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Structural analysis of complexes formed by Ethyl 4-phenylthiocarbamoyl piperazine-1-carboxylate with Ni(II), Zn(II) and Cd(II) through spectroscopic and DFT techniques

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#### Abstract:

A Piperazine derivative, Ethyl 4-phenylthiocarbamoyl piperazine-1-carboxylate and its Ni(II), Zn(II) and Cd(II) complexes have been synthesized and characterized by elemental analyses, magnetic susceptibility measurement, UV-Visible, FTIR, Raman spectroscopic and DFT methods. The Ni(II) and Zn(II) bind through the N and S sites of the two ligand Heptpc and N site of two pyridine molecules. However, the Cd(II) binds through the only N sites of the two ligand Heptpc and N site of two pyridine molecules. On the basis of various techniques used for the characterizations of the complexes, we found that the most possible geometry of the Ni(II) and Zn(II) complexes are distorted octahedral and of the Cd(II) complex is distorted tetrahedral.

Keywords: Piperazine derivatives, Heptpc, UV-Visible, FTIR, Raman, DFT.

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#### **1. Introduction**

Piperazine derivatives are among the important groups of the heterocyclic compounds, which consist of a six-membered ring containing two nitrogen atoms at opposite positions in the ring. The Piperazine derivatives are classified to have privileged structure and are frequently found in biologically active compounds across a number of different therapeutic uses such as antimicrobial, anti-tubercular, anticonvulsant, antidepressant, antiinflammatory, antimalarial, antiarrhythmic, antioxidant and antiviral etc. [1-3]. From the view point of coordination chemistry, the compounds which contain thiourea group are extremely versatile due to the ability to bridge a wide range of metals by coordinating through nitrogen or sulphur. Due to the catalytic, biologically induced reaction and clinical applications, there is an increasing interest to study the metal complexes of piperazine derivatives specially the transition metal complexes [4-6]. In present study, ethyl 4phenylthiocarbamoyl piperazine-1-carboxylate (Heptpc) and its complexes with Ni(II), Zn(II) and Cd(II) were synthesized. The synthesized complexes were formulated on the basis of analytical, spectral and magnetic measurement methods. The most possible geometry of the complexes was proposed using spectroscopic technique viz. elemental analyses, UV-Visible, FTIR and Raman spectroscopy. The density functional theory (DFT) approach has been also employed to obtain the geometry of the ligand (Heptpc) and its complexes. The Molecular electrostatic potential mapped surfaces and HOMO-LUMO of the Heptpc and the complexes are also computed by DFT method.

#### 2. Experimental Details:

#### 2.1 Materials and Instrumentations:

Ethylpiperazine-1-carboxylate and phenylisothiocyanate were purchased from Sigma-Aldrich and used without further purification. All solvents were purchased from Merck Chemicals, India and were dried and distilled following standard procedure before use. All reactions were carried out in open atmosphere. Carbon, Hydrogen and Nitrogen contents were estimated on a CHN Model CE-440 analyzer and on an Elemental Vario EL III Carlo Erba 1108 analyzer. By following standard procedures, the complexes were analyzed for their metal content, after decomposition with a mixture of conc. HNO<sub>3</sub> and HCl, followed by conc. H<sub>2</sub>SO<sub>4</sub> [7]. Magnetic susceptibility measurements were performed at room temperature on a Cahn Faraday balance using  $Hg[Co(NCS)_4]$  as the calibrant. The UV-Visible spectroscopy is used to obtain the geometry of the coordination compounds. The electronic spectra were recorded on a SIMADZU 1700 UV/VIS spectrophotometer at 300 K in DMSO solution. The FTIR technique is used to know the functional groups present in compounds. In order to assess the structures of the metal complexes with better precision, FTIR and Raman spectra of metal complexes were measured. The FTIR spectra were recorded in the range 400-4000 cm<sup>-1</sup> in KBr pellets on Spectrum 65 FT-IR spectrometer from PerkinElmer. The laser Raman spectra were recorded on a Raman spectrometer was from Renishaw Model: RM 1000 having grating of 2400 grooves/mm giving spectral resolution of ~1 cm<sup>-1</sup> at 50 micron slit opening The 514.5 nm  $Ar^+$  -laser was used as an excitation source delivering ~5 mW intensity at the sample. A microscope from Olympus with 50 x objectives was used to focus the laser on the sample and to collect the Raman scattered signal in back scattering geometry. The Raman spectra were recorded in the range 200-3500 cm<sup>-1</sup>. Spectrometer scanning, data collection and processing were done by a dedicated computer using Gram Wire software.

#### 2.2 Synthesis of ligand (Heptpc):

A mixture of ethylpiperazine-1-carboxylate (3 mL, 20 mmol) and phenylisothiocyanate (2.4 mL, 20 mmol) was refluxed in benzene (20 mL) at 45  $^{0}$ C for 6 h. A white precipitate was obtained upon cooling the reaction mixture in ice, which was filtered off, washed with methanol and ether and recrystallized from MeOH: CHCl<sub>3</sub> mixture (50:50 v/v).

