

Two new twisted helical nickel(II) and cobalt(III) octahedral monomer complexes: Synthesis and structural characterization

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Abstract. Two mononuclear complexes namely $[\text{Ni}^{\text{II}}(\text{L})]$ (**1**) and $[\text{Co}^{\text{III}}(\text{L})](\text{NO}_3)$ (**2**) of a hexacoordinating N_4O_2 donor Schiff base ligand were synthesized and characterized by single crystal X-ray studies. In compound **2** the central cobalt is in +3 oxidation state while 'in' compound **2**, the nickel ion is in +2 oxidation state. The two complexes are isostructural with octahedral coordination environment exhibiting helical twist topology. They also display strong H-bonding as well as $\text{CH}-\pi$ interactions to generate 1D chain.

Keywords. Coordination chemistry; nickel(II); cobalt(III); Schiff base; twisted helicity; supramolecular interactions.

1. Introduction

Over the last few years, there has been an immense research interest among the chemists towards the investigations of biological properties of nickel that lead to several structural and biochemical models.^{1,2} Variable oxidation states coupled with multitude of coordination geometries are the most interesting aspects that have been identified in the active site of many Ni-containing enzymes.³ Several biomimetic Ni^{II} complexes have been found to act as structural and functional models of metalloenzymes,⁴ such as the Ni-Fe hydrogenase^{5–7} or the CO dehydrogenase/acetyl coenzyme-A synthase,^{8,9} etc.

The importance of helicates is related to the development and the understanding of self-assembly in supramolecular chemistry¹⁰ that are frequently perceived in biology and in physics.^{11,12} Intense research activities have been focused on this new field in order to explore and apply its power of design and control for the selective preparation of complicated organized chemical architectures. The fundamental research on helicates has recently led to a new fascinating metallosupramolecular architectures based on multicomponents self-assemblies such as directional light-converting devices,¹³ inorganic two-dimensional racks, ladders¹⁴ and grids,¹⁵ intertwined catenanes and knots,¹⁶ and allosteric ionophores.¹⁷ On the other hand, $\text{CH}-\pi$,¹⁸ $\pi-\pi$,¹⁹ cation- π ,²⁰ anion- π ,²¹ etc. interactions have been found to play crucial roles in molecular

recognition, molecular assembly, and crystal packing of organic materials, nanomaterials and biomolecules.²² In this context, the occurrence of $\text{CH}\cdots\pi$ interactions in solid-state networks has been extensively described,^{18,19} and their importance as stabilizing weak forces have been clearly illustrated in molecular structures.^{19–22}

Hence, in this work, an octahedral complex, with NiO_2N_4 chromophore has been investigated (figure 1) along with an isostructural Co^{III} complex of the same ligand (scheme 1).

Both $[\text{Ni}^{\text{II}}\text{L}]\cdot\text{H}_2\text{O}$ (**1**) and $[\text{Co}^{\text{III}}\text{L}]\cdot\text{NO}_3$ (**2**) complexes were prepared by reacting equimolar quantities of M^{II} and (H_2L) (scheme 1) in acetonitrile in presence of two equivalents of triethylamine (TEA) as a base. Here, we are going to discuss the syntheses and structural characterization of two new Ni^{II} and Co^{III} octahedral complexes that exhibit twisted helicity and H-bonding as well as $\text{CH}-\pi$ interactions to generate 1D chain.

2. Experimental

2.1 Materials

Chemicals such as 3-methoxy-salicylaldehyde (vanillin), N,N'-bis(3-aminopropyl)-ethylene-diamine (Aldrich), $\text{Co}(\text{NO}_3)_2$, $\text{Ni}(\text{NO}_3)_2$ and triethylamine (TEA) (Merck, India) are of reagent grade and used without further purification. Solvents like methanol, ethanol, acetonitrile (Merck, India) were of reagent grade and used as received.

