CHAPTER-5

- **Chapter-5(A) :** Syntheses and Structural studies of Cobalt(II), Nickel(II), Zinc(II) and Cadmium(II) Selenocyanate complexes with tetradentate N_4-donor ligand.

- **Chapter-5(B) :** Zinc(II) and Cadmium(II) complexes with N_4-coordinate pyrazole based ligand: Syntheses, Characterizations and Structures.

CHAPTER-5(A)

Syntheses and Structural studies of Cobalt(II), Nickel(II), Zinc(II) and Cadmium(II) Selenocyanate complexes with tetradentate N_4-donor ligand.

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Syntheses and structural studies of cobalt(II), nickel(II), zinc(II) and cadmium(II) selenocyanate complexes with a tetradentate N_4-donor ligand

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Abstract

Four new selenocyanate containing mononuclear complexes of the types $[M(NCSe)(dbdmp)]ClO_4$ [M = Co(II), Zn(II)], $[Ni(dbdmp)(NCSe)_2]$ and $[Cd(dbdmp)(SeCN)_2]$ where 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 microanalysis, physico-chemical and spectroscopic methods. Crystal structures of the four complexes $[Co(NCSe)(dbdmp)]ClO_4$ (**1**) $[Ni(dbdmp)(NCSe)_2]$ (**2**), $[Zn(NCSe)(dbdmp)]ClO_4$ (**3**) and $[Cd(dbdmp)(SeCN)_2]$ (**4**) have been solved by single crystal X-ray diffraction studies and showed that complexes **1** and **3** have distorted trigonal bipyramidal geometry whereas complexes **2** and **4** have distorted octahedral geometry and the ligand dbdmp has two different isomers in the complexes **2** and **4**. In the complex **4**, selenium atom is bonded with cadmium(II) center whereas nitrogen atom of selenocyanate ion is coordinated with Co(II), Ni(II) and Zn(II) centers.

5(A).1. Introduction

Coordination chemistry of pseudohalogens as ligand in the transition metal complexes has attracted much attention among the researchers in the last decades. The selenocyanate ion is a triatomic ion and can acts as ambidentate ligand and is known to coordinate with metal ion through either nitrogen atom or selenium atom depends on the nature and coordination environment surrounding the metal ions [1-5]. Therefore, the selenocyanate ion can also act as terminal monodentate ligand or bridging ligand like pseudohalogens and can form mononuclear or polynuclear complexes with transition metals [6-19]. In the mononuclear complexes, it has been reported that Se-atom in $SeCN^-$ ion is bonded in complexes of metal atoms of class b character and N- atom in $SeCN^-$ ion bonded in complexes of metal atoms of class a character [20-23]. The number of selenocyanate containing mono- and polynuclear transition metal complexes is relatively less in the literature as selenium has weak affinity towards many transition metal ions.

As our interest is in the synthesis of mono- and polynuclear transition metal complexes with ligand dbdmp and pseudohalogens, we are interested to study the coordination behavior of selenocyanate ion with transition metal ions in presence of tetradentate N_4-coordinated dbdpm ligand. In this chapter, we report on the syntheses and characterizations of mononuclear complexes of the types $[M(NCSe)(dbdmp)]ClO_4$ [M = Co(II) and Zn(II)], $[Ni(dbdmp)(NCSe)_2]$ and $[Cd(dbdmp)(SeCN)_2]$. Crystal structures of the complexes were solved by single crystal X-ray diffraction studies and it showed that Ni(II) and Cd(II) complexes have six coordination with distorted octahedral geometry and five coordinated Co(II) and Zn(II) complexes have distorted trigonal bipyramidal geometry. In complex $[Cd(SeCN)(dbdmp)_2]$, coordination of Cd-Se is observed whereas other complexes [Co(II), Ni(II) and Zn(II)] have M-N coordination of $SeCN^-$ ion.

5(A).2. Experimental

5(A).2.1. Materials

The chemicals and solvents were of analytical grade and purchased from commercial sources. KSeCN (Aldrich) was of reagent grade and used as received. $M(ClO_4)_2.6H_2O$ [M = Cu(II), Co(II), Ni(II), Zn(II) and Cd(II)] were prepared by reaction of metal carbonate with dilute $HClO_4$ acid and followed by slow evaporation of the solution.

5(A).2.2. Syntheses of Complexes

Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only a small amount of material should be prepared, and it should be handled with caution.

5(A).2.2.1. [Co(NCSe)(dbdmp)]ClO_4 (1)

To a stirring methanol solution (10 ml) of $Co(ClO_4)_2.6H_2O$ (0.184 g, 0.5 mmol), ligand dbdmp (0.166 g, 0.5 mmol) in methanol (10 ml) was added drop by drop and the colour changed immediately to deep blue. After 10 min, KSeCN (0.079 g, 0.5 mmol) in minimum amount of water was added slowly to the mixture. This solution was stirred for 3 h at room temperature, filtered and bluish purple coloured crystals were obtained after slow evaporation of solvent. Yield. 0.185 g (62 %). Found C = 38.33, H = 5.43, N = 16.55 %. Anal calc for $C_{19}H_{32}N_7O_4SeClCo$: C = 38.30, H = 5.41, N = 16.46 %. IR (KBr pellet) cm^{-1}; ν($NCSe^-$), 2066 vs; ν(C = C) + ν(C = N)/pz ring, 1551 s, 1468 s; ν_{asmy}(Cl–O), 1085 br; δ(O–Cl–O), 624 s. UV-Vis spectra: λ_{max}/nm (ε_{max}/$mol^{-1}cm^{-1}$). 714 (33), 573 (293), 488 (120), 348 (3121), 243 (2276). Λ_M ($\Omega^{-1}cm^2\ mol^{-1}$) = 120. μ_{eff} = 3.87 BM.

5(A).2.2.2. [Ni(dbdmp)$(NCSe)_2$] (2)

This compound was synthesized using same method as for complex **1** except $Ni(ClO_4)_2.6H_2O$ was used instead of $Co(ClO_4)_2.6H_2O$ and 1 : 2 mole ratio of KSeCN was added. Blue coloured crystals were obtained after slow evaporation of solution. Yield. 0.175 g (58 %). Found C = 39.95, H = 5.42, N = 18.49 %. Anal calc for $C_{20}H_{32}N_8Se_2Ni$: C = 39.96, H = 5.37, N = 18.64 %. IR (KBr pellet) cm^{-1}; ν($NCSe^-$), 2086, 2111 vs; ν(C = C) + ν (C = N)/pz ring, 1559 s, 1466 s. UV-Vis spectra: λ_{max}/nm (ε_{max}/$mol^{-1}cm^{-1}$). 931 (11), 585 (38), 385 (463), 295 (857), 249 (2678). Λ_M ($\Omega^{-1}cm^2\ mol^{-1}$) = 12. μ_{eff} = 2.88 BM.

5(A).2.2.3. [Zn(NCSe)(dbdmp)]ClO_4 (3)

This compound was synthesized using same procedure as for complex **1** except $Zn(ClO_4)_2.6H_2O$ was used instead of $Co(ClO_4)_2.6H_2O$. Colourless crystals were obtained after slow evaporation of solution. Yield. 0.160 g (53 %). Found C = 38.01, H = 5.35, N = 16.15 %. Anal calc for $C_{19}H_{32}N_7O_4SeClZn$: C = 37.89,

H = 5.36, N = 16.28 %. IR (KBr pellet) cm^{-1}; ν(NCSe$^-$), 2074 vs; ν(C = C) + ν(C = N)/pz ring, 1552 s, 1468 s; ν_{asmy}(Cl–O), 1087 br; δ(O–Cl–O), 624 s. UV-Vis spectra: λ_{max}/nm (ε_{max}/$mol^{-1}cm^{-1}$). 217 (2744). Λ_M ($\Omega^{-1}cm^2\,mol^{-1}$) = 120.

5(A).2.2.4. [Cd(dbdmp)(SeCN)$_2$] (4)

This compound was synthesized using same procedure as for complex **1** except $Cd(ClO_4)_2.6H_2O$ was used instead of $Co(ClO_4)_2.6H_2O$ and 1:2 mole ratio of KSeCN was added. Colourless crystals were obtained after slow evaporation of solution. Yield. 0.195 g (59 %). Found C = 36.63, H = 4.91, N = 17.35 %. Anal calc for $C_{20}H_{32}N_8Se_2Cd_2$: C = 36.68, H = 4.93, N = 17.11 %. IR (KBr pellet) cm^{-1}; ν(NCSe$^-$), 2118, 2100 vs; ν(C = C) + ν(C = N)/pz ring, 1560 s, 1466 s. UV-Vis spectra: λ_{max}/nm (ε_{max}/$mol^{-1}cm^{-1}$). 219 (3089), 226 (3128). Λ_M ($\Omega^{-1}cm^2\,mol^{-1}$) = 10.

5(A).2.3. 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) were recorded on a Shimadzu 3600 in acetonitrile solution. Solution conductivity were measured in CH_3CN solution (~10^{-3} M) 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 Mettler UMX 5 balance, OMEGA temperature controller with a field strength of 0.8 Tesla using $Hg[Co(SCN)_4]$ as the reference.

5(A).3. X-ray Crystallography

Crystals of suitable size of complexes **1**, **2**, **3** and **4** were obtained by slow evaporation of methanol solution. The details of data collection and some important features of the refinement for the compounds **1**, **2**, **3** and **4** are given in Table 5(A).1 and selected bond lengths and angles are given in Table 5(A).2. Single crystal X-ray diffraction intensity data of the complexes were collected on Oxford X-CALIBUR-S CCD diffractometer with Cu-K_α radiation (λ = 1.54184Å) at 150 K for complex **1** and at 293 K for complexes **2** and **3**. 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 [24]. An absorption correction based on multi-scan method was applied [25]. All structures were solved by direct methods using SHELXTL [26] and refined by the full-matrix least-square based on F^2 technique using SHELXL-97 program package [27]. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located from difference Fourier map and treated as riding.

5(A).4. Results and Discussions

5(A).4.1. Syntheses

Four new mononuclear transition metal complexes $[M(NCSe)(dbdmp)]ClO_4$ [M = Co(II), Zn(II)], $[Ni(dbdmp)(NCSe)_2]$ and $[Cd(dbdmp)(SeCN)_2]$ were synthesized through one pot reaction of $M(ClO_4)_2.6H_2O$, ligand dbdmp and KSeCN ion in 1 : 1 : 1 [for Co(II) and Zn(II)] or 1: 1: 2 mole ratio [for M = Ni(II) and Cd(II)] in the presence of aqueous methanol at room temperature [Scheme 5(A).1]. There was no change of molecular composition of the complexes **1** and **3** when the reactions were carried out in different molar ratio of $SeCN^-$ ion and in different solvents. When the same reaction was carried out with $Cu(ClO_4)_2.6H_2O$, ligand dbdmp and $SeCN^-$ with different molar ratios, we always obtained reddish brown insoluble product. Molar conductivity measurement in CH_3CN solution (~10^{-3} M) shows that complexes $[M(NCSe)(dbdmp)]ClO_4$ [M = Co(II), Zn(II)] are 1:1 electrolyte (Λ_M ~ 120 $\Omega^{-1}cm^2mol^{-1}$) indicating the presence of counter anion in the molecules and there was no change of molar conductivity even after 2 h indicating no dissociation of the complexes in the solution [28].

The presence of counter anion was confirmed by IR spectra and single crystal X-ray diffraction studies. The complexes $[Ni(dbdmp)(NCSe)_2]$ (**2**) and $[Cd(dbdmp)(SeCN)_2]$ (**4**) are non ionic which were confirmed by conductance measurement (Λ_M ~ 12 $\Omega^{-1}cm^2mol^{-1}$), IR spectra and single crystal X-ray diffraction studies. The crystal structure determination of Cd(II) and Ni(II) complexes show the tetradentate N_4-coordinaing dbdmp ligand has two different isomers while coordination to Cd(II) and Ni(II) centers.

Table.5(A).1. Crystal parameters of complexes **1**, **2**, **3** and **4**.

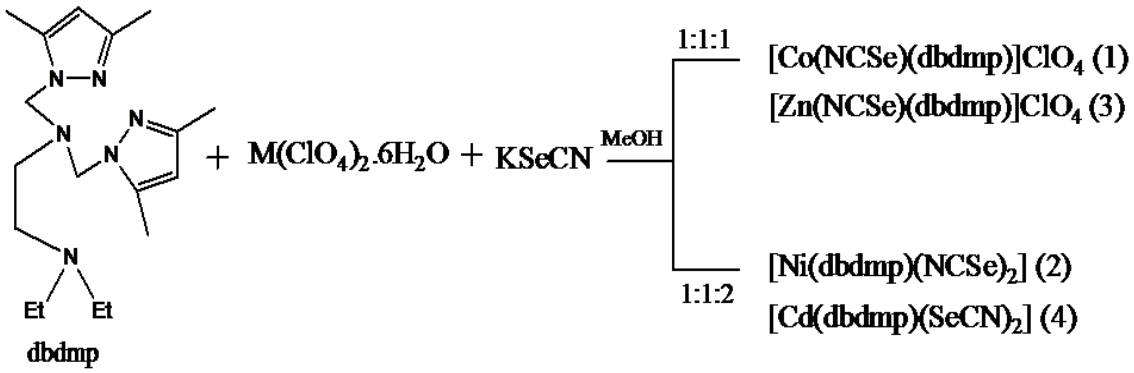
	[Co(NCSe)(dbdmp)]ClO_4 (1)	**[Ni(dbdmp)$(NCSe)_2$] (2)**	**[Zn(NCSe)(dbdmp)]ClO_4 (3)**	**[Cd(dbdmp)$(SeCN)_2$] (4)**
Empirical formula	$C_{19}H_{32}N_7O_4SeClCo$ (1)	$C_{20}H_{32}NiN_8Se$ (2)	$C_{19}H_{32}ZnN_7ClO_4Se$ (3)	$C_{20}H_{32}CdN_8Se_2$ (4)
Formula weight	595.86	601.17	602.30	654.86
Temperature (K)	150(2)	293(2)	293(2)	293(2)
Wavelength (Å)	1.54184	1.54184	1.54184	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	*$P2_1/c$*	*Pna21*	*$P2_1/c$*	*P-1*
a (Å)	14.9080(2)	14.5373(3)	14.9618(3)	8.7216(2)
b (Å)	12.1061(2)	18.1481(3)	12.1114(2)	10.8157(2)
c (Å)	14.6355(4)	10.0953(2)	14.6578(3)	14.2765(2)
α(°)	90	90	90	86.239(2)
β(°)	97.631(2)	90	97.839(2)	78.870(2)
γ(°)	90	90	90	77.070(2)
Volume ($Å^3$)	2617.99(9)	2663.39(9)	2631.29(9)	1287.52(4)
Z	4	4	4	2
Density (g/cm^3)	1.512	1.499	1.520	1.689
Absorption coefficient (mm^{-1})	7.990	4.350	4.133	3.698

F(000)	1220	1216	1232	648
θ range for data collection (°)	3.629 to 72.067	3.868 to 72.1020	4.5440 to 71.6580	3.8500 to 28.4170
Index ranges	$-18 \le h \le 18$,	$-17 \le h \le 17$	$-17 \le h \le 18$,	$-11 \le h \le 11$,
	$-14 \le k \le 14$,	$-14 \le k \le 22$	$-14 \le k \le 10$,	$-14 \le k \le 14$,
	$-17 \le l \le 18$	$-12 \le l \le 8$	$-17 \le l \le 12$	$-19 \le l \le 19$
Reflections collected	25285	6221	8193	62293
Independent reflections	5113	3212	4998	6348
	[*R*(int) = 0.0804]	[*R*(int) = 0.0216]	[*R*(int) = 0.0235]	[*R*(int) = 0.0513]
Max. and min. transmission	1.0000 and 0.19222	1.0000 and 0.59075	1.0000 and 0.56883	1.00000 and 0.56584
Data / restraints / parameters	5113 / 0 / 298	3212 / 1 / 281	4998 / 0 / 298	6348 / 0 / 280
Goodness-of-fit on F^2	1.015	1.053	1.033	1.064
Final R indices [I>2sigma(I)]	*R1* = 0.0672,	*R1* = 0.0320,	*R1* = 0.0539,	*R1* = 0.0412,
	wR2 = 0.1581	*wR2* = 0.0869	*wR2* = 0.0599	*wR2* = 0.0946
R indices (all data)	*R1* = 0.1007,	*R1* = 0.0336,	*R1* = 0.1527,	*R1* = 0.0502,
	wR2 = 0.1769	*wR2* = 0.0888	*wR2* = 0.1608	*wR2* = 0.0990
Largest diff. peak and hole (eA^{-3})	0.923 and -0.699	0.280 and -0.520	1.229 and -0.972	1.043 and -1.548
CCDC number	991575	991577	991576	996281

Table.5(A).2. Bond lengths (Å) and bond angles (˚) of Complexes **1**, **2**, **3** and **4**.