#### 2.3 Synthesis of the complexes [M(eptpc)<sub>2</sub>(py)<sub>2</sub>] {where M = Ni(II), Zn(II) and Cd(II)}:

The Synthesis procedure of metal complexes [M(eptpc)<sub>2</sub>(py)<sub>2</sub>] is as follow; M(OAc)<sub>2</sub>·xH<sub>2</sub>O (1 mmol) and Heptpc (2 mmol) were dissolved separately in 10 mL methanol-acetonitrile(1:1 v/v). The two mixtures thus prepared were mixed together and stirred for 2h. The solid precipitate was filtered, washed successively with ethanol-water mixture (50:50) and air dried. The precipitate was suspended in methanol to which pyridine (0.5 mL) was added and stirred for 1h. The resulting solution was filtered and kept for crystallization. Colored compound for analyses were obtained by slow evaporation of its methanol solution over a period of 25 days. All the complexes are air stable, non-hygroscopic amorphous solids. They are partially soluble in common organic solvents but soluble in DMF and DMSO and can be kept in desiccators over a prolonged period without any sign of decomposition. Scheme 1 depicts the synthesis of the ligand ethyl 4-phenylthiocarbamoyl piperazine-1-carboxylate (Heptpc) and metal complexes. For the preparation of the metal complexes, (Heptpc) is used as ligand and pyridine as coligand. The analytical Data, Color, Melting Point and Percentage Yield of ligand and the Metal Complexes are shown in table [1]



ethyl piperazine-1-carboxylate Phenylisothiocyanate ethyl 4-(phenylthiocarbamoyl)piperazine-1-carboxylate



Scheme [1]: Synthesis of ligand (Heptpc) and its metal complexes [M(eptpc)<sub>2</sub>(py)<sub>2</sub>]

#### 3. Results and Discussion:

#### 3.1 UV-Visible Spectra:

The UV-Visible spectra of the ligand Heptpc and the metal complexes  $[M(eptpc)_2(py)_2]$  are shown in the figure [1(a), (b), (c), (d) ]. The absorption region, band assignment and the geometry of the complexes are given in table [2]. The Ni(II) complex exhibited the absorption bands at 21010 and 27910 cm<sup>-1</sup>, attributed to  ${}^{3}A_{2}g \rightarrow {}^{3}A_{1}g(F)$  (v<sub>2</sub>), and  ${}^{3}A_{2}g \rightarrow {}^{3}T_{1}g(P)$  (v<sub>3</sub>) transitions [8]. The magnetic susceptibility measurements were performed at room temperature on a Cahn Faraday balance using Hg[Co(NCS)<sub>4</sub>] as the calibrant and observed the magnetic moment 2.88 B.M. This suggests the Ni(II) coordinate to (Heptpc+pyridine) in the distorted octahedral fashion whereas the Zn(II) and Cd(II) complexes have diamagnetic nature. But Zn(II) and Cd(II) complexes exhibit high energy

bands at 367, 310, 303 and 291–243 nm due to charge transfer/intraligand transitions [8]. Since Zn(II) may coordinate in the distorted octahedral as well as the distorted tetrahedral fashion according to nature but the spectral pattern of UV-Visible suggest for distorted octahedral geometry. However absorption bands of the Cd(II) complex suggest for its distorted tetrahedral geometry.

#### 3.2 Quantum chemical calculations of Heptpc and its metal complexes [M(eptpc)<sub>2</sub>(py)<sub>2</sub>]:

All quantum chemical calculations of Heptpc as well as its complexes with Ni(II), Zn(II) and Cd(II) have been performed with Gaussian 03 and Gauss View 4.1 program packages [9]. The optimization of the structures of ligand Heptpc have been done using DFT method with functional B3LYP and basis set 6-311++G(d,p) [10-13] whereas the geometry optimizations of complexes [M(eptpc)<sub>2</sub>(py)<sub>2</sub>]{where M = Ni(II), Zn(II) and Cd(II)} have been done using DFT method with functional B3LYP and basis sets 6-311++G(d,p){for C,H,N,O,S}/Lanl2DZ{for M = Ni(II), Zn(II) and Cd(II)}. The basis set Lanl2DZ [10-13] serves the purpose of including the pseudo potential of the core electrons in the metal atoms. Furthermore, this basis set is also compatible with other elements *viz*. C, H, N, S and O which are present in the complexes. The absence of imaginary harmonic frequencies confirms that the optimized structures are the global minimum energy conformations. The optimized structures of Heptpc and complexes [M(eptpc)<sub>2</sub>(py)<sub>2</sub>]{where M = Ni(II), Zn(II) and Cd(II)} are shown in the figures [2], [3], [4] and [5] respectively. The geometrical parameters viz. bond lengths and bond angles between the atoms participating in the coordination phenomenon are given in the table [3(a) and (b)].

