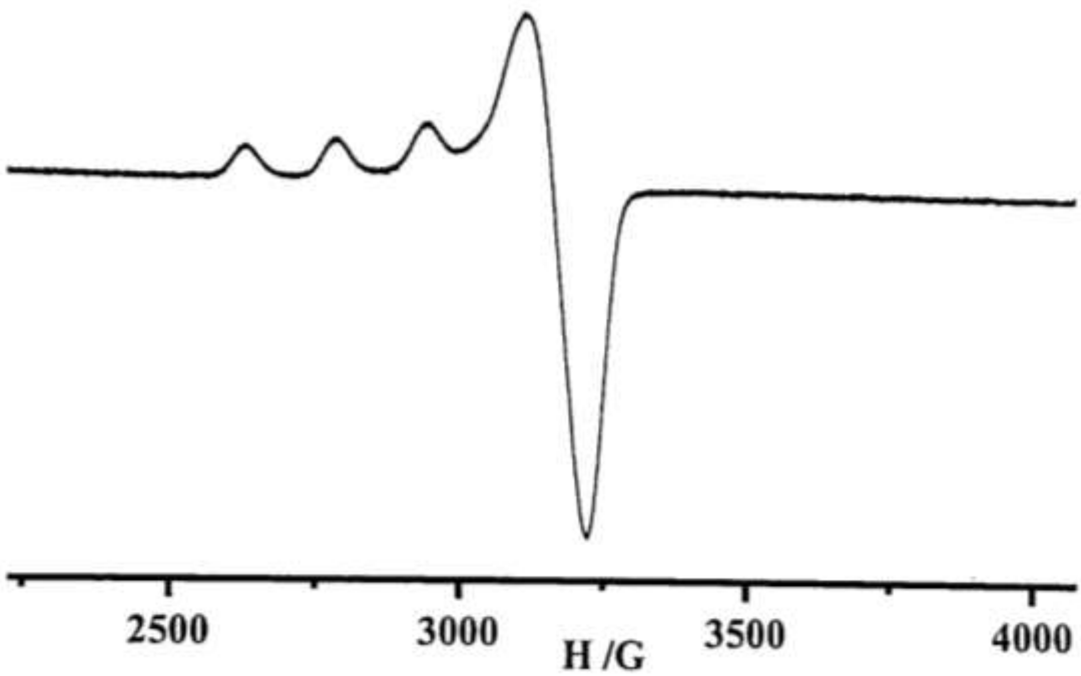


Figure 4(B).2 EPR spectrum of Cu(II) complex in DMSO solution at 77 K.

4(B).4.2.3. Electronic Spectra and Magnetic studies.

The UV-Visible spectra of both the complexes were recorded in CH_3CN (10^{-3}M) in the range of 200-900 nm. The high intensity bands appeared at <400nm are due to intra ligand n-π* and π - π * charge transfer transition. Generally, Cu(II) complex with trigonal bipyramidal or distorted trigonal bipyramidal geometry show two spectral bands - one in the region of 700 -750 nm (due to d_{xy}, $d_{yz} \rightarrow dz^2$)transition and another at 800- 870 nm (due to $d_{xy}, d_{x^2-y^2} \rightarrow dz^2$) transition whereas square pyramidal or distorted square pyramidal Cu(II) complexes show one spectral band in the region of 550-670 nm (due to d_{xz}, $d_{yz} \rightarrow d_{x^2-y^2}$) transition [16-19].Cu(II) complex show a broad one absorption band at 620 nm indicating complex have square pyramidal geometry and the band is due to d-d (d_{xz}, $d_{yz} \rightarrow d_{x^2-y^2}$) transition.

The magnetic susceptibility measurements in the powder sample show the effective magnetic moment (μ_{off}) of the complex at room temperature is 1.79 BM corresponding to one electron paramagnetism. It is reported by Mautner et al that dca bridged polynuclear Cu(II) complex show very weak interaction due to long Cu-Cu bond distance [20]. As the Cu-Cu distance is very high (> 6.0Å) in this complex, variable temperature magnetic study of the complex has not been carried out.