Bond Length (Å)							
[Co(NCSe)(dbdmp)]ClO_4 (1)		**[Ni(dbdmp)$(NCSe)_2$] (2)**		**[Zn(NCSe)(dbdmp)]ClO_4 (3)**		**[Cd(dbdmp)$(SeCN)_2$] (4)**	
Co(1)-N(7)	2.000(5)	Ni(1)-N(7)	2.005(4)	Zn(1)-N(7)	2.007(3)	Cd(1)-Se(1)	2.6731(5)
Co(1)-N(1)	2.038(5)	Ni(1)-N(8)	2.078(4)	Zn(1)-N(1)	2.042(3)	Cd(1)-Se(2)	2.7768(5)
Co(1)-N(5)	2.030(5)	Ni(1)-N(1)	2.109(4)	Zn(1)-N(5)	2.046(3)	Cd(1)-N(1)	2.405(3)
Co(1)-N(6)	2.140(4)	Ni(1)-N(5)	2.114(4)	Zn(1)-N(6)	2.152(3)	Cd(1)-N(5)	2.424(3)
Co(1)-N(3)	2.252(4)	Ni(1)-N(6)	2.254(4)	Zn(1)-N(3)	2.315(3)	Cd(1)-N(6)	2.528(3)
Se(1)-C(19)	1.769(5)	Ni(1)-N(3)	2.143(4)	Se(1)-C(19)	1.769(4)	Cd(1)-N(3)	2.470(3)
		Se(1)-C(19)	1.793(5)			Se(1)-Cd(19)	1.796(5)
		Se(2)-C(20)	1.804(4)			Se(2)-C(20)	1.807(5)

Bond Angles (º)							
[Co(NCSe)(dbdmp)]ClO_4 (1)		**[Ni(dbdmp)$(NCSe)_2$] (2)**		**[Zn(NCSe)(dbdmp)]ClO_4 (3)**		**[Cd(dbdmp)$(SeCN)_2$] (4)**	
N(7)-Co(1)-N(1)	104.6(2)	N(7)-Ni(1)-N(1)	96.23(17)	N(7)-Zn(1)-N(1)	104.73(15)	N(8)-C(20)-Se(2)	179.2(4)
N(7)-Co(1)-N(5)	104.6(2)	N(7)-Ni(1)-N(5)	100.70(17)	N(7)- Zn(1)-N(5)	104.93(15)	N(5)-Cd(1)-Se(1)	117.12(7)
N(1)-Co(1)-N(5)	113.74(18)	N(1)-Ni(1)-N(5)	89.16(15)	N(1)- Zn(1)-N(5)	114.13(12)	N(1)-Cd(1)-N(5)	141.13(10)
N(7)-Co(1)-N(6)	94.95(19)	N(7)- Ni(1)-N(6)	98.84(15)	N(7)- Zn(1)-N(6)	95.57(14)	N(6)-Cd(1)-Se(1)	93.48(7)
N(1)-Co(1)-N(6)	111.98(18)	N(1)-Ni(1)-N(6)	91.51(16)	N(1)- Zn(1)-N(6)	122.29 (11)	N(1)-Cd(1)-N(6)	86.32(11)
N(5)-Co(1)-N(6)	122.93(18)	N(5)-Ni(1)-N(6)	160.26(15)	N(5)- Zn(1)-N(6)	111.47 (12)	N(5)-Cd(1)-N(6)	91.91(11)
N(7)-Co(1)-N(3)	175.4(2)	N(7)-Ni(1)-N(3)	176. 37(16)	N(7)- Zn(1)-N(3)	175.39(14)	N(3)-Cd(1)-Se(1)	165.47(7)
N(1)-Co(1)-N(3)	78.35(17)	N(7)-Ni(1)-N(5)	100.70(17)	N(1)- Zn(1)-N(3)	76.96(11)	N(5)-Cd(1)-Se(1)	117.12(7)
N(5)-Co(1)-N(3)	77.11(16)	N(8)-Ni(1)-N(5)	85.84(16)	N(5)- Zn(1)-N(3)	77.97(11)	N(5)-Cd(1)-Se(2)	83.49(8)
N(6)-Co(1)-N(3)	80.57(15)	N(6)-Ni(1)-N(3)	83.08(14)	N(6)- Zn(1)-N(3)	79.97(11)	N(6)-Cd(1)-Se(2)	168.01(7)
N(7)-C(19)-Se(1)	179.5(5)	N(7)-Ni(1)-N(8)	90.49(17)	N(7)-C(19)-Se(1)	178.7(6)	Se(1)-Cd(1)-Se(2)	98.471(17)
		N(8)-Ni(1)-N(1)	172.28(16)			N(1)-Cd(1)-Se(2)	90.32(8)
		N(7)-C(19)-Se(1)	178.2(4)			N(7)-C(19)-Se(1)	176.0(6)
		N(8)-C(20)-Se(2)	179.2(4)			N(8)-C(20)-Se(2)	177.5(5)



Scheme.5(A).1. Syntheses of complexes.

In the complex [Cd(dbdmp)$(SeCN)_2$], selenium atom of the selenocyanate ion is coordinated with cadmium(II) center which was proved by IR spectroscopy and single crystal X-ray diffraction studies. Cadmium is a metal of class b character, so selenium atom in $SeCN^-$ ion is preferred to coordinate with cadmium. Other metal atoms Co(II), Ni(II) and Zn(II) are of class a character, so they preferred to coordinate with nitrogen atom of selenocyanate ion. The ambidentate behavior of $SeCN^-$ ion was confirmed by structural characterization of the complexes. All the complexes gave satisfactory microanalysis results confirming their composition. The diffraction quality crystals for structural studies were obtained by slow evaporation of the solution. The complexes are moderately soluble in common organic solvents such as acetonitrile, methanol, ethanol, dichloromethane, acetone etc.

5(A).4.2. Descriptions of Crystal Structures

5(A).4.2.1. [Co(NCSe)(dbdmp)]ClO_4 (1) and [Zn(NCSe)(dbdmp)]ClO_4 (3)

The molecular structures of complexes **1** and **3** were determined by the single crystal X-ray diffraction technique. The ORTEP diagrams with atom numbering schemes of the two complexes are shown in Fig.5(A).1 and Fig.5(A).2. The complexes **1** and **3** crystallize in a monoclinic crystal system with $P2_1/c$ space group. In both the complexes ligand dbdmp acts as tetradentate N_4-coordinated and bonded through two tertiary amines nitrogen atoms of *N*,*N*-diethylethylenediamine and two pyrazole rings' nitrogen atom around the metal ion. The complexes

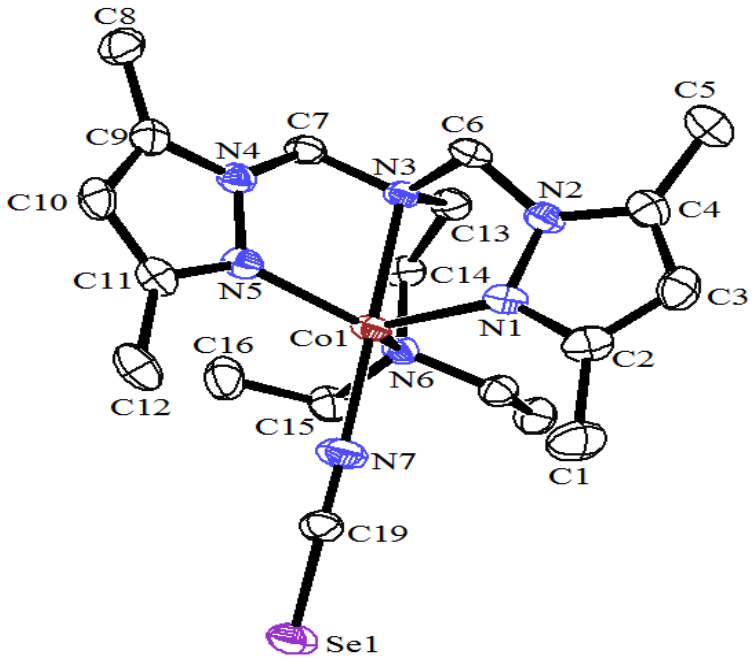


Fig.5(A).1. ORTEP diagram depicting the cationic part of the [Co(NCSe)(dbdmp)]ClO_4 **(1)** complex with atom numbering scheme (30% probability factor for the thermal ellipsoids. H-atoms are omitted for the clarity).

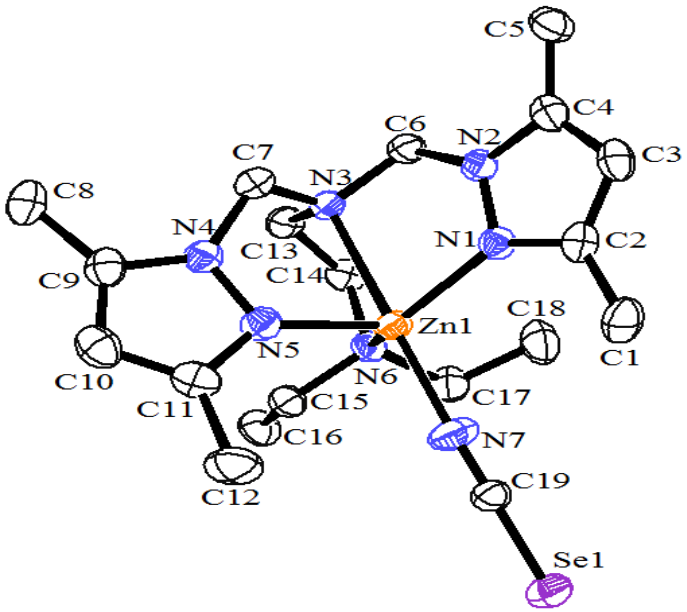


Fig.5(A).2. ORTEP diagram depicting the cationic part of the [Zn(NCSe)(dbdmp)]ClO_4 **(3)** complex with atom numbering scheme (30% probability factor for the thermal ellipsoids. H-atoms are omitted for the clarity).

$[M(NCSe)(dbdmp)]ClO_4$ [M = Co(II), Zn(II)] are penta coordinated where the central metal ion is coordinated by five nitrogen donors – four nitrogen atoms from the ligand dbdmp and one nitrogen atom from selenocyanide ion in the complexes. The coordination geometry around the metal center is best described as distorted trigonal bipyramidal which is revealed by the magnitude of the trigonality index τ of 0.87 and 0.88 for the complexes **1** and **3,** respectively [29]. In both the complexes, the equatorial positions are occupied by one tertiary nitrogen atom N(6) of ligand dbdmp and two nitrogen atoms N(1) and N(5) of pyrazole ring and the axial positions are occupied by another tertiary nitrogen atom N(3) of ligand dbdmp and nitrogen atom N(7) of selenocyanide ion. The terminal selenocyanide is attached via nearly linear to the metal ion as N(7)-C(19)-Se(1) angles are 179.5(5)º and 178.7(6)º for complexes **1** and **3**, respectively. The M-N bond distances in the trigonal planes lies in the range of 2.030(5)-2.152(3) Å. The axial M-N(3) bond distances are 2.252(4) and 2.315(3) Å and M-N(7) bond distances are 2.000(3) Å and 2.007(3) Å respectively for the complexes **2** and **4** which are shorter than M-N(3) distance. The axial bond N(3)-M-N(7) angles are 175.4° and 175.39° which is very close to 180°.

5.5(A).4.2.2. $[Ni(dbdmp)(NCSe)_2]$ (2) and $[Cd(dbdmp)(SeCN)_2]$ (4)

The ORTEP diagrams of the complexes **2** and **4** are shown in Fig.5(A).3 and Fig.5(A).4, selected bond length and bond angles are given in Table.5(A).2. The X-ray crystal structure determination confirmed that both $[Ni(dbdmp)(NCSe)_2]$ and $[Cd(dbdmp)(SeCN)_2]$ are nonionic, crystallized in *Pna21* and *P-1* space groups, respectively. In both the complexes, the M^{2+} cation have NiN_6 and CdN_4Se_2 chromophores with distorted octahedral geometry. Each metal center is coordinated by one molecule of ligand dbdmp containing three chelate rings and is bonded with four nitrogen atoms [N(1), N(3), N(5) and N(6)] of ligand (dbdmp) but the nature of coordination of the chelate rings of the ligand are different. The remaining two sites are occupied by two pendant $SeCN^-$ ligands, which binds the Ni(II) center through two N-atoms of two $SeCN^-$ ions whereas Cd(II) center binds through two Se-atoms of two $SeCN^-$ ions. The two $SeCN^-$ ions are coordinated in the cis position with respect to metal center in both the complexes.

