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unconventional С-Н···Н-С **Exploration π**–hole and of 1 of types supramolecular interactions in a trinuclear Cd(II) and a heteronuclear 2 Cd(II)-Ni(II) complex and experimental evidence for preferential site selection 3 of the ligand by 3d and 4d metal ions. 4

Saikat Banerjee,^a Antonio Bauzá,^b Antonio Frontera,^{*b} and Amrita Saha^{*a} 5

Abstract

In this present work we report synthesis and structural characterisations of a trinuclear cadmium (II) (1) and a di(phenoxido)-bridged dinuclear cadmium(II)-nickel(II) (2) complexes derived from a bicompartmental (N2O4) Schiff base ligand, H_2L . It has been observed that, in bicompartmental ligands the relatively small inner core is suitable for 3d metal ions and outer core can be occupied by different metal centers like 3d, 1s, 2s, 4d and 4f. We have experimentally established the above fact. In homotrinuclear complex 1 both inner (N2O2) and outer (O4) core has been occupied by cadmium (II) ions. Complex 1 upon reaction with NiCl_{2.6}H₂O produces heterodinuclar complex 2. Structural studies reveal that, in complex 1 terminal Cd units acquire trigonal prismatic geometry whereas the central Cd unit is eight coordinated. In case of complex 2 both nickel(II) and cadmium(II) ions are hexa-coordinated in a distorted octahedral environment. Both the complexes are studied using different spectroscopic 18 19 techniques. Complexes 1 and 2 exhibit important and relatively unexplored group of supramolecular interactions like π -hole, C-H··· π and C-H···H-C along with other hydrogen 20 21 bonding interactions. Theoretical DFT calculations are devoted to analyze these non covalent

24 Introduction

Schiff-base complexes play an important role in the development of modern coordination 25 chemistry and have various applications in the field of magnetism, catalysis, medicinal 26 chemistry, gas storage, electron transport processes and sensing.¹⁻⁹ Among the Schiff base 27 ligands acyclic compartmental ligands which contains two different sites are vastly used to 28 prepare homo and heteronuclear complexes. Such types of Schiff base ligands are achieved from 29 the condensation between diamines and salicylaldehyde with an appended alkoxy group at ortho 30 position to the phenoxido oxygen (salphen) (Scheme 1). The ligands have two different 31 tetradentate coordination core, inner core consists of two imine-N and two phenoxo-O atoms and 32 outer core involves two phenoxo-O and two alkoxy-O units. In case of homonuclear complexes 33 large number of di, tri, tetra and polynuclear complexes having 3d and 4d metals¹⁰⁻¹² are known 34 whereas heteronuclear complexes involves different 3d-1s, 3d-2s,¹³⁻¹⁹ 3d-3d,²⁰⁻³⁶ 3d-4d,³⁷⁻³⁸ and 35 3d-4f metal centers.³⁹⁻⁴⁸ 36

It has been observed that during formation of homo or heteronuclear complexes 37 bicompartmental ligands first form an intermediate known as "metallo-ligand reactant". This 38 metallo-ligand system further react with different metals ions with 1s, 2s, 3d, 4d and 4f 39 electronic configuations, ammonium ion, dicarboxylic acid and deprotonated diamine. The 40 mostly used transition metal centre among the divalent first row transition element to prepare 41 "metallo-ligand reactant" is Cu(II). In this case the Cu(II) center is coordinated with two imine-N 42 and two phenoxo-O atoms. Ni(II),^{22,26,32} Mn(II)²⁴ and Zn(II)³⁹⁻⁴² are also used for the same 43 purpose. In this context Salphen complexes containing zinc(II) need special mention. They have 44

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been widely used in the field of supramolecular chemistry,⁴⁹ catalysis⁵⁰ and transmetalation.⁵¹
Presence of available coordination site and presence of intermolecular Zn…O interactions
between the zinc(II) center of a salphen unit and phenolic oxygen of another are the two most
dominating facts to exhibit such types of behavior. It has been also observed that zinc salphen
moiety incorporated into a crown ether framework exhibit excellent binding affinity toward
cationic guest species.⁵²

The structural diversity of such complexes are achieved by interesting non covalent 51 interactions like hydrogen bonding, cation $-\pi$, anion $-\pi$, CH $-\pi^{53}$ and other less recognized forces. 52 such as, σ/π -hole,⁵⁴ and C-H···H-C interactions⁵⁴ etc. It is now well established that 53 supramolecular interactions deal with weak and reversible non covalent interactions which are 54 the basis of highly specific recognition, transport, and regulation mechanisms. It is vastly used to 55 understand the progress in many biological functions and drug design. Amongst supramolecular 56 interactions σ/π -holes interactions are very important but comparatively unexplored. In 1973 57 Birgi and Dunitz in a series of work explain the pathway along which a nucleophile attacks the π 58 -hole of a C=O group.⁵⁵ It has been observed that in a given group of the periodic table, σ/π -hole 59 interactions become more positive on going from the lower atomic number to the higher atomic 60 number. A positive π -hole interaction is highly directional in nature and observed between a 61 region with positive electrostatic potential of unpopulated π^* orbitals and electron dense region. 62 Recently, π -hole interactions has been observed in acyl carbons, ⁵⁶ SO₂ and SO₃ moieties, ⁵⁷ 63 RNO_2 molecules, ⁵⁸ XCN, XZO₂ (X=halogen, Z = pnictogen), etc. ⁵⁹ It is important to mention 64 that the nitro group plays a crucial role to modify the electronic nature of aromatic rings or 65 aliphatic chains. Therefore, it will participate in π -hole interactions and thus plays an important 66

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role in crystal engineering. Halogen bonding also needs special mention as it is important in thefield of biological systems and in the design of new materials.