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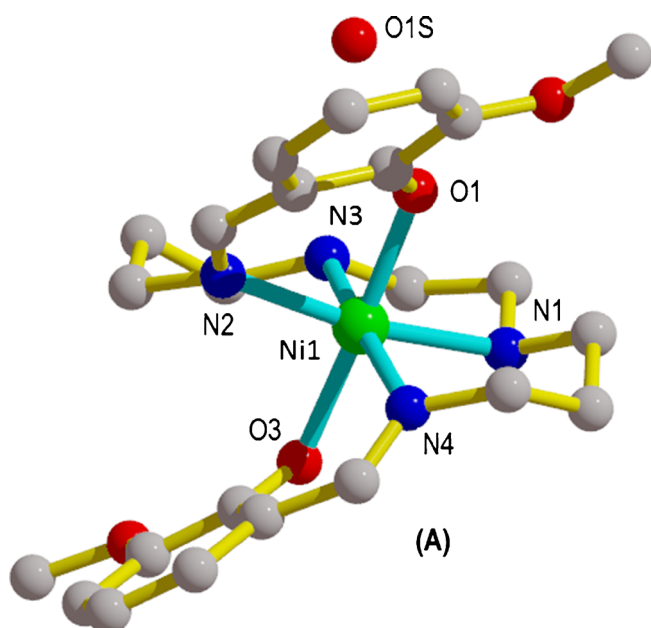
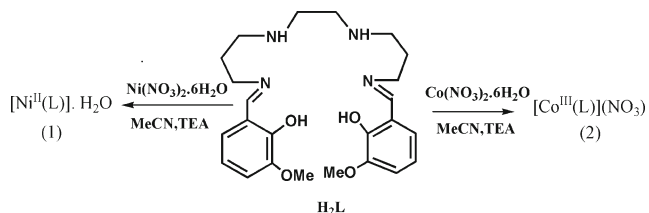


Figure 1. (a) Molecular view of complex **1**. All H-atoms are omitted for clarity. Symmetry code: a) x, y, z ; b) $-x, -y, 1/2+z$; c) $1/2-x, 1/2+y, 1/2+z$; d) $1/2+x, 1/2-y, z$.

2.1a Synthesis of ligand(H_2L): The Schiff base ligand was obtained by condensation of N,N'-bis(3-amino-propyl)ethylenediamine (1.74 g, 10 mmol.) and *o*-vanillin (3.04 g, 20 mmol.) in ethanol by stirring at 60°C for 4 hours, during which time a yellow solid separated out from the reaction mixture. The analytically pure solid was dried, and stored in vacuum over anhydrous $CaCl_2$ for subsequent use. Yield: 3.31 g (75%). Anal. Calcd. for $C_{24}H_{34}O_4N_4$ (MW = 442.55): C 65.13%, H 7.74%, N 12.65 %. Found: C 64.96%, H 7.75%, and N 12.42 %. 1H NMR (300 MHz, $CDCl_3$) (figure S1): δ 1.24 (s, 2H, imine*, not detectable precisely), 1.64–1.84 (m, 4H, methylene), 2.30–2.40 (d, 4H, methylene), 2.53–2.74 (d, 4H, methylene), 3.50–3.44 (d, 4H, methylene), 3.90 (s, 6H, methoxy), 6.88–7.28 (d, 2H, H4), (m, 6H, aromatic), 8.28 (s, 2H, azomethine), 13.3125 (s, 2H, phenoxo-OH).



Scheme 1. Schematic representation of formation of complexes.

2.1b Synthesis of $[Ni(L)](H_2O)(1)$: It was prepared by adding ligand (H_2L) (0.442 g, 1.0 mmol.) to a stirring acetonitrile solution (30 mL) of $Ni(NO_3)_2 \cdot 6H_2O$ (0.291 g, 1.0 mmol) to give a pale yellow solution, after a while a solution of TEA (0.202 g, 2.0 mmol) was added for the deprotonation of ligand which resulted in a brown solution. It was stirred for additional 20 m and filtered and then kept aside undisturbed for slow evaporation. After 3 days, the orange rectangular block-shaped crystals suitable for X-ray diffraction were formed. Yield: 2.83 g (55%). Anal. Calcd. for $C_{24}H_{34}N_4NiO_5$: C 55.72%, H 6.63%, N 10.83%. Found: C 55.96%, H 7.05%, and N 10.42 %.