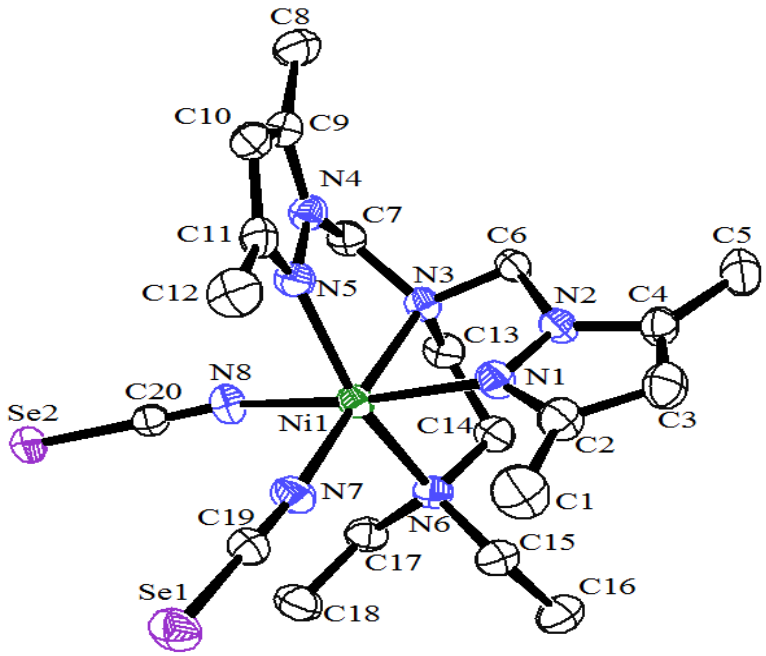


Fig.5(A).3. ORTEP diagram of the complex [Ni(dbdmp)$(NCSe)_2$] **(2)** with atom numbering scheme (30% probability factor for the thermal ellipsoids. H-atoms are omitted for the clarity).

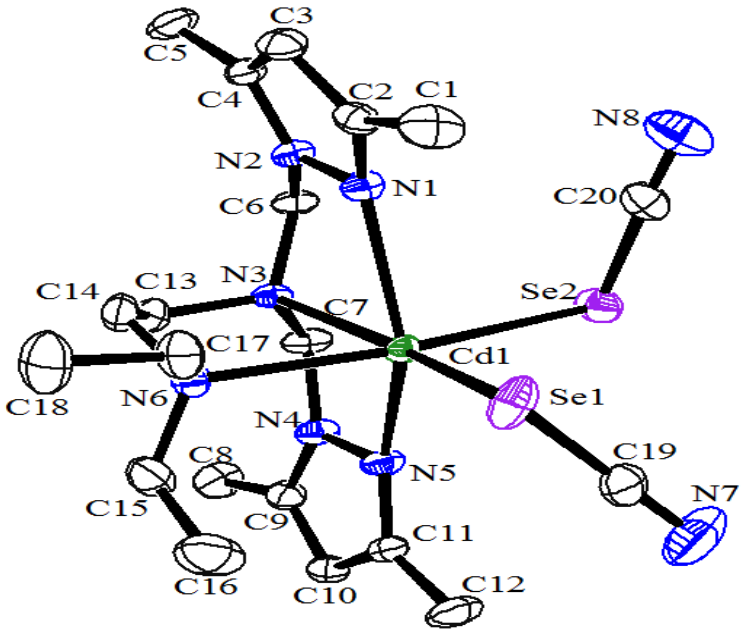


Fig.5(A).4. ORTEP diagram of the complex [Cd(dbdmp)$(SeCN)_2$] **(4)** with atom numbering scheme (30% probability factor for the thermal ellipsoids. H-atoms are omitted for the clarity).

In [Ni(dbdmp)$(NCSe)_2$] **(2)** complex, the octahedral nickel(II) center is coordinated by six nitrogen atoms N(1), N(3), N(5) N(6) N(7) and N(8) and the bond lengths of Ni-N(1) [2.109(4) Å), Ni-N(3) (2.143(4) Å], Ni(1)-N(5) [2.114(4) Å] Ni-N(6) [2.254(4) Å], Ni-N(7) [2.005(4) Å] and Ni-N(8) (2.078(4) Å) are different. The bond angles N(7)-Ni(1)-N(3) (176.37(16)º) and N(8)-Ni(1)-N(1) (172.28(16)º) are close to 180^0, whereas the axial bond angle N(5)-Ni(1)-N(6) [160.26(15)º] is distorted. The bond angles N(5)-Ni(1)-N(3), N(3)-Ni(1)-N(1), N(3)-Ni(1)-N(6) are 77.56(15)°, 80.60(15)° and 83.08(14)° respectively. The N-donor selenocyanate ions are coordinated to Ni(II) center in almost linear fashion (~179º). The complex **2** is slightly distorted with bond distances ranging from 2.005(4) to 2.254(3) Å and angles ranging between 83.08(14)° and 176.37(16)° (Table 5(A).2).

In the complex [Cd(dbdmp)$(SeCN)_2$] **(4)**, the equatorial plane of the octahedron is occupied by N(3) and N(6) of the dbdmp ligand and Se(1) and Se(2) of two $SeCN^-$ ions and the Cd(1)-N(3) (2.470(3) Å) and Cd(1)-N(6) (2.528(3) Å) bond distances are shorter than Cd(1)-Se(1)(2.673(5) Å) and Cd(1)-Se(2) (2.776(3)Å) bond distances. The axial positions are occupied by two nitrogen atoms N(1) and N(5) of ligand dbdmp and the Cd(1)-N(1) (2.405(3)Å) bond distance is nearly equal to the Cd(1)-N(5) (2.424(3) Å) bond distance. The Cd-Se bond lengths are comparable with those of reported for Se-bonded Cd(II) complex [30]. The equatorial bond angles N(3)-Cd(1)-Se(1) and N(5)-Cd(1)-Se(2) are 165.47(7)º and 168.01(7)º, respectively whereas the axial bond angle N(1)-Cd(1)-N(5) is 141.13(10)º. The bond angles N(3)-Cd(1)-N(6), N(1)-Cd(1)-N(3) and N(5)-Cd(1)-N(3) are $73.65(10)^0$, 71.28(9)º and 71.00(9)º, respectively. The different bond lengths [2.405- 2.776 Å] and bond angle [83.49º-168.01º] produce distortion in the molecule. The Se-donor selenocyanate ions are coordinated to Cd(II) center in almost linear fashion (~177º).

5(A).4.3. Spectral Data and Magnetic Data

5(A).4.3.1. IR Spectra

The IR spectra of the complexes were assigned in comparison to 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 complexes. The complexes **1** and **3** exhibit a very strong band at

2066 cm^{-1}, and 2076 cm^{-1}, respectively which are assigned to asymmetric stretching vibration of N-bonded terminal ν(NCSe$^-$) ion. The complex **2** exhibit two bands at 2086 and 2111 cm^{-1} (broad) and complex **4** exhibit two sharp but less intense peaks at 2118 and 2100 cm^{-1} due to asymmetric and symmetric stretching vibration of terminal ν(NCSe$^-$) ion. In general, N-bonded selenocyanate containing complexes have most intense band which appears at ~ 2070 cm^{-1} while for Se-bonded selenocyanete complexes, the band appears at ~ 2140 cm^{-1} with less intensity [31-32]. The IR spectra of complexes **1** and **3** exhibited a broad band at ~ 1085 cm^{-1} due to ν_{assy}(Cl-O) and a weak band at ~ 625 cm^{-1} due to δ(O-Cl-O) confirming the presence of perchlorate ion outside the coordination sphere in the complexes.

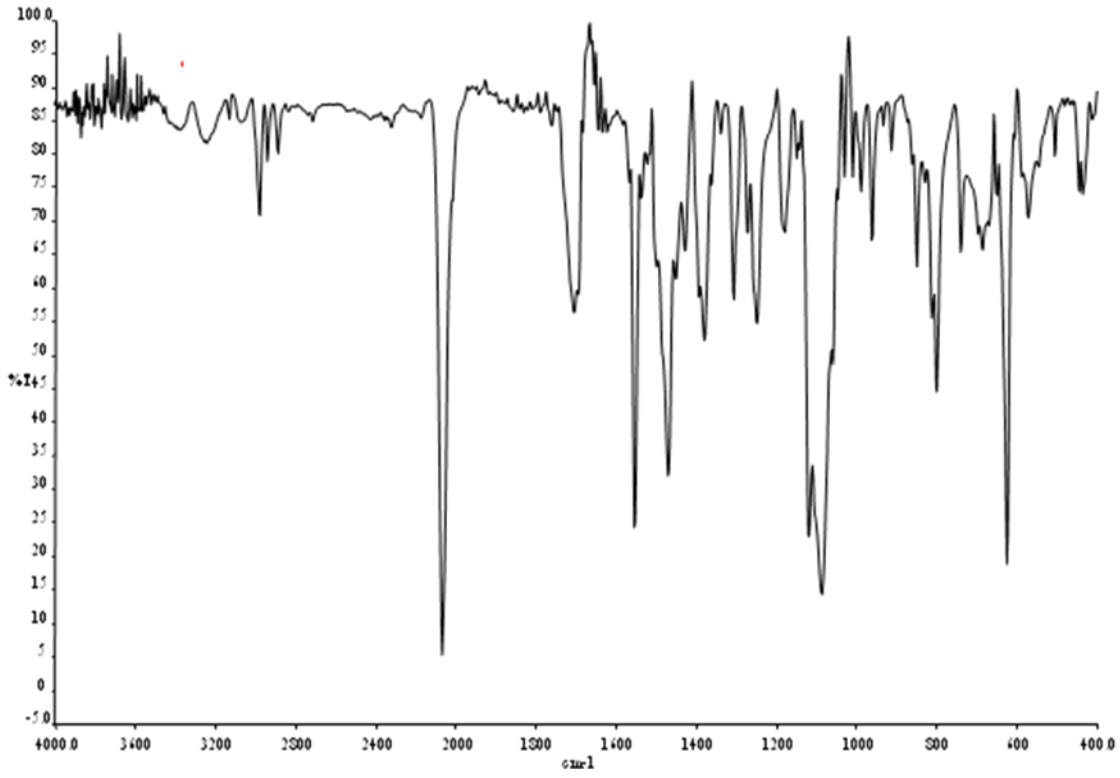


Fig.5(A).5. IR spectrum of [Co(NCSe)(dbdmp)]ClO_4 **(1)**.

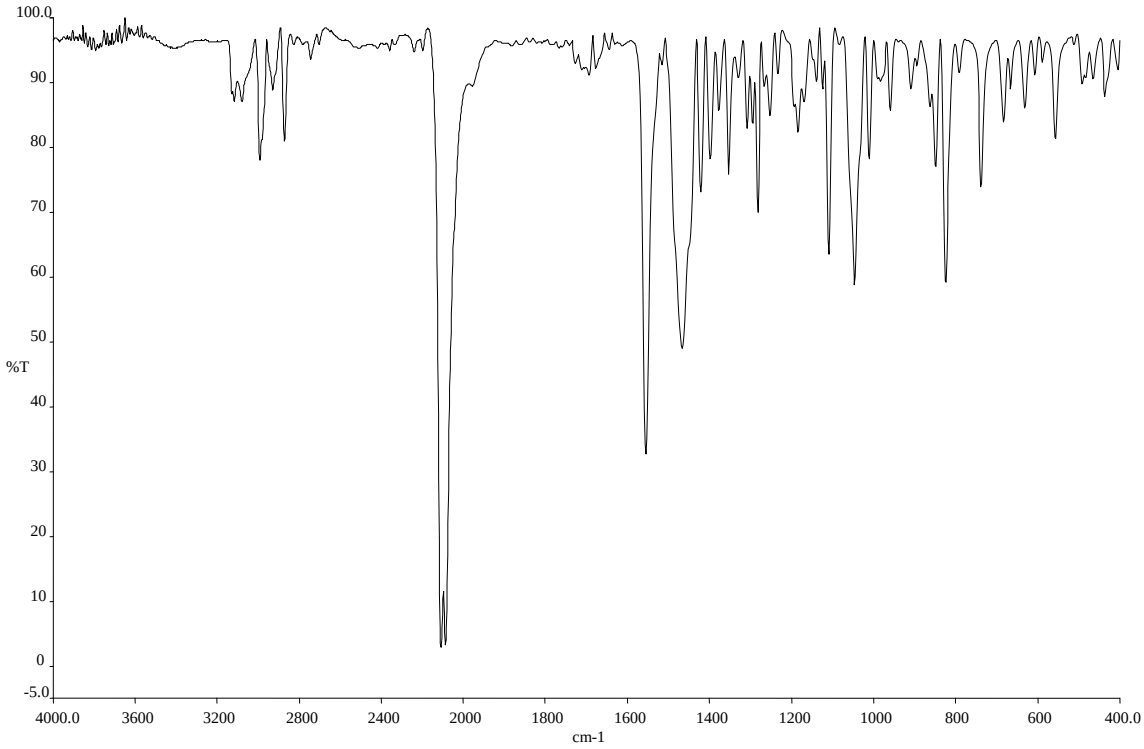


Fig.5(A).6. IR spectrum of $[Ni(dbdmp)(NCSe)_2]$ **(2)**.

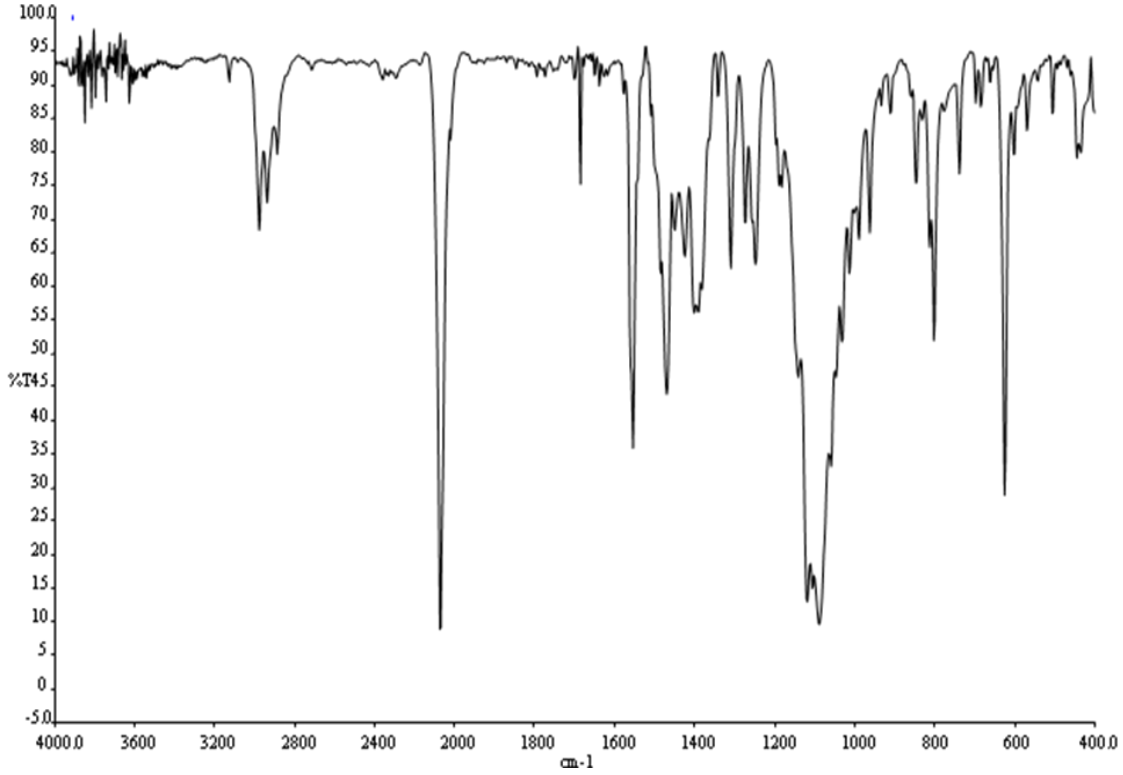


Fig.5(A).7. IR spectrum of $[Zn(NCSe)(dbdmp)]ClO_4$ **(3)**.