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In this work bicompartmental ligand, $H_2L(N,N)$ -bis(3- methoxysalicylidene)propylene-69 1.3-diamine)upon reaction with $Cd(NO_3)_2.4H_2O$ produced trinuclear 70 а complex $[Cd_3(L)_2(NO_3)_2](1)$. This trinuclear complex upon reaction with NiCl₂.6H₂O generate a 71 heterodinuclar Ni(II)-Cd(II) complex i.e. [{Ni^{II}L(CH₃OH)₂}CdCl₂].H₂O(**2**). In complex **1** Cd(II) 72 ions occupy both the coordination positions of the ligand, in complex 2 the inner Cd(II) centreis 73 easily replaced by the Ni(II) ion. Different spectroscopic studies are used to characterize both the 74 75 complexes. In contrast to the propensity of Cu(II) complexes to react with a second metal salt, only few products have been obtained from a mononuclear Ni(II) compounds.¹¹ 76

Most interesting observation in the supramolecular assembly of complex 1 and 2 is the 77 existence of remarkable π -hole, C-H··· π and C-H···H-C interactions along with other hydrogen 78 bonding interactions. In complex 1 π -hole interaction is established between the O atom of the 79 nitrato ligand and the C atom of the C=N bond. Molecular electrostatic potential (MEP) surface 80 analysis and the non covalent interaction (NCI) analysis of compounds 1 and 2 allow an 81 assessment of different nonbonding interactions and the extent to which these weak interactions 82 stabilize the complex. Briefly, the systems derived from the bi compartmental ligand, H_2L 83 exhibit in the solid state self-assemblies that are governed by an intricate combination of weak 84 interaction. They are thus interesting in the frontier research area of crystal engineering and 85 supramolecular chemistry. Thus, we have been motivated to explore this area further. 86

87 Experimental section

88 Materials and synthesis

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All reagent or analytical grade chemicals and solvents were purchased from commercial

92 diamine)

The tetradentate Schiff base ligand (**H**₂**L**) was prepared by the standard method.⁶⁰ Briefly, a mixture of o-vaniline (8.0 mmol, 1.217 g) and 1,3-diaminopropane (4.0 mmol, 0.296 g) in 50 mL methanol was heated to reflux for 2 h. The resulting light yellow colored Schiff base ligand (**H**₂**L**) was used for further reaction.

Synthesis of Schiff base ligand ($H_2L = N_1N'$ -bis(3- methoxysalicylidene)propylene-1,3-

97 **Preparation of [Cd₃(L)₂(NO₃)₂]** (1)

sources and used without further purification.

A 10 ml methanolic solution of cadmium nitrate (6.0 mmol, 1.848 g) was added to a 98 methanolic solution of H₂L (4.0 mmol) followed by addition of triethylamine (8.0 mmol, ~ 1.5 99 mL) and the resultant reaction mixture was heated to reflux for 4 h. The solution was then cooled 100 and filtered. Deep vellow colored crystals resulted from the slow evaporation of methanolic 101 solution of the complex at room temperature. Yield: 0.1880 g (82%). Anal. Calc. for 102 C₃₈H₄₀Cd₃N₆O₁₄: C 36.87%; H 3.09%; N 7.82%. Found: C 36.35%; H 3.07%; N 7.29%. IR (cm⁻ 103 ¹, KBr): υ (C=N) 1625 m; υ (C-N) 1225 s; ν (C-H) 730 s. UV-Vis, λ_{max} (nm), (ϵ (dm³mol⁻¹cm⁻¹)) 104 in DMF-CH₃CN (1:9, v/v): 268 (10420), 353 (4004). 105

¹H NMR (DMSO-d₆, 300 MHz) δ ppm: 1.81 (bs, 2H), 4.12 (bs, 4H), 6.27-6.9 (m, 4H), 8.178.32 (m, 2H)

¹³C NMR (DMSO-d₆, 75 MHz) δ ppm: 31.98 (-CH₂), 55.6 (-OCH₃), 63.9 (-CH₂), 113.44(-CH),

109 118.67 (-CH), 128.04 (-CH), 149.73 (-CH), 169.56 (-CH=N).

110 Preparation of $[{Ni^{II}L(CH_3OH)_2}CdCl_2].H_2O(2)$

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A 10 ml methanolic solution of nickel chloride (2.0 mmol, 0.4754 g) was added to a methanolic suspension of complex 1 (1.0 mmol) and the reaction mixture was stirred for 3 h at room temperature. Then the solution was filtered. Deep green colored crystals resulted from the slow evaporation of methanolic solution of the complex at room temperature.

115 Colour: Deep Green. Yield: 0.0996 g (75%). Anal. Calc. for $C_{21}H_{30}CdCl_2N_2NiO_7$: C 116 37.96%; H 4.55%; N 4.22%. Found: C 37.20%; H 4.15%; N 4.02%. IR (cm⁻¹, KBr): υ (C=N) 117 1620 m; υ (C-N) 1217 s; ν (C-H) 737 s. UV-Vis, λ_{max} (nm), (ε (dm³mol⁻¹cm⁻¹)) in DMF-CH₃CN 118 (1:9, ν/ν): 287 (28878), 370 (2123), 580 (195).

