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# Three mononuclear octahedral cobalt(III) complexes with salicylaldimine Schiff bases: Synthesis, characterization, phenoxazinone synthase mimicking activity and DFT study on supramolecular interactions

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#### Abstract

Three mononuclear facial cobalt(III) complexes,  $[Co(L)_2]ClO_4$  (1),  $[Co(L)(bzan)(N_3)]$ (2) and [Co(L)(bzan)(NCS)] (3) {HL = 2-(3-(dimethylamino)propyliminomethyl)-6ethoxyphenol and Hbzan = 1-benzoylacetone} were prepared and characterized by elemental and spectral analysis. X-ray crystal structure determination confirmed the structures of the complexes. Extended supra-molecular assemblies were generated in all three complexes through weak noncovalent interactions. Density functional theory (DFT) calculations were employed to understand and estimate the contribution of each interaction in the formation of the assembly using several theoretical models. Bader's theory of "atoms in molecules" (AIM) was also used to further describe the long range interactions and its role to stabilize different molecular assemblies. Complexes 2 and 3 are found to be efficient catalysts to perform the aerial oxidation

of 2-aminophenol to 2-aminophenoxazine-3-one and therefore may be used as functional models for copper(II) containing enzyme, phenoxazinone synthase.

*Keywords:* Cobalt(III); Schiff base; Phenoxazinone synthase mimicking activity; Supramolecular interactions; DFT study.

#### **1. Introduction**

Over the past several decades, many model complexes of cobalt(II) and cobalt(III) have been prepared and investigated, with particular emphasis on the reactivity of the metal ions in the trans methylation reaction and the reversible absorption of molecular oxygen [1-4]. Several cobalt(III) complexes have also been used to artificially model photosynthesis systems [5-7]. The most common approach to creating an artificial photosynthetic device involves the development of efficient and robust catalysts for each half reaction of water splitting, the oxidation of water to  $O_2$  and reduction of H<sup>+</sup> to H<sub>2</sub> [8-10]. Mononuclear series of cobaloxime complexes have widely been used by several groups as H<sub>2</sub> evaluator from aqueous solution. Dinuclear cobalt(III) complexes may function as mimics of the active biosites such as in methionine amino peptidase [11] and can show DNA cleavage activity [12]. Cobalt(III) in distorted octahedral and trigonal bipyramidal geometries have been identified in the metallohydrolase responsible for the removal of the N-terminal methionine from the protein chain [13]. Cobalt(III) Schiff base complexes have also drawn considerable attention in the past for their important biological applications [14-18]. On the other hand, Schiff bases themselves have been extensively studied in coordination chemistry due to their facile syntheses, easily tunable steric and electronic properties and their applications in different branches of science. Metal complexes of Schiff bases are important stereochemical models in main group and transition metal coordination chemistry [19-23]. The

complexes have wide applications, including bioinorganic chemistry, material science and magnetism, catalysis, separation and encapsulation, hydrometallurgy, metal clusters, transport and activation of small molecules etc [24-31]. Among several Schiff bases, salicylaldimine Schiff bases constitute a special class for their ability to bind more than one metal centres exploiting the bridging ability of phenoxo oxygen atom in it. Incorporation of additional groups in the salicylaldimine moieties may increase their denticity thereby making them more susceptible to form polynuclear complexes or may produce ligands having pendant donor atoms. Several pendant ligands have been used in a variety of chemical applications, e.g. in enzyme simulations [32], for the purpose of carrying a radionuclide into a target cell [33], in magnetic resonance imaging reagents [34], and for progressively more elaborate investigations for their structure/activity relationship [35-37]. In the present work, we have used three salicylaldimine Schiff bases to prepare three distorted octahedral cobalt(III) complexes,  $[Co(L)_2]ClO_4$  (1),  $[Co(L)(bzan)(N_3)]$ [Co(L)(bzan)(NCS)](3) [HL (2)=2-(3and (*dimethylamino*)propyliminomethyl)-6-ethoxyphenol, Hbzan = 1-benzoylacetone]. The structures have been confirmed by spectroscopy and single crystal X-ray crystallography highlighting such aspects like phenoxazinone synthase like activity.

The construction of supramolecular networks with interesting non-covalent interactions as binding forces is an appealing research topic now-a-days [38-42]. Several well established noncovalent interactions such as, hydrogen bonding,  $\pi$ -stacking, cation... $\pi$ , and C-H... $\pi$  forces, have been used to govern the organization of multicomponent supramolecular assemblies [43-46]. Moreover, other less recognized forces, such as,  $\sigma$ ... $\pi$ -hole, lone-pair... $\pi$  and anion... $\pi$ interactions, have also been utilized in many areas of chemistry and biochemistry [47-49]. The relevance of several noncovalent interactions has been broadly analyzed by means of theoretical

and experimental investigations [50-52]. In the present paper, the theoretical study is devoted to analyze the noncovalent interactions that govern the crystal packing of complexes 1, 2 and 3 focusing our attention to the remarkable C-H $\cdots$  $\pi$  and C-H $\cdots$ H-C interactions. Latter interaction has been studied in depth by Alvarez and coworkers [53,54]. Although C-H...H-C contacts in alkanes are among the weakest intermolecular interactions (~-0.4 kcal/mol for methane dimer), they are cumulative, resulting in larger dimerization energies in some cases (e.g. long open chains). For instance the complexation energy computed for the dimer of n-hexane is -4.5 kcal/mol [53]. At this stage, it is worthy to emphasize that supramolecular chemists usually analyze the non-covalent interactions in the X-ray structures that are shorter than the sum of van der Waals radii and they have a tendency to ignore all longer interactions in the crystal structures. Evidently, this is a simplistic view of crystal packing since interactions slightly longer also have an impact. That is, the difference in attraction (or repulsion) between a contact at the van der Waals distance and one that is slightly longer is not very much. Taking this in mind, in this theoretical study we also intend to exemplify this issue by computing the contribution of the long-range interactions in the assemblies retrieved from the solid state structures of the complexes reported herein.

