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A combined experimental and theoretical study on supramolecular assemblies in octahedral cobalt(III) salicylaldimine complexes having pendant side arms

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Abstract

complexes, $[Co(L^1)(N_3)_2(deen)]$ cobalt(III) Two mononuclear (1) and $[Co(L^2)(N_3)_2(DMSO)]$ (2), where HL¹ {2-(2-(diethylamino)ethyliminomethyl)-4-bromophenol} {2-(2-(diethylamino)ethyliminomethyl)-6-methoxyphenol} are tridentate HL^2 and and tetradentate Schiff bases, respectively and deen is a bidentate chelating ligand, N,N-diethyl-1,2diaminoethane, were prepared and characterized by elemental and spectral analysis. X-ray crystal structure determination confirmed the structures of the complexes. Both complexes are meridional isomers. The solid state structures show the participation of the organic ligands in concurrent conventional and unconventional C-H $\cdots\pi$ interactions along with hydrogen bonding. The energetic features of these interactions have also been studied by means of DFT calculations.

Keywords: Cobalt(III); Schiff base; Crystal Structure; Meridional; DFT study.

1. Introduction

Schiff bases have widely been studied in coordination chemistry particularly due to their facile syntheses and easily tunable steric and electronic properties. Metal complexes of Schiff bases are important stereochemical models in main group and transition metal coordination chemistry [1-5]. These complexes have various applications in bioinorganic chemistry, separation and encapsulation, catalysis, hydrometallurgy, metal clusters, material science and magnetism, transport and activation of small molecules etc [6-13]. Among numerous Schiff bases, salicylaldimine Schiff bases constitute a unique set for their ability to bind more than one metal centres exploiting the bridging ability of phenoxo oxygen atoms 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 complexes having pendant arms. Many such pendant ligands have been used in a variety of chemical applications, e.g. in MRI reagents, in enzyme simulations, in carrying a radionuclide into a target cell and also in exploring their geometry-activity correlation [14-19].

On the other hand, 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 [20-23]. Several cobalt(III) complexes have also been used to model artificially various photosynthesis systems [24-26]. The most common approach for creating an artificial photosynthetic device involves the development of efficient catalysts for the oxidation of H₂O to oxygen and reduction of H₃O⁺ to hydrogen [27-29]. Mononuclear cobaloxime complexes have extensively been used by several researchers to remove H₂ from H₂O. Dinuclear cobalt(III) complexes may mimic the active biosites e.g. in methionine amino peptidase [30] and may exhibit DNA cleavage activity [31].

Cobalt(III) of metallohydrolases are responsible for the removal of the N-terminal methionine from the protein chain [32]. Cobalt(III) Schiff base complexes have also attracted considerable attention for their biological applications [33-37].

 HL^1 In salicylaldimine Schiff bases. the present work, two HL^2 (diethylamino)ethyliminomethyl)-4-bromophenol} and (diethylamino)ethyliminomethyl)-6-methoxyphenol, have been used to prepare two new distorted octahedral cobalt(III) complexes, $[Co(L^{1})(N_{3})_{2}(deen)]$ (1) and $[Co(L^{2})(N_{3})_{2}(DMSO)]$ (2). These two Schiff bases, HL^1 and HL^2 , are not new and they have already been used by several groups to prepare many complexes of cobalt(III) [38] and various transition and non transition metals as well [39,40]. X-ray crystal structure determination confirmed the structures of complexes 1 and 2. The solid state structures show the participation of the organic ligands in C-H··· π interactions along with hydrogen bonding. The energetic features of these interactions have also been studied by means of DFT calculations. Herein, we report the synthesis, spectroscopic characterization, X-ray crystal structures, supramolecular interactions and Hirshfeld surface analysis of two new octahedral cobalt(III) complexes.