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120 Physical measurements

Elemental analysis for C, H and N was carried out using a Perkin–Elmer 240C elemental 121 analyzer. Infrared spectra (400–4000 cm⁻¹) were recorded from KBr pellets on a Nicolet Magna 122 IR 750 series-II FTIR spectrophotometer. Absorption spectra were measured using a UV-2450 123 spectrophotometer (Shimadzu) with a 1-cm-path-length quartz cell. Electron spray ionization 124 mass (ESI-MS positive) spectra were recorded on a MICROMASS Q-TOF mass spectrometer. 125 Measurements of ¹H NMR spectra were conducted using a Bruker 300 spectrometer in DMSO-126 d₆. Emission was examined by LS 55 Perkin-Elmer spectrofluorimeter at room temperature (298 127 K) in DMSO-Methanol (1:9, v/v) solution under degassed condition. 128

129 X-ray crystallography

Single crystal X-ray data of complexes **1** and **2** were collected on a Bruker SMART APEX-II CCD diffractometer using graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å) at room temperature. Data processing, structure solution, and refinement were performed using Bruker

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Apex-II suite program. All available reflections in $2\theta_{max}$ range were harvested and corrected for 133 Lorentz and polarization factors with Bruker SAINT plus.⁶¹ Reflections were then corrected for 134 absorption, inter-frame scaling, and other systematic errors with SADABS.⁶² The structures were 135 solved by the direct methods and refined by means of full matrix least-square technique based on 136 F^2 with SHELX-97 software package.⁶³ All the non hydrogen atoms were refined with anisotropic thermal parameters. C-H hydrogen atoms were inserted at geometrical positions with $U_{iso} = 1/2U_{eq}$ to those they are attached. Crystal data and details of data collection and refinement for 1 and 2 are summarized in Table 1.

Theoretical methods

The calculations of the non covalent interactions were carried out using the TURBOMOLE version 7.0⁶⁴ using the BP86-D3/def2-TZVP level of theory. To evaluate the interactions in the solid state, we have used the crystallographic coordinates. This procedure and level of theory 144 have been successfully used to evaluate similar interactions.⁶⁵ The interaction energies were 145 computed by calculating the difference between the energies of isolated monomers and their 146 assembly. The interaction energies were corrected for the Basis Set Superposition Error (BSSE) 147 using the counterpoise method.⁶⁶ 148

The NCI plot is a visualization index based on the electron density and its derivatives, and 149 enables identification and visualization of non covalent interactions efficiently. The isosurfaces 150 correspond to both favorable and unfavorable interactions, as differentiated by the sign of the 151 second density Hessian eigenvalue and defined by the isosurface color. NCI analysis allows an 152 assessment of host-guest complementarity and the extent to which weak interactions stabilize a 153 154 complex. The information provided by NCI plots is essentially qualitative, i.e. which molecular regions interact. The color scheme is a red-yellow-green-blue scale with red for ρ^+_{cut} (repulsive) 155

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and blue for ρ_{cut} (attractive). Yellow and green surfaces correspond to weak repulsive and weak attractive interactions, respectively.⁶⁷

158 Hirshfeld Surface analysis

Hirshfeld surface analysis have been done using Crystal Explorer version 3.1.⁶⁸ The normalized contact distance (d_{norm}) based on d_i and d_e has been determined by the given equation where r^{vdW} is the van der Waals (vdW) radius of the appropriate atom internal or external to the surface.

162
$$d_{\text{norm}} = \frac{(d_i - r_i^{\nu dW})}{r_i^{\nu dW}} + \frac{(d_e - r_e^{\nu dW})}{r_e^{\nu dW}}$$

 d_{norm} becomes negative for shorter contacts than vdW separations and becomes positive for contacts greater than vdW separations, and is displayed using a red–white–blue color scheme, where red highlights shorter contacts, white is used for contacts around the vdW separation, and blue is for longer contacts.⁶⁹

167 Results and Discussion

168 Syntheses, IR, UV/Vis spectra, photoluminescence properties of the Complexes

The Schiff base used in this work is a well known symmetrical tetradentate ligand (H₂L).⁶⁰ One 169 of the important aspects of this type of ligand (salphen) is that upon metalation the phenol 170 oxygen atoms of the ligand become negatively charged phenoxo groups, which have higher 171 coordination ability to another metal ion. Complex 1 was prepared by the reaction of 172 Cd(NO₃)₂.4H₂O with H₂L in 3:2 molar ratio in methanol in presence of few drops of trimethyl 173 amine. Complex 2 was prepared by mixing complex 1 with NiCl₂·4H₂O in methanol in a 1:1 174 molar ratio as shown in Scheme 1. Besides elemental analysis, all of the complexes were initially 175 characterized by IR spectroscopy. A strong and sharp band appeared at 1634 and 1619 $\rm cm^{-1}$. 176

