Synthesis, Spectroscopic and X-ray crystallographic Investigation of diperchlorate cadmium complex of o-phenanthroline

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Abstract - **o-phenanthroline is one of the most explored chelate systems out of many N-heterocyclic family of compounds, as it can easily form stable complexes with transition as well as non-transition cations. Moreover, planar nature of phenanthroline drawn considerable attention as it leads to intercalation or groove binding with DNA or RNA. Diperchlorate complex of Cd-o-phen is synthesized and characterized spectroscopically to verify its purity. The diperchlorate cadmium complex of bis chelating o-phenanthroline ligand formulated as [2Cd{C12H8N2)3}2 2(ClO4)2(C4H9N)(C5H5N)2]crystallizes in triclinic space group P-1 with Z=2 (two molecules per asymmetric unit).In the complex, both the cationic unit Cd(phen)$^+_3$ exhibit distorted octahedron with CdN6 coordination sphere involving six N atoms, each two from three bis chelating o-phen ligands. The counter perchlorate anions (ClO4)$^-$ remain free in the lattice along with solvent molecules pyridine and tetrahydropyrrole. All the three fused o-phen rings of both the molecules are orthogonal to each other with dihedral angles range from 72.8(4)° to 86.0(3)°.Halogen and oxygen of diperchlorate anions along with free solvent molecules pyridine and tetrahydropyrrole molecules play the decisive role in supperamolecular aggregation.**

Keywords: *metal perchlorate complex (Cd-o-phen); Spectroscopic; inter and intra molecular interactions*

I. INTRODUCTION

Wide range of complexing property [rigidity, planarity, aromaticity, basicity etc] as well as the redox stability of o-phenanthroline (o-phen) ligand at the different stoichiometric ratio results in a significant number of versatile materials. O-phen and its metal complexes possess potential technological applications, due to their high charge transfer mobility, bright light-emission and good electro and photo-active properties [1]-[5]. Among the d-block elements, Cd metal has been found in marine diatoms in the form of cadmium-dependent carbonic anhydrase. In addition, cadmium performs the same function as zinc in other anhydrases[6-8].As part of our ongoing research on metal diperchlorate complexes of o-phenanthroline, we report herethe synthesis, spectroscopic, characterization along with X-ray crystallographicinvestigation of cadmium complex of o-phen ligand.

II. EXPERIMENTAL

Synthesis and crystal growth

The aqueous deionized solution of cadmium perchlorate hexahydrate (1mmol) is added in the methanolic solution (20 ml,3mmol) of o-phenanthroline and the mixture is refluxed for about two hours at 45°C, resulting white coloured precipitate, filtered and washed with water and methanol successively. Yield 64%.The purified powder product readily soluble in DMF, DMSO, tetrahydropyrrole, pyridine, picoline solvents. To grow single crystals suitable for X-ray diffraction studies, synthesized powder is dissolved separately in pyridine, tetrahydropyrrole, picoline, DMF etc solvents. Few transparent blocks shaped single crystals are possible to grow from pyridine solvent using slow evaporation technique.

Spectroscopic Characterization

FT-IR spectroscopy

FT-IR spectra of o-phen and Cd-o-phen complex are recorded on a Perkin Elmer Spectrum GX FT-IR Spectrometer using KBr pellet technique. The spectra of free ligand and for the synthesized metal complex are recorded within the range of 4000-400 cm^{-1} in DMSO-d6 solution.

^{1}HNMR Spectroscopy

The ^{1}H NMR spectra of free o-phen ligand and its metal complex are recorded on a Bruker Advance DPX-200 spectrometer in d6-DMSO using 400 MHZ.

Structure solution and refinement

Three dimensional X-ray crystallographic data of an optimum size single crystal of Cd-o-phen complex is collected at room temperature on a Bruker Kappa Apex-II CCD-4 diffractometer [9] using graphite-monochromated MoKα radiation (λ = 0.71073 Å).Direct methods using SHELXS-97 [10] program, built in WinGX [11] program package is used to locate the phases to solve the crystal structure of Cd-o-phen complex and refined by full-matrix least square technique on F^2, using SHELXL-97 program of WinGX software. The values of $R[F^2> 2\sigma(F^2)]$ = 0.040 and S = 1.07 reveal the quality of the data. All hydrogen atoms are geometrically fixed and allowed to ride on the corresponding non-hydrogen atoms with C-H = 0.93Å. The final weighting scheme is $W = 1/[\sigma^2(F_o{}^2) + (0.0495P)^2 + 2.2797P]$ where $P = (F_o{}^2 + 2F_c{}^2)/3$. The residual electron density is '$\Delta\rho_{max}$' = 0.58 and '$\Delta\rho_{min}$= '-0.56' eÅ^{-3}, after the last cycle of refinement. ORTEP-III [12] and PLATON [13] programs within WinGX are used to prepare diagrams for publication.

