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MICROWAVE IRRADIATED SYNTHESIS AND H-BONDING NETWORK OF BIOLOGICALLY ACTIVE NANOCRYSTALLINE Cd(II) COMPLEX WITH HETEROATOM ('N' &'O') DONOR LIGANDS

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ABSTRACT

The post-transition diamagnetic complex of Cd(II) with benzimidazole ('N' Donor) and nitrite ion (nitrito-O, 'O' Donor) heteroatom ligands were synthesized and characterized by elemental analysis, estimation of metal ion, conductance (10^{-3} M complex solution), UV-Visible, IR, Far-IR, NMR spectra, SEM and X-ray diffraction (single crystal method). The complex was crystallized in orthorhombic $P2_12_12_1$ space group having a = 8.8701(3) Å,b = 11.5026(4) Å and c = 22.5665(8) Å. The interfacial angle of crystal are α = β = γ = 90°, volume and density of the crystallized complex were 2302.44(14) $Å^3$ and 1.612 mg/m^3 respectively. Cd(II) ion is surrounded by two oxygen atom of nitrite ion and three nitrogen atom of benzimidazole by distorted pentagonal bipyramidal structure. SEM images of the crystal also discussed the morphology. Biological activities against bacterial and fungal strains *viz., Klebsiella pnemoniae* and *salmonella typhi* (gram-negative bacteria), *Bacillus subtilis* (gram-negative bacteria) and pathogenic yeast *C. albicance* were carried out by Agar well diffusion method. On comparing benzimidazole the complex crystal shows potent activities against tested microorganisms.

Keywords: Cd(II) Complex, Benzimidazole, Microwave Irradiation, Nanocrystal, Pentagonal Bipyramidal

INTRODUCTION

Nitrogen and oxygen donor heteroatomic ligand was used to the efficient formation of coordination complexes with transition and post-transition metal ions due to the presence of lone pair of electrons on the donor atoms and vast bio-potential activities. Benzimidazole is one of the heterocyclic, monodentate, neutral and biologically active ligand which can coordinate through nitrogen atom of them[1-2]. In pharmaceutical industries, benzimidazole acts as a pharmacophore used to synthesized biologically active compounds.[3-4] its derivatives with transition metal ions play a vital role in bio-molecules *viz.,* vitamin B12 and metalloproteins. Benzimidazole is one of the imperative antimicrobial, anticancer, anti-inflammatory, antivirus, anti-ulcer, and anticonvulsant agent in biofield.[5-7]The nitrogen donor benzimidazole and its derivatives have two ring systems with different functional group leads to the change in physicochemical, geometry, pharmacokinetics property and bio-potential activities.[8-10]In the present exploration paying attention to the microwave irradiated synthesis, crystal structure and bio-potential activities of post-transition Cd(II) complex with benzimidazole ('N-donor) and nitrite ion ('O' donor).

EXPERIMENTAL

Materials and Methods

All the chemicals such as benzimidazole (Alfa Aesar), sodium nitrite, CH_3OH, C_2H_5OH, DMSO, DMF and Cadmium nitrite were purchased from scientific suppliers and used as such without further purification. They are all AnalaR grade.

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Elements present in the synthesized crystal were detected from Thermo Finnegan make, Flash EA1112 series CHNS(O) analyzer instrument. The conductivity of the 10^{-3} M complex in CH_3CN at 30^0C was carried out using Systronic Conductivity Bridge. The UV-visible spectrum of the complex by diffused reflectance spectra (DRS) method was measured by using Varian carry-5000 model UV-Visible spectrophotometer. IR spectrum of benzimidazole and Cd(II) complex were carried out at 4000-400 cm^{-1} wave number using Schimadzu FT-IR8400s spectroscopy with KBr pellet technique. The ^{1}H-NMR and ^{13}C-NMR spectra of the diamagnetic Cd(II) complex and ligand INH were recorded in the DMSO-d6 solvent on a 500 MHz FT NMR spectroscopy using Tetramethylsilane as an internal standard. Bruker D8 Venture SC-XRD system is used for structure determination of single crystal. It is a combination of two X-ray sources (Mo & Cu) with a highly accurate goniometer. The photon 100 CMOS detector is optimized for both Mo(Kα) and Cu(Kα) radiation. The wavelength is fully automated. The bio-potential activities (antibacterial and antifungal) Cd(II) complex were done by *in-vitro* Agar well diffusion method using the standard Amikacin and Ketoconazole and also comparing with free benzimidazole.