#### 2. Experimental section

All chemicals used were purchased from Sigma-Aldrich and were of reagent grade. They were used without further purification.

**Caution!!!** Although no problems were encountered in this work, perchlorate salts containing organic ligands and azide complexes are potentially explosive. Only a small amount of the material should be prepared and it should be handled with care.

#### 2.1. Preparations

#### 2.1.1. Preparation of the ligand, 2-(3-(dimethylamino)propyliminomethyl)-6-ethoxyphenol (HL)

The tetradentate  $N_2O_2$  donor Schiff base ligand HL was prepared by refluxing N,Ndimethyl-1,3-diaminopropane (1 mmol, 0.125 mL) with 3-ethoxysalicylaldehyde (1 mmol, 0.166 g) in methanol (20 mL) for ca. 1 h. The ligand was not isolated and the methanol solution was used directly for the preparation of complexes.

#### 2.1.2. Preparation of $[Co(L)_2]ClO_4(1)$

A methanol solution of cobalt(II) perchlorate hexahydrate (0.5 mmol, 0.182 g) was added to the methanol solution of the ligand HL and refluxed for 1 h. Diffraction quality dark brown single crystals of complex **1** were obtained after few days on slow evaporation of the solution in open atmosphere.

Yield: 0.40 g (61%). Anal. Calc. for  $C_{28}H_{42}CoN_4ClO_8$  (FW 657.04): C, 51.18; H, 6.44; N, 8.53. Found: C, 51.12; H, 6.38; N, 8.60 %; IR (KBr, cm<sup>-1</sup>): 1618 ( $\upsilon_{C=N}$ ), 3006-2928 ( $\upsilon_{CH}$ ), 1082 ( $\upsilon_{ClO4}$ ).UV-Vis,  $\lambda_{max}$  (nm), [ $\varepsilon_{max}$  (L mol<sup>-1</sup> cm<sup>-1</sup>)] (DMSO), 275 (9.1 × 10<sup>3</sup>), 325 (5.2 × 10<sup>3</sup>), 522 (7.1 × 10<sup>2</sup>). Magnetic moment: diamagnetic.

#### 2.1.3. Preparation of $[Co(L)(bzan)(N_3)]$ (2)

A methanol solution of cobalt(II) perchlorate hexahydrate (1 mmol, 0.365 g) was added to the methanol solution of the ligand HL followed by the addition of methanol solution of 1benzoylacetone (Hbzan) (1 mmol, 0.162 g) and refluxed for 1 h. An aqueous methanol solution of sodium azide (1 mmol, 0.065 g) was then added to it and refluxed further for ca. 1 h.

Diffraction quality dark brown single crystals of complex 2 were obtained after few days on slow evaporation of the solution in open atmosphere.

Yield: 0.30 g (65%). Anal. Calc. for  $C_{24}H_{30}CoN_5O_4$  (FW 511.46): C, 56.36; H, 5.91; N, 13.69. Found: C, 56.30; H, 5.86; N, 13.76 %; IR (KBr, cm<sup>-1</sup>): 1625 ( $\upsilon_{C=N}$ ), 2026 ( $\upsilon_{N3}$ ), 1556 ( $\upsilon_{C=O}$ ), 2923 ( $\upsilon_{CH}$ ). UV-Vis,  $\lambda_{max}$  (nm), [ $\varepsilon_{max}$  (dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>)] (CH<sub>3</sub>CN), 243 (1.4 × 10<sup>4</sup>), 275 (1.1 × 10<sup>4</sup>), 328 (4.1 × 10<sup>3</sup>), 494 (2.1 × 10<sup>2</sup>), 703 (1.4 × 10<sup>2</sup>). Magnetic moment: diamagnetic.

#### 2.1.4. Preparation of [Co(L)(bzan)(NCS)] (3)

A methanol solution of cobalt(II) perchlorate hexahydrate (1 mmol, 0.365 g) was added to the methanol solution of the ligand HL followed by the addition of methanol solution of 1benzoylacetone (Hbzan) (1 mmol, 0.162 g) and refluxed for 1 h. An methanol solution of sodium thiocyanate (1 mmol, 0.081 g) was then added to it and refluxed further for ca. 1 h. Diffraction quality dark brown single crystals of complex **3** were obtained after few days on slow evaporation of the solution in open atmosphere.

Yield: 0.30 g (65%). Anal. Calc. for C<sub>25</sub>H<sub>30</sub>CoN<sub>3</sub>O<sub>4</sub>S (FW 527.51): C, 56.92; H, 5.73; N, 7.9. Found: C, 56.85; H, 5.67; N, 8.04 %; IR (KBr, cm<sup>-1</sup>): 1623 ( $\nu_{C=N}$ ), 2107 ( $\nu_{NCS}$ ), 1513 ( $\nu_{C=O}$ ), 2982-2888 ( $\nu_{CH}$ ). UV-Vis,  $\lambda_{max}$  (nm), [ $\epsilon_{max}$  (dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>)] (CH<sub>3</sub>CN), 246 (1.1 × 10<sup>4</sup>), 272 (9.9 × 10<sup>3</sup>), 326 (3.5 × 10<sup>3</sup>), 492 (2.4 × 10<sup>2</sup>), 746 (1.2 × 10<sup>2</sup>). Magnetic moment: diamagnetic.