III. RESULT AND DISCUSSION

FT-IR Spectroscopy

FT-IR Spectra of o-phen and Cd-o-phen complex is shown in **Figure1** and **Figure2**, respectively. To confirm the metal-ligand complexation, a comparative study of the IR spectra of the Cd-o-phen complex with that of the free o-phen ligand is carried out. The band v(Cd-N) at 418 cm^{-1} which is absent in the spectra of the free ligand o-phenanthroline, suggests metal(Cd) bonding with the nitrogen atoms of o-phenanthroline ligand. The absorption band v(C=N) and v(C=C) of o-phenanthroline are shown at 1618 cm^{-1} and 1504 cm^{-1} while these stretching vibrations are shifted to comparative higher frequency in the Cd-o-phen complex to 1623 cm^{-1} and 1592 cm^{-1}, confirming the participation of the C=N of o-phenanthroline in bonding. This bonding is also confirmed by the change of C-H stretching frequency of Cd-o-phen complex which is located at 3064-2850 cm^{-1}. Further, the peak at 1084 cm^{-1} corresponds to asymmetric stretching vibration of Cl-O, suggesting the presence of anion ClO4$^-$in the lattice, which is in agreement with X-ray crystallographic data. Characteristic IR bands (cm^{-1}) of o-phen and Cd-o-phen complex are assigned based on some reported data [14]-[17] which are listed below.

FT-IR (KBr pellet,cm^{-1}) :o-phen ligand :3417 (b,s) v(OH) , 3059-2851(b,w)v(C-H), 1618&1587(m) v(C=N), 1504(m) v(C=C), 1137 &1091 (sh,m) v(C-C), 875&738(s) v(C-H)oop.

Cd-o-phen:3439 (b,s) v(OH) , 3064-2850v(C-H), 1623&1592(m) v(C=N), 1518(m) v(C=C), 1225&1148 (w) v(C-C), 1084 (s) v_{as}(ClO$_4$), 622(s) δ(ClO$_4$), 845&724(s) v(C-H)oop ,418(vw) v(Cd-N)
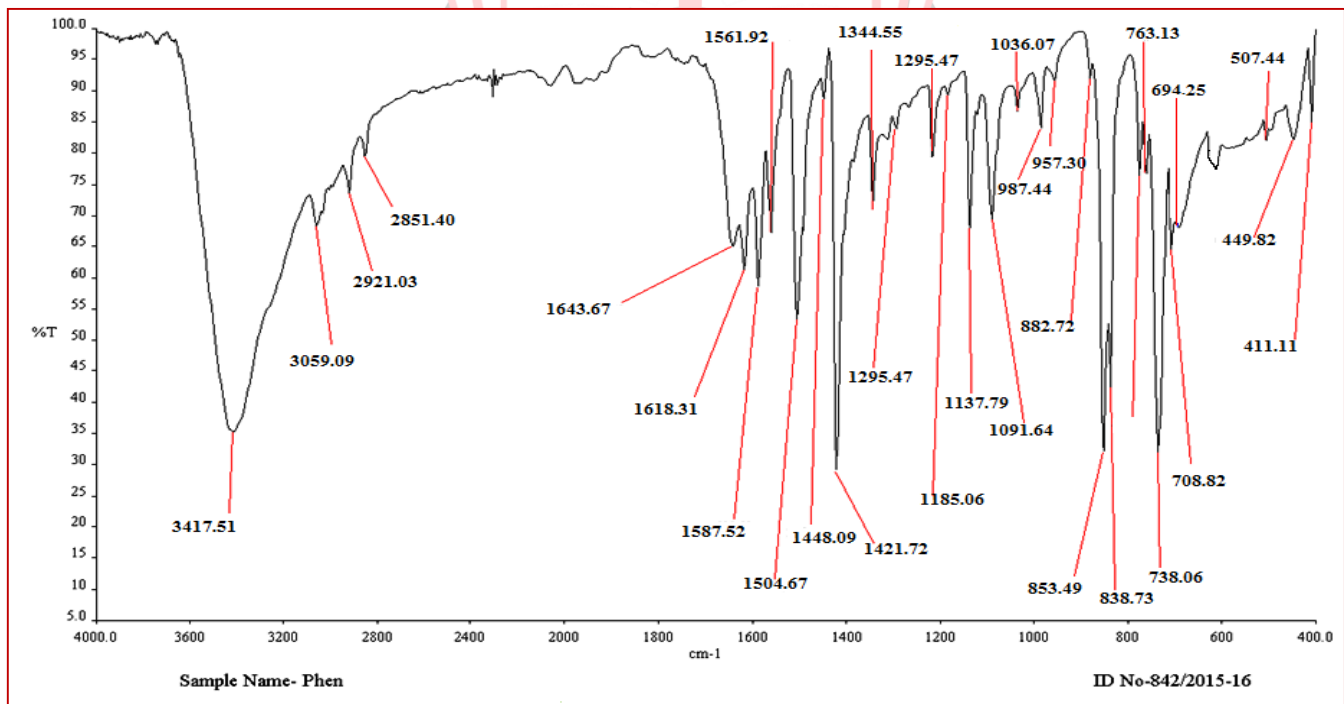