Preparation of Complex

Cd(II) crystal was synthesized by mixing benzimidazole1.52 g (6.48 mmol) in 5ml methanol with 2g(3.24 mmol) of $Cd(NO_3)_2.4H_2O$ in 5ml methanol and sodium nitrite 0.90g (6.52 mmol) in ethanol solution was mixed then the mixture was irradiated on a microwave oven for 10 seconds. The precipitated colorless complex was filtered, washed with 1:1 ethanol:water and dried. The crystal is stable at room temperature and the yield is 80%.

RESULTS AND DISCUSSION

UV Spectra

The UV-spectra of the complex shows the charge transfer spectra at 267 nm (MLCT) and 338 nm (LMCT) due to the completely filled d orbital of Cd(II) metal ion in the complex. The charge transfer spectra (C-T band) only possible in the complex.[11]

IR Spectrum

The IR spectrum of benzimidazole shows the ν(C=H) at 3112 cm^{-1} , ν(N=H) at 3063cm^{-1} ν(C-C) at 1620 cm^{-1} and ν (C-C) in ring at 1458cm^{-1}stretching frequencies in the free state but after complexation these frequencies are shifted to3174 cm^{-1} 3057 cm^{-1}3112 cm^{-1} 1622 cm^{-1} 1462cm^{-1}, the ν(N-H) in plane and out of plane stretching frequencies at 617 cm^{-1} and 626 cm^{-1}upon coordination through the nitrogen atom of benzimidazole these stretching frequencies are shifted to 582 cm^{-1}, 578 cm^{-1}respectively confirming the planarity changes during complexation and further it is concluded the effective formation of complexes. [12] Nitrite ion shows the ν_a (ONO) asymmetric and symmetric stretching ν_{sy}(ONO) frequencies at 1270 cm^{-1} and1362 cm^{-1}respectively. The separation of asymmetric and symmetric frequency calculates by Δ^a factor. The Δ^a factor value is at 112 cm^{-1} which depend upon the degree of symmetry of the nitrito-O group in the complex.[13] Higher the value of Δ^a indicating the N=O and N-O bonds are nonequivalent which increases the degree of symmetry.

FAR-IR Spectra

Far-IR spectra of the synthesized crystal confirming by the metal linked atom capability. Obviously, the far IR spectra of the complex show the stretching frequencies at 429 cm^{-1} is ascribed to the ν(M-N) linkage of benzimidazole nitrogen donor site.[14] The nitrite ion (ambidentate ligand) can coordinate through the oxygen donor site is confirming by ν(M-O) at 344 cm^{-1}

NMR- Spectra

The ^{1}H-NMR spectrum of benzimidazole shows the chemical shift values at 12.50 ppm for N-H proton (singlet), 8.25 ppm for N=C-H (singlet) and 7.17-7.20 ppm for aromatic proton (multiplet). In diamagnetic Cd(II) complex the N-H chemical shift value shifted to downfield at 12.63 ppm whereas N=C-H is not shifted (8.25 ppm). The aromatic protons are slightly shifted to downfield at 7.21-7.63 ppm.[15-16] The ^{13}C-NMR spectra of the ligand give four different chemical shift values corresponding to the carbon atom present in the benzimidazole (ligand). The N=C at 141.90 ppm, C2 at 138.09 ppm, C3 at

121.71 ppm and C4 at 115.36 ppm. In complex, these are shifted to downfield at 143.43ppm, 137.01 ppm, 122.64 ppm, and 115.52 ppm respectively indicating the effective formation of coordination complex site through the nitrogen atom of benzimidazole.[17]