#### **3.3 Molecular electrostatic potential and Frontier molecular orbital analysis:**

The molecular electrostatic potential (MEP) mapped surfaces illustrate the continuous charge distributions of molecules three dimensionally which give clear signature of the interactions

and the reactive sites of the molecules. The MEP mapped surface of the molecules are computed by DFT method at 6-311++G(d,p){for C,H,N,O,S}/Lanl2DZ{for M = Ni(II), Zn(II) and Cd(II) level of calculation. The MEP mapped surfaces of the Heptpc (a) and its complexes ([b] Ni (II), [c] Zn (II), [d] Cd (II) ) are shown in figure [6]. In color scheme of the MEP plot, the red region shows the negative electrostatic potentials i.e atoms with lone pairs; the blue region shows the positive electrostatic potentials and the green region cover the parts of the molecule where electrostatic potentials are close to zero. The intensity of the color is directly proportional to the absolute value of the potential energy. Frontier molecular orbitals (FMOs) refer to the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) which is used to determine the molecular reactivity, excitation properties and the electron transport phenomenon [14, 15]. The outermost higher energy orbital (HOMO) acts as an electron donor while the lowest energy orbital (LUMO) acts as an electron acceptor. The energies of the HOMO-LUMO orbital of the molecules, calculated by DFT method, are found to be negative, this signifies that the molecules are stable [16]. The HOMO-LUMO plots for the Heptpc (a) and its complexes ([b] Ni (II), [c] Zn (II), [d] Cd (II) ) are shown in figure [7]. The electronic transition from the ground state to the excited state due to a transfer of electrons from the HOMO to LUMO levels is mainly due to  $\pi$ ... $\pi$ transition. The positive phases are red and the negative ones are green. The small energy gap of molecules is termed as soft while the large energy gaps are termed as hard molecules. The hardness value  $(\eta)$  of a molecule can be defined by the formula [17]

#### $\eta = \{-\varepsilon_{\text{HOMO}} + \varepsilon_{\text{LUMO}}\}/2$

where  $\varepsilon_{HOMO}$  and  $\varepsilon_{LUMO}$  are the energies of the HOMO and LUMO molecular orbital. The soft molecules are high reactive, high polarisable and less stable than the hard ones because soft molecules need small energy for excitation. It can be seen from figure [6] the Cd-complex is softest among the other complexes and Heptpc, which needs less energy for the excitation

from the ground state to excited state i.e. the polarisability vary as  $Cd \rightarrow Ni \approx Zn$  in decreasing order. The HOMO-LUMO energy gap for the Ni and Zn complexes are approximately equal values. This suggests the same type of geometrical structures of the Ni and Zn complexes. This confirms the results obtained by the UV-Visible spectral analysis.

#### 3.2 Vibrational (FTIR and Raman band) analysis of Heptpc and the Complexes:

The FTIR and Raman spectra of the ligand Heptpc and the metal complexes  $[M(eptpc)_2(py)_2]$ {where M = Ni(II), Zn(II) and Cd(II) are recorded to obtain the binding sites of the metals to the ligand. The FTIR and Raman spectra of the ligand Heptpc and the metal complexes are shown in the figures [8] and [9] respectively. The bands, which show clear changes after the complex formation have been emphasized. The vibrational modes of Raman and IR bands are assigned [18-20] with the help of DFT calculation and the DFT results have been also used to understand the experimental results.

The v(C-H) of the two pyridine molecules in Ni and Zn complexes exhibited a very weak IR band at 3243 cm<sup>-1</sup>, whereas it was found to be absent in Cd complex. But a broad band at 3239 cm<sup>-1</sup> in the Raman spectra is observed in all the three complexes corresponding to v(C-H) vibration. This may be due to different type of geometry of Cd complex than those of Ni and Zn complexes, which influences the charge distribution i.e. vibrational energy responsible for v(C-H) vibration of pyridine. A very strong and sharp Raman band is observed at 3069 cm<sup>-1</sup> in all the three complexes, which is assigned as v(C-H) of the both ligand molecules present in complexes. The Raman band at 3012 cm<sup>-1</sup> and IR bands at 3011 and 2983 cm<sup>-1</sup> corresponding to N-H stretching are observed in the ligand Heptpc but these are completely absent in all the three complexes, which suggested that the removal of H atom from –NH group and concomitant binding of metals to N sites of two ligand Heptpc and two coligands pyridine leads to the complex formation. The Raman bands at 2998 cm<sup>-1</sup> and 2913 cm<sup>-1</sup> and IR band at 2983 cm<sup>-1</sup> attributed to C-H stretching of piperazine rings in pure ligand