2. Experimental

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

2.2.1. Synthesis of $[Co(L^1)(N_3)_2(deen)]$ (1) {HL¹ =2-(2-(diethylamino)ethyliminomethyl)-4bromophenol}

A methanol solution of 5-bromosalicylaldehyde (1 mmol, 0.201 g) and N,N-diethyl-1,2diaminoethane (1mmol, 0.140 mL) was refluxed for 1 h to prepare tridentate N₂O donor Schiff base 2-(2-(diethylamino)ethyliminomethyl)-4-bromophenol (HL¹). The Schiff base was not isolated and was used directly for the preparation of complex **1**. A methanol solution of cobalt(II) perchlorate hexahydrate (1 mmol, 0.365 g) was added to the methanol solution of the Schiff base and refluxed for 1 h. An methanol solution of N,N-diethyl-1,2-diaminoethane (1 mmol, 0.140 mL) along with aqueous-methanol solution of sodium azide (2 mmol, 0.130 g) was then added to it and refluxed further for ca. 1 h. Diffraction quality dark brown single crystals of complex **1** were obtained after few days on slow evaporation of a DMSO solution of the complex in open atmosphere.

Yield: 0.30 g [based on Co(II)] 54%. Anal. Calc. for $C_{19}H_{34}BrCoN_{10}O$ (FW 557.39): C, 40.94; H, 6.15; N, 25.13, Found: C, 40.88; H, 6.08; N, 25.20%; IR (KBr, cm⁻¹): 1637 ($\nu_{C=N}$), 2021 (ν_{N3}), 3232, 3293 (ν_{N-H}), 2968-2806 (ν_{CH}). UV-Vis, λ_{max} (nm), [ϵ_{max} (L mol⁻¹ cm⁻¹)] (DMSO), 261 (1.5 × 10⁴), 333 (8.7 × 10³), 325 (9.5 × 10³), 509 (9.1 × 10²). Magnetic moment: diamagnetic.

2.2.2. Synthesis of $[Co(L^2)(N_3)_2(DMSO)]$ (2) {HL² =2-(2-(diethylamino)ethyliminomethyl)-6-methoxyphenol

A methanol solution of 3-methoxysalicylaldehyde (1 mmol, 0.152 g) and N,N-diethyl-1,2-diaminoethane (deen) (1mmol, 0.140 mL) was refluxed for 1 h to prepare tetradentate N_2O_2 donor Schiff base 2-(2-(diethylamino)ethyliminomethyl)-6-methoxyphenol (HL²). The Schiff

base was not isolated and was used directly for the preparation of complex **2**. A methanol solution of cobalt(II) perchlorate hexahydrate (1 mmol, 0.365 g) was added to the methanol solution of the Schiff base and refluxed for 1 h. An aqueous methanol solution of sodium azide (2 mmol, 0.130 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 a DMSO solution of the complex in open atmosphere.

Yield: 0.30 g [based on Co(II)] 64%. Anal. Calc. for $C_{16}H_{27}CoN_8O_3S$ (FW 470.46): C, 40.85; H, 5.78; N, 23.82. Found: C, 40.80; H, 5.72; N, 23.89%; IR (KBr, cm⁻¹): 1635 ($\upsilon_{C=N}$), 2015 (υ_{N3}), 2998-2820 (υ_{CH}). UV-Vis, λ_{max} (nm), [ε_{max} (L mol⁻¹ cm⁻¹)] (DMSO), 270 (1.1 × 10⁴), 327 (9.5 × 10³), 512 (8.4 × 10²). Magnetic moment: diamagnetic.

2.3. Physical measurements

Elemental analyses (carbon, hydrogen and nitrogen) were performed on a Perkin-Elmer 240C elemental analyzer. Infrared spectra in KBr (4500-400 cm⁻¹) were recorded using a PerkinElmer Spectrum Two FTIR spectrophotometer. Electronic spectra in DMSO (900-200 nm) were recorded on a PerkinElmer Lambda 35 UV-Vis spectrophotometer. Fluorescence spectra in DMSO 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.