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177	respectively for complex 1 and 2, due to azomethine $v(C=N)$. In complex 1, stretching
178	frequencies at 1385 and 1290 cm ⁻¹ were tentatively assigned to $v(NO_3^-)$. In complex 2, a broad
179	band appeared at 3443 cm ⁻¹ , which may be assigned to the O-H stretching of the MeOH or of
180	the crystallized water molecule. The electronic spectra of complexes 1 and 2 are recorded in
181	DMF-CH ₃ CN (1:9 v/v) mixture of solvent. Both the complexes exhibit two sharp absorption
182	bands around 270 nm and 350 nm. These absorption bands can be assigned to $n \to \pi^*$ or $\pi \to \pi^*$
183	transitions of the Schiff-base ligands. Besides these bands, a broad absorption band is observed
184	in the visible region for complex 2 at 580 nm which can be assigned to the spin-allowed d-d
185	transition ${}^{3}T_{1g}(F) \leftarrow {}^{3}A_{2g}$. ⁷⁰ ¹ H NMR spectrum of complex 1 was performed using d ₆ -DMSO as
186	solvent. For complex 1 aromatic protons appeared within 6.27-6.90 ppm, where as aliphatic
187	protons appeared around 4.32 ppm and 1.80 ppm respectively. Azomethine CH=N proton
188	appeared at 8.3 ppm. In ¹³ C NMR spectrum of complex 1, the aromatic carbon atoms appeared
189	within 113-118 ppm. Whereas, the imine carbon atom (-CH=N) appeared at 169.53 ppm.
190	Aliphatic carbon atoms and carbon atom of the methoxy group appeared around 31, 63 and 55
191	ppm respectively. (Figure S3-S6) Fluoresence spectrum of the free ligand complex 1 and 2 were
192	performed in DMF-CH ₃ CN (1:9 v/v) mixture of solvent. Free ligand H_2L upon excitation gives a
193	broad fluorescent emission band at 458 nm. Complex 1 upon excitation at 353 nm gives an
194	intense emission peak was observed at 492 nm.(Figure 3) This type of luminescence may be
195	attributed to the intraligand $(\pi \rightarrow \pi^*)$ transition and the red shift in complex 1 may presumably
196	be due to the metal coordination. ⁷¹⁻⁷⁶ For complex 2 , upon excitation at 287 nm and 370 nm
197	respectively, no significant fluorescent emission band was observed mainly due to presence of
198	Ni(II) ion in the moiety.

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200 Description of the crystal structures of [Cd₃(L)₂(NO₃)₂] (1)

Compound 1 crystallized from slow diffusion of methanol solvent and it has monoclinic 201 space group P21/c. The crystal structure of $[Cd_3(L)_2(NO_3)_2]$ (1) is presented in Figure 1. Selected 202 bond lengths and angles for complex 1 are given in table 2. The core structure of 1 contains a 203 Cd3 unit. The two terminal Cd atoms Cd1 and Cd2 are located in the inner N2O2 cavities of the 204 two Schiff base ligands and are each bonded to a bidentate nitrate anion, resulting in a trigonal 205 prismatic geometry. Both Cd1 and Cd2 atoms lie slightly above the N2O2 plane by 0.792 A°. 206 207 The central metal atom Cd3 is eight coordinated and is encapsulated in the O8 cavity formed by four phenolic oxygen atoms (0,0) and four methoxy oxygen atoms (0,0). Thus the bridging 208 phenoxo oxygen atoms of the deprotonated Schiff base ligand L^{2-} connect each terminal Cd atom 209 210 to the central Cd atom forming bis(u-phenoxo) bridged Cd(II) - Cd(II) motifs. The three Cd(II) ions are nearly linear with a Cd(1)-Cd(3)-Cd(2) angle of 172.34° and Cd-Cd distances are similar 211 3.556Å and 3.546 Å for Cd1-Cd3 and Cd3-Cd2 respectively. The Cd-N, Cd-O (phonolic), Cd-O 212 213 (methoxy) bond distances are 2.249 Å, 2.242 Å and 2.63 Å respectively and these values are comparable with those found in other Schiff base complexes of Cd.¹¹ The Cd-O bond distances 214 varies in the extensive range which indicate different types of interaction between the Cd(II) ion 215 and the O atoms within the molecule. Presence of three carbon backbone makes the ligand 216 flexible and the two N2O2 planes of the Schiff base are crossed with dihedral angles of 66.77° 217 respectively. 218

In complex 1 self assembly by week π -hole interactions is observed. Cadmium coordinated nitrate ions interact with imine C-H moieties through delocalized π - electron cloud. As a result one trinuclear unit is interlinked with two neighboring trinuclear units to generate a two dimensional sheet. Presence of $\pi \dots \pi$ interactions between phenyl rings of same molecule (intramolecular) and two adjacent molecules (intermolecular) further stabilizes the structure. The
distance between the centers of two rings is 3.952 Å.

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226 Description of the crystal structures of [{Ni^{II}L(CH₃OH)₂}CdCl₂].H₂O (2)

Compound 2 crystallized from slow diffusion of methanol solvent and it has 227 monoclinic space group P2₁/n. A perceptive view and atom numbering scheme of the 228 asymmetric unit of [{Ni^{II}L(CH₃OH)₂}CdCl₂].H₂O (2) is presented in figure 2. Selected bond 229 lengths and angles of complex 2 are given in table 3. One molecule of complex 1 upon reaction 230 with NiCl₂.6H₂O generates complex 2. Monomeric unit of Complex 2 consists of one [NiL] unit, 231 one cadmium ion, two chloride anions and two methanol molecule. In the structure a 232 crystallographic two fold axis passes through the cadmium atom. Crystal structure clearly reveals 233 that the Ni(II) ion has replaced the Cd(II) from the inner core of the Schiff base ligand of 234 complex 1. Ni(II) ion is present in a hexa coordinated octahedral geometry where the basal 235 plane is formed by the two imine N atoms N(1) and N(2), and two phenoxido O atoms O(1) and 236 O(3), of the schiff base. Two methanol molecules coordinated axially to the metal centre (O5, 237 O6) through the oxygen center to complete the coordination. The Cd(II) molecule is present as a 238 terminal unit where it is coordinated with two phenolic oxygen atoms (O1,O3), two methoxy 239 oxygen atoms (O2,O4) of the Schiff base ligand and two chloride ions resulting a highly 240 distorted octahedral geometry. The bridging phenoxo oxygen atoms of the deprotonated Schiff 241 base ligand L²⁻ connect terminal Cd atom to the Ni(II) atom forming bis(µ-phenoxo) bridged 242 Cd(II) - Ni(II) motif with metal metal separation of 3.390Å. Terminal Cd-phenoxo bond 243 distances (2.2595Å) are significantly shorter than the Cd-methoxy bond distances (2.5265Å). 244 Whereas Cd-Cl bond distances (2.4667Å) are shorter than the corresponding Cd-methoxy bond 245