Heptpc are observed, but after the complexation the Raman bands at 2998 cm<sup>-1</sup> is shifted to the higher wavenumber at 3006 cm<sup>-1</sup> whereas the Raman band at 2913 cm<sup>-1</sup> and IR band at 2983 cm<sup>-1</sup> disappeared. A very weak band at 2870 cm<sup>-1</sup> in Raman spectra of pure ligand Heptpc is shifted to the lower wavenumber 2866 cm<sup>-1</sup> after complexation in all the three complexes. The IR band at 1698 cm<sup>-1</sup> corresponding to v(C=O) of pure Heptpc disappeared in the complexes. Similarly, the two very sharp bands at 1596 and 1527 cm<sup>-1</sup> in the Raman spectra of the three complexes are observed which was not found in the Raman spectra of pure heptpc. These bands are assigned as scissoring of C-H group. This signifies the change in the charge cloud of ligand Heptpc before and after the complex formation. The two neighbouring Raman bands at 1457 and 1441 cm<sup>-1</sup> attributed to the contributions of N-H bending, scissoring of C-H mode and C=N stretching of thiourea group of pure Heptpc are shifted to lower wavenumber at 1454 and 1438 cm<sup>-1</sup> respectively in all three complexes. This is due to removal of H from –NH group and binding of metals to same N site. Therefore, the Raman bands at 1454 and 1438 cm<sup>-1</sup> complexes exhibited the vibrational modes [ $\beta$  (M-N<sub>p</sub>-C<sub>p</sub>) + v (C=C)<sub>p1+p2</sub> +  $\beta$  (C-H)] where M= Ni, Zn and Cd. We observed three new bands at 1332, 1311 and 1293 cm<sup>-1</sup> in the Raman spectra of the complexes, which is assigned as contribution of vibrational modes  $[\beta (N_{p1}-M-N_{p2}) + v_{as}(C-N)_{p1+p2} + v_{as}(C-C)_{p1+p2}]$ . This again proves the binding of metals through N site of pyridine molecules. The Raman band at 1257 cm<sup>-1</sup> attributed to the twisting of  $CH_2$  of piperazine ring plus N=C=N(H) bending of thiourea in the pure Heptpc is split into two bands at 1252 and 1241 cm<sup>-1</sup> after the complex formation. The removal of H atom from -NH group leads to the formation of deprotonated thiourea group, which give two bands at 1252 and 1241 cm<sup>-1</sup>. A very strong and sharp band at 1206 cm<sup>-1</sup> is assigned as C-H bending of the benzene ring in Heptpc which is red shifted with decreasing Raman activity as we go Cd $\rightarrow$ Ni $\approx$ Zn. This suggests interestingly that the complexes are less polarisable as we go to Cd $\rightarrow$ Ni $\approx$ Zn order which is also explained by theoretically calculated

HOMO-LUMO energy gap as shown in figure [7]. The new band at 1081 cm<sup>-1</sup> in Raman spectra of complexes (Fig 3), assigned as the vibrational modes  $[v_{as}(N-M)_{p1+p2} + \beta_{as(tr)}(C-N-m)]$  $C)_{p_1+p_2} + \beta_{(tr)} (C-C-C)_{p_1+p_2}$ ], gives clear evidence of metal binding. The two Raman bands at 1046 (vw) and 1033 cm<sup>-1</sup> due to the vibrational modes [v (C-C)<sub>pz</sub>+  $\beta$ <sub>(tr)</sub> (C-N-C)<sub>pz</sub>+  $\beta$ (thiourea)+ v (C-O)] are coupled and shifted to the lower wavenumber at 1029 cm<sup>-1</sup> in the Zn and Ni complexes having contribution from the a new vibrational modes  $[v_{as}(N-Ni)_{p1+p2}+\phi]$ (p1+p2)] whereas in case of Cd complex, the band at 1046 cm<sup>-1</sup> is not found to be shifted and the band at 1033 cm<sup>-1</sup> is shifted to the same position at 1029 cm<sup>-1</sup> in all complexes. This shows that the different type of coordination property of thiourea group with Cd(II) and Ni(II) (or Zn(II)). The most strong and highest Raman active band in the whole range of Raman spectra appeared at 998 cm<sup>-1</sup> in all the three complexes, which is not present in the Heptpc before the complex formation. This band belongs to the metal coordinated modes in addition to the possible contribution of vibrational modes of pyridine molecules i.e.  $[\gamma(C-N-$ M)<sub>p2</sub>+r(C-H)<sub>op</sub>+r (ring)<sub>p2</sub>]. A strong Raman band at 934 cm<sup>-1</sup> attributed to [{ $\beta_{(tr)}$  (N=C=NH)+v  $(C-S)_{pz}$  thiourea+ v(ring)<sub>pz</sub>+  $\varphi(bz)$  of the pure Heptpc was absent in the complexes. However, it is split in two components, one at 952 cm<sup>-1</sup> assigned as  $v(ring)_{pz} + v(C-O) + \phi(bz)$  and other at 922 cm<sup>-1</sup> corresponding to metal coordinated mode and pyridine molecules,  $\tau$ (M- $N_p$ )+r(C<sub>2</sub>H<sub>2</sub>)<sub>p</sub>.