#### 2.2. Physical measurements

Elemental analyses (carbon, hydrogen and nitrogen) were performed on a Perkin-Elmer 240C elemental analyzer. Infrared spectra in KBr (4500-400 cm<sup>-1</sup>) were recorded using a PerkinElmer Spectrum Two FTIR spectrophotometer. Electronic spectra (900-200 nm) were

recorded on a PerkinElmer Lambda 35 UV-Vis spectrophotometer. Fluorescence spectra in acetonitrile were obtained on a Hitachi F-7000 Fluorescence spectrophotometer at room temperature. The magnetic susceptibility measurements were done with an EG & PAR vibrating sample magnetometer, model 155 at room temperature and diamagnetic corrections were made using Pascal's constants. The powder XRD data were collected on a Bruker D8 Advance X-ray diffractometer using Cu K<sub> $\alpha$ </sub> radiation ( $\lambda = 1.548$  Å) generated at 40 kV and 40 mA. The PXRD spectra were recorded in a 20 range of 5-50° using 1-D Lynxeye detector at ambient conditions.

#### 2.3. X-ray crystallography

Single crystals of three complexes having suitable dimensions were used for data collection using a Bruker SMART APEX II diffractometer equipped with graphitemonochromated Mo K<sub> $\alpha$ </sub> radiation ( $\lambda = 0.71073$  Å) at 150 K. Molecular structures were solved using the SHELX-97 package [55]. Hydrogen atoms were placed in their geometrically idealized positions and constrained to ride on their parent atoms. Multi-scan empirical absorption corrections were applied to the data using the program SADABS [56]. A summary of the crystallographic data is given in Table 1. Selected bond lengths and bond angles of three complexes are given in Tables 2 and 3, respectively.

#### 2.4. Hirshfeld Surface Analysis

Hirshfeld surfaces [57-59] and the associated two-dimensional (2D) fingerprint [60-62] plots were calculated using Crystal Explorer [63], with bond lengths to hydrogen atoms set to standard values [64]. For each point on the Hirshfeld isosurface, two distances,  $d_e$  (the distance from the point to the nearest nucleus external to the surface) and  $d_i$  (the distance to the nearest

nucleus internal to the surface), are defined. The normalized contact distance  $(d_{norm})$  based on  $d_e$ and  $d_i$  is given by

$$d_{norm} = \frac{(d_i - r_i^{vdw})}{r_i^{vwd}} + \frac{(d_e - r_e^{vdw})}{r_e^{vwd}}$$

where  $r_i^{vdW}$  and  $r_e^{vdW}$  are the van der Waals radii of the atoms. The value of  $d_{norm}$  is negative or positive depending on intermolecular contacts being shorter or longer than the van der Waals separations. The parameter  $d_{norm}$  displays a surface with a red-white-blue color scheme, where bright red spots highlight shorter contacts, white areas represent contacts around the van der Waals separation, and blue regions are devoid of close contacts. For a given crystal structure and set of spherical atomic electron densities, the Hirshfeld surface is unique [65] and thus it suggests the possibility of gaining additional insight into the intermolecular interaction of molecular crystals.

#### 2.5. Theoretical methods

The calculations of the noncovalent interactions were carried out using the TURBOMOLE version 7.0 [66] 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 have been successfully used to evaluate similar interactions [67-70]. The interaction energies were computed by calculating the difference between the energies of isolated monomers and their assembly. The interaction energies were corrected for the Basis Set Superposition Error (BSSE) using the counterpoise method [71]. The "atoms-in-molecules" (AIM) [72] analysis was performed at the BP86-D3/def2-TZVP level of theory. The calculation of AIM properties was done using the AIMAII program [73].

#### 2.6. Catalytic oxidation of 2-aminophenol

 $10^{-4}$  M solutions of the complexes in acetonitrile were treated with a  $10^{-2}$  M solution of oaminophenol under aerobic conditions at  $25^{0}$ C. The reaction was followed spectrophotometrically by monitoring the increase in the absorbance maxima at ~433 nm.  $10^{-4}$  M solutions of the complexes were mixed with at least 10 equivalents of substrate to maintain pseudo-first order conditions to determine the dependence of rate on the substrate concentration and various kinetic parameters. The rate of the reaction was derived from the initial rate method.

#### 3. Results and discussion

#### 3.1. Synthesis

The tetradentate  $N_2O_2$  donor Schiff base ligand, HL, was synthesized by 1:1 condensation of N,N-dimethyl-1,3-diaminopropane with 3-ethoxysalicylaldehyde in methanol following the literature method [74-77]. The ligand was not isolated and the methanol solution was used directly for the preparation of complexes.

A methanol solution of HL was made to react with cobalt(II) perchlorate hexahydrate under reflux to prepare mononuclear bis-ligand complex,  $[Co(L)_2]ClO_4$  (1). Cobalt(II) is readily oxidised to cobalt(III) by areal oxygen in presence of the Schiff base ligands producing strong crystal field, as was also observed in similar complexes [78]. We have repeated the reaction in N<sub>2</sub> atmosphere but no complex could be isolated. On the other hand, to stop the formation of this type of bis-ligand complex, we have reacted cobalt(II) with HL in presence of suitable coordinating anions, e.g. benzoylacetonate (bzan) and azide. The result is the formation of  $[Co(L)(bzan)(N_3)]$  (2), where three coordinating sites of cobalt(III) are occupied by the deprotonated Schiff base. Two oxygen atoms from bzan coordinate cobalt(III) and the remaining

site is occupied by a terminal azide. Complex **3** was prepared in a similar method as that of **2**, except that thiocyanate was added (instead of azide), which coordinated the sixth coordinated site of cobalt(III) leading to the formation of [Co(L)(bzan)(NCS)] (**3**). The formation of all three complexes is shown in Scheme 1.