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distances but longer than the Cd-phenoxo bond distances. The small value of the average 246 deviation of the four oxygen atoms from the least square O4 plane clearly suggests that the four 247 oxygen atoms of O-phenoxo and O-methoxy unit exists in almost planer form. The displacement 248 of Cd(1) from the least square O4 plane is 0.082 Å which suggests that the metal is perfectly 249 placed inside the O4 compartment. The range of bond angle around the Cd center are 65.39(8)-250 159.99(8)°. The Ni-imine (2.026(3) Å and 2.033(3) Å) and Ni-phenoxo (2.003(2)Å and 251 1.993(2)Å) bond distances which lie in the usual range³² are shorter than the Ni-O (methanol) 252 bond distances (2.142(3)Å and 2.158(3)Å respectively). The small value of the average deviation 253 of the four oxygen atoms from the least square N2O2 plane clearly suggests that the four oxygen 254 atoms of O-phenoxo and O-methoxy unit exists in almost planer form. The displacement of 255 Ni(1) from the least square N2O2 plane is 0.013 Å which suggests that the metal is perfectly 256 placed inside the N2O2 compartment. This result clearly suggests that small size of Ni(II) center 257 has more preference towards the inner core compared to the relatively large Cd(II) ion. 258

The orientation of ligands around the metal center is such that is no π - π stacking interaction is observed. But the molecule displays various interesting hydrogen bonding interactions. The molecule contains water molecule as solvent of crystallization. It exhibits both intramolecular and intermolecular hydrogen bonding with Ni-coordinated methanolic O-H and Cd-coordinated chlorine atoms and thus forming 2D sheet in bc plane.

264 Computational Study

The theoretical study is devoted to analyze the non covalent interactions that govern the crystal packing of compounds 1 and 2 focusing our attention to the remarkable π -hole, C-H··· π and C-H···H-C interactions. In 1, the absence of good H-bond donors facilitates the formation of a π hole bonding interaction involving the C atom of the C=N bond and the nitrate. This type of

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bonding has attracted attention to the scientific community in the last years⁷⁷ and has been analyzed in the present study along with other interactions. In **2**, the conventional H-bonding interactions are important due to the presence of the coordinated MeOH that is a very good Hbond donor.

In Figure 4 we show the representation of an infinite chain found in the solid state of compound 273 1 where interesting and unconventional interactions are established. Apart from long range van 274 der Waals interactions between the organic ligands, two additional interactions are present. One 275 of both is a π -hole interaction between the O atom of the nitrato ligand and the C atom of the 276 C=N bond. The O···C distance is slightly shorter (3.20 Å) than the sum of van der Waals radii 277 (i.e., 3.22 Å). The importance of π -hole interactions in crystal engineering and other fields have 278 been recently reviewed.⁵⁴ We have computed the MEP surface of a theoretical model that 279 consists of the Schiff-base ligand used in this work coordinated to a Cd(II) metal center. The 280 MEP surface of this simple model shows a positive electrostatic potential over the C atom of the 281 C=N bond, therefore it is well suited for interacting with electron rich molecules, thus explaining 282 the formation of the π -hole interaction in **1**. The second interaction that we focus our attention is 283 established between two aromatic H atoms and the nitrato ligand (Figure 4A). This interaction 284 can be viewed as C-H···O hydrogen bonding interactions; however the directionality 285 (perpendicular approach) does not correspond to a hydrogen bond. Certainly, it resembles a T-286 shape stacking interaction, where the π -system of the nitrate anion is involved. To evaluate the 287 unconventional interactions observed in 1, we have used two theoretical models that are shown 288 in Figure 4C, D. In the first theoretical model (Figure 4C), both π -hole and C-H···NO₃ 289 interactions are evaluated along with other long range van der Waals interactions. The computed 290 interaction energy is $\Delta E_3 = -27.7$ kcal/mol confirming the importance of this intricate 291

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292 combination of interactions. In the second model the nitrato ligand has been substituted by nitrito (see small arrow in Figure 4D) and, consequently, the π -hole interaction is not formed. The 293 interaction energy is reduced to $\Delta E_4 = -24.3$ kcal/mol. The contribution the π -hole interaction 294 can be evaluated by difference, which is $\Delta E_3 - \Delta E_4 = -3.4$ kcal/mol, confirming its importance in 295 the crystal packing of compound 1. In order to characterize the interactions in 1, we have also 296 computed the NCI plot that is shown in Figure 4E. A small green isosurface can be observed 297 between one oxygen atom of the nitrito ligand and the C atom of the C=N bond, thus confirming 298 the existence of the π -hole interaction. More extended surfaces can be observed between the 299 aromatic rings and other aliphatic groups that characterize the long range van der Waals 300 interactions. Moreover, another isosurface is observed between the nitrato ligand and both C-H 301 aromatic groups (Figure 4E). This surface is extended all over the nitrato ligand instead of the 302 303 formation of two small isosurfaces between the H and O atoms. This indicates that the interaction cannot be defined as H-bonding and, instead, it is better described as a C-H $\cdots\pi$ 304 interaction involving the whole π -system of the electron rich nitrato ligand. 305