2.4. X-ray crystallography

Single crystals of both complexes having suitable dimensions, were used for data collection using a Bruker SMART APEX II diffractometer equipped with graphite-

monochromated Mo K α radiation ($\lambda = 0.71073$ Å) at 150 K. Molecular structures were solved using the SHELX-14/7 package [41]. Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms, attached to nitrogen, were located by difference Fourier maps and were kept at fixed positions. All other 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 [42]. A summary of the crystallographic data is given in Table 1. Selected bond lengths and bond angles are given in Tables 2 and 3, respectively.

2.5. Hirshfeld Surface Analysis

Hirshfeld surfaces [43-45] and the associated two-dimensional (2D) fingerprint [46-48] plots were calculated using Crystal Explorer, [49] with bond lengths to hydrogen atoms set to standard values [50]. 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

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

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 [51] and thus it suggests the possibility of gaining additional insight into the intermolecular interaction of molecular crystals.

2.6 Theoretical methods

The calculations of the noncovalent interactions were carried out using the TURBOMOLE version 7.0 [52] 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 [53-56]. 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 [57]. The low spin configuration of the Co metal centers has been used for the calculations.

3. Results and discussion

3.1. Synthesis

Two Schiff base ligands, HL^1 and HL^2 , were synthesized by the condensation of N,Ndiethyl-1,2-diaminoethane with 5-bromosalicylaldehyde and 3-methoxysalicylaldehyde respectively in methanol following the literature method [58,59]. The Schiff base ligands were not isolated and used directly for the preparation of complexes. Methanol solution of HL^1 was made to react with cobalt(II) in presence of suitable anionic and neutral coordinating ligands, azide and deen to produce $[Co(L^1)(N_3)_2(deen)]$ (1), where cobalt(II) is in situ oxidised to cobalt(III). This oxidation is obviously favoured in presence of Schiff base ligands having

stronger crystal field [60]. In this complex, three coordinating sites of cobalt(III) are occupied by the deprotonated tridentate Schiff base. Two azide ions coordinate cobalt(III) and the remaining site is occupied by a neutral deen molecule. On the other hand, a potential tetradentate Schiff base, HL^2 was then used for preparing complex **2**. Any additional neutral coordinating ligand was not added. This leads to the formation of $[Co(L^2)(N_3)_2(DMSO)]$ (**2**). The complexes could not be prepared under Ar or N₂ atmosphere. It is, therefore, concluded that the reactions are initiated by the aerial oxidation of cobalt(II) to cobalt(III). Formation of both complexes is shown in Scheme 1. It is to be noted here that ligand HL^2 is potential tetradentate ligand, however, in forming complex **2**, it behaves as tridentate one, keeping the remaining donor site pendant. Keeping in mind the novel role of pendant ligands in enzyme simulations [61], in carrying a radionuclide into a target cell [62], in magnetic resonance imaging reagents [63] etc, the present findings may provide insight and serve as a prototype for preparing other such complexes.



Scheme 1: Preparation of complexes 1 and 2.

Schiff bases usually exist in their zwitterionic forms. Thus it is quite rational to assume that HL^1 and HL^2 remain in their zwitterionic forms. When the Schiff base coordinates the metal, the deprotonation occurs. The liberated proton could easily be abstracted by the tertiary amine nitrogen atom of a free deen molecule, thereby making the potential bidentate diamine (deen) into a monodentate one. The primary amine nitrogen atom of deen then coordinates cobalt(III) and at the final stage of the reaction tertiary amine is deprotonated and this deprotonation is favoured by the hydroxide ions produced by the reduction of O_2 during the areal oxidation of cobalt(II). A tentative mechanism is given in Scheme 2