2.1c Synthesis of $[Co(L)](NO_3)(2)$: It was prepared in the same way as for $[Ni(L)](H_2O)$ with the exception that $Co(NO_3)_2 \cdot 6H_2O$ (0.293 g, 1.0 mmol) was taken instead of $Ni(NO_3)_2 \cdot 6H_2O$. In 3 days, the dark brown block-shaped crystals suitable for X-ray diffraction were formed. Yield: 4.37 g (78%). Anal. Calcd. for $C_{24}H_{32}CoN_5O_7$: C 51.33%, H 5.74%, N 12.47 %. Found: C 50.96%, H 5.75%, and N 12.49 %.

2.2 Physical measurements

Elemental analyses were carried out using a Perkin-Elmer 240 elemental analyzer. 1H NMR spectrum was recorded on a Bruker 300 MHz NMR spectrometer using trimethylsilane as an internal standard in $CDCl_3$. Electronic spectra were recorded from Agilent 8453 UV-vis diode-array spectrophotometer.

2.3 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 ($\lambda = 0.71073 \text{ \AA}$). Data collection, reduction, structure solution, and refinement were performed using the Bruker APEX-II suite (v2.0-2) program. All available reflections to $2\theta_{\max}$ were harvested and corrected for Lorentz and polarization factors with Bruker SAINT plus. Reflections were then corrected for absorption, inter frame scaling, and other systematic errors with SADABS.²³ The structures were solved by the direct methods and refined by means of full matrix least-square technique based on F^2 with SHELX-97 software package.²⁴ All the non-hydrogen atoms were refined with anisotropic thermal parameters. All the hydrogen atoms belonging to carbon and nitrogen atoms were placed in their geometrically idealized positions, while hydrogen atoms on oxygen atoms

of non-coordinated water was found on the difference Fourier map, and all of them were constrained to ride on their parent atoms. Drawings of molecules were generated with the program DIAMOND-3.0 and PLATON-1.16. The crystallographic data for **1** and **2** are given in table 1.

3. Results and Discussion

Synthesis $[\text{Ni}^{\text{II}}(\text{L})]\cdot\text{H}_2\text{O}$ and $[\text{Co}^{\text{III}}(\text{L})](\text{NO}_3)$ complexes were prepared by reacting the respective (Ni^{II} and Co^{II}) metal ions with 1 equivalent of hexacoordinating ligand H_2L in presence of 2 equivalents of TEA in acetonitrile. It was interesting to note that Co^{II} ion is oxidized to Co^{III} in presence of hard-donor (N_4O_2) atoms probably by the atmospheric oxygen as evidenced from the charge balance of the formed complex and also by BVS calculations (*vide infra*).

3.1 Structural description

The structure of $[\text{Ni}(\text{L})](\text{H}_2\text{O})(\mathbf{1})$ is shown in figure 1. The complex **1** crystallizes in a *orthorhombic* space group *Pna*21. The coordination sphere of the hexacoordinated Ni^{II} metal centre is surrounded by N_4O_2 atoms of the Schiff base ligand (H_2L). The four N

atoms (namely N1, N2, N3 and N4) from the N,N'-bis(3-amino-propyl)ethylenediamine part of the ligand are coordinated to nickel(II) centre and the two O atoms (O1 and O3) from the phenolic $-\text{OH}$ groups of the two *o*-vanillin moieties of ligand, coordinate axially to the metal centre thereby forming a complete octahedral geometry. The Ni-N bond distances are in the range 2.020–2.096 Å and Ni-O bond distances 2.038–2.040 Å. All the bond distances are found to be almost identical. Bond distances and bond angles are listed in table 2a.