5(A).4.3.2. Electronic spectra and magnetic Data

The electronic spectra of complexes **1 - 4** were recorded in acetonitrile solution. Complex **1** shows three absorption bands at 714, 573 and 488 nm with molar absorption coefficient 33, 293 and 120 $mol^{-1}cm^{-1}$, respectively which could be assigned to d-d or ligand-to-metal charge transfer transition of a high spin trigonal bipyramidal cobalt(II) complex. Complex **2** shows two absorption bands in the visible regions at 931 and 585 nm with molar extinction coefficients 11 and 38 $mol^{-1}cm^{-1}$, respectively which are attributed to d-d transitions. No characteristic bands have been observed for complexes **3** and **4** in the visible region. Spectral bands below 400 nm due to intraligand charge transfer transition in all the complexes **1-4**.

Room temperature magnetic susceptibility of complex **1** was 3.87 BM and this result indicates the presence of high spin cobalt(II) complex with three unpaired spin. For the complex **2**, it showed two electrons paramagnetism (μ_{eff} ~ 2.88 BM) indicating octahedral geometry of the complex.

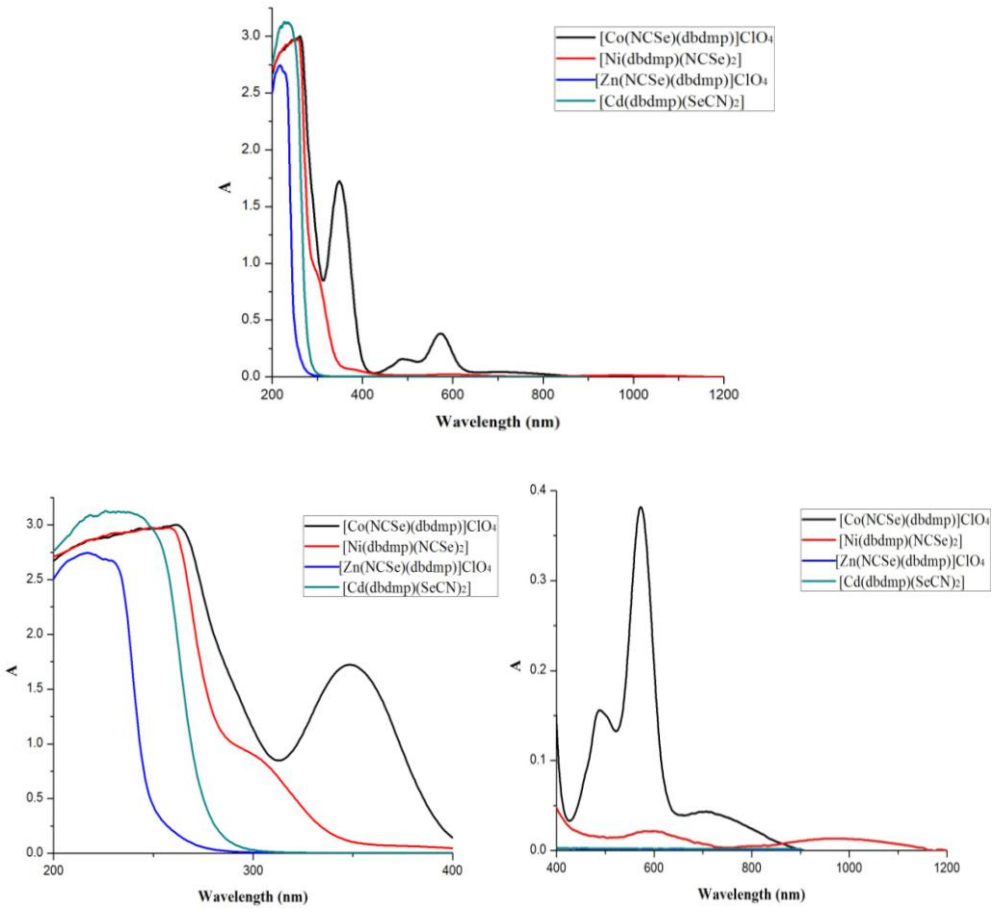


Fig.5(A).8. Electronic spectra of complexes 2-4 in CH_3CN at 25°C (10^{-3} M).

5(A).5. Conclusions

Four mononuclear complexes of the type [M(NCSe)(dbdmp)]ClO_4 [M = Co(II), Zn(II)], [Ni(dbdmp)$(NCSe)_2$] and [Cd(dbdmp)$(SeCN)_2$] where dbdmp = *N*,*N*-diethyl-*N′*,*N′*-bis((3,5-dimethyl-*1H*-pyrazol-1-yl)methyl)ethane-1,2-diamine have been synthesized and characterized. Structural studies show that complexes **1** and **3** have distorted trigonal bipyramidal geometry whereas complexes **2** and **4** have distorted octahedral geometry. The ligand dbdmp has two different isomers in in the complexes [Ni(dbdmp)$(NCSe)_2$] and [Cd(dbdmp)$(SeCN)_2$]. In complex **4**, selenium atom of $SeCN^-$ ion is bonded with cadmium(II) center which was confirmed by IR and crystal structure determination.

5(A).6. References:

1. S. Odabaşıoğlua, R. Kurtarana, A. Azizoglua, H. Karab, S. Özc, O. Atakolc, *Cent. Eur. J. Chem.* 7 (2009) 402.
2. A. D. Jana, A. K. Ghosh, D. Ghoshal, G. Mostafa, N. R. Chaudhuri, *Cryst. Eng. Comm.* 9 (2007) 304.
3. Z. D. Georgousis, P. C. Christidis, D. Hadjipavlou-Litina, C. A. Bolos, *J. Mol. Struct.* 837 (2007) 30.
4. S. Jana, P. Bhaumik, K. Harms, S. Chattopadhyay, *Polyhedron* 78 (2014) 94.
5. B. A. Leita, B. Moubaraki, K. S. Murray, J. P. Smith, *Polyhedron* 24 (2005) 2165.
6. P. M. Secondo, J. M. Land, R. G. Baughman, H. L. Collier, *Inorg. Chim. Acta* 309 (2000) 13.
7. F. A. Cotton, C. A. Murillo, Q. Zhao, *Inorg. Chem.* 48 (2009) 11755.
8. M. Wriedt, C. Näther, *Chem. Commun.* 46 (2010) 4707.
9. S. N. Shukla, P. Gaur, S. Mathews, S. Khan, A. Srivastava, *J. Coord. Chem.* 61 (2008) 3913.
10. D. M. Duggan, D. N. Hendrickson, *Inorg. Chem.* 13 (1974) 2929.
11. M. Fettouhi, B. A. Al-Maythalony, M. N. Shaikh, M. I. M. Wazeer, A. A. Isab, *Polyhedron* 30 (2011) 1262.
12. S. Sain, T. K. Maji, G. Mostafa, T.-H. Lu, M. Y. Chiang, N. R. Chaudhuri, *Polyhedron* 21 (2002) 2293.
13. S. C. Manna, S. Mistri, E. Zangrando, *Inorg. Chim. Acta* 413 (2014) 166.
14. A. Beheshti, W. Clegg, H. Fallah, *Inorg. Chim. Acta* 322 (2001) 1.
15. J. Ribas, M. Monfort, I. Resino, B. K. Ghosh, X. Solans, M. Font-Bardia, *Polyhedron* 17 (1998) 1735.
16. R. R. Choudhury, C. R. Choudhury, S. R. Batten, S. Mitra, *Struct Chem.* 19 (2008) 645.
17. A. D. Jana, S. C.Manna, G. M. Rosair, M. G. B. Drew, G. Mostafa, N. R. Chaudhuri, *Cryst. Growth Des.*7 (2007) 1365.
18. J. Klingele, D. Kaase, M. Schmucker, Y. Lan, G. Chastanet, J.-F. Létard, *Inorg. Chem.* 52 (2013) 6000.

19. W. A. Gobeze, V. A. Milway, J. Olguín, G. N. L. Jameson, S. Brooker, *Inorg. Chem.* 51 (2012) 9056.
20. A. H. Norbury, *Advances in Inorganic Chemistry and Radiochemistry, Academic Press, New York* (1975) 17.
21. R. A. Bailey, S. L. Kozak, T. W. Michelsen, W. N. Mills, *Coord. Chem. Rev.* 6 (1971) 407.
22. A. M. Golub, H. Kohler, V. V. Skopenko, *Chemistry of Pseudohalides, Elsevier, New York* (1986).
23. J. L. Burmeister, *Coord. Chem. Rev.* 105 (1990) 77.
24. Agilent (2011). *CrysAlis PRO*. Agilent Technologies UK Ltd, Yarnton, England.
25. G. M. Sheldrick, *SAINT, 5.1 ed. Siemens Industrial Automation Inc., Madison, WI* (1995).
26. G. M. Sheldrick, *SADABS, Empirical Absorption Correction Program, University of Gottingen, Gottingen, Germany* (1997).
27. G. M. Sheldrick, *SHELXTL Reference Manual (Version 5.1), Bruker AXS, Madison, WI* (1997).
28. W. J. Geary, *Coord. Chem. Rev.* 7 (1971) 81.
29. A. W. Addision, T. N. Rao, J. Reedijk, J. Van Rijn, G. C. Verschoor, *J. Chem. Soc., Dalton Trans.* (1984) 1349.
30. C. R. Choudhury, S. K. Dey, N. Mondal, S. Mitra, V. Gramlich, *Inorg. Chim. Acta* 353 (2003) 217.
31. F. A. Cotton, D. M. L. Goodgame, M. Goodgame, T. E. Haas, *Inorg. Chem.* 1 (1962) 565.
32. J. L. Burmeister, L. Williams, *Inorg. Chem.* 5 (1966) 1113.

CHAPTER-5(B)

Zinc(II) and Cadmium(II) complexes with N_4-coordinate pyrazole based ligand: Syntheses, Characterizations and Structures.

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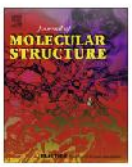

Zinc(II) and Cadmium(II) complexes with N_4-coordinate pyrazole based ligand: Syntheses, characterization and structure

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Abstract

A series of six new mononuclear zinc(II) complexes of the type [Zn(X)(dbdmp)]Y **(1-6)** (X = N_3^- / NCO^- / NCS^-, Y = ClO_4^- / PF_6^- and dbdmp = *N*,*N*-diethyl-*N′*,*N′*-bis((3,5-dimethyl-*1H*-pyrazol-1-yl)methyl)ethane-1,2-diamine), two binuclear cadmium(II) complexes [{Cd(dbdmp)}$_2$(μ-N_3)$_2$](Y)$_2$ **(7-8)** and three mononuclear cadmium(II) complexes [Cd(NCO)(dbdmp)]Y (Y = ClO_4^- / PF_6^-) **(9-10)** and [Cd(NCS)$_2$(dbdmp)] **(11)** have been synthesized and characterized by physico-chemical methods. Crystal structures of the complexes [Zn(N_3)(dbdmp)]ClO_4 **(1)**, [{Cd(dbdmp)}$_2$(μ-N_3)$_2$](ClO_4)$_2$ **(7)**, [Cd(NCO)(dbdmp)]ClO_4 **(9)** and [Cd(NCS)$_2$(dbdmp)] **(11)** have been solved by single crystal X-ray diffraction studies and showed that [Zn(N_3)(dbdmp)]ClO_4 **(1)** and [Cd(NCO)(dbdmp)]ClO_4 **(9)** have distorted trigonal bipyramidal geometry, [Cd(NCS)$_2$(dbdmp)] **(11)** and [{Cd(dbdmp)}$_2$(μ-N_3)$_2$](ClO_4)$_2$ **(7)** have distorted octahedral geometry.

5(B).1. Introduction

In the previous chapters we have described the synthesis, characterization, structures and properties of transition metal complexes of tetradentate ligand dbdmp with different pseudohalides. As an extention of such work, in this chapter we have studied the coordination behaviour of ligand dbdmp with Zn(II) and Cd(II) ion in combination with pseudohalides. The synthesized ligand dbdmp showed distorted trigonal bipyramidal geometry with transition metal ions in the presence of pseudohalides. So we are interested to examine the coordination behaviour of zinc(II) and cadmium(II) ions in the presence of ligand dbdmp and pseudohalides as their d^{10} configuration provides a wide range of symmetries and coordination numbers. A large number of mono, bi- and polynuclear complexes of copper(II), cobalt(II), nickel(II) with azide or thiocyanate or isocyanate have been reported but number of papers on zinc(II) and cadmium(II) complexes with pseudohalides are relatively less [1-8]. Among the pseudohalides containing cadmium complexes, the number of isocyanate containing cadmium complexes structurally characterized is rare [9].

The synthesis and characterization of zinc (II) and cadmium (II) complexes with pyrazole based ligand are of considerable interest because of their potential application in the field of catalysis [10-11], molecular sieves and luminescence materials [12-13]. Zinc is an important element in the bio-system and plays an important role in the active centers in metalloenzymes. Pyrazole containing ligand and their metal complexes also have biological activities [14]. A number of zinc(II) complexes with nitrogen containing heterocyclic ligand have been synthesized and characterized and studied their biological activity [15-16].

In this chapter, we describe the syntheses, characterizations and structures of zinc(II) and cadmium(II) complexes with pseudohalies like azide / thiocyanate or isocyanate and tetradentate N_4-coordinate pyrazole based ligand *N*,*N*-diethyl-*N*′,*N*′-bis((3,5-dimethyl-*1H*-pyrazol-1-yl)methyl)ethane-1,2-diamine (dbdmp). All zinc(II) complexes and NCS^- and NCO^- containing cadmium(II) complexes are mononuclear, whereas azide containing cadmium(II) complexes are binuclear.

5(B).2. Experimental

5(B).2.1. Materials

The chemicals and solvents were of analytical grade and purchased from commercial sources. $Zn(CH_3COO)_2{\cdot}2H_2O$ (Qualigens, India), $Cd(CH_3COO)_2{\cdot}2H_2O$ (SRL, India), NH_4PF_6 (Aldrich) were of reagent grade and used as received. $M(ClO_4)_2{\cdot}6H_2O$ [(M = Zn(II) and Cd(II)] were prepared by reaction of metal carbonate with dilute $HClO_4$ acid and followed by slow evaporation of the solution.

5(B).2.2. Syntheses of Complexes

5(B).2.2.1.$[Zn(N_3)(dbdmp)]ClO_4$ (1)

To a stirring methanol solution (5 ml) of $Zn(ClO_4)_2{\cdot}6H_2O$ (0.186 g, 0.5 mmol), ligand dbdmp (0.166 g, 0.5 mmol) in methanol (10 ml) was added drop by drop. After 10 min, NaN_3 (0.033 g, 0.5 mmol) in water (1 ml) was added slowly to the mixture. This solution was stirred for 3 h at room temperature, filtered and kept for slow evaporation. Block shaped colourless crystals were obtained after five days which were washed with diethyl ether and dried in vacuo. Yield. 0.150 g (56 %). Found C = 40.15, H = 6.05, N = 23.28 %. Anal calc for $C_{18}H_{32}N_9O_4ClZn$: C = 40.08, H = 5.98, N = 23.37 %. IR (KBr pellet) cm^{-1}; ν(C_2H_5 + CH_3), 2984, 2943 m; ν(N_3^-), 2079 vs; ν(C = C) + ν (C = N)/pz ring, 1551 s, 1466 s; ν_{asmy}(Cl–O), 1106 br; δ(O–Cl–O), 624 s. UV-Vis spectra: λ_{max}/nm (in CH_3CN)(ε_{max}/$mol^{-1}cm^{-1}$) 215 (28048). Λ_M ($\Omega^{-1}cm^2\,mol^{-1}$) = 122.