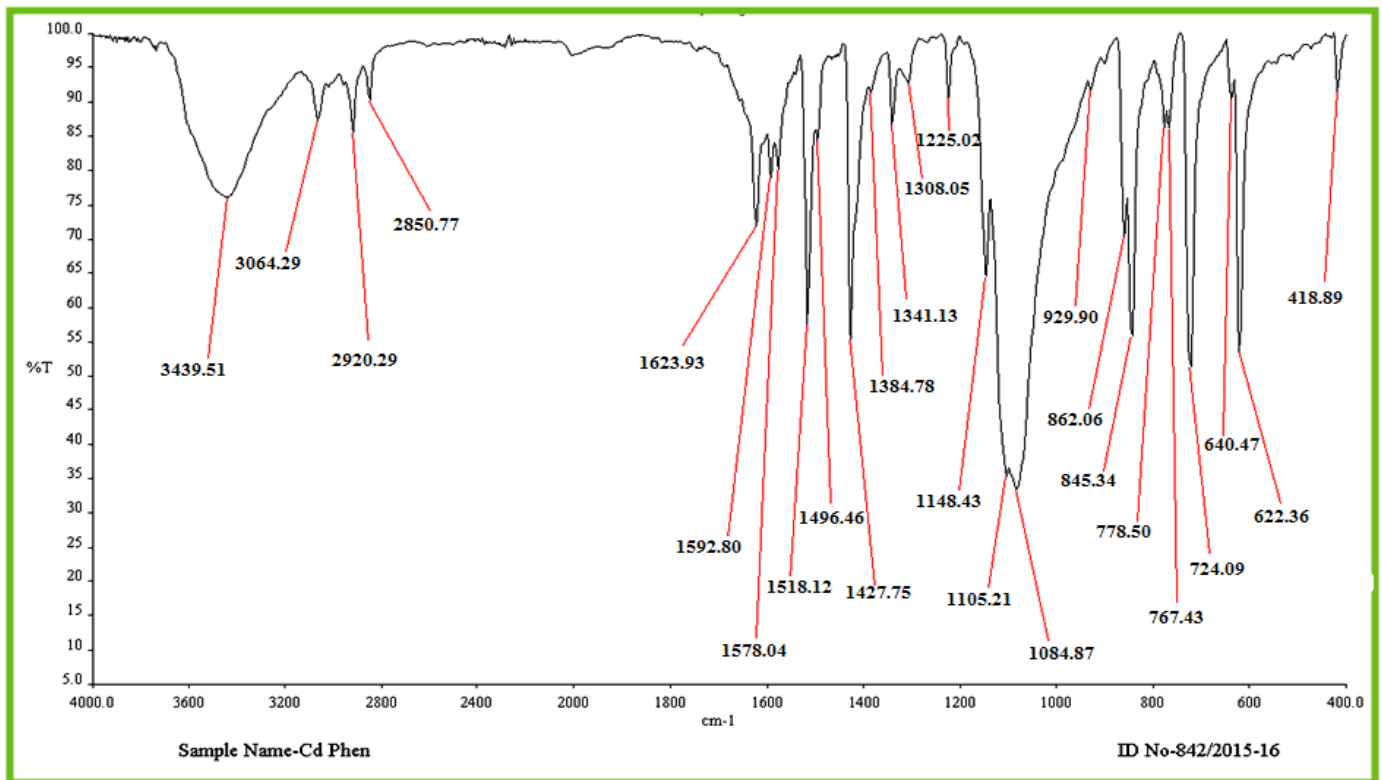**Figure 1 FT-IR spectra of o-phen ligand**

Figure 2 FT-IR spectra of Cd-o-phen complex

^{1}HNMR spectroscopy

^{1}HNMR spectra for free o-phen ligand and those of Cd-o-phen complex are depicted in **Figure 3** and **Figure 4**, respectively. The phenanthroline molecule consists of four pairs of equivalent protons and resonates within the range of 7.6-9.2 ppm. A doublet at 9.19-9.17 ppm is assigned to protons attached to C2 and C11 whereas, those at 8.24-8.21 ppm are due to protons at C4 and C9. Similarly, singlet at 7.77-7.76 ppm is assigned to protons attached to C6 , C7 and quartet in the range 7.63-7.60 ppm arises due to protons at C3 and C10 while almost all resonance suffers downfield shift in Cd-o-phen complex [18]-[20].^{1}H NMR assignments for o-phen and Cd-o-phen complex are listed below:

o-phen ligand (DMSO-d6,400 MHZ): δ 9.189 H2 &H11 ,8.238 H4 &H9 , 7.769H6 &H7, 7.616 H3 &H10 **Cd-o-phen complex :** δ 9.254H2 &H11, 8.319H4 &H9, 7.854H6 &H7, 7.705 H3 &H10
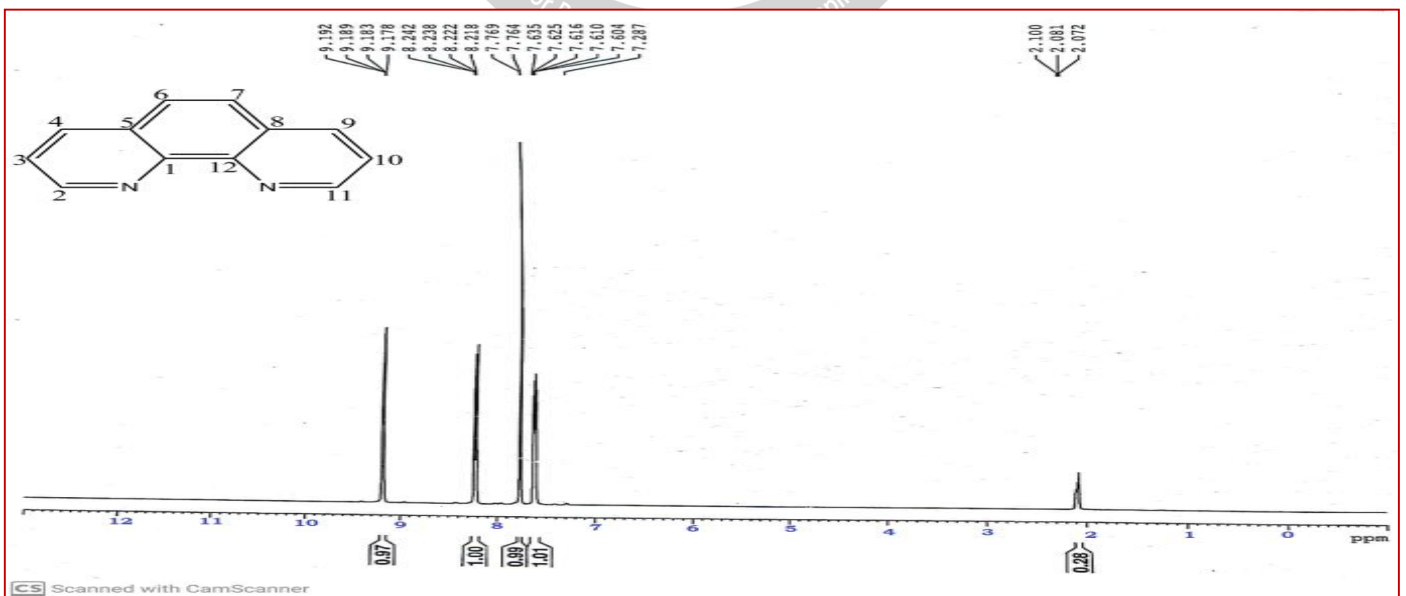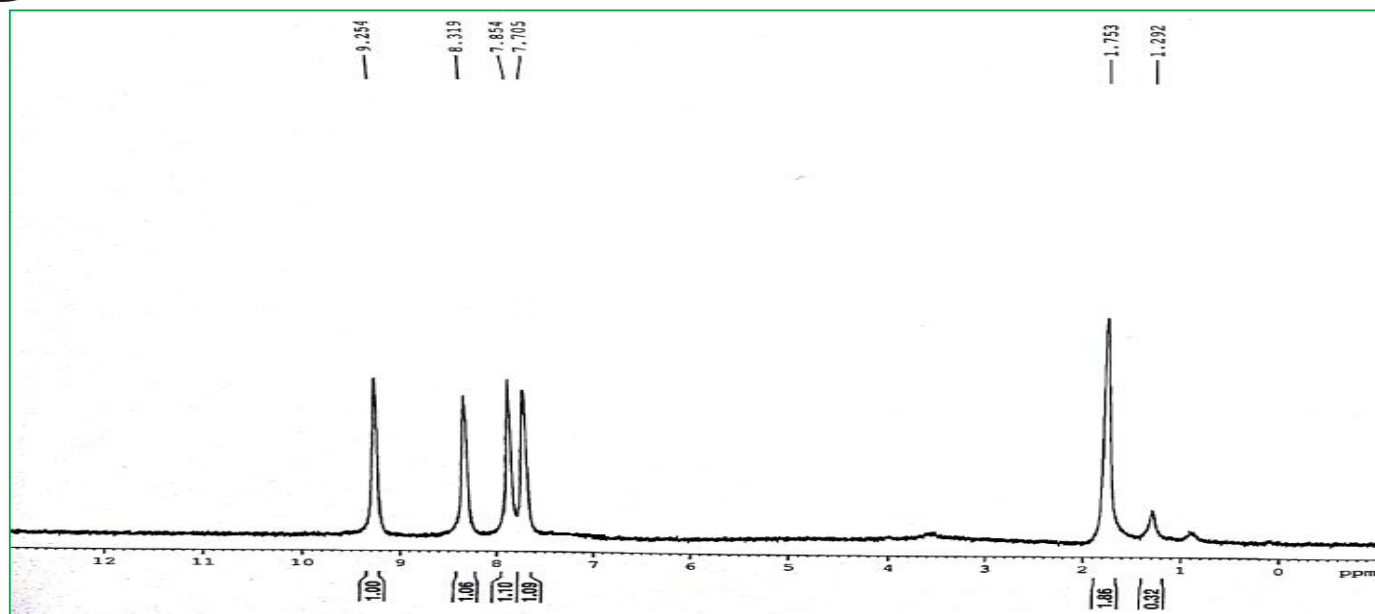

Figure 3 ^{1}HNMR spectra of o-phen ligand

Figure 4 ^{1}HNMR spectra of Cd-o-phen complex

Crystallographic analysis of [2Cd{C12H8N2)3}22(ClO4)2(C4H9N)(C5H5N)2]