306

In Figure 5 we show the representation of self-assembled dimer found in the solid state of 307 compound 2 that is governed by two symmetrically related $O-H\cdots Cl$ interactions. Moreover the 308 methyl groups of the MeOH ligands form C-H $\cdots\pi$ interactions (at 2.61 Å of the closest C atom 309 of the ring). C-H···H-C interactions are likely present involving the H-atoms of the methyl 310 groups since they are close to each other. The C-H···H-C interaction has been recently studied 311 in depth by Alvarez and coworkers.⁵⁴ Although dihydrogen contacts in alkanes are among the 312 weakest intermolecular interactions (\sim -0.4 kcal/mol for methane dimer), these interactions are 313 314 cumulative and resulting in larger dimerization energies in some cases (e.g. long open chains).

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For instance the complexation energy computed for the dimer of *n*-hexane is -4.5 kcal/mol.⁷⁷ In 315 addition, the association energies for dimers of some polyhedranes (tetrahedrane, adamantane, 316 octahedrane, cubane and dodecahedrane) are also strong, reaching -3.0 kcal/mol for 317 dodecahedrane.⁷⁷ We have computed the molecular electrostatic potential MEP surface of 318 compound 2 in order to rationalize the formation of the electrostatically driven interactions (see 319 Figure 5B). It can be observed that the most positive region corresponds to the hydroxyl group of 320 the MeOH due to the enhancement of the acidity of the H atom upon coordination to Ni(II). 321 Moreover, the most negative region correspond to the chlorido ligands thus the formation of the 322 323 O-H···Cl H-bond is electrostatically very favored.

To evaluate the intricate combination of interactions observed in the self-assembled dimer of 2, 324 we have used several theoretical models (using the crystallographic coordinates) that are shown 325 326 in Figure 5C, D. We have used DFT calculations at the BP86-D3/def2-TZVP level of theory since it is a good compromise between the accuracy of the method and the size of the system. 327 The interaction energy of the self-assembled dimer ($\Delta E_1 = -35.6$ kcal/mol, Figure 5B) is very 328 large basically due to the contribution of both H-bonding interactions. In an effort to estimate the 329 contribution of the weak C–H $\cdots\pi$ and C–H \cdots H–C interactions, we have computed an additional 330 model where the methanol molecules have been replaced by water ligands (see small arrows 331 Figure 5D). As a result the interaction is reduced to $\Delta E_2 = -29.8$ kcal/mol that is the contribution 332 of the H-bonding interactions, confirming their strong nature as anticipated by the MEP analysis. 333 The contribution of the weaker C–H··· π and C–H···H–C interactions can be estimated by 334 difference, which is -5.8 kcal/mol. In order to characterize the interactions shown in Figure 5, 335 we have computed the non covalent interaction (NCI) plot of this compound. The NCI plot is a 336 337 visualization index that enables identification and visualization of non covalent interactions

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efficiently. The NCI analysis allows an assessment of host-guest complementarity and the extent 338 to which weak interactions stabilize a complex. The information provided is essentially 339 qualitative, that is, which molecular regions interact. The representation of the NCI plot 340 computed for compound 2 is shown in Figure 5E. An extended region can be observed between 341 the aromatic rings and the methyl groups of the methanol ligands, thus characterizing the C-342 $H \cdots \pi$ interaction (the green surface corresponds to weak interaction). Small isosurfaces are also 343 present between the chlorido and the hydroxyl groups that confirm the existence of both 344 hydrogen bonding interactions. Finally, a green isosurface is also observed between the methyl 345 346 groups that confirm the existence of the C–H···H–C interactions.

347 Hirshfeld Surface analysis

Supramolecular interactions are further investigated using Hirshfeld Surface analysis. Complexes 348 1 and 2 are mapped over d_{norm} (range of -0.1 to 1.5Å), shape index (range of -1.0 – 1.0Å) and 349 350 curvedness (range of -4.0 - 0.4) respectively and presented in figure 6 and figure S7 respectively. During mapping surfaces are kept transparent for visualization of different supramolecular 351 interactions. For Complex 1, H-bonding interactions between the O atom of nitrate ion and H 352 353 atoms of aromatic ring of o-vaniline has been predominantly found as bright red area in the Hirshfeld surfaces. Other longer and weaker interactions appeared as light colour in the surfaces. 354 Fingerprint plots consist of all type of intermolecular interactions. So, fingerprint plots need to be 355 decomposed to have idea of individual contacts. In the decomposed fingerprint plot, 356 complementary regions are obtained where one molecule acts as a donor (de > di) (bottom left of 357 fingerprint plot) and the other as an acceptor (de < di) (bottom right of fingerprint plot). For 358 complex 1, O...H/H...O, N...H/H...N and H...H contacts comprise 29.7%, 2.8% and 46.1% of the 359 total Hirshfeld surface where O···H interactions comprise around 14.3% of the total Hirshfeld 360