5(B).2.2.2. $[Zn(N_3)(dbdmp)]PF_6$ (2)

A methanol solution (5 ml) of ligand dbdmp (0.166 g, 0.5 mmol) was added drop wise to a stirring solution of $Zn(CH_3COO)_2{\cdot}2H_2O$ (0.110 g, 0.5 mmol) in the same solvent (10 ml). To this NaN_3 (0.032 g, 0.5 mmol) in water (1 ml) was added slowly. After 10 min NH_4PF_6 (0.082 g, 0.5 mmol) in water (1 ml) was added and the colorless solution was stirred for 5 h, filtered and kept at room temperature for slow evaporation. After few days block shaped pale yellow colored crystals were obtained. Yield. 0.180 g (61 %). Found C = 36.75, H = 5.54, N = 21.76 %. Anal calc for

$C_{18}H_{32}N_9PF_6Zn$: C = 36.96, H = 5.51, N = 21.55 %. IR (KBr pellet) cm^{-1}; $\nu(C_2H_5 + CH_3)$, 2980, 2952 m; $\nu(N_3^-)$, 2088 vs; ν(C = C) + ν (C = N)/pz ring, 1552 s, 1464 s; $\nu(PF_6^-)$, 865 s. UV-Vis spectra: λ_{max}/nm (in CH_3CN) (ε_{max}/$mol^{-1}cm^{-1}$) 214 (25836). Λ_M ($\Omega^{-1}cm^2\,mol^{-1}$) = 120.

5(B).2.2.3. [Zn(NCO)(dbdmp)]ClO_4 (3)

This complex was prepared by following the same procedure as for complex **1** except NaNCO was used instead of NaN_3. Colorless crystals were obtained after slow evaporation of solvent. Yield. 0.200 g (68 %). Found C = 42.23, H = 5.74, N = 18.35 %. Anal calc for $C_{19}H_{32}N_7O_5ClZn$: C = 42.31, H = 5.78, N = 18.18 %. IR (KBr pellet) cm^{-1}; $\nu(C_2H_5 + CH_3)$, 3149, 2924 m; $\nu(NCO^-)$, 2233 vs; ν(C = C) + ν (C = N)/pz ring, 1528 s, 1423 s; ν_{asmy}(Cl–O), 1088 vs; δ(O–Cl–O), 628 s. UV-Vis spectra: λ_{max}/nm (in CH_3CN) (ε_{max}/$mol^{-1}cm^{-1}$) 219 (27563). Λ_M ($\Omega^{-1}cm^2\,mol^{-1}$) = 118.

5(B).2.2.4. [Zn(NCO)(dbdmp)]PF_6 (4)

This complex was prepared by following the same procedure as for complex **2** except NaNCO was used instead of NaN_3. Colorless crystals were obtained after slow evaporation of solvent. Yield. 0.165 g (56 %). Found C = 39.23, H = 5.49, N = 16.85 %. Anal calc for $C_{19}H_{32}N_7OF_6PZn$: C = 39.02, H = 5.51, N = 16.76 %. IR (KBr pellet) cm^{-1}; $\nu(C_2H_5 + CH_3)$, 3123, 2926 m; $\nu(NCO^-)$, 2235 vs; ν(C = C) + ν(C = N)/pz ring, 1555 s, 1416 s; $\nu(PF_6^-)$, 846 s. UV-Vis spectra: λ_{max}/nm (in CH_3CN) (ε_{max}/$mol^{-1}cm^{-1}$) 217 (23885). Λ_M ($\Omega^{-1}cm^2\,mol^{-1}$) = 115.

5(B).2.2.5. [Zn(NCS)(dbdmp)]ClO_4 (5)

This complex was prepared by following the same procedure as for complex **1** except KSCN was used instead of NaN_3. Colorless crystals were obtained after slow evaporation of solvent. Yield. 0.197 g (71 %). Found C = 41.23, H = 5.79, N = 17.39 %. Anal calc for $C_{19}H_{32}N_7O_4ClSZn$: C = 41.09, H = 5.81, N = 17.65 %. IR (KBr pellet) cm^{-1}; $\nu(C_2H_5 + CH_3)$, 2980 m; $\nu(NCS^-)$, 2076 vs; ν(C = C) + ν (C = N)/pz ring, 1552 s, 1468 s; ν_{asmy}(Cl–O), 1089 vs; δ(O–Cl–O), 625 s. UV-Vis spectra: λ_{max}/nm (in CH_3CN) (ε_{max}/$mol^{-1}cm^{-1}$) 220 (24763). Λ_M ($\Omega^{-1}cm^2\,mol^{-1}$) = 114.

5(B).2.2.6. $[Zn(NCS)(dbdmp)]PF_6$ (6)

This complex was prepared by following the same procedure as for complex **2** except KSCN was used instead of NaN_3. Colorless crystals were obtained after slow evaporation of solvent. Yield. 0.187 g (63 %). Found C = 37.83, H = 5.40, N = 16.45 %. Anal calc for $C_{19}H_{32}N_7SF_6PZn$: C = 37.98, H = 5.37, N = 16.32 %. IR (KBr pellet) cm^{-1}; $\nu(C_2H_5 + CH_3)$, 3146, 2988 m; $\nu(NCS^-)$, 2066 vs; $\nu(C = C) + \nu(C = N)$/pz ring, 1558, 1468 s; $\nu(PF_6^-)$, 845 s. UV-Vis spectra: λ_{max}/nm (in CH_3CN) (ε_{max}/$mol^{-1}cm^{-1}$) 221 (23989). Λ_M ($\Omega^{-1}cm^2\,mol^{-1}$) = 117.

5(B).2.2.7. $[\{Cd(dbdmp)\}_2(\mu\text{-}N_3)_2](ClO_4)_2$ (7)

To a stirring solution of $Cd(ClO_4)_2 \cdot 6H_2O$ in methanol, ligand dbdmp (0.166 g, 0.5 mmol) was added into it. After 5 min NaN_3 (0.032 g, 0.5 mmol) in water (1 ml) was added. This solution was stirred for 4 h then filtered and kept for slow evaporation. Colorless needle shaped crystals were obtained after 3 days. Yield. 0.240 g (82 %). Found C = 36.76, H = 5.46, N = 21.75 %. Anal calc for $C_{36}H_{64}N_{18}O_8Cd_2Cl_2$: C = 36.87, H = 5.50, N = 21.50 %. IR (KBr pellet) cm^{-1}; $\nu(C_2H_5 + CH_3)$, 3131, 2972 m; $\nu(N_3^-)$, 2031, 2073 vs; $\nu(C = C) + \nu(C = N)$/pz ring, 1552 s, 1464 s; $\nu_{asmy}(Cl–O)$, 1075 vs; $\delta(O–Cl–O)$, 624 s. UV-Vis spectra: λ_{max}/nm (in CH_3CN) (ε_{max}/$mol^{-1}cm^{-1}$). 217 (29973). Λ_M ($\Omega^{-1}cm^2\,mol^{-1}$) = 195.

5(B).2.2.8. $[(dbdmp)Cd(\mu\text{-}N_3)]_2(PF_6)_2$ (8)

$Cd(CH_3COO)_2 \cdot 2H_2O$ (0.133 g, 0.5 mmol) was dissolved in of methanol (5 ml) and ligand dbdmp (0.166 g, 0.5 mmol) in methanol (10 ml) was added into it. To this solution, NaN_3 (0.032 g, 0.5 mmol) in water (1 ml) was added. After 15 min NH_4PF_6 (0.82 g, 0.5 mmol) was dissolved in water (1 ml) and added drop by drop. This yellow colored solution was stirred for 4 h, filtered and kept for slow evaporation. White colored needle shaped crystals were obtained after 2 days. Yield. 0.198 g (69 %). Found C = 34.46, H = 5.08, N = 19.83 %, Anal calc for $C_{36}H_{64}N_{18}F_{12}Cd_2P_2$: C = 34.21, H = 5.10, N = 19.95 %. IR (KBr pellet) cm^{-1}; $\nu(C_2H_5 + CH_3)$, 2986, 2928, 2875 m; $\nu(N_3^-)$, 2093, 2038 vs; $\nu(C = C) + \nu(C = N)$/pz ring, 1556 s, 1469 s; $\nu(PF_6^-)$, 841 s. UV-Vis spectra: λ_{max}/nm (in CH_3CN)(ε_{max}/$mol^{-1}cm^{-1}$) 215 (26530). Λ_M ($\Omega^{-1}cm^2\,mol^{-1}$) = 210.

5(B).2.2.9. [Cd(NCO)(dbdmp)]ClO_4 (9)

This complex was prepared by following the same procedure as for complex **7** except NaNCO was used instead of NaN_3. Colorless crystals were obtained after slow evaporation of solvent. Yield. 0.210 g (72 %). Found C = 38.86, H = 5.49, N = 16.85 %. Anal calc for $C_{19}H_{32}N_7O_5Cd_1Cl_1$: C = 38.92, H = 5.50, N = 16.72 %. IR (KBr pellet) cm^{-1}; ν(C_2H_5 +CH_3), 3132, 2972 m; ν(NCO^-), 2202 vs; ν(C = C) + ν(C = N)/pz ring, 1552 s, 1464 s; ν_{asmy}(Cl–O), 1094 vs; δ(O–Cl–O), 624 s. UV-Vis spectra: λ_{max}/nm (in CH_3CN) (ε_{max}/$mol^{-1}cm^{-1}$) 214 (28937). Λ_M ($\Omega^{-1}cm^2\,mol^{-1}$) = 125.

5(B).2.2.10. [Cd(NCO)(dbdmp)]PF_6 (10)

This complex was prepared by following the same procedure as for complex **8** except NaNCO was used instead of NaN_3. Colorless crystals were obtained after slow evaporation of solvent. Yield. 0.195 g (62 %). Found C = 36.02, H = 5.12, N = 15.39 %. Anal calc for $C_{19}H_{32}N_7O_1Cd_1P_1F_6$: C = 36.12, H = 5.10, N = 15.52 %. IR (KBr pellet) cm^{-1}; ν(C_2H_5 +CH_3), 2986, 2931 m; ν(NCO^-), 2227 vs; ν(C = C) + ν(C = N)/pz ring, 1556 s, 1474, 1469 s; ν(PF_6^-), 842 s. UV-Vis spectra: λ_{max}/nm (in CH_3CN) (ε_{max}/$mol^{-1}cm^{-1}$) 216 (27687). Λ_M ($\Omega^{-1}cm^2\,mol^{-1}$) = 122.

5(B).2.2.11. [Cd$(NCS)_2$(dbdmp)] (11)

This complex was prepared by following the same procedure as for complex **7** except KSCN was used instead of NaN_3. Colorless crystals were obtained after slow evaporation of solvent. Yield. 0.140 g (49 %). Found C = 42.86, H = 5.70, N = 19.85 %, Anal calc for $C_{20}H_{32}N_8S_2Cd$: C = 42.81, H = 5.75, N = 19.97 %. IR (KBr pellet) cm^{-1}; ν(C_2H_5 +CH_3), 2984, 2868 m; ν(NCS^-), 2074, 2041 vs; ν(C = C) + ν (C = N)/pz ring, 1556 s, 1462 s. UV-Vis spectra: λ_{max}/nm (in CH_3CN) (ε_{max}/$mol^{-1}cm^{-1}$) 211 (27567). Λ_M ($\Omega^{-1}cm^2\,mol^{-1}$) = 10.

5(B).2.3. Physical Measurements

The IR spectrums were recorded on a Perkin-Elmer FT-IR spectrometer RX1 spectrum using KBr pellets. The micro analysis (C, H and N) were carried out using a Perkin-Elmer IA 2400 series elemental analyzer. UV-Vis spectra (900 – 190 nm) were recorded on a Perkin-Elmer spectrophotometer model Lambda 35 in acetonitrile solution. Solution conductivity were measured in CH_3CN solution (10^{-3} M) using Equip-Tronics conductivity meter (model no. EQ-660A).

5(B). 3. X-ray Crystallography

The details of data collection and some important features of the refinement for the compounds **1**, **7, 9** and **11** are given in Table 5(B).1 and selected bond lengths and angles are given in Table 5(B).2. Colourless crystals of suitable size of complexes were obtained by slow evaporation of methanol solution. Single crystal X-ray diffraction intensity data of the complexes **1** and **11** were collected at 293 K using Bruker APEX-II CCD diffractometer equipped with graphite monochromated Mo-K_α radiation (λ = 0.71073 Å) and Oxford X-CALIBUR-S CCD diffractometer with Cu-K_α radiation (λ = 1.54184 Å) at 150 K for complex **7** and at 293 K for complex **9**. Data reduction was carried out using the program Bruker SAINT [17] and CrysAlisPro, Agilent Technologies, Version 1.171.35.19 [18]. An absorption correction based on multi-scan method [19] was applied. 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 [20] respectively. All calculations were carried out using WinGX system Ver-1.64 [21]. All hydrogen atoms were located from difference Fourier map and treated as riding. All non hydrogen atoms were refined with anisotropic displacement coefficients.

Table 5(B).1. Crystal parameters of Complexes **1**, **7**, **9** and **11**.