3.2. Description of the structures

#### $3.2.1. [Co(L)_2]ClO_4(1)$

Complex 1 crystallizes in the triclinic space group P1. A perspective view of complex 1 along with the selective atom numbering scheme is shown in Figure 1. The structure

determination reveals that the complex consists of a discrete cationic mononuclear unit  $[Co(L)_2]^+$ along with a non-coordinating perchlorate anion. The cobalt(III) center is in a six-coordinate octahedral environment, being bonded to two imine nitrogen atoms, N(2) and N(4), two amine nitrogen atoms, N(1) and N(3), and two phenoxo oxygen atoms, O(1) and O(3), from two deprotonated Schiff base ligands (L), which occupy facial positions (fac isomer). The closest conformation of saturated six membered chelate rings, Co(1)-N(1)-C(3)-C(4)-C(5)-N(2) and Co(1)-N(3)-C(17)-C(18)-C(19)-N(4), are half-chair, with puckering parameters [79] q = 0.697(8)Å,  $\theta = 163.3(7)^\circ$ ,  $\varphi = 170(3)^\circ$  and q = 0.744(8)Å,  $\theta = 16.1(7)^\circ$ ,  $\varphi = 345(2)^\circ$ , respectively. The N(1)-Co(1)-N(2) and N(3)-Co(1)-N(4) angles are 84.7(3)° and 83.8(3)°, respectively and are typical of a six membered chelate ring [80]. The Co-N<sub>imine</sub> distances {1.919(7)-1.954(8) Å} is shorter than the Co-N<sub>amine</sub> distances {2.077(7)-2.123(7) Å} [81].

#### $3.2.2. [Co(L)(bzan)(N_3)] (2)$

Complex 2 crystallizes in the monoclinic space group  $P2_1/c$ . A perspective view of complex 2 along with the selective atom numbering scheme is shown in Figure 2. The structure determination reveals that the complex consists of a discrete mononuclear unit  $[Co(L)(bzan)(N_3)]$ . The cobalt(III) center is coordinated by one amine nitrogen atom, N(1), one imine nitrogen atom, N(2), and one phenoxo oxygen atom, O(3), from one deprotonated Schiff base ligand (L)<sup>-</sup>, and two carbonyl oxygen atoms, O(1) and O(2), of a benzoylacetonate ligand (bzan). The sixth coordination site of cobalt(III) is occupied by a nitrogen atom, N(3) of a terminal azide to complete its octahedral geometry. The Schiff base ligand coordinates cobalt(III) in facial fashion. The Co-N<sub>imine</sub> distance {1.898(2) Å} is shorter than the Co-N<sub>amine</sub> distance {2.055(2) Å}, as were also observed in similar systems [82]. The saturated six membered chelate ring Co(1)-N(1)-C(13)-C(14)-C(15)-N(2), present an half-chair conformation

with puckering parameters [79] q = 0.672(2) Å,  $\theta = 10.6(3)^\circ$ ,  $\varphi = 335.0(13)^\circ$ . The N(1)-Co(1)-N(2) angle is 86.82(9)° and is typical of a six membered chelate ring. The terminal azide is quasi-linear with the N-N-N angle being 176.0°(3).

#### 3.2.3. [Co(L)(bzan)(NCS)] (**3**)

Complex **3** crystallizes in the monoclinic space group  $P2_1/c$ . A perspective view of complex **3** along with the selective atom numbering scheme is shown in Figure 3. The structure determination reveals that the complex consists of a discrete mononuclear unit [Co(L)(bzan)(NCS)]. The cobalt(III) center is coordinated by one amine nitrogen atom, N(1), one imine nitrogen atom, N(2), and one phenoxo oxygen atom, O(3), from one deprotonated Schiff base ligand (L)<sup>-</sup>, and two carbonyl oxygen atoms, O(1) and O(2), of a benzoylacetonate ligand (bzan). The sixth coordination site of cobalt(III) is occupied by a nitrogen atom, N(3) of a terminal thiocyanate to complete its octahedral geometry. The Schiff base ligand coordinates cobalt(III) in facial fashion. The Schiff base ligand coordinates cobalt(III) in meridional fashion. The Co-N<sub>imine</sub> distance {1.905(2) Å} is shorter than the Co-N<sub>amine</sub> distance {2.058(2) Å}, as were also observed in similar systems [82]. The saturated six membered chelate ring Co(1)-N(1)-C(13)-C(14)-C(15)-N(2), present an half-chair conformation with puckering parameters [79] q = 0.662(2) Å,  $\theta = 169.25(17)^\circ$ ,  $\varphi = 158.4(11)^\circ$ . The N(1)-Co(1)-N(2) angle is 88.29(8)° and is typical of a six membered chelate ring [83].

#### 3.3. Geometrical preferences

One meridional and five facial geometrical isomers are possible for any octahedral bisligand complexes of asymmetric tridentate ligand (e.g. HL) (Scheme 2). However, in present

case, only the facial one having amine nitrogen, imine nitrogen and phenoxo oxygen atoms in trans positions ((a) in Scheme 2) has been formed exclusively, as confirmed by X-ray analysis.



**Scheme 2:** Possible facial (a-e) and meridional (f) (geometrical) isomers of complex **1**; N<sup>A</sup>, N<sup>I</sup> and O indicate imine nitrogen, amine nitrogen and phenoxy oxygen atoms, respectively.