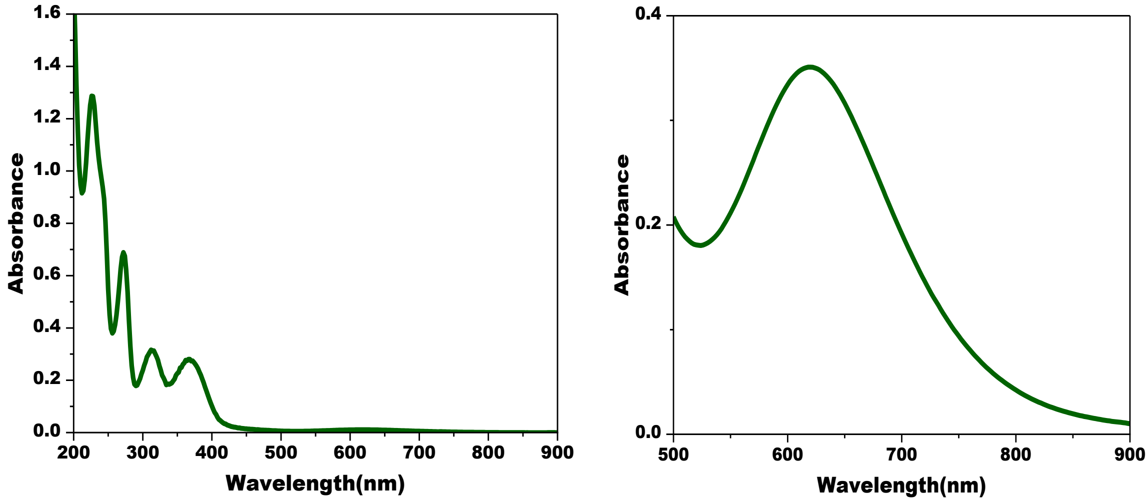
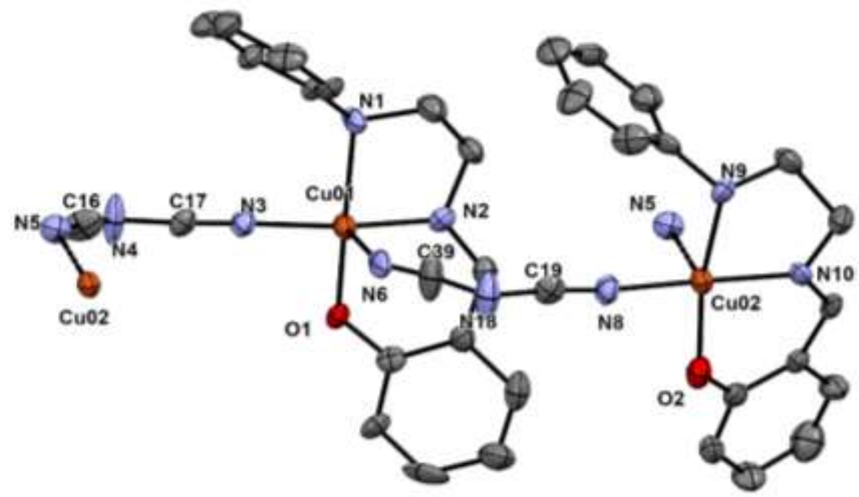


Figure 4(B).3. Electronic Spectra of Cu(II) complex in CH_3CN (10^{-3} M)