surface and the H…O interactions comprise around 15.4% of the total Hirshfeld surface. In the 361 decomposed fingerprint plot of complex 1, $O \cdots H$ interactions are represented by a spike (d_i = 362 0.92 Å, $d_e = 1.22$ Å) in the bottom left (donor) area where as H···O interactions are represented 363 by a spike ($d_i = 1.21$ Å, $d_e = 0.91$ Å) in the bottom right (acceptor) region (Figure S8).For 364 complex 2, O...H/H...O, Cl...H/H...Cl and H...H contacts comprise 5.4%, 15.9% and 57.8% of 365 the total Hirshfeld surface where Cl...H interactions comprise around 6.3% of the total Hirshfeld 366 surface and the H···Cl interactions comprise around 9.6% of the total Hirshfeld surface. In the 367 decomposed fingerprint plot of complex 2, Cl···H interactions are represented by a spike ($d_i =$ 368 0.85 Å, $d_e = 1.45$ Å) in the bottom left (donor) area where as H···Cl interactions are represented 369 by a spike ($d_i = 1.44$ Å, $d_e = 0.86$ Å) in the bottom right (acceptor) region (Figure S8). 370

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372 Life Time Measurements

Lifetime data of the complex 1 was studied at 298 K in acetonitrile solution upon excited at 368 nm. The average fluorescence decay life time has been measured for the complex 1 using the given formula ($\tau_f = a_1\tau_1 + a_2\tau_2$, where a_1 and a_2 are relative amplitude of decay process). The average fluorescence lifetime of complex is 0.3244 nSec. (Figure 7, Table S1)

377 Concluding remarks

We have synthesized and structurally characterized one trinuclear cadmium (II) (1) and one di(phenoxido)-bridged dinuclearcadmium(II)-nickel(II) (2) complexes derived from a bicompartmental (N2O4) Schiff base ligand. Crystal structure of complex 2 has proved preferential selection of inner core of the N2O4 donor Schiff base ligand by 3d metal ion in comparison with a 4d metal ion. The supramolecular assemblies observed in the solid state

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383 architectures of both complexes features have been further investigated theoretically using DFT calculations. Supramolecular structure of complex 1 exhibits remarkable π -hole and C-H $\cdots\pi$ 384 interactions. Moreover, complex 2 exhibits weak C-H···H-C interactions between H-atoms of 385 closely spaced methyl groups along with other non-covalent interactions. The theoretical 386 study, by means of the NCI plot, has confirmed the existence of these interactions which have 387 been rationalized using MEP surfaces. More importantly, we have calculated the energetic 388 contribution of each interaction, which can be helpful to develop scoring functions. Hirshfeld 389 surface mapping and fingerprint plotting have been done to visualize the close contacts 390 391 qualitatively.

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403

404 Appendix A. Supplementary data

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405 CCDC 1062044-1062045 contain the supplementary crystallographic data for complexes 2 and 1 respectively. These be obtained free of 406 data can charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data 407 Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or 408 email:deposit@ccdc.cam.ac.uk. 409

410 Notes & References

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- 564

565 Table1 Crystal parameters and selected refinement details for complexes 1 and 2

Compound	1	2
Empirical formula	$C_{38}H_{40}Cd3N_6O_{14}$	C ₂₁ H ₃₀ CdCl ₂ N ₂ NiO ₇
Formula weight	1141.99	664.47
Temperature (K)	296(2)	273
Crystal system	Monoclinic	Monoclinic
Space group	$P2_{l}/c$	P 21/n
<i>a</i> (Å)	20.0254(6)	10.2934
<i>b</i> (Å)	8.8925(2)	15.9246(5)
<i>c</i> (Å)	23.9742(6)	15.9021(5)
$\alpha(^{\circ})$	90	90
β(°)	100.745(1)	102.203(2)
γ(°)	90	90
Volume (Å ³)	4194.37(19)	2547.75(15)
Ζ	4	4
$D_{\rm calc} ({\rm g}{\rm cm}^{-3})$	1.809	1.685
Absorption	1.518	1.821
coefficient (mm ⁻¹)		
<i>F</i> (000)	2264	1304
θ Range for data	1.03-24.55	1.83-30.23
collection (°)	26	
Reflections	58462	43947

567	collected		
	Independent	6990/0.0324	7304/0.0310
568	reflections / R_{int}		
	Observed	5933	5773
569	reflections [I> $2\sigma(I)$]		
570	Data / restraints /	6990/ 0/553	7304/1/319
	parameters		
571	Goodness-of-fit on	1.027	1.043
	F^2		
572	Final	R1 = 0.0238;	R1 = 0.0351;
	indices[I> $2\sigma(I)$]	wR2 = 0.0622	wR2 = 0.0936.
573			
574	<i>R</i> indices (all data)	R1 = 0.0320;	R1 = 0.0485;
		wR2 = 0.0736	wR2 = 0.1025
575	Largest diff. peak /	0.450/-0.312	1.217/-0.513
	hole (e $Å^{-3}$)		

Table2. Selected bond lengths (Å) and bond angles (°) for complex 1

Complex 1

Cd3O1	2.744(3)	Cd301A	2.762(3)
Cd3 –O2	2.260(2)	Cd3 –O2A	2.276(2)
Cd3 –O3	2.243(3)	Cd3 –O3A	2.268(2)
Cd3 –O4	2.495(3)	Cd3 –O4A	2.521(2)
Cd1-N1	2.241(3)	Cd2–N1A	2.237(3)
Cd1 –N2	2.257(3)	Cd2 –N2A	2.262(3)
Cd1 –O2	2.235(2)	Cd2 –O2A	2.216(2)
Cd1 –O3	2.224(2)	Cd2 – O3A	2.215(2)