It is difficult to explain the stability of this particular facial isomer with the help of electronic factor, because there should be competition between two ( $\pi$  acceptor) imine groups in the trans disposition for accepting electrons from the same d-orbitals of cobalt(III), minimizing the back-bonding stabilization. However, two chelate rings {O(1)-C(12)-C(7)-C(8)-N(2)-Co(1) and Co(1)-N(1)-C(3)-C(4)-C(5)-N(2)} are orthogonal to each other (89.45<sup>0</sup>) in this disposition and therefore non-bonding interaction in this facial isomer is expected to be low. Besides the requirement of efficient crystal packing, this seems to be responsible for its exclusive formation.



Scheme 3: Possible facial (a-c) and meridional (d) (geometrical) isomers of complexes 2 and 3;  $N^A$ ,  $N^I$  and O indicate imine nitrogen, amine nitrogen and phenoxo oxygen atoms, respectively {X= azide (in 2) or thiocyanate (in 3)}.

On the other hand, one meridional and three facial geometrical isomers are possible for both complexes 2 and 3 (Scheme 3). However, in present case, only the facial isomers of both complexes have been formed exclusively, where azide nitrogen atoms are in the opposite site to the phenoxo oxygen atoms ((d) in Scheme 3), as confirmed by X-ray analysis.

#### 3.4. Powder X-ray diffraction

The experimental powder XRD patterns of the bulk product of all three complexes are in good agreement with simulated XRD patterns from single crystal X-ray diffraction, confirming purity of the bulk samples. The simulated patterns were calculated from the single crystal structural data (cif file) using the CCDC Mercury software. Figure 4 shows the experimental and simulated powder XRD patterns of complex **3**.

#### 3.5. Hirshfeld surface analysis

The Hirshfeld surfaces for complexes 1, 2 and 3 are mapped over  $d_{norm}$ , shape index and curvedness (Figure 5). The surfaces are shown as transparent to allow visualization of the molecular moiety around which they are calculated. The dominant interaction between  $C \cdots H / C$ H…C for all complexes can be seen in the Hirshfeld surfaces as red spots on the d<sub>norm</sub> surface in Figure 5. Other visible spots in the Hirshfeld surfaces correspond to H...H contacts. The small extent of area and light color on the surface indicate weaker and longer contact other than hydrogen bonds. The C···H / H···C interactions appear as distinct spikes in the 2D fingerprint plot (Figure 6). Complementary regions are visible in the fingerprint plots where one molecule acts as a donor  $(d_e > d_i)$  and the other as an acceptor  $(d_e < d_i)$ . The fingerprint plots can be decomposed to highlight contributions from different interaction types, which overlap in the full fingerprint [84]. The proportions of C···H / H···C interactions comprise 7.8, 20.8 and 23.5 % of the Hirshfield surfaces for each molecule of complexes 1, 2 and 3 respectively. The C-H interaction is represented by lower spike ( $d_i = 1.69$ ,  $d_e = 1.08$  Å in 1,  $d_i = 1.6$ ,  $d_e = 1.1$  Å in 2 and  $d_i = 1.54$ ,  $d_e = 1.06$  Å in 3) and the H···C interaction is also represented by another spike ( $d_i =$ 1.08,  $d_e = 1.69$  Å in 1,  $d_i = 1.1$ ,  $d_e = 1.62$  Å in 2 and  $d_i = 1.06$ ,  $d_e = 1.55$  Å in 3) by upper spike and can be viewed as bright red spots on the  $d_{norm}$  surface.

#### 3.6. IR, electronic and fluorescence spectra and magnetic property

In the IR spectra of all three complexes, distinct bands due to azomethine (C=N) stretching vibrations appears in the region of 1618-1625 cm<sup>-1</sup>. Sharp bands at 2026 and 2017 cm<sup>-1</sup> indicate the presence of terminal azide and thiocyanate in the IR spectra of complexes **2** and **3**, respectively. The characteristic absorption band for non-coordinated perchlorate anion appeared at 1082 cm<sup>-1</sup> in the IR spectrum of complex **1**. Bands in the range of 3006-2806 cm<sup>-1</sup> due to alkyl

C-H bond stretching vibrations are customarily noticed in the IR spectra of all complexes [85-88].

Electronic spectra of complexes are recorded in acetonitrile medium at room temperature in the range 200-800 nm. In all three complexes, the low-spin octahedral ground term is  ${}^{1}A_{1g}$  and there are two spin-allowed transitions,  ${}^{1}A_{1g} \rightarrow {}^{1}T_{1g}$  and  ${}^{1}A_{1g} \rightarrow {}^{1}T_{2g}$  [89]. The electronic spectra of **1**, **2** and **3** display one low energy absorption band each at 522, 703 and 746 nm, respectively, attributable to one of the two expected transitions for any low-spin cobalt(III) in octahedral geometry, as mentioned above. In the high energy region, all complexes show intense absorption bands around 243-275 nm, corresponding to  $\pi$ - $\pi$ \* transitions, and bands around 325-328 nm, attributed to the charge transfer transition from the coordinated ligands to the cobalt(III) centres (LMCT) [90-92]. All complexes show emissions with maxima in the range of 380-385 nm in the UV region, upon excitation around 325 nm in acetonitrile at room temperature.

All three complexes are diamagnetic as expected for low-spin cobalt(III) complexes [89].