An ORTEP view of the Cd-o-phen with thermal ellipsoids drawn at 50% probability level showing atomic numbering scheme is depicted in **Figure 5.** The crystal data, data collection and refinement parameters are listed in **Table 1**. Cadmium complex of o-phenanthroline formulated as **[2Cd{C$_{12}$H$_8$N$_2$)$_3$}$^+$$_2$2(ClO$_4$)$^-$$_2$(C$_4H_9$N)(C$_5H_5$N)$_2$]** in presence of solvent molecules crystallizes in triclinic crystal system with space group P-1 with Z=2 (two molecule per asymmetric unit). In both the molecules of Cd-o-phen complex, Cd, exhibits distorted octahedral geometry involving two N-atoms of three bis chelating o-phen ligands. There are two uncoordinated perchlorate anions (ClO$_4$)$^-$ for each molecules of the asymmetric unit along with one solvent molecule of tetrahydropyrrole and one molecule of solvent pyridine are free in the lattice. Coordination covalent bond lengths and bond angles surrounding Cd ion for both the molecules (molecule A & molecule B) are listed in **Table 2a** and **Table 2b.**The bite angles (N1-Cd1-N2,N3-Cd1-N4,N5-Cd1-N6,N7-Cd2-N8,N9-Cd2-N10,N11-Cd2-N12) involving bis chelating o-phen ligand coordinating to Cd for both the molecules ranges from 70.5(4)° to 72.5(5)°. The other angles surrounding Cd ranges from 90.5(5)° to 160.6(4)° confirming distorted octahedral coordination in both the molecules. The dihedral angles [72.8(4)° to 86.0(3)°] between any two planner fourteen membered fused o-phen ring systems of three o-phen ligands of both the molecules (molecule A & molecule B) confirm almost an orthogonal orientation of the o-phen molecules to each other. The **[2Cd{C$_{12}$H$_8$N$_2$)$_3$}$^+$$_2$2(ClO$_4$)$^-$$_2$(C$_4H_9$N)(C$_5H_5$N)$_2$]**metal complex is stabilized due to collective contributions of about a dozen of C-H…O hydrogen bond interactions and couple of significant Cl-O…π interactions , direction specific C–H…π and π…π intra and inter molecular interactions .Diperchlorate anion acts as a bridging moiety thereby interlinking cation to anion forming a supperamolecular aggregation. Both, the halogen Cl and the oxygens of (ClO4)$^-$anions contribute maximum, either as a donor or acceptor in the molecular stability as shown in **Figure 6 and Figure 7**. In couple of hal(Cl)-O… π interactions wherein Cl1 & Cl2 do not take part but it is the Cl3 & Cl4 which contributes for the molecular stabilities. The details of inter and intra molecular interactions are tabulated in **Table 3**. Out of five, three C-H... π interactions are due to the donor moieties of solvent tetrahydropyrrole, and pyridine connecting to the o-phen ring plane while the reaming two[C26-H26...Cg30, C50-H50…Cg5] are connecting two Cd-o-phen cation unit .All five C-H…π interactions are type–V interaction according to Maleon at all [21]. **Figure 8** display the part of molecular packing diagram showing C–H…π inter molecular interactions between solvent molecule and Cd-o-phen unit (molecule A) in the molecular structure. The intermolecular π…π interaction involve, π-centre of two 6 membered rings of Cd-o-phen unit namely C4-C45-C6-C7-C11-C12(Cg10) & C64-C65-C66-C67-C71-C72 (Cg33) contributing to molecular packing which is depicted in the **Figure 9.**

Table 1 Crystallographic data, intensity data collection and refinement parameters

Chemical formula	:	**[2Cd{C$_{12}$H$_8$N$_2$)$_3$}$_2$2(ClO$_4$)$_2$(C$_4$H$_9$N)(C$_5$H$_5$N)$_2$]**
Molecular weight	:	1703.862 amu
Crystal description	:	Block shape
Crystal system, Space group	:	Triclinic, P-1

a	:	12.7660(4)Å
b	:	13.2286(5)Å
c	:	13.4021(5)Å
α	:	86.904(2) °
β	:	73.617(2)°
γ	:	75.270(2)°
Volume (V)	:	2099.66(13)Å^3
Z	:	2[with two molecules per asymmetric unit]
ρ_c	:	1.52Mg/m^3
μ	:	0.71 mm^{-1}
Instrument used	:	Bruker Kappa APEX-II CCD Diffaractometer
F(000)	:	980
Temperature during data Collection	:	293 K
Radiation type, Wavelength (λ)	:	MoKα, 0.71073 Å
Radiation source	:	Fine-focus sealed tube
Mode of data collection		ω - 2θ scan mode
θ range for data collection (°)	:	$\theta_{min} = 1.6°$, $\theta_{max} = 27.6°$
Total number of measured reflections	:	25018
Total number of independent reflections	:	12927
Limiting indices ; h, k, l	:	-16 to16, -17 to 17, -17 to 15
Refinement method	:	Full Matrix Least Square of $|F|^2$
Number of parameters	:	1109
Goodness of fit on $|F|^2$	:	1.07
Final R indices [I > 2σ(I)]	:	$R_1 = 0.0403$, $wR_2 = 0.1021$
R indices (all data)	:	$R_1 = 0.0498$, $wR_2 = 0.1114$
Largest difference peak and hole	:	$\Delta\rho_{min} = -0.56$ eÅ^{-3} $\Delta\rho_{max} = 0.58$eÅ^{-3}
Software used to data Collection	:	Bruker Kappa Apex-II
Software used to cell refinement	:	Bruker SAINT
Software used to solve the structure	:	SHELXS – 97
Software used to refine the structure	:	SHELXL – 97
Software used for molecular Graphics	:	PLATON & ORTEP

Table 2(a) (Molecule-A) Coordination sphere [(Bond lengths (Å) & Bond angles(°)] surrounding Cd1

Bond lengths(Å)

Cd1-N1	2.332(12)	Cd1-N3	2.316(13)	Cd1-N5	2.320(13)

Cd1-N2	2.399(14)	Cd1-N4	2.345(14)	Cd1-N6	2.335(15)

Bond angles(°)

N1-Cd1-N2	70.5 (4)	N2-Cd1-N3	101.5(5)	N3-Cd1-N5	156.5(5)
N1-Cd1-N3	104 (4)	N2-Cd1-N4	90.5(5)	N3-Cd1-N6	92.3(5)
N1-Cd1-N4	159.3(5)	N2-Cd1-N5	98.7(4)	N4- Cd1-N5	96.8(5)
N1-Cd1-N5	94.1(4)	N2-Cd1-N6	159.6(5)	N4- Cd1-N6	108.4(5)
N1-Cd1-N6	91.8(5)	N3-Cd1-N4	71.2(5)	N5-Cd1-N6	71.9(5)