The IR band at 880 cm<sup>-1</sup> [ $\beta$ (ring)<sub>pz</sub>+r(CH<sub>2</sub>)<sub>pz</sub>+scis(N<sub>pz</sub>=C=O)+v(C-O)] shifted to 871 cm<sup>-1</sup> due to redistribution of charge over the Heptpc molecule on complex formation leading to the red shift of this band. Whereas, the band at 817 cm<sup>-1</sup> in the IR spectra of pure Heptpc, which is mainly due to ring breathing of piperazine and benzene disappeared in the complexes. In Raman spectra of the complexes, a strong band due to rocking modes of the M-N (M = Ni, Zn, Cd) and C-H bonds of two pyridine molecules is observed at 770 cm<sup>-1</sup>. The Raman spectra of the complexes exhibited two strong and very sharp bands at 701 and

 $679 \text{ cm}^{-1}$ . Similarly the IR spectra of the complexes exhibited a new band at 698 cm<sup>-1</sup>, which was not observed in pure Heptpc. The Raman band at 701 cm<sup>-1</sup> and IR band at 698 cm<sup>-1</sup> are due to the asymmetric stretching of the metal coordinated bond with N atoms of both ligand Heptpc (i.e M-N<sub>L</sub> bond) and the band at 679 cm<sup>-1</sup> is due to the asymmetric stretching of the metal coordinated bond with N atoms of both pyridine molecules (i.e M-N<sub>p</sub> bond) and trigonal bending of (C-N-C) plus (C-C-C) of pyridine rings. A very sharp band at 629 cm<sup>-1</sup> of the pure Heptpc is split into the two weak bands on either side of the 629 cm<sup>-1</sup>, one towards higher wavenumber at 638 cm<sup>-1</sup> which gets broadened in the complexes and the other towards lower wavenumber at 614 cm<sup>-1</sup>.

Appearance of a new band at 532 cm<sup>-1</sup> [v(M-N)<sub>p</sub>] in the Raman spectra of Cd complex suggests the formation of bond between the Cd<sup>2+</sup> and N sites of both pyridine. In case of Zn and Ni complexes the bands corresponding to v(M-N)<sub>p</sub> and v(M-S)<sub>L</sub> appeared at 580 and 427 cm<sup>-1</sup> respectively. The IR band at 477 cm<sup>-1</sup>[ $\beta$ (N-H)+  $\beta$ (thiourea)] of Heptpc split into two components in the complexes, one at 474 cm<sup>-1</sup> due to [ $\beta$ (N<sub>p</sub>-M-S)+ $\gamma$ (ring)<sub>p</sub>, where M=Zn and Ni] in case of the Zn and Ni complexes whereas due to [ $\beta$ (N<sub>p</sub>-Cd-N<sub>p</sub>)+ $\gamma$ (ring)<sub>p</sub>] for Cd complex and the other at 490 cm<sup>-1</sup> that is more clear and sharp in the Zn and Ni complexes than in Cd complex. The IR band at 490 cm<sup>-1</sup> mainly corresponds to [ $\beta$ (N<sub>p</sub>-M-S)+r(N<sub>L</sub>-M-N<sub>L</sub>)+ $\gamma$ (ring)<sub>p</sub>] in the Zn and Ni complexes and [ $\beta$ (N<sub>p</sub>-Cd-N<sub>p</sub>)+r(N<sub>L</sub>-d-N<sub>L</sub>)+ $\gamma$ (ring)<sub>p</sub>] in the Cd complex. The IR band at 490 cm<sup>-1</sup> mainly corresponds to [ $\beta$ (N<sub>p</sub>-M-S)+r(N<sub>L</sub>-M-N<sub>L</sub>)+ $\gamma$ (ring)<sub>p</sub>] in the Zn and Ni complexes and [ $\beta$ (N<sub>p</sub>-Cd-N<sub>p</sub>)+r(N<sub>L</sub>-d-N<sub>L</sub>)+ $\gamma$ (ring)<sub>p</sub>] in the Zn and Ni complexes and [ $\beta$ (N<sub>p</sub>-Cd-N<sub>p</sub>)+r(N<sub>L</sub>-d-N<sub>L</sub>)+ $\gamma$ (ring)<sub>p</sub>] in the Zn and Ni complexes and [ $\beta$ (N<sub>p</sub>-Cd-N<sub>p</sub>)+r(N<sub>L</sub>-d-N<sub>L</sub>)+ $\gamma$ (ring)<sub>p</sub>] in the Zn and Ni complexes and [ $\beta$ (N<sub>p</sub>-Cd-N<sub>p</sub>)+r(N<sub>L</sub>-d-N<sub>L</sub>)+ $\gamma$ (ring)<sub>p</sub>] in the Cd complex. The above discussion suggests that the metal ions (Zn(II) and Ni(II)) bonded through nitrogen and thione sulfur sites of deprotonated ligand (eptpc) and nitrogen site of co-ligand (pyridine) form a chelate ring whereas Cd(II) bonded through only nitrogen site of deprotonated ligand (eptpc) and nitrogen site of co-ligand (pyridine). This indicates the similar type of the geometry of the complexes of Zn(II) and Ni(II) whereas Cd(II) complex has different type geometry. This support the result obtained by UV-Visible absorption