Crystal Structure Depiction of the Complex[18-19]

In the crystal structure of Cd(II) ion is seven coordinated by three donor nitrogen atom of benzimidazole (3 units) ligand and four oxygen atoms of each anionic nitrite ions. Cd(II) ions show distorted pentagonal bipyramidal structure with N1, N4,N6 from benzimidazole and O1, O2, O3, O4 from nitrite ion. All the atoms are coplanar in nature and the complex is crystallized by orthorhombic crystal system with $P2_12_12_1$ space group. The unit cell parameters $a \neq b \neq c$(a= 8.8701, b = 11.5026,c = 22.5665) but the angle is equal to 90° ($\alpha = \beta = \gamma = 90°$). The selected bond angles of metal coordinate bonds are N_6-Cd-N_1 at 169°, N_6-Cd-N_4 at 92.99°, N_1-Cd-N_4 at 96.85°, O_2-Cd-O_1 at 49° and O_4-Cd-O_2 at 79.45° are also confirming the coordination site and structure of the crystal.

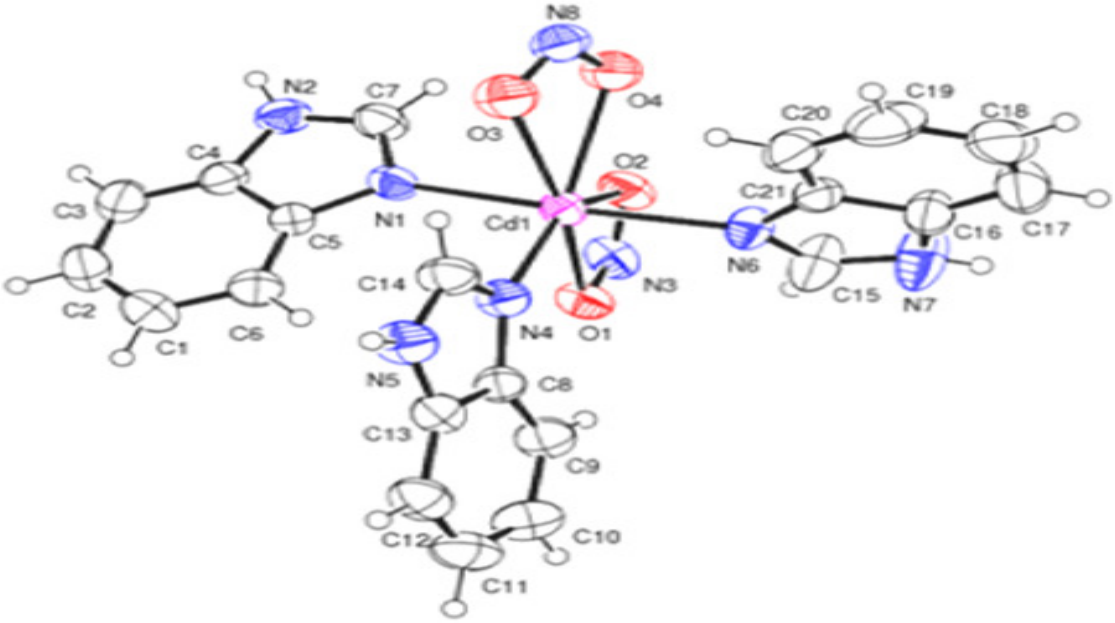


Fig.-1: Crystal Structure of Cd(II) Complex

Table-1: Crystal Data and Structure Refinement for Cd(II) Complex

Identification code	G11	
Empirical formula	C_{21} H_{18} Cd N_8 O_4	
Formula weight	558.83	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 8.8701(3) Å	α= 90°.
	b = 11.5026(4) Å	β= 90°.
	c = 22.5665(8) Å	γ = 90°.
Volume	2302.44(14) $Å^3$	
Z	4	
Density (calculated)	1.612 Mg/m^3	
Absorption coefficient	0.994 mm^{-1}	