Table 2(b) (Molecule-B) Coordination sphere [(Bond lengths (Å)& Bond angles(°)] surrounding Cd2

Bond lengths (Å)

Cd2-N7	2.339(13)	Cd2-N9	2.345(13)	Cd2-N11	2.339(13)
Cd2-N8	2.351(13)	Cd2-N10	2.408(14)	Cd2-N12	2.361(12)

Bond angles(°)

N7-Cd2-N8	72.5(5)	N8-Cd2-N9	97.1(5)	N9-Cd2-N11	94.9(4)
N7-Cd2-N9	154.6(5)	N8-Cd2-N10	109.7(5)	N9-Cd2-N12	100.2(5)
N7-Cd2-N10	90.6(5)	N8-Cd2-N11	157.5(5)	N10-Cd2-N11	92.2(5)
N7-Cd2-N11	103.2(4)	N8-Cd2-N12	88.0(4)	N10-Cd2-N12	160.6(4)
N7-Cd2-N12	102.4(4)	N9-Cd2-N10	70.7(5)	N11-Cd2-N12	71.1(5)

Table 3 Intra and inter molecular hydrogen bond, π-π, C-H…π, and Cl-O…π interactions along with symmetry codes

(A) Hydrogen bond interactions

D-H…A	D-H (Å)	H…A (Å)	D-A (Å)	∠D-H…A (°)
C(2)-H(2)...O(4)	0.92	2.41	3.3(3)	159
C(13)-H(13)...O(6)i	0.93	2.51	3.39(2)	159
C(15)-H(15A)...O(3)ii	0.93	2.44	3.35(3)	168
C(26) -H(26) ...O(14)	0.93	2.55	3.02(3)	112
C(30)-H(30)...O(16)i	0.93	2.55	3.35(2)	144
C(32)-H(32)...O(16)i	0.93	2.52	3.35(3)	148
C(34)-H(34) ...O(7)i	0.93	2.52	3.25(4)	135
C(39)-H(39) ...O(7)iii	0.93	2.53	3.40(3)	155
C(54)-H(54) ...O(10)iv	0.93	2.54	3.40(3)	154
C(62) -H(62)...O(5)v	0.93	2.48	3.34(4)	154
C(66) -H(66)...O(6)vi	0.93	2.58	3.45(3)	150

(B)π-π interaction

Cg(I)- Cg(J)	d[Cg(I)…Cg(J)] (Å)	α (°)	β (°)	γ (°)	Slippage	Cg(I)…P Å	Cg(J)...P Å
Cg(10) -Cg(33)vii	3.601(9)	2.67	14.8	16.6	0.919	3.4631	-3.4749

(C) X-H…π interaction

C-H(I)…Cg(J)	d(H-Cg) (Å)	d(C-Cg) (Å)	C-H…Cg (°)	γ (°)	H…P (Å)	Type
C(26) -H(26)…Cg(30)viii	2.98	3.76(2)	143	9.16	-2.94	V
C(50)-H(50)…Cg(5)ii	2.95	3.72(18)	143	12.94	2.87	V
C(76)-H(76)… Cg(12)	2.94	3.55(4)	123	13.53	2.86	V
C(83)-H(83B)…Cg(27)	2.60	3.56(4)	169	16.61	-2.49	V
C(84)-H(84B)…Cg(11)iv	2.57	3.48(4)	157	12.19	-2.51	V

(D) Y-Z…π interaction

Cl-O(I)…Cg(J)	d(Z-Cg) (Å)	d(Y-Cg) (Å)	Y-Z…Cg (°)	γ (°)	O…P (Å)
Cl(3)-O(10)…Cg(4)ii	3.27(2)	4.249(9)	129.3(11)	12.41	3.194
Cl(3)-O(10)…Cg(8)ii	3.77(2)	4.387(9)	108.8(10)	16.19	-3.620
Cl(3)-O(12)…Cg(1)ii	3.74(2)	4.533(9)	116.4(12)	29.34	3.260
Cl(3)-O(12)…Cg(10)ii	3.24(2)	3.999(10)	113.0(11)	7.26	3.220
Cl(4)-O(14)…Cg(33)viii	3.40(2)	3.983(10)	108.7(11)	4.47	-3.390
Cl(4)-O(16)…Cg(29)viii	3.38(18)	4.248(9)	121.3(9)	10.79	-3.323