Scheme 2: Probable mechanistic pathway for the preparation of complex 1

3.2. Description of the structures

3.2.1. Complex $[Co(L^1)(N_3)_2(deen)]$ (1)

Complex 1 crystallizes in the triclinic space group $P\overline{1}$. A perspective view of the complex along with the selective atom numbering scheme is shown in Figure 1. The structure determination reveals that the complex consists of a discrete mononuclear unit $[Co(L^1)(N_3)_2(deen)]$. The cobalt(III) center is coordinated by one imine nitrogen atom, N(2), one amine nitrogen atom, N(1), and one phenoxo oxygen atom, O(1), from one deprotonated Schiff

base ligand $(L^1)^-$, and two nitrogen atoms, N(3) and N(4), from two terminal azides, respectively. The sixth coordination cite of cobalt(III) is occupied by an amine nitrogen atom, N(5), from a Nsubstituted amine, (deen), to complete its octahedral geometry. The potential bidentate diamine (deen) therefore binds cobalt(III) in monodentate fashion. However, the diamine (deen) is unsymmetrical and it is, therefore, perhaps not too unexpected that the primary amine coordinates but the hindered diethylamine group does not.

The Schiff base ligand coordinates cobalt(III) in meridional fashion. The Co-N_{imine} distance {1.883(4) Å} is shorter than the Co-N_{amine} distance {2.077(5) Å}, as were also observed in similar systems [64]. The saturated five membered chelate ring Co(1)-N(1)-C(5)-C(6)-N(2), present an envelope conformation with puckering parameters q(2) = 0.438(6) Å, $\varphi = 249.1(6)^{\circ}$ [65]. The N(1)-Co(1)-N(2) angle is 86.02(18)° and is typical of a five membered chelate ring [66]. The terminal azides are quasi-linear with the N-N-N angles being 175.4(6) and 176.2(5)°. The torsion angle between two terminal azides is 6.9(4)°.

The hydrogen atom, H(55A), attached to amine nitrogen atom, N(5), is participated in hydrogen bonding interaction (Table 4) with the symmetry related azide nitogen atom, N(7)^a {symmetry transformation $^{a} = 1-x,2-y,1-z$ } of neighbouring molecule. The hydrogen bonding interaction leads to the formation of a dimeric supramolecular structure as shown in Figure 2. There are no other significant supramolecular interactions present in the complex.

3.2.2. Complex $[Co(L^2)(N_3)_2(DMSO)]$ (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 3. The structure determination reveals that the complex consists of a discrete mononuclear unit

 $[Co(L^2)(N_3)_2(DMSO)]$. The cobalt(III) center is coordinated by one imine nitrogen atom, N(2), one amine nitrogen atom, N(1), and one phenoxo oxygen atom, O(1), from one deprotonated Schiff base ligand $(L^2)^2$, and two nitrogen atoms, N(3) and N(4), from two terminal azides, respectively. The sixth coordination cite of cobalt(III) is occupied by an oxygen atom, O(3), from a DMSO molecule to complete its octahedral geometry. The Schiff base ligand coordinates cobalt(III) in meridional fashion. The Co-N_{imine} distance {1.876(3) Å} is shorter than the Co-N_{amine} distance {2.064(3) Å}, as were also observed in similar systems [64]. The N(1)-Co(1)-N(2) angle is 86.37(14)° and is typical of a five membered chelate ring [66]. Terminal azides are quasi-linear with the N-N-N angles being 175.7(4) and 176.1°(5). The torsion angle between two terminal azides is 134.2(2)°.

3.3. IR, electronic and fluorescence spectra

In the IR spectra of complexes **1** and **2**, distinct bands due to azomethine (C=N) stretching vibrations appear at 1637 and 1635 cm⁻¹, respectively [58]. Strong bands at 2021 and 2015 cm⁻¹ indicate the presence of terminal azides in the IR spectra of complexes **1** and **2**, respectively. Sharp bands at 3293 and 3232 cm⁻¹ indicate N-H stretching vibrations in the IR spectrum of complex **1**. Bands in the range of 2998-2806 cm⁻¹ due to alkyl C-H bond stretching vibrations are customarily noticed in the IR spectra of both complexes.