F(000)	1120
Crystal size	0.200 x 0.150 x 0.100 mm^3
Theta range for data collection	2.467 to 24.997°.
Index ranges	-9<=h<=10, -13<=k<=12, -26<=l<=26
Reflections collected	37912
Independent reflections	4057 [R(int) = 0.0538]
Completeness to theta = 24.997°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7452 and 0.6728
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4057 / 3 / 319
Goodness-of-fit on F^2	1.104
Final R indices [I>2sigma(I)]	R1 = 0.0255, wR2 = 0.0406
R indices (all data)	R1 = 0.0448, wR2 = 0.0473
Absolute structure parameter	-0.028(11)
Extinction coefficient	n/a
Largest diff. peak and hole	0.502 and -0.473 e. $Å^{-3}$

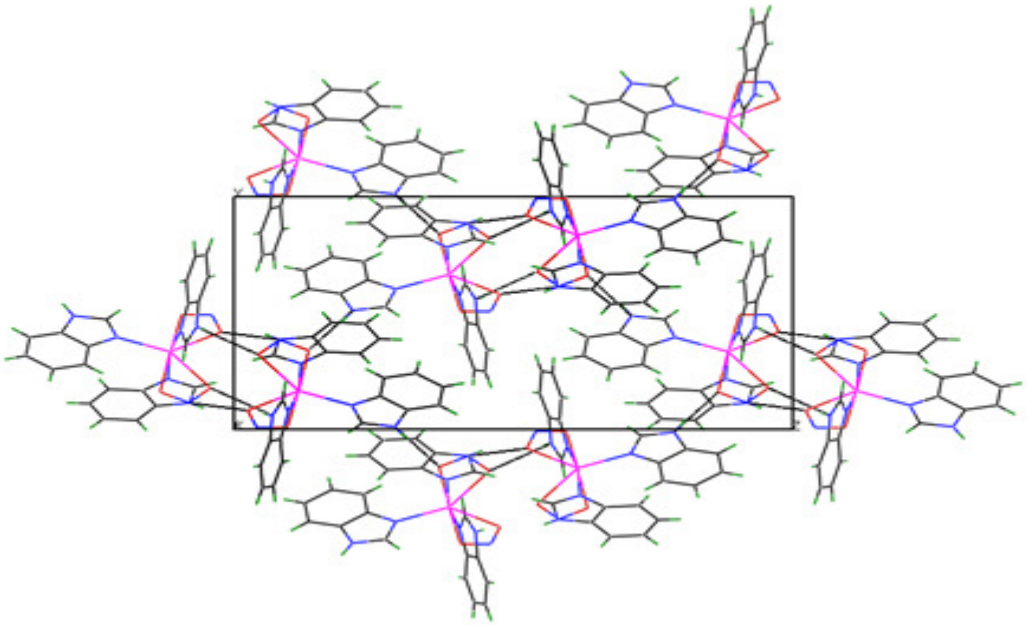


Fig.-2: 3-D Network of H-Bonded Cd(II) Complex

SEM Image of the Crystal

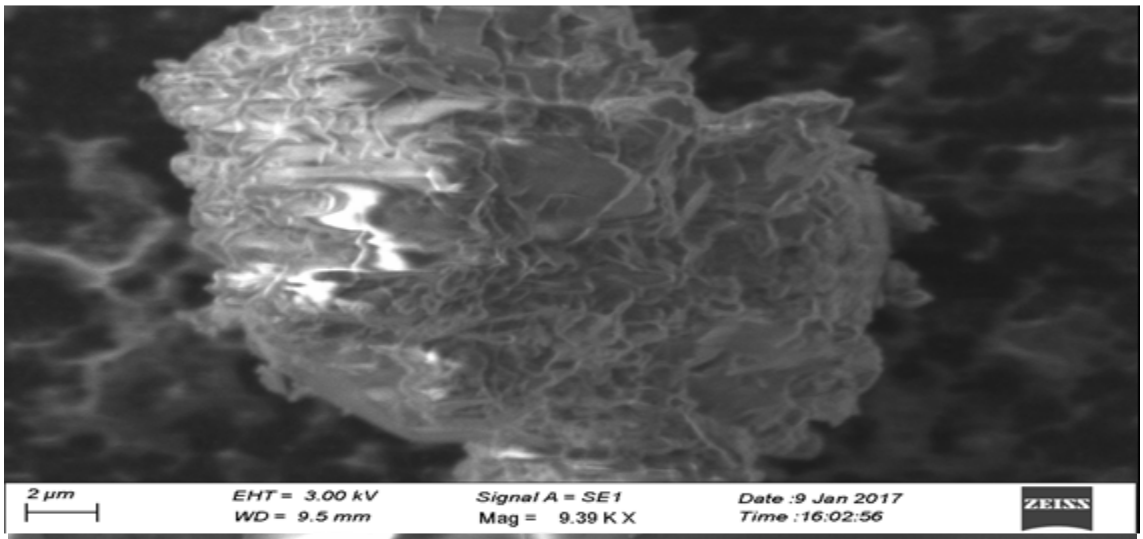
The morphological and structural properties of Cd(II) complex were evaluated by using a SEM image (scanning electron microscope). The SEM images magnifying under different size (2µm, 3µm, 10µm & 20µm). The SEM image of the crystal confirmed by the heterogeneity and Nanocrystal nature of the complex.[20]