#### 3.7. Theoretical calculation on supramolecular interactions in solid state

In Figure 7A we show the representation of an infinite 1D chain found in the solid state of complex **1** that is governed by the formation of two equivalent C-H··· $\pi$  and C-H···H-C interactions. We have used a theoretical model that consists of one dimer taken from this infinite chain (using the crystallographic coordinates). We have computed its interaction energy (see Figure 7B), which is  $\Delta E_1 = -10.3$  kcal/mol that can be initially attributed to the contribution of both C-H··· $\pi$  and C-H···H-C interactions (see dashed lines) along with long range. In an effort to estimate the contribution of the C-H···H-C interaction, we have computed an additional model where the aromatic ring has been changed by a double bond (see small arrows in Figure 7C). As a result the interaction is significantly reduced to  $\Delta E_1 = -0.5$  kcal/mol that is the contribution of

the weak C-H···H-C interaction. This value is in good agreement with pervious calculations of methane dimer. To evaluate the contribution from long-range dispersion interactions between the bulk of the two molecules, we have used an additional theoretical model (see Figure 7D) where the methyl groups that participate in both C-H··· $\pi$  and C-H···H-C interactions have been replaced by H atoms (see small arrows in Figure 7D). In this dimer, all interatomic distances are longer that the sum of the corresponding van der Waals radii. Remarkably, the interaction energy is significant  $\Delta E_3 = -4.9$  kcal/mol confirming that the long range interactions are an important part of the total interaction energy (~47%).

A similar study has been done for complex 2. In Figure 8A we represent a part of the crystal packing this complex, where an infinite 1D chain formed, that is governed by the formation of C-H··· $\pi$  and C-H···H-C interactions. We have firstly used a theoretical model that consists of one dimer taken from this infinite chain (using the crystallographic coordinates). In this dimer, two symmetrically related C-H···H-C interactions are formed involving both ethoxy arms. Moreover, four C-H $\cdots\pi$  interactions are also established involving aliphatic and aromatic H atoms. We have used a theoretical model of this self-assembled dimer (see Figure 8B) and the interaction energy is large  $\Delta E_4 = -23.9$  kcal/mol. In an effort to estimate the contribution of the C-H···H-C interaction, we have computed an additional model where the methyl group of each ethoxy arm has been replaced by a H atom (see small arrows in Figure 8C). As a result the interaction is slightly reduced to  $\Delta E_5 = -21.1$  kcal/mol and the difference with  $\Delta E_4$  is the contribution of both C-H···H-C interactions (-2.8 kcal/mol). To evaluate the contribution of the aliphatic C-H··· $\pi$  interaction we have used an additional model where the methyl groups that participate in both C-H $\cdots\pi$  and C-H $\cdots$ H-C interaction has been replaced by H atoms (see Figure 8D). As a result the interaction energy is reduced to  $\Delta E_6 = -17.8$  kcal/mol and its difference with

respect to  $\Delta E_5$  is the contribution of the aliphatic C-H… $\pi$  interactions (-3.3 kcal/mol). Finally, to evaluate the contribution of long-range dispersion interactions between the bulk of the two molecules, we have used an additional theoretical model where the aromatic ring has been changed by a double bond (see small arrows in Figure 8E). The resulting interaction energy is  $\Delta E_7 = -8.4$  kcal/mol, which corresponds to the contribution of long range interactions. These results confirm that focusing excessively on individual short contacts may lead to ignore the crucial influence of relevant longer-range interactions.

A simpler study has been done for complex **3** since it does not exhibit C-H···H-C interactions in the solid state. In Figure 9A we represent a self-assembled dimer that is formed in the solid state, where two types of C-H··· $\pi$  are formed involving both ethoxy arms. The interaction energy of this self-assembled dimer (see Figure 9A) is  $\Delta E_3 = -11.0$  kcal/mol that corresponds to the four C-H··· $\pi$  and long range interactions. To evaluate the contribution of latter interactions between the bulk of the two molecules, we have used an additional theoretical model (see Figure 9B) where the ethyl groups have been replaced by H atoms. As a result the interaction energy is reduced to  $\Delta E_2 = -5.1$  kcal/mol. Therefore the contribution of long range interactions is an important part of the total binding energy (~29%) confirming the crucial role of these interactions in the solid state.

Finally, we have used the Bader's theory of "atoms in molecules", which provides an unambiguous definition of chemical bonding, to further demonstrate the existence of long range interactions in complexes **1** and **2**. The AIM theory has been successfully used to characterize and understand a great variety of interactions. In Figure 10 we show the AIM analysis of the long-range dimers described above in Figures 7D and 8E for **1** and **2**, respectively. In both cases (all interatomic distances are longer that the sum of the van der Waals radii) it can be observed

the presence of several bond (red spheres) and ring (yellow spheres) critical points and bond paths (dashed lines) inter-connecting several atoms thus confirming the existence of the long range interactions.

#### 3.8. Phenoxazinone synthase like activity

To check the ability of the complexes to oxidize o-aminophenol to 2-aminophenoxazine-3-one (phenoxazinone synthase mimicking activity),  $10^{-2}$  M acetonitrile solution of oaminophenol were mixed separately with 10<sup>-4</sup> M solution of each complex, and the spectra were recorded for up to 4 h at room temperature. It was found that both complexes 2 and 3 are showing phenoxazinone synthase mimicking activity, but complex 1 is not. The time dependent spectral profiles for a period of 4 h after the addition of o-aminophenol in acetonitrile solution of 2 and 3 are shown in Figure 11. The gradual increase of peak (characteristic of the phenoxazinone absorption) intensity at ~433 nm implies the catalytic conversation of oaminophenol to 2-aminophenoxazine-3-one in aerobic conditions. A blank experiment without catalyst under identical conditions does not show significant growth of the band at ~433 nm. To understand the extent of the catalytic efficiency,  $10^{-4}$  M solutions of the complexes were treated with substrate (o-aminophenol) under pseudo-first order conditions. Time scan at the  $\lambda_{max}$ of 2-aminophenoxazine-3-one was carried out for a period of 200 min. The initial rate was determined from the slope of the absorbance versus time plot. This has been repeated thrice and the average value was taken. Rate saturation kinetics of complex 3 is clearly indicated in Figure 12 (initial rate of the reaction versus concentration of the substrate plot). This observation indicates that an intermediate complex substrate adduct is formed at a pre-equilibrium stage and that the irreversible substrate oxidation is the rate determining step of the catalytic cycle. This type of saturation rate dependency on the concentration of the substrate may be treated with the