Electronic spectra of complexes are recorded in DMSO medium at room temperature in the range 200-900 nm. Both complexes exhibit low-energy absorptions around 510 nm attributable to a transition in the visible region of a low-spin cobalt(III) in octahedral geometry. In the high energy region, both complexes show intense absorption bands within 260-270 nm, corresponding to π - π * transitions, whereas bands around 325 nm, are attributed to the charge transfer transition from the coordinated unsaturated ligands to the cobalt(III) centres (LMCT).

All complexes show emissions with maxima around 380 nm in the UV region, upon excitation at 325 nm in DMSO at room temperature.

3.4. Hirshfeld surface analysis

The Hirshfeld surfaces for both complexes are mapped over d_{norm}, shape index and curvedness (Figure 4). The surfaces are shown as transparent to allow visualization of the molecular moiety around which they are calculated. The dominant interaction between N and H atoms for complexes 1 and 2 can be seen in the Hirshfeld surfaces as red spots on the d_{norm} surface in Figure 4. 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 N···H/H···N interactions appear as distinct spikes in the 2D fingerprint plot (Figure 5). 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 [67]. The proportions of $N \cdots H/H \cdots N$ interactions comprise 26 and 30.5% for 1 and 2, respectively. The N···H interaction is represented by lower spike ($d_i = 1.26$, $d_e = 0.86$ Å in 1 and $d_i = 1.4$, $d_e = 1.0$ Å in 2) and the H···N interaction is also represented by another spike ($d_i =$ 0.89, $d_e = 1.28$ Å in 1 and $d_i = 1.0$, $d_e = 1.33$ Å in 2) by upper spike {Figure 5} and can be viewed as bright red spots on the d_{norm} surface {Figure 4}.

3.5. Geometrical preferences

Both complexes 1 and 2 may have three facial and two meridional isomers (Scheme 3). However, in present case, only the meridional isomers of both complexes having azide nitrogen atoms in trans positions ((e) in Scheme 3) have been formed exclusively, as confirmed by X-ray analysis. This may be due to the fact that when azides are in trans dispositions, dipole-dipole

interactions between two azide moieties are minimized which in turn minimizes the energy of the system. The dipole-dipole interactions are increased in all other possible isomers where azides are in cis orientation. This is responsible for the formation of meridional isomers as the sole products both in case of complexes 1 and 2.



Scheme 3: Possible facial (a-c) and meridional (d-e) (geometrical) isomers of complexes 1 and 2; N^A , N^I and O indicate imine nitrogen, amine nitrogen and phenoxy oxygen atoms, respectively{X= deen (in 1) or DMSO (in 2)}.

3.6. Magnetic properties

Both complexes are diamagnetic as expected for low-spin cobalt(III) complexes [68].

3.7. DFT study on supramolecular interactions

The theoretical study is devoted to analyze the noncovalent interactions that govern the crystal packing of complexes 1 and 2 focusing our attention to the remarkable C-H··· π interactions. The importance of this interaction in the solid state has been studied in depth by Nishioa [69]. In this type of bonding, the π -system is an arene, commonly a six or five membered ring. Studies on the importance of this interaction in more unconventional π -systems like double

or triple bonds are scarcely found in the literature. Herein we also analyze the importance of the unconventional C-H··· π interaction involving the azide ligand as π -donor. From X-ray solid state structure of the complexes (Figures 1 and 3), it can be observed that the N¹,N¹-diethylethane-1,2-diamine co-ligand in **1** is mono-coordinated via the primary amine group instead of the more basic tertiary amine group. This unexpected N-coordination is likely due to the formation of an intramolecular hydrogen bond (see Figure 1) that compensates the coordination with the less basic amine group.