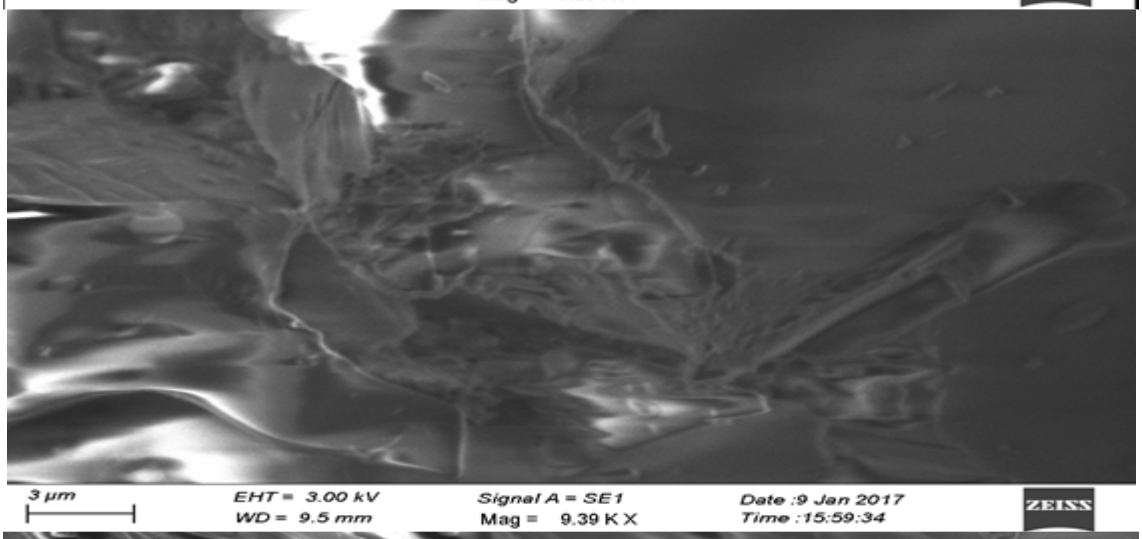
Bio-Potential Activities of the Crystal

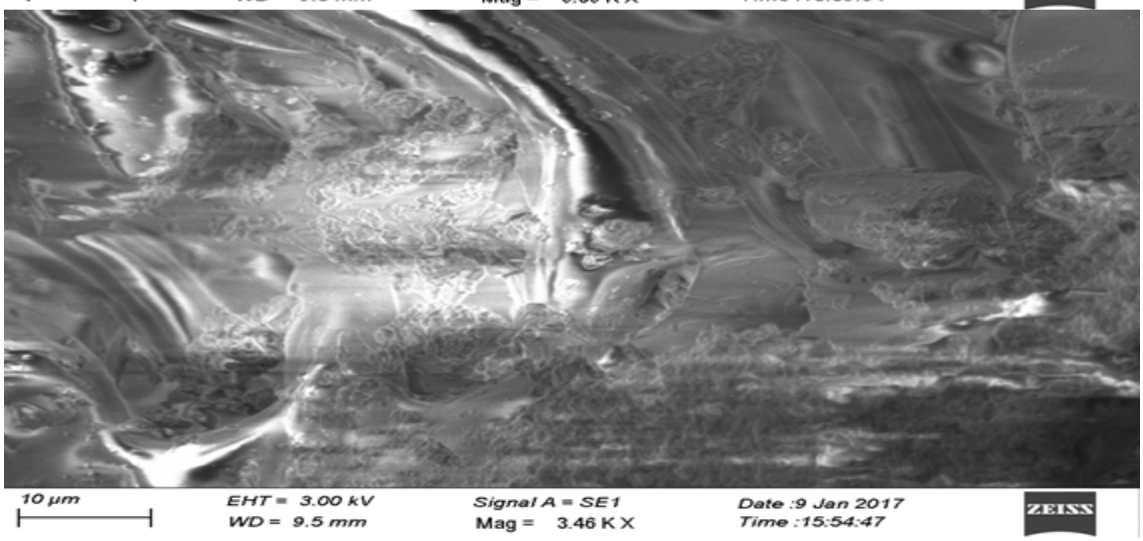
Bio-potential activities of benzimidazole and its Cd(II) complex were carried out by Agar well diffusion method using gram-negative bacteria *Klebsiella pneumonia* and pathogenic yeast *C. albicance*. The results indicating that the compound shows enhanced antibacterial and antifungal activities on comparing the standard as well as a ligand.

The enhanced activity of the complex explain on basis of ligand structure, donor site of ligand (N/O) and overtone's chelation theory concept which is explain on the basis of lipophilicity of the complex which is

an significant factor that controls the antibacterial/antifungal activity because of the lipid membrane that surrounds the cell favors the passage of only lipid soluble matter. Chelation is further increases the delocalization of π-electrons over the ring in the ligand which enhance the lipophilicity of the metal complex.[21-22]