	$[Zn(N_3)(dbdmp)]ClO_4$ (1)	**$[\{Cd(dbdmp)\}_2(\mu\text{-}N_3)_2](ClO_4)_2$ (7)**	**$[Cd(NCO)(dbdmp)]ClO_4$ (9)**	**$[Cd(NCS)_2(dbdmp)]$ (11)**
Empirical formula	$C_{18}H_{32}N_9O_4ClZn$	$C_{36}H_{64}Cd_2Cl_2N_{18}O_8$	$C_{19}H_{32}CdN_7O_5Cl$	$C_{20}H_{32}CdN_8S_2$
Formula weight	539.35	1172.77	586.38	561.09
Temperature (K)	295(2)	150.0(10)	293(2)	293(2)
Wavelength (Å)	0.71073	1.54184	1.54184	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$C2/c$
a (Å)	8.5154(6)	8.56730(10)	8.6201(2)	34.460(6)
b (Å)	19.2104(13)	21.6683(3)	21.9666(7)	8.1191(15)
c (Å)	14.4727(10)	12.8970(2)	13.0473(4)	18.700(3)
~(°)	90	90	90	90
(°)	91.937(2)	100.106(2)	99.630(3)	99.965(7)
¥(°)	90	90	90	90
Volume ($Å^3$)	2366.2(3)	2357.04(6)	2435.75(12)	5153.0(16)
Z	4	2	4	8
Density (g/cm^3)	1.514	1.653	1.599	1.446

Absorption coefficient (mm^{-1})	1.195	8.850	8.572	1.033
F(000)	1128	1200	1200	2344
θ range for data collection (°)	1.76 to 32.25	4.01 to 71.94	3.98 to 71.63	1.20 to 25.24
Index ranges	$-12 \le h \le 11$,	$-6 \le h \le 10$,	$-6 \le h \le 10$,	$-38 \le h \le 38$,
	$-25 \le k \le 27$,	$-25 \le k \le 26$,	$-26 \le k \le 25$,	$-9 \le k \le 9$,
	$-20 \le l \le 21$	$-15 \le l \le 13$	$-16 \le l \le 14$	$-20 \le l \le 21$
Reflections collected	37274	8877	9189	20831
Independent reflections	7704	4645	4651	3845
	[*R*(int) = 0.0386]	[*R*(int) = 0.0313]	[*R*(int) = 0.0404]	[*R*(int) = 0.0402]
Data / restraints / parameters	7704/ 0 / 304	4645 / 0 / 304	4651 / 0 / 298	3845 / 0 / 280
Goodness-of-fit on F^2	1.029	1.079	1.171	1.039
Final *R* indices [*I*>2sigma(*I*)]	*R1* = 0.0324,	*R1* = 0.0440,	*R1* = 0.0665,	*R1* = 0.0312,
	w*R2* = 0.0777	w*R2* = 0.1276	w*R2* = 0.1710	w*R2* = 0.0773
R indices	*R1* = 0.0404,	*R1* = 0.0461,	*R1* = 0.0746,	*R1* = 0.0389,
(all data)	w*R2* = 0.0809	w*R2* = 0.1304	w*R2* = 0.1756	w*R2* = 0.0820
Largest diff. peak and hole (eA^{-3})	0.737 and -0.535	2.153 and -1.629	1.344 and -0.933	0.286 and -0.464
CCDC number	932054	890814	957335	890813

Table 5(B).2. Bond lengths (Ǻ) and bond angles (°) of Complexes **1**, **7**, **9** and **11**.

Bond Lengths (Å)

[Zn(N_3)(dbdmp)]ClO_4 (1)		**[{Cd(dbdmp)}$_2$(μ-N_3)$_2$](ClO_4)$_2$ (7)**		**[Cd(NCO)(dbdmp)]ClO_4 (9)**		**[Cd(NCS)$_2$(dbdmp)] (11)**	
Zn(1)-N(7)	2.0001(13)	Cd(1)-N(1)	2.289(3)	Cd(1)-N(1)	2.293(7)	Cd(1)-N(7)	2.223(3)
Zn(1)-N(5)	2.0517(11)	Cd(1)-N(3)	2.453(3)	Cd(1)-N(3)	2.445(7)	Cd(1)-N(8)	2.315(4)
Zn(1)-N(1)	2.0713(12)	Cd(1)-N(5)	2.307(3)	Cd(1)-N(5)	2.290(7)	Cd(1)-N(5)	2.357(3)
Zn(1)-N(6)	2.1176(11)	Cd(1)-N(6)	2.376(3)	Cd(1)-N(6)	2.351(7)	Cd(1)-N(1)	2.369(3)
Zn(1)-N(3)	2.3046(12)	Cd(1)-N(7)	2.222(4)	Cd(1)-N(7)	2.157(7)	Cd(1)-N(3)	2.483(3)
		Cd(1)-N(8)	2.617(4)			Cd(1)-N(6)	2.540(3)
		Cd(1)---Cd(1i)	5.4701(4)				

Bond Angles (º)

[Zn(N_3)(dbdmp)]ClO_4 (1)		**[{Cd(dbdmp)}$_2$(μ-N_3)$_2$](ClO_4)$_2$ (7)**		**[Cd(NCO)(dbdmp)]ClO_4 (9)**		**[Cd(NCS)$_2$(dbdmp)] (11)**	
N(7)-Zn(1)-N(5)	107.60(5)	N(6)-Cd(1)-N(8)	163.24(12)	N(1)-Cd(1)-N(6)	100.1(3)	N(7)-Cd(1)-N(3)	169.28(12)
N(1)-Zn(1)-N(6)	125.71(4)	N(7)-Cd(1)-N(3)	172.14(13)	N(7)-Cd(1)-N(3)	169.4(3)	N(7)-Cd(1)-N(5)	108.10(12)
N(5)-Zn(1)-N(1)	111.43(5)	N(1)-Cd(1)-N(5)	138.47(12)	N(5)-Cd(1)-N(1)	136.0(2)	N(8)-Cd(1)-N(6)	163.59(13)
N(7)-Zn(1)-N(3)	175.76(5)	N(7)-Cd(1)-N(6)	107.59(13)	N(7)-Cd(1)-N(6)	113.2(3)	N(1)-Cd(1)-N(5)	143.17(11)
N(5)-Zn(1)-N(6)	109.44(4)	N(3)-Cd(1)-N(8)	86.54(11)	N(5)-Cd(1)-N(6)	96.3(2)	N(7)-C(19)-S(1)	176.0(4)
N(7)-N(8)-N(9)	176.59(15)	N(8)-N(9)-N(7)	176.5(4)	N(7)-C(19)-O(5)	178.6(9)	N(8)-C(20)-S(2)	175.4(4)

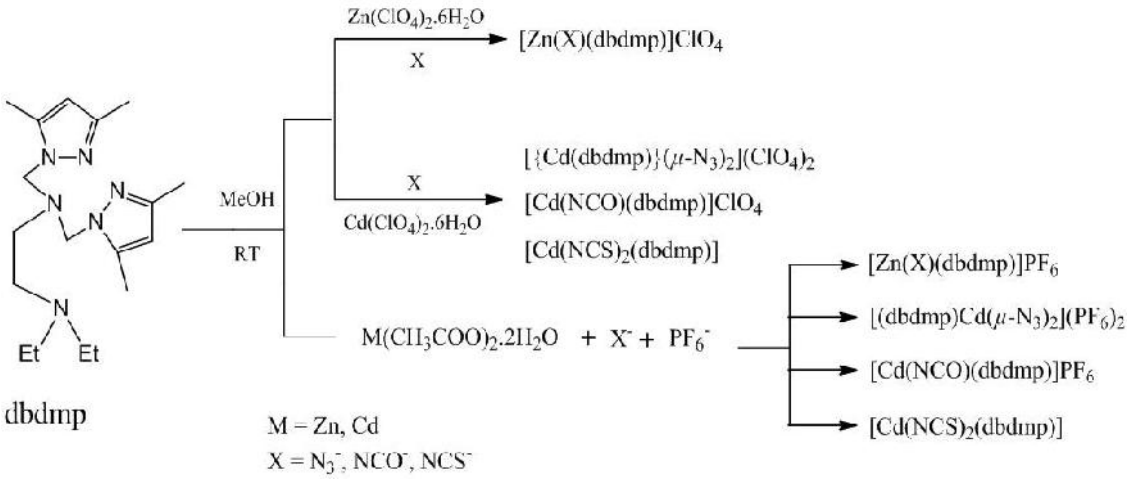
5(B).4. Results and Discussions

5(B).4.1. Syntheses

The mononuclear complexes of the type [Zn(X)(dbdmp)]Y **(1-6)** have been synthesized by reacting $Zn(ClO_4)_2 \cdot 6H_2O$ / $Zn(CH_3COO)_2 \cdot 2H_2O$, tetradentate N_4-coordinate ligand dbdmp, X (N_3^-/ NCO^-/ NCS^-) and Y (ClO_4^- / PF_6^-) ions in 1: 1: 1: 1 mole ratio in the presence of aqueous methanol at room temperature and isolated as stable colorless crystals in good yield [Scheme 5(B).1]. There is no change of composition of the complexes even with excess addition of X^- ions in the reaction. The molar conductivity measurement in CH_3CN solution (~10^{-3} M) shows all the zinc complexes are 1:1 electrolyte (Λ_M ~120 $\Omega^{-1}cm^2mol^{-1}$) [22]. There was no change of molar conductivity even after 2h indicating no decomposition of the complexes in the solution. Furthermore, the presence of counter anion was confirmed by IR spectra and single crystal X-ray diffraction studies of $[Zn(N_3)(dbdmp)]ClO_4$ (1) [Fig.5(B).1]. All complexes gave satisfactory microanalysis results confirming their molecular composition. The complexes are stable in air and moderately soluble in acetonitrile, methanol, ethanol, dichloromethane, acetone etc.

Mononuclear cadmium(II) complexes [Cd(NCO)(dbdmp)]Y and $[Cd(NCS)_2(dbdmp)]$ and binuclear cadmium(II) complexes $[\{Cd(dbdmp)\}_2(\mu\text{-}N_3)_2](Y)_2$ (Y = ClO_4^-/ PF_6^-) were obtained as colourless compound through one pot reaction of $Cd(ClO_4)_2 \cdot 6H_2O$ / $Cd(CH_3COO)_2 \cdot 2H_2O$, ligand dbdmp, pseudohalides (N_3^- / NCO^- / NCS^-) and PF_6^- in 1: 1: 1: 1 mole ratio in presence of aqueous methanol at room temperature. IR spectral data shows that azide ion containing compounds **7** and **8** are binuclear. This was also confirmed by single crystal X-ray diffraction studies of complex $[\{Cd(dbdmp)\}_2(\mu\text{-}N_3)_2](ClO_4)_2$ **(7)** [Fig.5(B).2]. Isocyanate containing complexes **9** and **10** are mononuclear with distorted trigonal bipyramidal geometry which is confirmed by single crystal diffraction studies of the complex $[Cd(NCO)(dbdmp)]ClO_4$ **(9)** [Fig.5(B).3]. The $[Cd(NCS)_2(dbdmp)]$ **(11)** complex is non ionic which is confirmed by conductance measurement (Λ_M ~10 $\Omega^{-1}cm^2mol^{-1}$), IR spectra and single crystal X-ray diffraction studies. This complex $[Cd(NCS)_2(dbdmp)]$ (**11**) has different molecular composition than corresponding zinc complexes **5** and **6**. The important point is that except two cadmium azide complexes **7** and **8**, all zinc and cadmium complexes **1-6** and **9-11** are mononuclear. The azide containing cadmium complexes **7** and **8** are binuclear with

double end-to-end (μ-1,3) coordination mode. The molar conductivity measurement in CH_3CN solution (~10^{-3}M) shows the complexes **9** and **10** are 1:1 electrolyte (Λ_M ~120 $\Omega^{-1}cm^2$ mol^{-1}) whereas complexes **7** and **8** are 1:2 electrolyte (Λ_M >180 $\Omega^{-1}cm^2mol^{-1}$) indicating the presence of counter anion in the molecule [22]. All complexes gave satisfactory microanalysis results confirming their molecular composition. The diffraction quality crystals for structural studies were obtained by slow evaporation of the solution. The complexes are stable in air and moderately soluble in acetonitrile, methanol, ethanol, dichloromethane, acetone etc.



Scheme.5(B).1. Syntheses of complexes.

In the study presented here, the present N_4-coordinated tetradentate pyrazole containing ligand form penta coordinated mononuclear complexes with trigonal bipyramidal geometry and six coordinated mono- or binuclear distorted octahedral geometry with zinc(II) and cadmium(II) in presence of pseudohalides like azide or thiocyanate or isocyanate. Similar, tetradentate N_4-coordinated pyridyl-pyrazole based ligand form five coordinated mononuclear complexes with trigonal bipyramidal geometry and six coordinated binuclear complexes with distorted octahedral geometry with same metal ions and same pseudohalides [23-25]. Therefore, we can conclude that pyrazole containing tetradentate N4-coordinated ligand form mononuclear complexes with either trigonal bipyramidal or distorted octahedral geometry and binuclear complexes with distorted octahedral geometry with Zn(II) and Cd(II) ions in the presence of pseudohalides like azide, thiocyanate or isocyanate, although zinc(II) and cadmium (II) prefer to form tetrahedral complexes [26]. Another important point

is that most of the reported azide bridged binuclear cadmium(II) complexes have end-on (μ-1,1) coordination mode of bonding [23, 27-28] but the compound $[\{Cd(dbdmp)\}_2(\mu\text{-}N_3)_2](ClO_4)_2$ **(7)** synthesized by us has rare end-to-end (μ-1,3) coordination mode of bonding.

5(B).4.2. Description of Crystal Structures

5(B).4.2.1. $[Zn(N_3)(dbdmp)]ClO_4$ (1)

The ORTEP representation of the cationic part of complex $[Zn(N_3)(dbdmp)]ClO_4$ is shown in Fig. 5(B).1. Selected bond length and bond angles are given in Table 5(B).2. The structure of $[Zn(N_3)(dbdmp)]ClO_4$ consists of monomeric $[Zn(N_3)(dbdmp)]^+$ cation and crystallized in monoclinic crystal system with centro symmetric space group $P2_1/c$. The ligand dbdmp is tetradentate, utilized all the four potential N_4-donor sites N(1), N(3), N(5), N(6) for bonding in the complex. As shown in Fig.1, the zinc atom is five coordinated and the geometry around zinc(II) can be best described as distorted trigonal bipyramidal as indicated by the magnitude of the trigonality index ² ~ 0.835 [² = (α – β)/60, where α and β are the two largest coordination angles]. For the perfect square pyramidal and trigonal bipyramidal geometries, the ² -values are zero and unity, respectively [29]. The zinc(II) ion is coordinated by five nitrogen donor atoms- four nitrogen atoms from ligand dbdmp and one nitrogen [N(7)] of terminal azide ion. In the basal plane, there are three nitrogen atoms N(1), N(5) and N(6) of ligand dbdmp and axial plane are occupied by N(3) of dbdmp and N(7) of terminal azide ion. The bond lengths are in the range of 2.0517(11) to 2.117(11) Å in the equatorial plane and axial bond Zn-N(3) (2.304(12) Å) is longer than Zn-N(7) 2.0001(13) (Å). The Zn-N(7) distance 2.0001(13) Å is comparable with the corresponding distance (1.978-2.036 Å) given for other mononuclear five coordinated zinc(II) azido complex previously reported [23-25]. The bond angle Zn(1)-N(7)-N(8) is 129.71º but the bond angle (176.60º) of terminal azide ion N(7)-N(8)-N(9) is close to 180º. The axial bond angle is 175.76(5)º but the equatorial bond angles are in the range of 109.44(4) to 125.71(4)º.

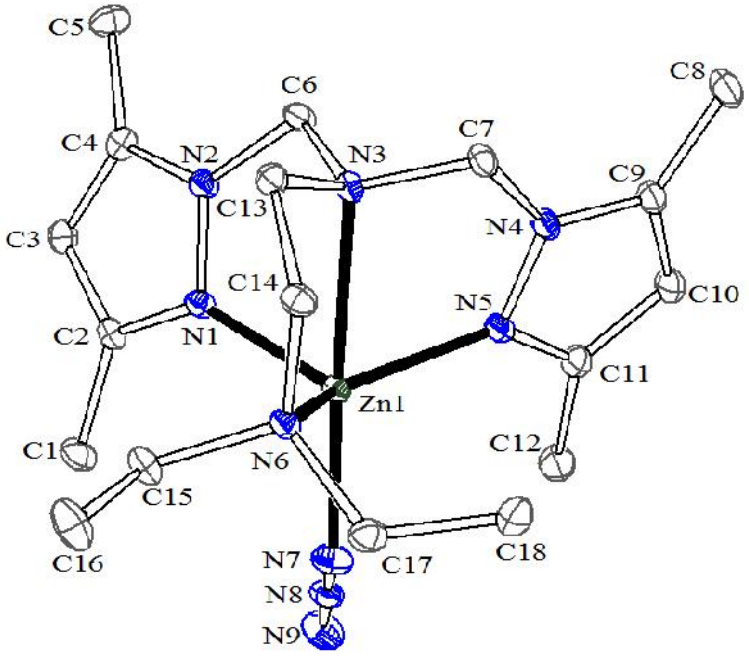


Fig. 5(B).1. ORTEP diagram depicting the cationic part of the $[Zn(N_3)(dbdmp)]ClO_4$ **(1)** complex with atom numbering scheme (30% probability factor for the thermal ellipsoids. H-atoms are omitted for the clarity).