The structure of $[\text{Co}(\text{L})](\text{NO}_3)$ (**2**) is shown in figure 2. The complex **2** crystallizes in a *orthorhombic* space group *Pccn*. The coordination environment around the Co^{III} metal centre is same as that of complex **1**. The four N atoms (N1 and N2 and their symmetry related counter parts) from the N,N'-bis(3-aminopropyl)ethylenediamine part of the ligand coordinate to Co1 to form the square plane and two O atoms (O2 and its symmetry related counter part) from the phenolic $-\text{OH}$ groups of two *o*-vanillin moieties, occupy the axial positions giving an octahedral geometry. The Co-N bond distances are in the range 1.933–1.976 Å while Co-O bond distances are almost equal (~ 1.890 Å). The shorter axial Co-O bond length than the equatorial Co-N bond length is in conformity with the results observed previously in cobalt(III) complexes of comparable ligand environment²⁵ (table 2b).

Table 1. Crystallographic data and details of the structure determination for **1–2**.

	1 (CCDC No.-894740)	2 (CCDC No.-894739)
Formula	$\text{C}_{24}\text{H}_{32}\text{N}_4\text{NiO}_4\cdot\text{H}_2\text{O}$	$\text{C}_{24}\text{H}_{32}\text{CoN}_4\text{O}_4\cdot\text{N O}_3$
FW	517.24	561.48
Crystal System	Orthorhombic	Orthorhombic
Space group	<i>Pna</i> 21 (No. 33)	<i>Pccn</i> (No. 56)
<i>a</i> /Å	37.5238(12)	7.4561(3)
<i>b</i> /Å	7.5017(2)	18.4285(6)
<i>c</i> /Å	8.6868(3)	19.1192(7)
α /°, β /°, γ /°	90	90
<i>V</i> /Å ³	2445.27(13)	2627.07(17)
<i>Z</i>	4	4
ρ_{calc} /g cm ^{−3}	1.405	1.420
$\mu(\text{Mo-K}\alpha)$ /mm ^{−1}	0.836	0.705
<i>F</i> (000)	1096	1176
Theta Min-Max [°]	1.1, 32.6	2.1, 27.1
Index ranges	−56: 56 ; −11: 11 ; −13: 13	−9: 9 ; −23: 23 ; −24: 24
Reflection collected	35271	20284
Independent reflections (<i>R</i> _{int})	7937 (0.038)	2908 (0.026)
No. Of Parameter	361	174
GOF	1.11	1.026
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)]	0.0509 ((6648)	0.0355 (2261)
w <i>R</i> ₂ (all data)	0.1012	0.0979
Min. and Max. Resd. Dens./e Å ^{−3}	−0.93, 0.38	−0.27, 0.30

Table 2. Summary of bond distances and bond angles of complexes **1** and **2**.

(i) Complex 1 .			
Bond lengths (Å)		Bond angles (°)	
Ni1- N1	2.020(10)	N1- Ni1- N4	88.56(9)
Ni1- N4	2.057(3)	N1- Ni1- O3	93.19(8)
Ni1- O3	2.073(2)	N4- Ni1- O3	84.15(8)
Ni1- O1	2.0819(17)	N1- Ni1- O1	90.04(8)
Ni1- N3	2.116(3)	N4- Ni1- O1	92.17(8)
Ni1- N2	2.066(2)	O3- Ni1- O1	175.04(7)
Bond angles (°)			
N1- Ni1- N2	169.91(10)	N1- Ni1- N3	83.57(10)
N4- Ni1- N2	88.56(9)	N4- Ni1- N3	169.05(10)
O3- Ni1- N2	92.83(8)	O3- Ni1- N3	88.69(9)
O1- Ni1- N2	84.53(8)	O1- Ni1- N3	95.42(9)
		N3- Ni1- N2	88.47(10)
(ii) Complex 2 .			
Bond lengths (Å)		Bond angles (°)	
Co1- O2	1.8901(12)	O2a- Co1- N1a	89.55(5)
Co1- O2a	1.8901(12)	N1- Co1- N1a	93.61(6)
Co1- N1	1.9332(15)	O2- Co1- N2	85.90(6)
Co1- N1a	1.9332(15)	O2- Co1- N2a	89.95(6)
Co1- N2	1.9742(15)	N1- Co1- N2a	90.12(6)
Co1- N2a	1.9742(15)	N1- Co1- N2	174.32(6)
Bond angles (°)			
O2- Co1- O2a	174.30(5)	O2a- Co1- N2	89.95(6)
O2- Co1- N1	89.55(5)	O2a- Co1- N2a	85.90(6)
O2- Co1- N1a	94.36(5)	N1- Co1- N2a	90.12(6)
O2a- Co1- N1	94.36(5)	N1a- Co1- N2a	174.32(6)
		N2- Co1- N2a	86.49(6)