As a first approximation to rationalize the different assemblies observed in the solid state of complexes 1 and 2, we have computed their Molecular Electrostatic Potential (MEP) surfaces that are shown in Figure 6. As expected, in both complexes the most negative regions (red surface) correspond to the azide ligands on the extension of the N₃ σ -bonds. The most positive region in 1 is the N-H bond; therefore it is well suited for establishing H-bonds with the azide groups. In complex 2 the most positive region corresponds to the CH₃ groups of the coordinated DMSO molecule. Unexpectedly, the positive potential MEP value in this region (+38 kcal/mol) is identical to that observed in complex 1 for the N-H group, which is better hydrogen bond donor.

In Figure 7A, we show the representation of an infinite zig-zag 1D chain found in the solid state of complex 1 that is governed by the successive interaction of self-assembled dimers (see Figure 7B). Each dimer is generated due to the formation of two equivalent N-H…N, C-H…Br and C-H… π interactions. These dimers propagate in the solid state by means of unconventional C-H… π interactions where the π -system is provided by the azide ligand (see Figure 7D). We have used two theoretical models that are two dimers taken from this infinite chain (using the crystallographic coordinates). The interaction energy of the self-assembled

dimer (see Figure 8B) is $\Delta E_1 = -25.3$ kcal/mol that can be attributed to the contribution of N-H…N, C-H…Br and C-H… π interactions (see dashed lines). In an effort to estimate the contribution of the C-H…Br and C-H… π interactions, we have computed an additional model where the azide ligands have been replaced by hydrido ligands (see small arrows in Figure 7C). As a result the interaction is significantly reduced to $\Delta E_2 = -10.7$ kcal/mol that is the contribution of the weak C-H…Br and C-H… π interactions. The contribution of both H-bonds can be estimated by difference, which is -14.6 kcal/mol. This large interaction energy for the N-H…N H-bonds is in good agreement with the MEP analysis commented above. Remarkably, the binding energy computed for the other dimer (see Figure 7D) where two symmetrically related unconventional C-H… π interactions are established is large ($\Delta E_3 = -20.3$ kcal/mol) confirming the importance of this type of interactions in the solid state.

A similar study has been done for complex 2. In Figure 8A we represent a part of the crystal packing in this complex, where an infinite 1D chain is formed, that is governed by the formation, among others, of C-H·· π interactions involving the aromatic ring of the Schiff base ligand. In fact this ring interacts with an ethyl group by one side of the π -system (denoted as C-H·· π_1) and with the methyl group of the DMSO by the opposite side (denoted as C-H·· π_2). To evaluate these C-H·· π interactions, we have used two theoretical models (using the crystallographic coordinates) that are shown in Figures 8B and 8C. In the first dimer (C-H·· π_1), two conventional-H·· π interactions are formed involving one N-ethyl group and one unconventional C-H·· π interaction involving one aromatic H atom and the azide ligand (see Figure 8B). The interaction energy is large $\Delta E_4 = -13.0$ kcal/mol confirming the importance of this intricate combination of C-H·· π interactions. In the second dimer (C-H·· π_2), a conventional C-H·· π interaction is established between the methyl group of DMSO and the aromatic ring. In

addition, a bifurcated hydrogen bonding interaction between two DMSO hydrogen atoms and the azide ligand (see Figure 8C) is established. This interaction strongly agrees with the MEP surface shown in Figure 6B, where the most positive region was observed between the Me groups of DMSO. Consequently, the interaction energy is large $\Delta E_5 = -18.4$ kcal/mol due to the contribution of both interactions.