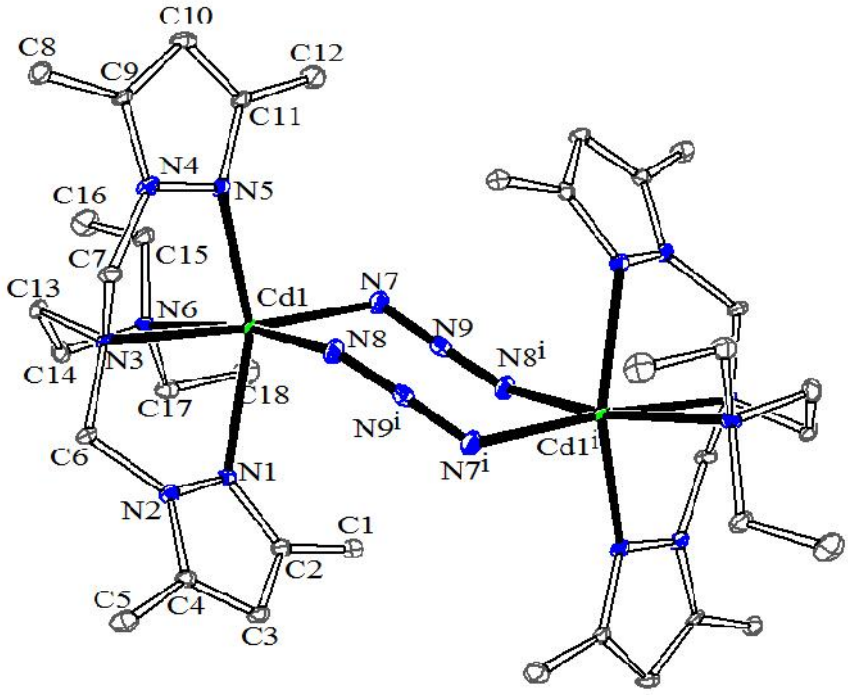


Fig. 5(B).2. ORTEP diagram depicting the cationic part of the $[\{Cd(dbdmp)\}_2(\mu\text{-}N_3)_2](ClO_4)_2$ **(7)** complex with atom numbering scheme (30% probability factor for the thermal ellipsoids. H-atoms are omitted for the clarity).

5(B).4.2.2. [{Cd(dbdmp)}$_2$(μ-N_3)$_2$](ClO$_4$)$_2$ (7)

The molecular structure of the dimeric cationic moiety of complex **7** is crystallized in monoclinic crystal system with centro symmetric space group *P2$_1$/c*. Atom-lebeling scheme is shown in Fig. 5(B).2 and selected bond lengths and angles for the metal coordination sphere of the structure are given in Table 5(B).2. The structure shows that the two azide ions bridges two cadmium(II) centers by adopting end-to-end (μ-1,3) coordination mode. The geometry around each cadmium is distorted octahedral and each cadmium center is blocked by three five membered chelate ring. The double end-to-end azide bridges link two symmetry related centers forming an eight-membered Cd-($\mu_{1,3}$-N_3)$_2$-Cd bridging ring and forms chair conformation. The Cd-N(7) bond (2.222(4) Å) is much shorter than Cd-N(8) bond (2.617(4) Å)) of azide ion which might be caused by azide ion-azide ion repulsion in the two CdN_3 moieties. Each cadmium is bonded to four nitrogen atoms-two tertiary nitrogen atoms N(3) and N(6) from ligand and two nitrogen atoms (N(7), N(8)) from two azide ions in the equatorial position and the two pyrazole nitrogen atoms N(5) and N(1) at the axial position. In the basal plane, the bond lengths Cd-N(6) (2.375 Å), Cd-N(7) (2.221 Å), Cd-N(8) (2.616 Å) and Cd-N(3) (2.453 Å) are approximately equal. The two axial lengths Cd-N(5) (2.307(3) Å) and Cd-N(1) (2.289 Å) are nearly equal. The bond angles N(7)-Cd(1)-N(3) is 172.15º and N(1)-Cd(1)-N(5) is 138.46º. This is a dimeric structure and the bond length of Cd(1)-N(7) and Cd(1i)-N(7i) are equal (2.221 Å). Since the distance between Cd-N(8) (2.617(4) Å) is longer than Cd-N(7) bond (2.222(4) Å), it can be concluded that the interaction between Cd and N(8) of azide ion is very weak. The bridging azide ions are quasilinear as is reflected in the N(7)-N(9)-N(8) bond angle 176.5(4)º. The Cd----Cd distance is 5.4701(4) Å which lie in the normal rang found for related end-to-end (μ-1,3) azide bridged compounds [30].

5(B).4.2.3. [Cd(NCO)(dbdmp)]ClO$_4$ (9)

The ORTEP diagram of the cationic part of the complex [Cd(NCO)(dbdmp)]ClO_4 is shown in Fig.5(B).3 and selected bond length and bond angles are given in Table.5(B).2. The structure of [Cd(NCO)(dbdmp)]ClO_4 consists of monomeric $[Cd(NCO)(dbdmp)]^+$ cation and crystallized in monoclinic crystal system with centro symmetric space group *P2$_1$/c*. As shown in Fig.5(B).3, the cadmium atom is five

coordinated where four coordination sites are occupied by four nitrogen atom [N(1), N(3), N(5) and N(6)] of ligand dbdmp and one nitrogen [N(7)] of terminal NCO^- ion. The geometry around cadmium(II) ion can be best described either as distorted trigonal bipyramidal or as distorted square pyramidal as indicated by the magnitude of the trigonality index $^2 \sim 0.55$. The equatorial plane is occupied by N(1), N(5) and N(6) atoms of ligand dbdmp and the two axial plane is occupied by N(3) of dbdmp and N(7) of terminal NCO^- ion. The equatorial bond lengths are in the range of 2.290(6) Å to 2.351(7) Å and axial bond lengths are 2.157(7) Å and 2.445(7) Å. The Cd-N(NCO) bond length is comparable to other reporte Cd-N(NCO) bond lengths (2.238(5) Å and 2.194(4) Å) of mononuclear cadmium(II) isocyanate complex [9] and (2.329(2) Å) of polynuclear cadmium(II) isocyanate complex [31]. The bond angle N(3)-Cd(1)-N(7) is 169.35º but the bond angle of terminal NCO^- ion N(7)-C(19)-O(5) (178.60º) is close to 180º. The axial bond angle is 169.4(3)º and equatorial bond angles are in the range of 96.3(4)º to 136.0(2)º.

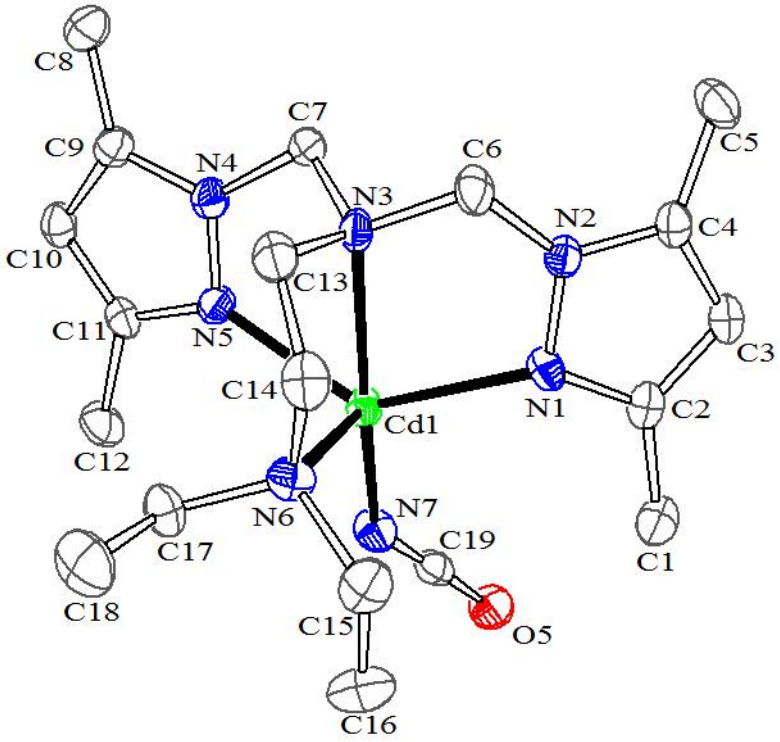


Fig.5(B).3. ORTEP diagram depicting the cationic part of the $[Cd(NCO)(dbdmp)]ClO_4$ **(9)** complex with atom numbering scheme (30% probability factor for the thermal ellipsoids. H-atoms are omitted for the clarity).

5(B).4.2.4. [Cd(NCS)$_2$(dbdmp)] (11)

The ORTEP representation of the complex [Cd(NCS)$_2$(dbdmp)] (**11**) is shown in Fig. 5(B).4. Selected bond length and bond angles are given in Table 5(B).2. The structure of [Cd(NCS)$_2$(dbdmp)] reveals that complex **11** is a non-ionic complex and crystallized in monoclinic crystal system with space group *C2/c*, where two NCS^- ions are attached in cis position with respect to Cd(II) atom. The geometry around Cd(II) ion is distorted octahedral with CdN_6 coordination environment ligated by four nitrogen atoms of ligand dbdmp [N(1), N(3), N(5) and N(6)] and two nitrogen of terminal thiocyanate ions. The basal plane of complex consists of two tertiary amines' nitrogen atoms of dbdmp [N(3) and N(6)] and two nitrogen atoms [N(7) and N(8)] of two terminal thiocyanate ions while the axial position is occupied by N(1) and N(5) nitrogen atoms of pyrazole ring of dbdmp.

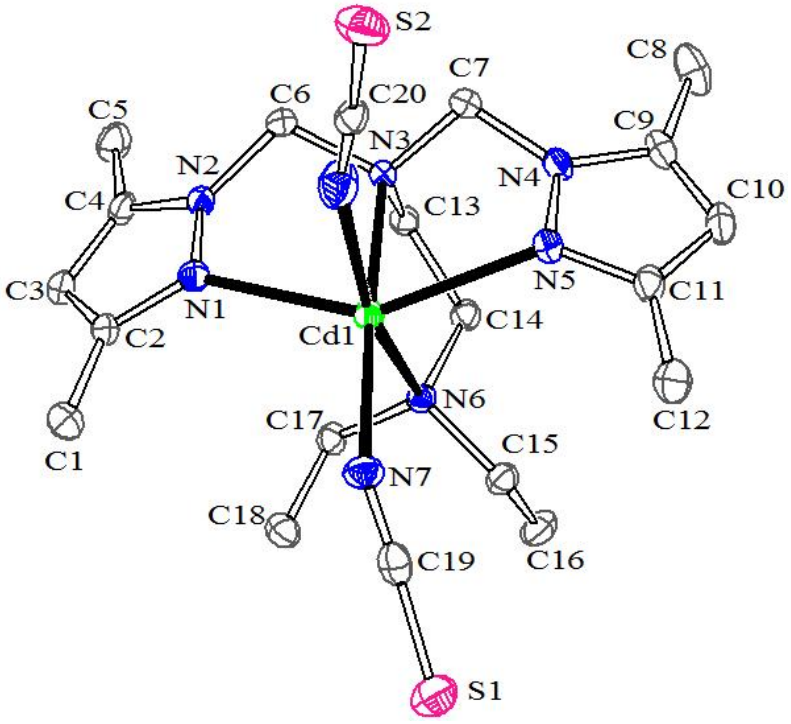


Fig.5(B).4. ORTEP diagram of the complex [Cd(NCS)$_2$(dbdmp)] **(11)** with atom numbering scheme (30% probability factor for the thermal ellipsoids. H-atoms are omitted for the clarity).

The two axial bond lengths Cd(1)-N(1) and Cd(1)-N(5) are 2.369(3) Å and 2.357(3) Å, respectively and the equatorial bond lengths are in the range of 2.223(3) Å-2.540(3) Å. The equatorial bond angles N(7)-Cd(1)-N(3) and N(8)-Cd(1)-N(6) are 169.28(12)º and 163.59(13)º, respectively whereas the axial bond angle N(1)-Cd(1)-N(5) is 143.17(11)º. The terminal N-donor thiocyanate ions are coordinated to Cd(II) center in almost linear fashion (~176º). The two Cd-N(NCS) bond distances are in the range of 2.223-2.540 Å and is comparable with corresponding value (2.343 Å) given by other hexacoordinated NCS containing Cd(II) complexes reported earlier [32-34]. The four Cd-N(dbdmp) bonds are in the range of 2.315 Å-2.480 Å in all the three cadmium (II) complexes **7**, **9** and **11**, but the Cd-N(NCS)bond lengths (2.223(3) Å and 2.540(3) Å) are longer than Cd-N(NCO) bond length 2.157(7) Å.

5(B).4.3. IR Spectra

The IR spectra of the complexes were assigned in comparison of the IR spectra of the ligand. In free ligand, two strong bands are found at 1555 cm^{-1} and 1459 cm^{-1} which are assigned as ν(C = C) and ν(C=N) bands of pyrazole ring. All the complexes also 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 complexes. IR spectra of complexes **1-2** exhibited a sharp peak in the region of 2079-2088 cm^{-1} due to asymmetric stretching vibration of terminal ν(N_3^-) ion. For complexes **3** and **4**, a sharp band appeared at ~ 2233 cm^{-1} due to asymmetric stretching vibration of N- bonded terminal ν(NCO^-) ion. Two sharp bands in the range 2031-2073 cm^{-1} for **7** and at 2096-2057 cm^{-1} for **8** indicating the bridging mode of coordination of azide ion in the complexes [35]. One sharp peak at ~ 2220 cm^{-1} is observed in the IR spectra of complexes **9** and **10** indicating the coordination of NCO^- ion. An intense band appeared in the region of 2046-2076 cm^{-1} due to asymmetric stretching vibration of N-bonded terminal ν(NCS^-) ion for the complexes **5**, **6** and **11**. The IR spectra of complexes **1, 3, 5, 7** and **9** shows a broad band in the region of 1100 cm^{-1} and a weak band at 625 cm^{-1} confirm the presence of perchlorate ion as counter anion. An intense band at ~ 850 cm^{-1} confirms the presence of PF_6^- counter anion for the complexes **2**, **4, 6, 8** and **10** respectively.