Where,

Cg(1)= Cd1-N1-N2-C11-C12, Cg(3)=Cd1-N5-N6-C35-C36,

Cg(4)=N1-C1-C2-C3-C4-C12 , Cg(5)=N2-C7-C8-C9-C10-C11,

Cg(8)=N5-C25-C26-C27-C28-C36,Cg(10)=C4-C5-C6-C7-C11-C12,

Cg(11)=C16-C17-C18-C19-C23-C24,Cg(12)=C28-C28-C30-C31-C35-C36,

Cg(27)=N9-C49-C50-C51-C52-C60,Cg(29)=N11-C61-C62-C63-C64-C72,

Cg(30)=N12-C67-C68-C69-C70-C71,Cg(33)=C64-C65-C66-C67-C71-C72

Symmetry Codes : (i)-1+x,y,z (ii) x,y,1+z (iii) x,1+y,z (iv) 1+x,y,z

(v) x,1+y,1+z (vi) -1+x,1+y,1+z (vii) x,-1+y,-1+z   (viii) x,y,-1+Z
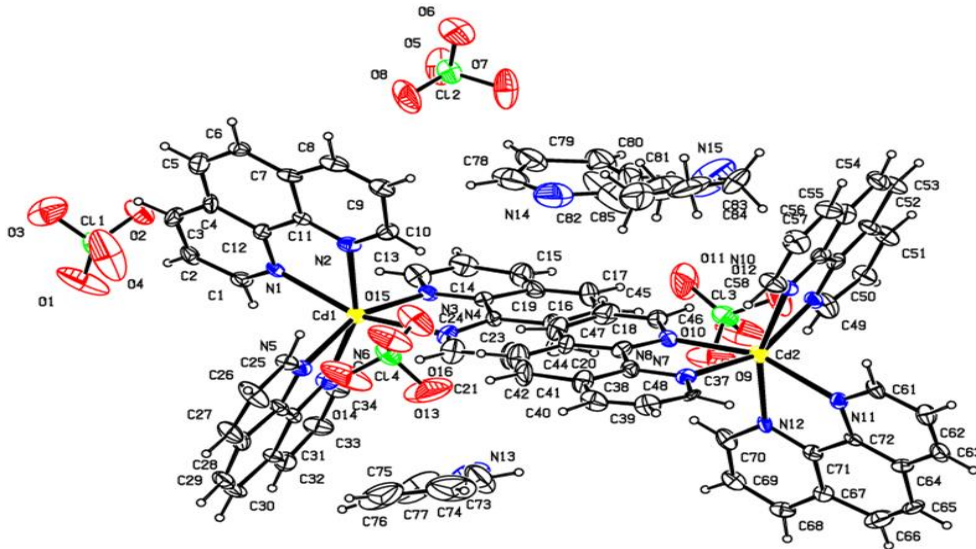

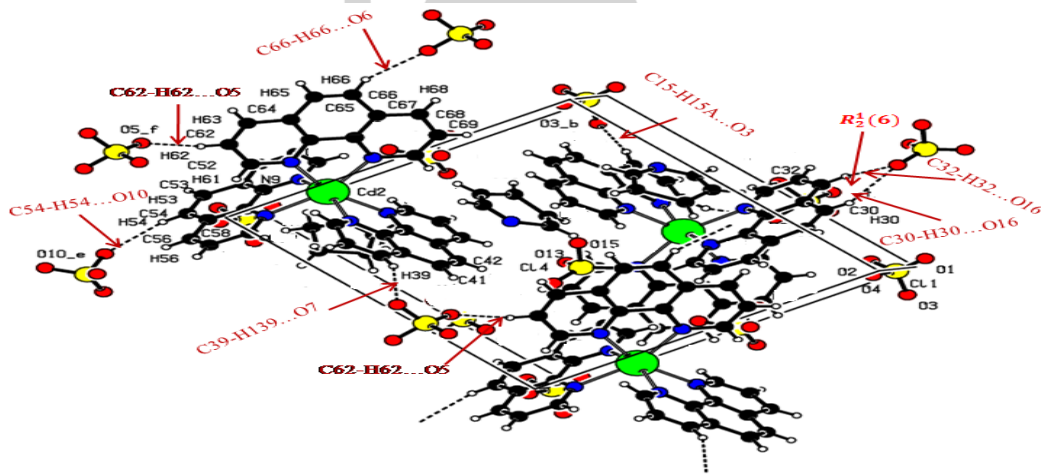**Figure 5 ORTEP view of the Cd-o-phen complex with thermal ellipsoids at 50% probability level**

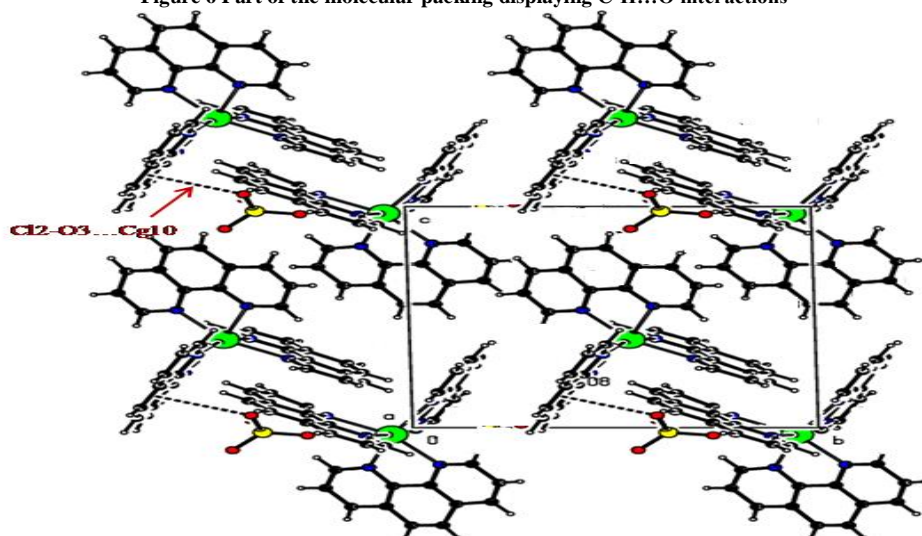**Figure 6 Part of the molecular packing displaying C-H…O interactions**