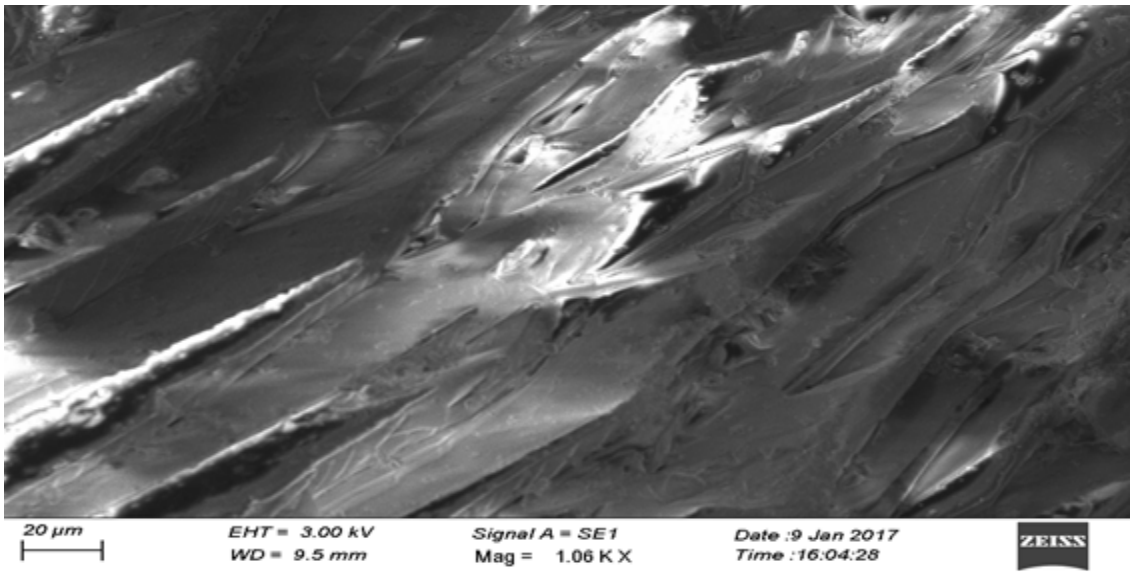


Fig.-3 SEM Images of Cd(II) Complex

Table-2: Selected Bond lengths [Å] and angles [°] for Cd(II) Complex

C(1)-C(6)	1.378(7)
C(1)-C(2)	1.385(8)
C(1)-H(1)	0.9300
C(2)-C(3)	1.364(7)
C(2)-H(2)	0.9300
C(3)-C(4)	1.370(7)
C(3)-H(3)	0.9300
C(4)-N(2)	1.389(6)
C(4)-C(5)	1.391(7)
C(5)-C(6)	1.388(6)
C(5)-N(1)	1.390(6)
C(6)-H(6)	0.9300
C(7)-N(1)	1.323(6)
C(7)-N(2)	1.336(7)
C(7)-H(7)	0.9300
C(8)-C(9)	1.378(6)
O(3)-N(8)-O(4)	112.6(4)
N(3)-O(1)-Cd(1)	102.5(3)
N(3)-O(2)-Cd(1)	94.5(3)
N(8)-O(3)-Cd(1)	95.3(3)
N(8)-O(4)-Cd(1)	101.9(3)
N(4)-Cd(1)-N(6)	92.99(15)
N(4)-Cd(1)-N(1)	96.85(15)
N(6)-Cd(1)-N(1)	169.06(15)
N(4)-Cd(1)-O(4)	133.68(14)
N(6)-Cd(1)-O(4)	83.96(14)
N(1)-Cd(1)-O(4)	92.63(14)
N(4)-Cd(1)-O(1)	96.77(13)
N(6)-Cd(1)-O(1)	87.95(13)
N(1)-Cd(1)-O(1)	86.16(13)
O(4)-Cd(1)-O(1)	129.12(12)
N(4)-Cd(1)-O(3)	86.08(14)
N(6)-Cd(1)-O(3)	102.21(14)
N(1)-Cd(1)-O(3)	83.28(13)
O(4)-Cd(1)-O(3)	50.15(11)
O(1)-Cd(1)-O(3)	169.32(13)

N(4)-Cd(1)-O(2)	146.62(13)
N(6)-Cd(1)-O(2)	85.90(12)
N(1)-Cd(1)-O(2)	83.25(13)
O(4)-Cd(1)-O(2)	79.45(12)
O(1)-Cd(1)-O(2)	49.86(11)
O(3)-Cd(1)-O(2)	126.80(12)

Fig.-4 Zone of Inhibition of Cd(II) Complex

Supplementary Materials

Crystallographic data for the Cd(II) complex have been deposited to the Cambridge Crystallographic data Centre. 12, Union Road, Cambridge CB2 1E2, UK.

CCDC number for the complex is 1523352. Copies of this information of the compounds obtained from Cambridge Crystallographic Data Centre with free of cost by the following the link. http://www.ccdc.cam.ac.uk/deposit@ccdc.cam.ac.uk

CONCLUSION

Cd(II) complex synthesized using benzimidazole and nitrite ion as ligands with microwave heating. The complex crystallized with distorted pentagonal bipyramidal structure having a= 8.8701, b = 11.5026, c = 22.5665 and angle $\alpha = \beta = \gamma = 90°$. The crystal is non-electrolyte, coordinate through the nitrogen atom of benzimidazole and oxygen atom of nitrite ion. It is biologically active against the tested microorganisms. The complex is Nanocrystalline in nature.

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