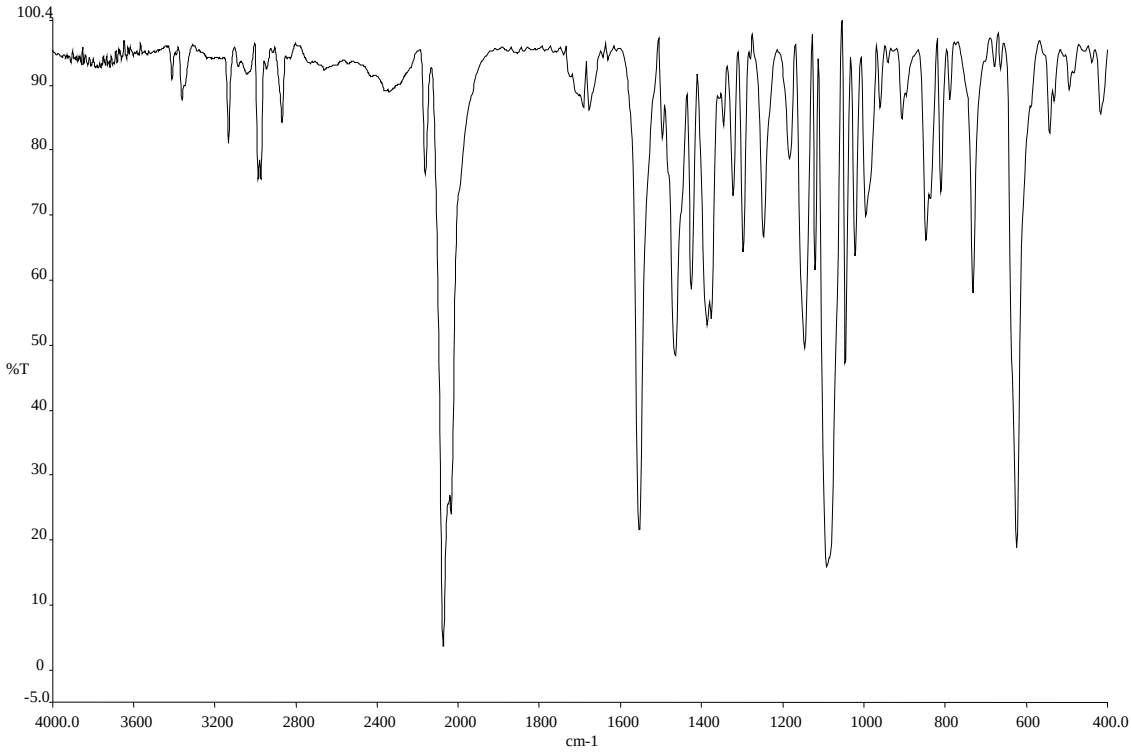


Fig.5(B).5. IR spectrum of [{Cd(dbdmp)}$_2$(μ-N_3)$_2$](ClO$_4$)$_2$ **(7)**.

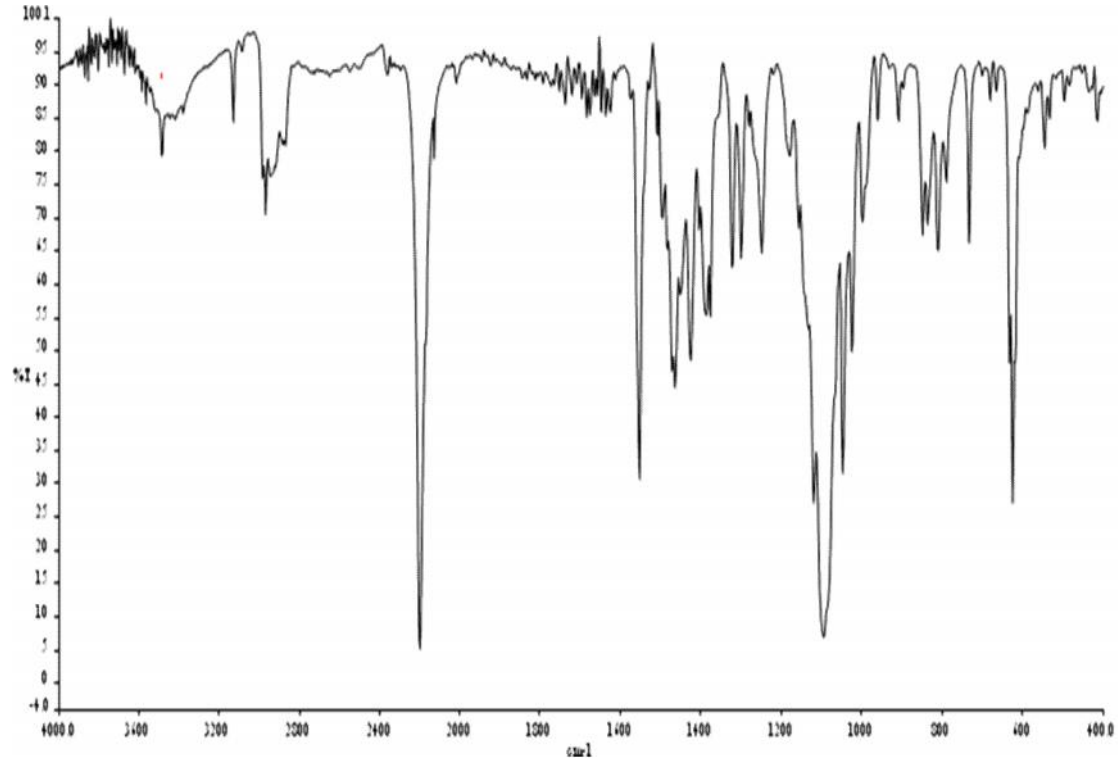


Fig.5(B).6. IR spectrum of [Cd(NCO)(dbdmp)]ClO$_4$ **(9)**.

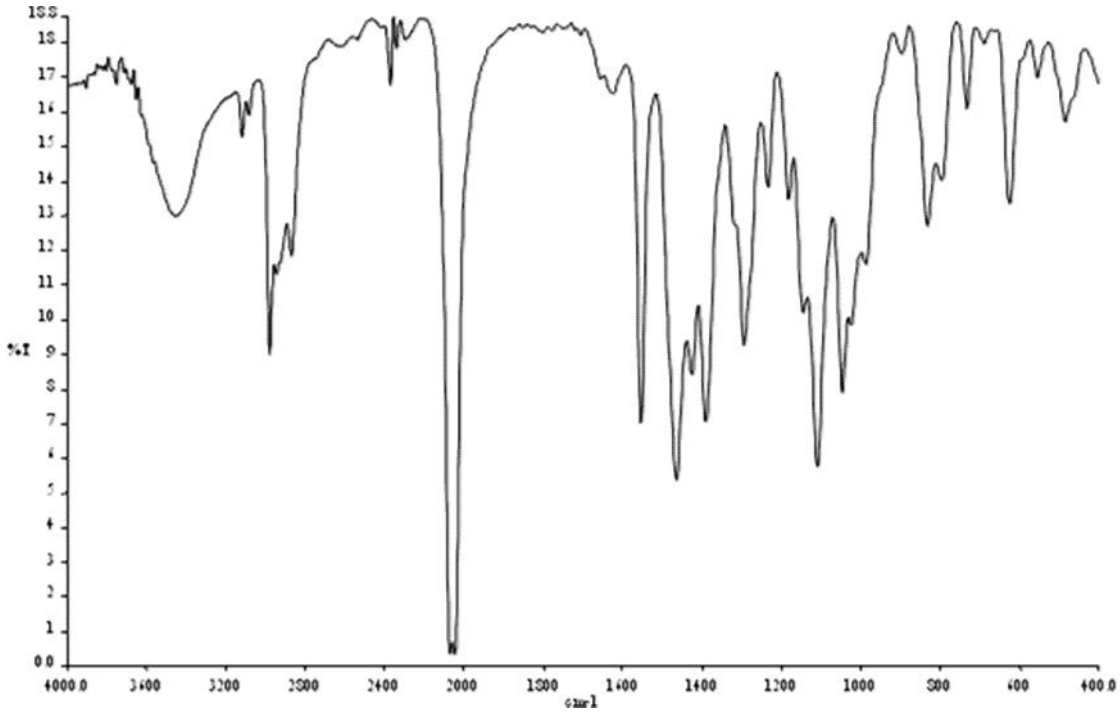


Fig.5(B).7. IR spectrum of [Cd(dbdmp)$(NCS)_2$] **(11)**.

5(B).5. Conclusion

This chapter describes the syntheses and characterizations of mononuclear zinc(II) complexes [Zn(X)(dbdmp)]Y (X= N_3^- / NCO^- / NCS^- and Y = ClO_4^- / PF_6^-), mononuclear cadmium(II) complexes [Cd$(NCS)_2$(dbdmp)] and [Cd(NCO)](dbdmp)]Y and binuclear azide bridged cadmium(II) complexes [{Cd(dbdmp)}$_2$(μ-N_3)$_2$](Y)$_2$ (Y = PF_6^- / ClO_4^-). The single crystal X-ray structure shows five coordinated cadmium(II) and zinc(II) complexes have distorted trigonal bipyramidal geometry with MN_5 (M = Cd and Zn) coordination environment, [Cd$(NCS)_2$(dbdmp)] (4) has octahedral geometry and the geometry around each cadmium atom in binuclear azide bridged cadmium (II) complex [{Cd(dbdmp)}$_2$(μ-N_3)$_2$]$(ClO_4)_2$ has distorted octahedral geometry. The prefered geometry for pyrazole containing N_4-coordinating tetradentate ligand is either trigonal bipyramidal or distorted octahedral for zinc(II) and cadmium(II) complexes in presence of N_3^- / NCS^- / NCO^- ions and binuclear azide bridged cadmium(II) complex has end-to-end (μ-1,3) bridging coordination mode.

5(B).6. References:

1. R. Ghosh, S. H. Rahaman, G. M. Rosair, B. K. Ghosh, *Inorg. Chem. Commun.* 10 (2007) 61.
2. B. Holló, Z. D. Tomić, P. Pogány, A. Kovács, V. M. Leovac, K. M. Szécsényi, *Polyhedron* 28 (2009) 3881.
3. B. N. Sarkar, S. Choubey, K. Bhar, S. Chattopadhyay, P. Mitra, B. K. Ghosh, *J. Mol. Struct.* 994 (2011) 306.
4. N. G. Spiropulos, G. C. Chingas, M. Sullivan, J. T. York, E. C.Brown, *Inorg. Chim. Acta* 376 (2011) 562.
5. Y. F. Ji, R. Wang, S. Ding, C. F. Du, Z. L. Liu, *Inorg. Chem. Commun.* 16 (2012) 47.
6. A. A. Hoser, W. Schilf, A. S. Chelmieniecka, B. Kolodziej, B. Kamieński, E. Grech, K. Woźniak, *Polyhedron* 31 (2012) 241.
7. S. Satapathi, S. Das, K. Bhar, R. K. Kumar, T. K. Maji, B. K. Maji, *Polyhedron* 30 (2011) 387.
8. L. Sun, X. Li, N. Yu, S. Chen, S. Yao, H. Deng, *Inorg. Chem. Commun.* 24 (2012) 241.
9. L. K. Das, M. G.B. Drew, A. Ghosh, *Inorg. Chim. Acta* 394 (2013) 247.
10. G. Bentabed-Ababsa, F. Blanco, A. Derdour, F. Mongin, F. Trecourt, G. Queguiner, R. Ballesteros, B. Abarca, *J. Org. Chem.* 74 (2009) 163.
11. M. Fujita, Y. J. Kwon, S. Washizu, K. Ogura, *J. Am. Chem. Soc.* 116 (1994) 1151.
12. H. A. Habib, A. Hoffmann, H. A. Hoppe, G. Steinfeld, C. Janiak, *Inorg. Chem.* 48 (2009) 2166.
13. H. Z. Dong, J. Zhao, S. H. Gou, H. B. Zhu, *Polyhedron* 28 (2009) 1040.
14. S. B. Kumar, M. Zala, A. Solanki, M. Rangrez, P. Parikh, E. Suresh, *Polyhedron* 36 (2012) 15.
15. K. Ghosh, P. Kumar, N. Tyagi, *Inorg. Chim. Acta* 375 (2011) 77.
16. H. L.Wu, K. T. Wang, B. Liu, F. Kou, F. Jia, J. Yuan, Y. Bai, *Inorg. Chim. Acta* 384 (2012) 302.
17. Bruker, *SAINT (Version 6.36a) Bruker AXS Inc., Madison, Wisconsin, USA* 2002.
18. Agilent, *CrysAlis PRO*. *Agilent Technologies UK Ltd, Yarnton, England*

(2011).

19. Bruker, *SMART (Version 5.625) and SADABS (Version 2.03a) Bruker AXS Inc., Madison, Wisconsin, USA* 2001.
20. G. M. Sheldrick, SHELXS97 and SHELXL97: *Programs for Crystal Structure Solution and Refinement, University of Göttingen, Germany* 1997.
21. L. J. Farrugia, *J. Appl. Cryst.* 32 (1999) 837.
22. W. J. Geary, *Coord. Chem. Rev.* 7 (1971) 81.
23. S. B. Kumar, M. Zala, *J. Indian Chem. Soc.* 90 (2013) 1.
24. J. Banerjee, D. Bose, S. H. Rahaman, R. D. B. Walsh, M. J. Zaworotko, B. K. Ghosh, *Ind. J. Chem.* 43A (2004) 1119.
25. H.-Yu Qian, Z.-Lu You, *Synthesis and Reactivity in Inorganic, Metal-Organic and Nano-Metal Chemistry* 39 (2009) 193.
26. M. W. Njoroge, S. O. Ojwach, G. S. Nyamato, B. Omondi, J. Darkwa, *J. Coord. Chem.* 66 (2013) 1626.
27. S. Ray, S. Konar, A. Jana, S. Jana, A. Patra, S. Chatterjee, J. A. Golen, A. L. Rheingold, S. S. Mandal, S. K. Kar, *Polyhedron* 33 (2012) 82.
28. B. Machura, I. Nawrot, K. Michalik, *Polyhedron* 31 (2012) 548.
29. A. W. Addison, T. N. Rao, J. Reedijk, J. Van Rijn, G. C. Verschoor, *J. Chem. Soc., Dalton Trans.* (1984) 1349.
30. M. A. S. Goher, F. A. Mautner, A. K. Hafez, M. A. M. Abu-Youssef, C. Gspan, A. M.-A. Badr, *Polyhedron* 22 (2003) 975.
31. X. Zhu, Y. Guo, Y.-L. Zou, *Acta Cryst. Section E* E65 (2009) m1506.
32. H. Chowdhury, R. Ghosh, S. H. Rahaman, G. M. Rosair, B. K. Ghosh, *Ind. J. Chem.* 44A (2005) 687.
33. H. Chowdhury, R. Ghosh, S. H. Rahaman, B. K. Ghosh, *Polyhedron* 26 (2007) 5023.
34. K. K. Sarkar, B. G. Chand, A. D. Jana, G. Mostafa, C. Sinha, *Inorg. Chim. Acta.* 359 (2006) 695.
35. R. Corte´s, M. Drillon, X. Solans, L. Lezama, T. Rojo, *Inorg. Chem.* 36 (1997) 677.