4. Summary

In summary, the synthesis and characterization of two new mononuclear octahedral cobalt(III) complexes with potential tri and tetradentate salicylaldimine Schiff bases are described in the paper. X-ray crystal structure determination confirmed the structures of the complexes. Both the complexes are meridional isomers. The isolation and crystal structure determination of the complex **2** unambiguously shows that the potential tetradentate Schiff base acting as tridentate ligand, keeping the remaining donor site (i.e. methoxy) pendant. Pendant donors do have the potential to be used as attachment points for other molecules, thereby facilitating the formation of homo and hetero polynuclear complexes. At the same time, they may perturb the metal ions at additional coordination sites, in competition with external substrates. The structural motifs are therefore important ones in influencing the development in coordination chemistry in future. Furthermore, the solid state structures show the participation of the organic ligands in concurrent conventional and unconventional C-H… π interactions along with hydrogen bonding. The energetic features of these interactions have also been studied by means of DFT calculations.

Acknowledgement

Crystallographic data of both complexes were collected at the DST-FIST, India-funded single crystal diffractometer facility at the Department of Chemistry, Jadavpur University.

Appendix A. Supplementary data

CCDC 1408892 and 1408891 contain the supplementary crystallographic data for complexes **1** and **2**, 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 http://dx.doi.org/10.1016/j.poly.2014.11.012.

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Acceptic

	1	2	
Formula	C ₁₉ H ₃₄ BrCoN ₁₀ O	C ₁₆ H ₂₇ CoN ₈ O ₃ S	
Formula Weight	557.39	470.46	
Crystal System	Triclinic	ic Monoclinic	
Space group	$P\overline{1}$	$P2_{1}/c$	
a(Å)	9.5571(3)	8.8590(8)	
b(Å)	10.4978(4)	10.2398(10)	
c(Å)	14.5828(5)	24.106(2)	
α(°)	109.508(2)	90	
β(°)	103.638(2)	95.784(6)	
γ(°)	99.324(2)	90	
d(calc) [g/cm ³]	n ³] 1.432 1.436		
μ [mm ⁻¹]	2.239	2.239 0.919	
F(000)	576	984	
Total Reflections	19586	31083	
Unique Reflections	4859	4208	
Observed data[$I > 2 \sigma(I)$]	3122	3284	
No of parameters	277	262	
R(int)	0.041	0.056	
R1, wR2(all data)	0.0930, 0.1517	0.0706, 0.1535	
R1, wR2([I > 2 $\sigma(I)$]	0.0576, 0.1374	0.0530, 0.1402	

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

D

Co(1)-O(1) 1.879(4) 1.878(3) Co(1)-O(3) - 1.950(2) Co(1)-N(1) 2.077(5) 2.064(3) Co(1)-N(2) 1.883(4) 1.876(3) Co(1)-N(2) 1.883(4) 1.876(3) Co(1)-N(3) 1.955(5) 1.947(3) Co(1)-N(4) 1.957(5) 1.968(3) Co(1)-N(5) 1.976(4) -
Co(1)-O(3) - 1.950(2) Co(1)-N(1) 2.077(5) 2.064(3) Co(1)-N(2) 1.883(4) 1.876(3) Co(1)-N(3) 1.955(5) 1.947(3) Co(1)-N(4) 1.957(5) 1.968(3) Co(1)-N(5) 1.976(4) -
Co(1)-N(1) 2.077(5) 2.064(3) Co(1)-N(2) 1.883(4) 1.876(3) Co(1)-N(3) 1.955(5) 1.947(3) Co(1)-N(4) 1.957(5) 1.968(3) Co(1)-N(5) 1.976(4) -
Co(1)-N(2) 1.883(4) 1.876(3) Co(1)-N(3) 1.955(5) 1.947(3) Co(1)-N(4) 1.957(5) 1.968(3) Co(1)-N(5) 1.976(4) -
Co(1)-N(3) 1.955(5) 1.947(3) Co(1)-N(4) 1.957(5) 1.968(3) Co(1)-N(5) 1.976(4) -
Co(1)-N(4) 1.957(5) 1.968(3) Co(1)-N(5) 1.976(4) -
Co(1)-N(5) 1.976(4) -

Table 2: Selected bond lengths (\AA) of complexes 1 and 2.