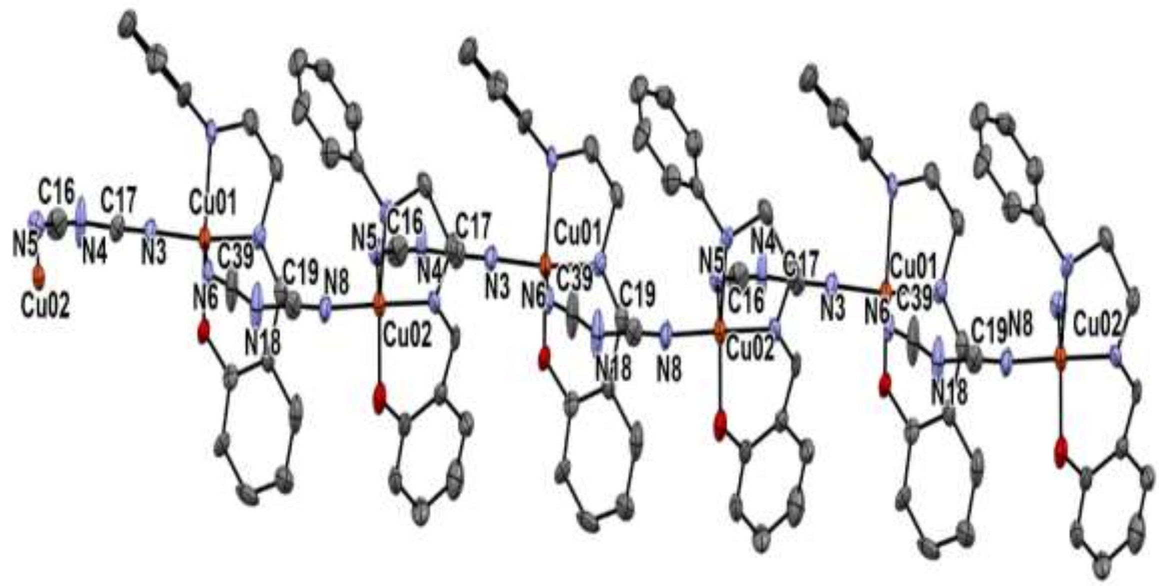
4(B).4.3. Description of crystal structure

4(B).4.3.1. Crystal structure of $\{[Cu(L2)\{N(CN)_2\}](CH_3CN)\}_n$

The ORTEP diagram of the complex is shown in Fig. 4(B).4. Details of crystallographic data collection are given in the Table 4(B).1 and the selected bond lengths and bond angles of the copper coordination sphere are given in Table 4(B).2. The complex crystallizes in triclinic crystal system with space group *P-1*. The asymmetric unit of the complex Fig. 4(B).4(a) consists of two copper(II) centres, two bridging ligand dca and two Schiff base N2O donor ligand. In the structure, each Cu(II) centre has N_4O coordination environment and two copper(II) centres are covalently linked by Cu-N-C-N-C-N-Cu, leading to the formation of one dimensional polymeric chain. The geometry around each copper centre is distorted square pyramidal (τ = 0.1). In the basal plane, there are three nitrogen atoms- two nitrogen atoms from tridentate ligand and one nitrogen atom from bridging dca and one oxygen atom from phenol and the apical position is occupied by N atom of another dca. The bond lengths around copper(II) centres are Cuo1-N1H (2.119Å), Cu01-N2 (1.919(12)Å), Cu01-O1 (1.932(12)Å), Cu01-N3(1.919(10)Å) and Cu01-N(62.462(18)Å) are not equal. The bond lengths of bridging dca between two copper centres are CuO2-N5(2.476Å), N5-C16(1.102Å) C16-N4(1.308Å), N4-C17(1.308Å), C17-N3(1.171Å), N3-Cu01(1.934Å). The distances between Cu …. .Cu in the molecule is 6.973 Å which is shorter than single μ-$_{1,5}$ dca bridged pyrazolyl containing N_3-donor polynuclear copper(II) complex with square pyramidal geometry [19].



(a)



(b)

Figure. 4(B).4. (a). ORTEP diagram of the asymmetric unit of Cu(II) complex with atom numbering scheme. Hydrogen atom and CH_3CN molecule are omitted for clarity. (b). ORTEP diagram of the 1D polymeric chain of Cu(II) complex with atom numbering scheme.