technique i.e. distorted octahedral geometry of the complexes  $[Zn(eptpc)_2(py)_2]$  and  $[Ni(eptpc)_2(py)_2]$  and distorted tetrahedral geometry of the complex  $[Cd(eptpc)_2(py)_2]$ .

The IR band at 429 cm<sup>-1</sup> due to bending of N-H bond in the Heptpc disappeared after the complex formation. This shows the removal of H atom from –NH group and binding of the metals to this site. The Raman bands at 359 and 225 cm<sup>-1</sup> of pure Heptpc due to the vibrations of the thiourea group disappeared completely after the complex formation and a broad Raman band at 395 cm<sup>-1</sup> of the Heptpc is shifted and converted to a sharp and strong band at 408 cm<sup>-1</sup> due to v(M-S) [where M = Ni, Zn, Cd]. This again confirms the formation of metal complexes.

#### 4. Conclusion and Output:

This study was undertaken in many stages. In first stage, ligand Heptpc was synthesized as depicted in scheme 1. In second stage, metal complexes of Ni, Zn and Cd were prepared using Heptpc as ligand and pyridine as coligand (scheme 1). Since the Single crystals of the complexes could not be isolated from the solutions, no direct structural information could be obtained. Therefore, in third stage, the most possible geometries of the complexes were proposed using elemental analyzer, Magnetic data and UV-Visible spectroscopy. Further in fourth stage, we characterized the ligand Heptpc and the metal complexes using the vibrational spectroscopic (FTIR and Raman) techniques to access the binding of metals. The Zn and Ni bind with N and S sites of the two ligand Heptpc and two N sites of two pyridine molecules in Zn/Ni complex but in Cd complex, Cd binds to only N sites of the two ligand Heptpc and two N sites of two pyridine molecules of the binding phenomenon. The DFT calculations were performed with many possible structures of the complexes as input for geometry optimizations but only the geometry presented in this work are converged, for which the harmonic frequency found to be imaginary. Thus DFT calculation further strongly proves that

the proposed geometry of the complexes is most possible and acceptable. By using various technique, we proposed the distorted octahedral geometry of complexes -  $[Zn(eptpc)_2(py)_2]$  and  $[Ni(eptpc)_2(py)_2]$  and distorted tetrahedral geometry of complex -  $[Cd(eptpc)_2(py)_2]$ . This study concludes that the technique viz. elemental analyses, UV-Visible, FTIR, Raman and DFT method are good enough to propose the most possible geometry of complex molecules.

#### <sup>a</sup> Abbreviations:

v =stretching;  $\beta =$ bending;  $\delta =$  deformation;  $\gamma =$  out-of-plane bending;  $\tau =$ torsion; r = rocking;  $\varphi =$  ring breathing; twist= twisting;  $\omega =$ wagging; tr= trigonal; pz= piperazine ring; bz= benzene ring; op= out of plane.

p1 and p2 are the two pyridine rings; L1 and L2 are the two ligand (Heptpc/eptpc), where Heptpc is pure and eptpc (deprotonated Heptpc) is coordinating ligand.

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#### **References:**

 J. Faist, W. Seebacher, R. Saf, R. Brun, M. Kaiser, R. Weis, Eur. J. Med. Chem., 47 (2012) 510-519.

[2] K. Kulig, J. Sapa, D. Maciag, B. Filipek, B. Malawska, Arch. Pharm., 340 (2007) 466-475.