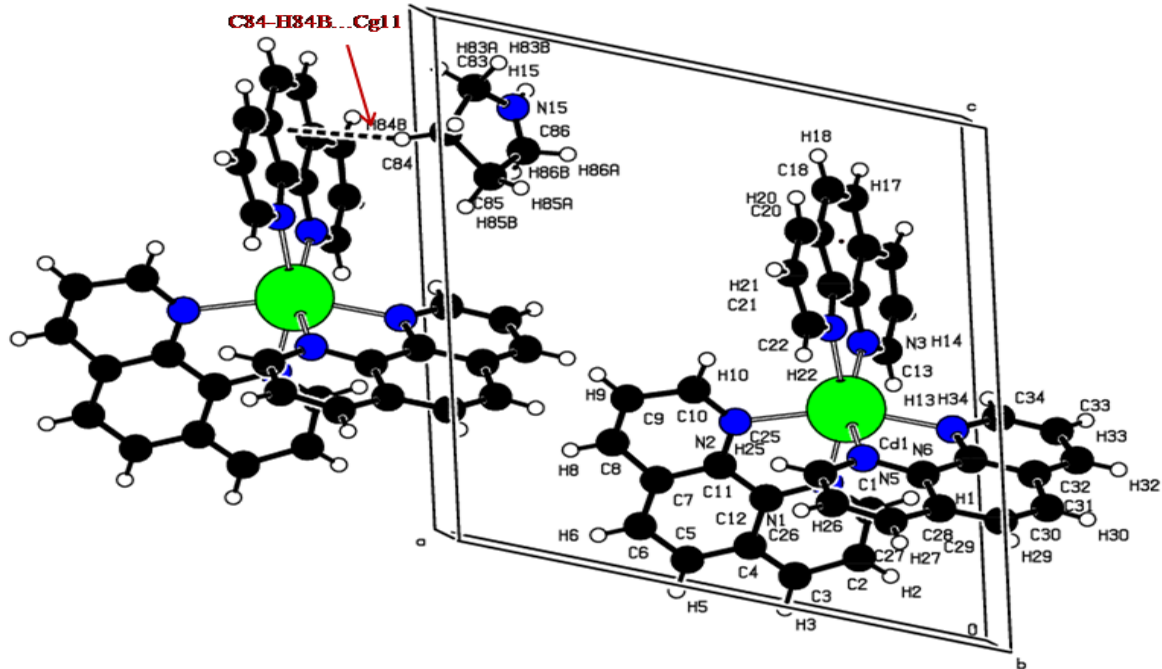**Figure 7 Part of the molecular packing displaying Cl-O…Cg interactions**

Figure 8 Part of the molecular packing displaying C-H…Cg interactions
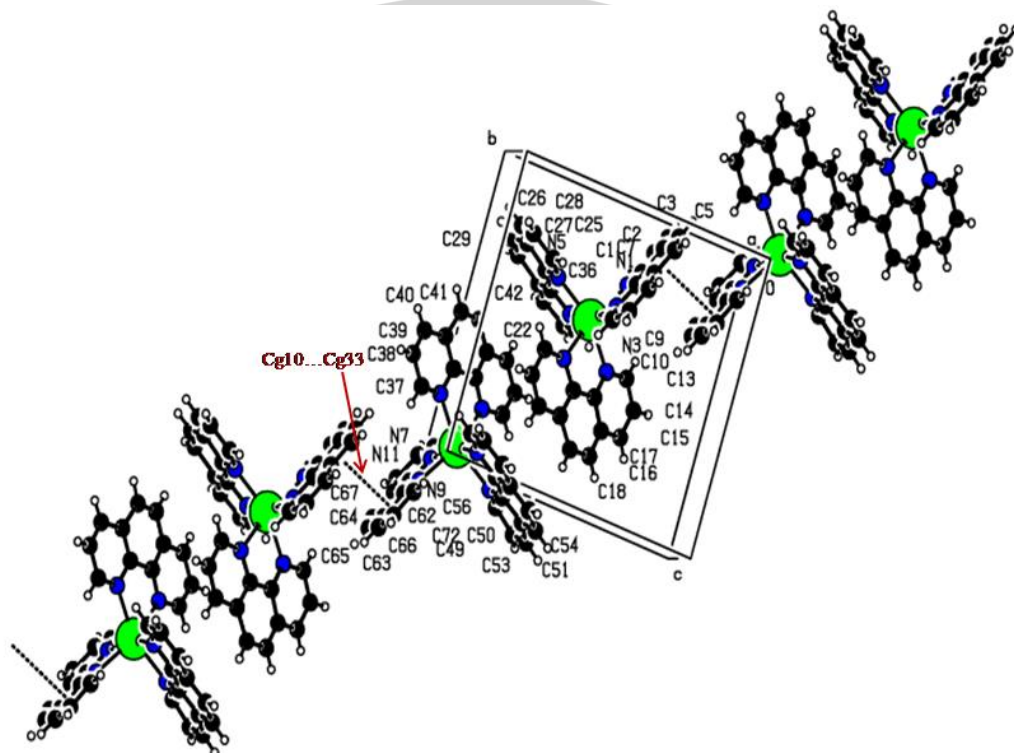

Figure9 Part of the molecular packing displaying Cg…Cg interactions

CONCLUSION

Dinuclear cadmium complex of o-phen ligand is synthesized & crystallized using 1:1 pyridine-tetrahydropyrrole solvent. Central metal Cd exhibits distorted octahedral geometry. There are two molecules per asymmetric unit-each molecule of the asymmetric unit consists of one cation unit[Cd(phen)$_3$]$^+$,two anions (Clo4)$^-$ and one solvent pyridine along with one tetrahydropyrrole solvent free in the lattice. Both the molecules of the asymmetric unit are very similar in the molecular dimension. All the three fused o-phen rings are perpendicular to each other facilitating diperchlorate anions to act as a bridging moiety connecting cation to anion and vice-versa resulting in supperamolecular aggregation.

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