Table 4(B).2 Bond lengths (Å) and angles (º) of Cu(II) complex

Bond lengths (Å)		Bond angles (º)	
Cu01-O1	1.932(10)	O1-Cu01-N3	91.8(4)
Cu01-N2	1.919(12)	O1-Cu01-N1	164.0(4)
Cu01-N3	1.934(12)	O1-Cu01-N6	96.0(4)
Cu01-N1	2.119(12)	N2-Cu01-O1	90.8(5)
Cu01-N6	2.462(18)	N2-Cu01-N3	170.7(5)
Cu02-O2	1.925(11)	N2-Cu01-N1	83.2(5)
Cu02-N10	1.938(11)	N2-Cu01-N6	91.2(5)
Cu02-N9	2.118(12)	N3-Cu01-N1	91.9(5)
Cu02-N51	2.476(16)	N3-Cu01-N6	97.4(5)
Cu02-N8	1.945(12)	N1-Cu01-N6	99.0(5)
		O2-Cu02-N10	90.1(5)
		O2-Cu02-N9	165.3(5)
		O2-Cu02-N5[1]	96.6(4)
		O2-Cu02-N8	91.3(5)
		N10-Cu02-N9	83.9(5)

4(B).5. Conclusion

One new polynuclear Cu(II) complex has been synthesized by the reaction of N_2O donor Schiff base ligand {((2- (phenyl amino)ethyl)imino)methyl}phenol (HL2) and bridging ligand dca and characterized. Structural characterization by single crystal X-ray diffraction data shows the complexes has polymeric structure and each copper center has distorted square pyramidal geometry and two copper centers are bridged by one dca molecule with μ-$_{1,5}$ coordination mode.

4(B).6. References

1 S. Raje, N. Mondivagu, M. Chahal, R. J. Butcher, R. Angamuthu. Chem. Asian J. 13 (2018) 1458.

2. B. Kumari, S. Kundu, K. Ghosh, M. Banerjee, S. K. Pradhan, S. M. Islam, P. Brandão, V. Félix, D. Das. Dalton Trans. 47 (2018) 14008.

3 A. Ghosh, D. Das. Dalton Trans. 44 (2015) 11797.

4. H. Peng, Y. L, Zhong, W. Che. Synth. React. Inorg. Met.Org. Nano-Met. Chem. 38 (2008) 677.

5. S. S. Qian, X. S. Cheng, Z. L. You, H. L. Zhu. Russian J. Coord. Chem. 39 (2013) 704.

6. S. J. Munshi, M. Guin, S. Kundu, S. B. Kumar. J. Ind. Chem. Soc. 98 (2021) 100080.

7. S. J. Munshi, M. H. Sadhu, S. Kundu, C. Savani, S. B. Kumar. J. Mol. Struct. 1209 (2020) 127984.

8. Rigaku OD Crys Alis PRO. Rigaku Oxford Differaction Ltd, Yarnton, England (2018).

9. Agilent, CrysAlis PRO. Agilent Technologies UK Ltd, Yarnton, England (2011).

10. G. M. Sheldrick. SAINT, 5.1st edn. Siemens Industrial Automation Inc., Madison, WI (1995).

11. G. M. Sheldrick, Program for Refinement of Crystal Structures, University of Göttingen, Germany (1997).

12. L. J. Farrugia. J. Appl Cryst. 32 (1999) 837.

13. L. J. Farrugia. J. Appl. Cryst. 30 (1997) 565.

14 K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds. Part B. Applications in Coordination, Organometallic, and Bioinorganic Chemistry, fifth ed., Wiley, New York (1997) 116.

15 H. Kohler, A. Kolbe, G. Lux, Z. Anorg. Allg. Chem. 428 (1977) 103.

16 M. H. Sadhu, S. B. Kumar, J. K. Saini, S. S. Purani, T. R. Khanna. Inorg. Chim. Acta 466 (2017) 219.

17 U. Mukhopadhayay, I. Bernal, S.S. Massoud, F. A. Moutner. Inorg. Chim. Acta 357 (2004) 3673.

18 B.J. Hathaway, in: G. Wilkinson, R.D. Gillard, J.A. McCleverty (Eds.), Comprehensive Coordination Chemistry, vol. 5, Pergamon Press, Oxford, England (1987) 533.

19 S.S. Massoud, M.M. Lemieux, L.L. Quan, R. Vicente, J. H. Albering, F. A. Mautner. Inorg. Chim. Acta 388 (2012) 71.

20 F. A. Mautner, M. Mikuriya, H. Ishida, H. Sakiyama, F. R. Louka, J. W. Humphrey, S. S. Massoud. Inorg. Chim. Acta 362 (2009) 4073.