	1	2
O(1)-Co(1)-O(3)	-	87.11(11)
O(1)-Co(1)-N(1)	177.79(18)	177.96(12)
O(1)-Co(1)-N(2)	94.53(18)	95.16(13)
O(1)-Co(1)-N(3)	90.87(19)	88.89(14)
O(1)-Co(1)-N(4)	90.8(20)	88.82(14)
O(3)-Co(1)-N(1)	-	91.39(12)
O(3)-Co(1)-N(2)	-	177.42(12)
O(3)-Co(1)-N(3)	-	91.29(12)
O(3)-Co(1)-N(4)	-	89.62(12)
N(1)-Co(1)-N(2)	86.02(18)	86.37(14)
N(1)-Co(1)-N(3)	91.27(19)	92.54(14)
N(1)-Co(1)-N(4)	87.10(19)	89.78(14)
N(2)-Co(1)-N(3)	90.40(19)	87.54(14)
N(2)-Co(1)-N(4)	89.29(19)	91.64(14)
N(3)-Co(1)-N(4)	178.4(20)	177.49(14)
O(1)-Co(1)-N(5)	83.35(17)	-
N(1)-Co(1)-N(5)	96.17(17)	-
N(2)-Co(1)-N(5)	177.22(17)	-
N(3)-Co(1)-N(5)	87.84(19)	-
N(4)-Co(1)-N(5)	92.54(19)	-

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

	D–H···A	D–H	Н…А	D…A	∠D–H…A
	N(5)-H(55A)····N(7) ^a	0.89	2.28	3.149(7)	165
), donor;	H, hydrogen; A, accepto	or. Symmetr	ry transform	nation $^{a} = 1-x$,	2-y, 1-z.
				G	0
	R				
	ALR I				
	CIR				
С	CIP .				
C					
C					

Table 4: Hydrogen bond distances (Å) and angles (°) of complex 1.



Figure 1: Perspective view of the complex 1 with selective atom-numbering scheme. Hydrogen atoms are omitted for clarity.



Figure 2: Hydrogen bonding interaction in complex 1. Selected hydrogen atoms are omitted for clarity. Symmetry transformation a = 1-x, 2-y,1-z.

C



Figure 3: Perspective view of the complex 2 with selective atom-numbering scheme. Hydrogen atoms are omitted for clarity.



Figure 4: Hirshfeld surfaces mapped with dnorm (left), shape index (middle) and curvedness (right) of complex 1 (top) and complex 2 (bottom).



Figure 5: Fingerprint plot: Full {left side} and resolved $N \cdots H/H \cdots N$ contact {right side} contributed to the total Hirshfeld Surface area of complex 1 (top) and complex 2 (bottom).

R



Figure 6: MEP surfaces of complexes 1 and 2. Energies at selected points of the surfaces are given in kcal/mol.



Figure 7: (A) X-ray fragment of complex **1**, H-atoms omitted for clarity. (B-D) Theoretical models used to evaluate the C-H···Br and C-H··· π interactions. Distances in Å.

Rocki



Figure 8: (A) X-ray fragment of complex 2, highlighting the C-H··· π interactions. (B-C) Theoretical models used to evaluate the C-H··· π , and H-bonding interactions. Distances in Å.

Graphical Abstract (Pictogram)

A combined experimental and theoretical study on supramolecular assemblies in octahedral cobalt(III) salicylaldimine complexes having pendant side arms

Kousik Ghosh, Abhisek Banerjee, Sumit Roy, Antonio bauzá, Antonio Frontera, Shouvik Chattopadhyay



Graphical Abstract (Synopsis)

A combined experimental and theoretical study on supramolecular assemblies in octahedral cobalt(III) salicylaldimine complexes having pendant side arms

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

Meridional isomers of two mononuclear cobalt(III) complexes with salicylaldimine Schiff bases were prepared and characterized. The energetic features of conventional and unconventional supramolecular interactions have also been studied by means of DFT calculations.