- [3] A. Pietrzycka, M. Stepniewski, A.M. Waszkielewicz, H. Marona, Acta Pol Pharm, 63 (2006) 19-24.
- [4] A.Y. Louie, T.J. Meade, Chem. Rev., 99 (1999) 2711-2734.
- [5] Z. Balcarová, J. Kaspárková, A. Zákovská, O. Nováková, M.F. Sivo, G. Natile, V. Brabec, Mol. Pharmacol., 53 (1998) 846-855.
- [6] R.Bakhtiar, E.I. Ochiai, General Pharmacology: The Vascular System, 32 (1999) 525-540.
- [7] A.I. Vogel, A Text Book of Quantitative Inorganic Analysis, third ed., ELBS, Longman, London, (1969).
- [8] A.B.P. Lever Inorganic Electronic Spectroscopy, second ed., Elsevier, Amsterdam (1984).
- [9] M.J. Frisch, J.A. Pople, Gaussian 03, Revision A.1, Gaussian, Inc., Pittsburgh, 2003.
- [10] A.D. Becke, J. Chem. Phys, 98 (1993) 5648-5652.
- [11] C. Lee, W. Yang, R.G. Parr, Phys. Rev. B, 37 (1988) 785-789.
- [12] J.M.L. Martin, C. Van Alsenoy, GAR2PED, University of Antwerp, (1995).
- [13] M. Biczysko, P. Panek, V. Barone, Chem. Phys. Lett., 475 (2009) 105-110.
- [14] M. Belletête, J.F. Morin, M. Leclerc, G. Durocher, J. Phys. Chem. A, 109 (2005) 6953-6959.
- [15] D. Zhenming, S. Heping, L. Yufang, L. Diansheng, L. Bo, Spectrochim. Acta-A Mol. Biomol. Spectrosc., 78 (2011) 1143-1148.
- [16] S.W. Xia, X. Xu, Y.L. Sun, Y.L. Fan, Y.H. Fan, C.F. Bi, D.M. Zhang, L.R. Yang, Chin.J. Struct. Chem. 25 (2006) 849
- [17] K. Fukui, Science, 218 (1982) 747-754.
- [18] K. Nakamoto, Infra and Raman spectra of Inorganic and coordination compounds, PartA, 6<sup>th</sup> ed, John Wiley & Sons, (2008)

[19] K. Nakamoto, Infra and Raman spectra of Inorganic and coordination compounds, PartB, 6<sup>th</sup> ed, John Wiley & Sons, (2009)

[20] J. R. Ferraro, K. Nakamoto, C. W. Brown, Introductory Raman Spectroscopy, 2<sup>nd</sup> ed, Elsevier, (2003)

#### **Figure Captions**

Figure 1(a): The UV/VIS. spectra of the pure ligand Heptpc in the region 200-500 nm

Figure 1(b): The UV/VIS. spectra of the  $[Ni(eptpc)_2(py)_2]$  in the region 200-500 nm

Figure 1(c): The UV/VIS. spectra of the [Zn(eptpc)<sub>2</sub>(py)<sub>2</sub>] in the region 200-500 nm

Figure 1(d): The UV/VIS. spectra of the [Cd(eptpc)<sub>2</sub>(py)<sub>2</sub>] in the region 200-500 nm

Figure 2: Optimized structure of the Heptpc by DFT method

Figure 3: Optimized structure of [Ni(eptpc)<sub>2</sub>(py)<sub>2</sub>] by DFT method.

Figure 4: Optimized structure of [Zn(eptpc)<sub>2</sub>(py)<sub>2</sub>] by DFT method.

Figure 5: Optimized structure of [Cd(eptpc)<sub>2</sub>(py)<sub>2</sub>] by DFT method.

Figure 6: Molecular Electrostatic potential surface maps of Heptpc (a) and its metal complexes ( [b] Ni (II), [c] Zn (II), [d] Cd (II) ).

Figure 7: The HOMO-LUMO plots for the (a) Heptpc and its complexes ([b] Ni (II), [c] Zn (II), [d] Cd (II) ).

Figure 8: Experimental FT-IR spectra of Heptpc and Ni(II), Zn(II) and Cd(II) complexes in the region 350-4000 cm<sup>-1</sup>.

Figure 9(a): Experimental Raman spectra of Heptpc and Ni(II), Zn(II) and Cd(II) complexes in the region 200-1000 cm<sup>-1</sup>.

Figure 9(b): Experimental Raman spectra of Heptpc and Ni(II), Zn(II) and Cd(II) complexes in the region 900-1750 cm<sup>-1</sup>.

Figure 9(c): Experimental Raman spectra of Heptpc and Ni(II), Zn(II) and Cd(II) complexes in the region 2600-3500 cm<sup>-1</sup>.

#### **Tables Captions:**

 Table 1: Analytical Data, Colour, Melting Point, and Percentage Yield of ligand and the

 Metal Complexes

 Table 2: Electronic absorption spectral data of the ligand(Heptpc) and complexes in DMSO

 Solution

Table 3(a): Selected bond lengths of complexes [M(eptpc)<sub>2</sub>(py)<sub>2</sub>] (where M=Ni, Zn, Cd) calculated by DFT method.

Table 3(b): Selected bond angles of complexes [M(eptpc)<sub>2</sub>(py)<sub>2</sub>] (where M=Ni, Zn, Cd) calculated by DFT method.