Cd1-O5	2.543(4)	Cd2 – 05A	2.474(3)
Cd3Cd1	3.556	Cd3Cd2	3.546
O1-Cd3-O2	61.41(7)	O1A-Cd3-O2A	60.34(8)
O2-Cd3-O3	73.85(8)	O2A-Cd3-O3A	73.70(8)
O3-Cd3-O4	66.23(8)	O3A-Cd3- O4A	65.41(8)
N1-Cd1-N2	90.2(1)	N1A-Cd2-N2A	88.4(1)
N1-Cd1-O2	83.49(9)	N1A-Cd2-O2A	84.6(1)
N2-Cd1-O3	83.0(1)	N2A-Cd2-O3A	82.28(9)
O2Cd1O3	74.70(8)	O2A-Cd2-O3A	75.91(8)
O5-Cd1-O6	51.7(1)	O5A-Cd2-O6A	50.9(1)
Cd3-O2-Cd1	104.54(8)	Cd3–O2A–Cd2	104.27(9)
C9-C10-C11	116.10	Cd3–O3A–Cd2	104.59(8)
C9A-C10A-C11A	121.15		

Table 3. Selected bond lengths (Å) and bond angles (°) for complete	x 2
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		Complex 2		
Ni1–N1	2.026(3)		Ni1–O1	2.003(2)
Ni1 –N2	2.033(3)		Ni2 –O3	1.993(2)
Cd101	2.262(2)		Cd102	2.528(2)
Cd1 –O3	2.257(2)		Cd104	2.525(3)
Ni1–O5	2.158(3)		Cd1–Cl1	2.4811(8)
Ni1 –06	2.142(3)		Cd1–Cl2	2.452(1)
Ni1Cd1	3.390			

N1-Ni1-N2	98.7(1)	N1-Ni1-O1	90.5(1)
O3-Ni2-N2	91.1(1)	Cl1-Cd1-O2	86.59(6)
N1-Ni1-O3	169.5(1)	01-Ni1-O3	79.94(9)
O1 Cd1O3	69.25(8)	O3-Cd1-O4	65.45(8)
O1 Cd1O2	65.39(8)	Cl1-Cd1-Cl2	120.42(3)
C9-C10-C11	115.8(5)	Cl1-Cd1-O4	88.46(7)



Scheme 1. The route to the syntheses of complexes 1 and 2

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653

654



Fig. 4. (A) X-ray fragment of 1. (B-D) Theoretical models used to evaluate the C–H $\cdots \pi$, and Hbonding interactions. Distances in Å. (E) MEP surface of a model compound of complex 1. (F) NCI plot of the dimer of compound 1.



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Fig. 5. (A) X-ray fragment of 2. (B) MEP surface of compound 1. (C,D) Theoretical models used
to evaluate the non covalent interactions. Distances in Å. (E) NCI plot of the dimer of compound
2.

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Fig. 6. Hirshfeld Surface mapped over d_{norm} for complexes 1 and 2.



Fig. 7.Time-resolved fluorescence decay curves (logarithm of normalized intensity vs time in ns) of Complex $1 (\bullet)$ and (\bullet) indicates decay curve for the scattered.



Graphical Abstract (Synopsis)

Exploration of unconventional π -hole and C-H····H-C types of supramolecular interactions in a trinuclear Cd(II) and a heteronuclear Cd(II)-Ni(II) complex and experimental evidence for preferential site selection of the ligand by 3d and 4d metal ions.

Saikat Banerjee,^a Antonio Bauzá,^b Antonio Frontera,^{*b} and Amrita Saha^{*a}

Abstract

In this present work we report synthesis and structural characterisations of a trinuclear cadmium (II) (1) and a di(phenoxido)-bridged dinuclear cadmium(II)–nickel(II) (2) complexes derived from a bicompertmental (N2O4) Schiff base ligand, H_2L . It has been observed that, in bicompertmental ligands the relatively small inner core is suitable for 3d metal ions and outer core can be occupied by different metal centers like 3d, 1s, 2s, 4d and 4f. We have experimentally established the above fact. In homotrinuclear complex 1 both inner (N2O2) and outer (O4) core has been occupied by cadmium (II) ions. Complex 1 upon reaction with NiCl₂.6H₂O produces heterodinuclar complex 2, where 3d nickel(II) ion easily replaced relatively large cadmium(II) ion. Structural studies reveal that, in complex 1 terminal Cd units acquire trigonal prismatic geometry whereas the central Cd unit is eight coordinated. In case of complex 2 both nickel(II) and cadmium(II) ions are hexa-coordinated in a distorted octahedral environment. Both the complexes are studied using different spectroscopic techniques. Complexes 1 and 2 exhibit important and relatively unexplored group of supramolecular interactions like π -hole, C-H… π and C-H…H–C along with other hydrogen bonding

interactions. Theoretical DFT calculations are devoted to analyze these noncovalent interactions. Several computational tools like MEP surface analysis and NCI analysis are utilized to explain and illustrate such interactions.

Graphical Abstract (Pictogram)

Saikat Banerjee,^a Antonio Bauzá,^bAntonio Frontera,^{*b} and Amrita Saha^{*a}