Michaelis-Menten model. This may also, upon linearization, give a double reciprocal Lineweaver-Burk plot which is used to analyze different parameters, viz. V<sub>max</sub> (Maximum reaction velocity), K<sub>M</sub> (Michaelis constant), and K<sub>cat</sub> (Turnover number). The initial rate versus substrate concentration plot and Lineweaver-Burk plot for complex 3 are shown in Figures 12 and 13, respectively.  $K_M$  values for complexes 2 and 3 are 5.08 x 10<sup>-4</sup> M and 5.75 x 10<sup>-4</sup> M, respectively. Similarly  $V_{max}$  values are 4.04 x 10<sup>-4</sup> M<sup>-1</sup> (for 2) and 4.29 x 10<sup>-4</sup> M<sup>-1</sup> (for 3). The  $K_{cat}$  value is obtained by dividing the  $V_{max}$  by the concentration of the complex used, and are found to be 4.12  $S^{-1}$  and 4.29  $S^{-1}$  for complexes 2 and 3, respectively. A probable mechanistic pathway for the oxidation of o-aminophenol to 2-aminophenoxazine-3-one is shown in Scheme 4. Initially, o-aminophenol forms adduct with complexes replacing the monodentate coligands, azide in 2 and thiocyanate in 3. This results in the formation of an o-aminophenol radical by the reaction with molecular dioxygen regenerating complexes 2 or 3. In the next step, the oaminophenol radical may be oxidized to o-benzoquinone monoamine, which, in turn, may be converted to 2-aminophenoxazine-3-one by the reaction with dioxygen and o-aminophenol (Scheme 4). It is to be noted here that complex 3 is inactive towards the phenoxazinone synthase mimicking activity. This may be correlated with its structure. It is a bis-ligand complex and does not contain any monodentate ligand, which could be replaced with o-aminophenol initiating catalysis. Similar mechanism has also been proposed by other groups [93,94].



Scheme 4: Probable mechanistic pathway for the oxidation of o-aminophenol to 2aminophenoxazine-3-one

#### 4. Conclusion

Three new mononuclear octahedral facial cobalt(III) complexes with a Schiff base ligand have been synthesized and X-ray characterized. The solid state structures show the participation of the organic ligand in concurrent C-H··· $\pi$  and C-H···H-C interactions involving the methoxy arm and the aromatic ring. The energetic features of these interactions have also been studied by means of DFT calculations. Moreover, it has been shown that long range interactions that are usually ignored by supramolecular chemists are very relevant in the stabilization of the different

assemblies observed in the solid state of all three complexes. Complexes 2 and 3 are found to show to phenoxazinone synthase mimicking activity.

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#### Appendix A. Supplementary data

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CCDC 1408890, 1419342 and 1419343 contain the supplementary crystallographic data for complexes **1**, **2** and **3**, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at <u>http://dx.doi.org/10.1016/j.poly.2014.11.012</u>.

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	1	2	3
Formula	C <sub>28</sub> H <sub>42</sub> CoN <sub>4</sub> ClO <sub>8</sub>	C <sub>24</sub> H <sub>30</sub> CoN <sub>5</sub> O <sub>4</sub>	C <sub>25</sub> H <sub>30</sub> CoN <sub>3</sub> O <sub>4</sub> S
Formula Weight	657.04	511.46	527.51
Crystal System	Triclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 1	$P2_{1}/c$	$P2_{1}/c$
a(Å)	8.2535(5)	12.9436(3)	10.5078(3)
b(Å)	10.0987(6)	8.8914(2)	19.1109(6)
c(Å)	11.0825(7)	20.9537(6)	13.1236(4)
α (°)	97.162(4)	90	90
β(°)	109.189(4)	98.045(1)	106.458(2)
γ(°)	106.444(3)	90	90
d(calc) [g/cm <sup>3</sup> ]	1.343	1.423	1.386
μ[mm <sup>-1</sup> ]	0.662	0.759	0.797
F(000)	346	1072	1104
Total Reflections	11303	35682	34282
Unique Reflections	6210	4553	4234
Observed data[ $I > 2 \sigma(I)$ ]	3109	3412	3513
No of parameters	379	307	307
R(int)	0.041	0.049	0.041
R1, wR2(all data)	0.0764, 0.2040	0.0597, 0.1055	0.0429, 0.0806
R1, wR2([ $I > 2 \sigma(I)$ ]	0.0699, 0.1945	0.0396, 0.0975	0.0326, 0.0756

 Table 1: Crystal data and refinement details of complexes 1, 2 and 3.