### Table 1

	Empirical			Yield		Elemental			
Compounds	formula	<i>M.P</i> .	Colour	(%)		Analysis			
	(Weight in gm.)	$(^{0}C)$		(mg)		%Found			7
						(calcd.)			
					С	Н	N	S	М
Heptpc	$C_{14}H_{19}N_2O_2S$	235	White	85	60.27	6.81	10.02	11.47	
	(279.50)				( 60.18)	( 6.78)	(10.03)	(11.45)	
[Ni(eptpc) <sub>2</sub> (py) <sub>2</sub> ]	$C_{38}H_{46}N_6O_4S_2Ni$	320	Brown	78	62.07	6.31	11.48	8.74	7.98
	(734.98)				(62.05)	(6.26)	(11.52)	(8.76)	(7.90)
[Zn(eptpc) <sub>2</sub> (py) <sub>2</sub> ]	$C_{38}H_{46}N_6O_4S_2Zn \\$	278	Colorless	67	61.47	6.20	11.34	8.65	8.80
	(742.36)				(61.45)	(6.16)	(11.25)	(8.70)	(8.85)
[Cd(eptpc) <sub>2</sub> (py) <sub>2</sub> ]	$C_{38}H_{46}N_6O_4S_2Cd$	286	Colorless	74	57.87	5.88	10.68	8.14	14.35
	(788.82)				(57.82)	(5.83)	(10.72)	(8.17)	(14.28)

### Table 2

Table 2				
Compounds	Magnetic moment (B.M.)	Absorption (cm <sup>-1</sup> )	Band assignment	Geometry
Heptpc			LCT	
[Ni(eptpc) <sub>2</sub> (py) <sub>2</sub> ]	2.88	21010, 27910	${}^{3}A_{2}g \rightarrow {}^{3}A_{1}g(F) (v_{2}), {}^{3}T_{1}g(P)$ (v <sub>3</sub> )	Distorted Octahedral
[Zn(eptpc) <sub>2</sub> (py) <sub>2</sub> ]	Diamagnetic	29500-31000	IL/CT	Distorted Octahedral
[Cd(eptpc) <sub>2</sub> (py) <sub>2</sub> ]	Diamagnetic	29500-31000	IL/CT	Distorted tetrahedral

### Table 3(a):

Bond	Bond length (M=Ni)	Bond length $(M=Zn)$	Bond	Bond length
(where M=Ni, Zn)				
M-N <sub>p1</sub>	1.911	2.276	Cd-N <sub>p1</sub>	2.399
M-N <sub>p2</sub>	1.913	2.288	Cd-N <sub>p1</sub>	2.399
$M-N_1$	2.988	2.144	Cd-N <sub>1</sub>	2.234
<b>M-N</b> <sub>2</sub>	2.988	2.144	Cd-N <sub>1</sub>	2.234
$M-S_1$	2.348	2.741		CI
M-S <sub>2</sub>	2.348	2.741		
Table 3(b):			J.	2
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### Table 3(b):

Bond angle	Bond angle	Bond angle	Bond angle	Bond angle
(where M=Ni, Zn)	(M=Ni)	(M=Zn)		
$N_{p1}$ -M- $N_{p2}$	179.99	179.99	$N_{p1}$ -Cd- $N_{p2}$	80.10
$N_{p1}$ -M-S <sub>1</sub>	89.88	89.88	N <sub>1</sub> -Cd-N <sub>2</sub>	120.94
$N_{p2}$ -M- $S_2$	90.12	92.43	N <sub>p1</sub> -Cd-N <sub>1</sub>	95.88
$N_{p1}$ - $M$ - $N_1$	93.65	92.19	N <sub>p2</sub> -Cd-N <sub>2</sub>	95.89
$N_{p2}$ -M- $N_2$	93.65	92.19	$N_{p2}$ -Cd- $N_1$	127.30
N <sub>p2</sub> -M-N <sub>1</sub>	86.34	87.81	$N_{p1}$ - $M$ - $N_2$	127.30
N <sub>p1</sub> -M-N <sub>2</sub>	86.34	87.81		
N <sub>p1</sub> -M-S <sub>2</sub>	89.88	87.57		
N <sub>p2</sub> -M-S <sub>1</sub>	90.12	92.43		
S <sub>1</sub> -M-S <sub>2</sub>	86.34	87.81		
N <sub>1</sub> -M-N <sub>2</sub>	172.69	175.62		

























#### Highlights:

- The synthesis of Ni(II), Zn(II) and Cd(II) complexes of ethyl 4-phenylthiocarbamoyl piperazine-1-carboxylate is reported.
- The coordination properties of the metals are investigated by using UV-Visible, FTIR, and Raman spectroscopic technique.
- The optimized geometry, HOMO-LUMO and MEPS calculated results performed by DFT method fully support the experimental results.

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