	1	2	3
Co(1)-O(1)	1.879(6)	1.8946(17)	1.9042(17)
Co(1)-O(2)	-	1.9029(16)	1.8858(14)
Co(1)-O(3)	1.861(6)	1.8938(17)	1.8567(14)
Co(1)-N(1)	2.077(7)	2.0552(19)	2.0580(19)
Co(1)-N(2)	1.919(7)	1.898(2)	1.9050(19)
Co(1)-N(3)	2.123(7)	1.950(3)	1.926(2)
Co(1)-N(4)	1.954(7)	- 2	-

**Table 2**: Bond lengths (Å) of complexes 1, 2 and 3.

	1	2	3
O(1)-Co(1)-O(2)	-	94.17(7)	93.69(7)
O(1)-Co(1)-O(3)	178.3(3)	88.52(7)	82.89(7)
O(1)-Co(1)-N(1)	89.6(3)	173.40(8)	92.62(7)
O(1)-Co(1)-N(2)	91.1(3)	86.65(8)	175.16(8)
O(1)-Co(1)-N(3)	90.7(3)	90.73(9)	88.54(8)
O(1)-Co(1)-N(4)	89.3(3)	-	2
O(2)-Co(1)-O(3)	-	85.71(7)	90.31(7)
O(2)-Co(1)-N(1)	-	92.37(8)	173.35(8)
O(2)-Co(1)-N(2)	-	179.18(8)	85.59(7)
O(2)-Co(1)-N(3)	-	87.24(9)	88.94(7)
O(3)-Co(1)-N(1)	88.9(3)	92.96(8)	92.54(7)
O(3)-Co(1)-N(2)	87.9(3)	94.21(9)	92.32(8)
O(3)-Co(1)-N(3)	90.8(3)	172.83(9)	171.33(8)
O(3)-Co(1)-N(4)	91.8(3)	-	-
N(1)-Co(1)-N(2)	84.7(3)	86.82(9)	88.29(8)
N(1)-Co(1)-N(3)	179.6(3)	88.60(10)	89.14(8)
N(1)-Co(1)-N(4)	96.6(3)	-	-
N(2)-Co(1)-N(3)	95.0(3)	92.86(10)	96.24(9)
N(2)-Co(1)-N(4)	178.7(3)	-	-
N(3)-Co(1)-N(4)	83.8(3)	-	-

Table 3: Selected bond angles (°) of complexes 1, 2 and 3.

#### Legends to the figures

Figure 1: Perspective view of the complex 1 with selective atom-numbering scheme. Hydrogen atoms are not shown for clarity.

**Figure 2:** Perspective view of the complex **2** with selective atom-numbering scheme. Hydrogen atoms are omitted for clarity.

Figure 3: Perspective view of the complex 3 with selective atom-numbering scheme. Hydrogen atoms are omitted for clarity.

**Figure 4:** Experimental and simulated powder XRD patterns of complex **3**, confirming the purity of the bulk materials.

Figure 5: Hirshfeld surfaces mapped with  $d_{norm}$  (top), shape index (middle) and curvedness (bottom).

Figure 6: Fingerprint plot: Full (top) and resolved into  $C \cdots H / H \cdots C$  contact contact (bottom) contributed to the total Hirshfeld Surface area of complex 1 (left), complex 2 (middle) and complex 3 (right).

**Figure 7:** (A) X-ray fragment of complex 1, highlighting the C-H··· $\pi$  and C-H···H-C interactions. (B-D) Theoretical models used to evaluate the C-H··· $\pi$ , C-H···H-C and long range interactions (Distances in Å).

**Figure 8:** (A) X-ray fragment of complex **2**, highlighting the C-H··· $\pi$  and C-H···H-C interactions. (B-D) Theoretical models used to evaluate the C-H··· $\pi$ , C-H···H-C and long range interactions (Distances in Å).

**Figure 9:** (A) X-ray fragment of complex **3**, highlighting the H-bonds and  $\pi \cdots \pi$  stacking interactions. (B) Theoretical models used to evaluate the  $\pi \cdots \pi$  stacking interactions (Distances in Å).

**Figure 10:** AIM analysis of two long-range models of complexes **1** and **2**. Bond and ring critical points are represented by red and yellow spheres, respectively. The bond paths connecting bond critical points are also represented by dashed lines.

**Figure 11:** The UV-Vis spectral profiles indicating the increment of 2-aminophenoxazine-3-one at 433 nm upon addition of  $10^{-2}$  M o-aminophenol to the  $10^{-4}$  M of complexes **2** (a) and **3** (b) at room temperature.

**Figure 12:** The Initial rate vs substrate concentration plot for the oxidation of o-aminophenol in dioxygen-saturated acetonitrile catalyzed by complex **3** at room temperature.

Figure 13: The Linear Lineweaver-Burk plot for the oxidation of o-aminophenol catalyzed by complex 3 at room temperature.

X C C F













Figure 6















# **Graphical Abstract (Pictogram)**

Three mononuclear octahedral cobalt(III) complexes with salicylaldimine Schiff bases: Synthesis, characterization, phenoxazinone synthase mimicking activity and DFT study on supramolecular interactions

Kousik Ghosh, Sumit Roy, Anindya Ghosh, Abhisek Banerjee, Antonio Bauzá, Antonio Frontera, Shouvik Chattopadhyay



# **Graphical Abstract (Synopsis)**

Three mononuclear octahedral cobalt(III) complexes with salicylaldimine Schiff bases: Synthesis, characterization, phenoxazinone synthase mimicking activity and DFT study on supramolecular interactions

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Three mononuclear octahedral facial cobalt(III) complexes have been synthesized and characterized. The structures have been confirmed by single crystal X-ray analysis. Supramolecular interactions in solid state in them have been analysed with DFT study. Two complexes show phenoxazinone synthase mimicking activity.

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