Symmetry code: a = 1/2-x, 1/2-y, z.

Space-filling representation of [Ni(L)] and [Co(L)]⁺ clearly demonstrates mononuclear single-stranded helical structures for both the complexes figures S2 and S3. It is generally accepted that a central metal ion

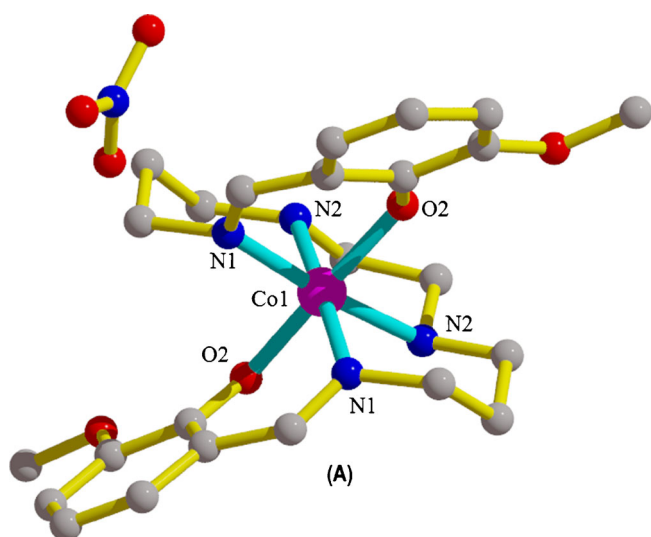


Figure 2. (a) Molecular view of complex **2**. All H-atoms are omitted for clarity. Symmetry code: a) x,y,z; b) 1/2+x, -y, 1/2-z; c) -x, 1/2+y, 1/2-z; d) 1/2-x, 1/2-y, z; e) -x, -y, -z; f) 1/2-x, y, 1/2+z; g) x, 1/2-y, 1/2+z; h) 1/2+x, 1/2+y, -z.

which is too small to fit into the cavity of the bound multidentate ligand may generate such topology. Steric interactions between the extremities of the strand induce a slight twisting of the ligand, reminiscent of that found in organic helicenes.²⁶ Several acyclic polyglycols and linear podands wrap around group I and II metals²⁷ as exemplified by the carbocyclic antibiotic monensin which gives the mononuclear single-stranded helical complex.²⁸ Here the helical twist is favoured by the attachment of rigid and bulky terminal aromatic groups (*o*-vanillin) to comparatively flexible central N,N'-bis(3-aminopropyl)ethylenediamine moiety. The angles between the two planes constructed from two *o*-vanillin moieties is found to be 30.92° and 36.06° for complexes **1** and **2**, respectively which clearly demonstrate the fact of helical twisting observed in **1** and **2**.

In case of complex **1** there is one non-coordinated water molecule (O1S) that is involved in four-ways H-bonding interactions namely, N1-H1...O1S, N3-H45...O1S, O1S-H55...O1 and O1S-H40...O3. It forms two H-bonds with two amine nitrogen atoms N1, N3 and with two phenolate oxygen atoms (O1 and O3) belonging to two neighbouring complexes on either sides (figure 3a). Spiral binding of complex **1** through H-bonding is shown in figure 3b. In cobalt(III) complex

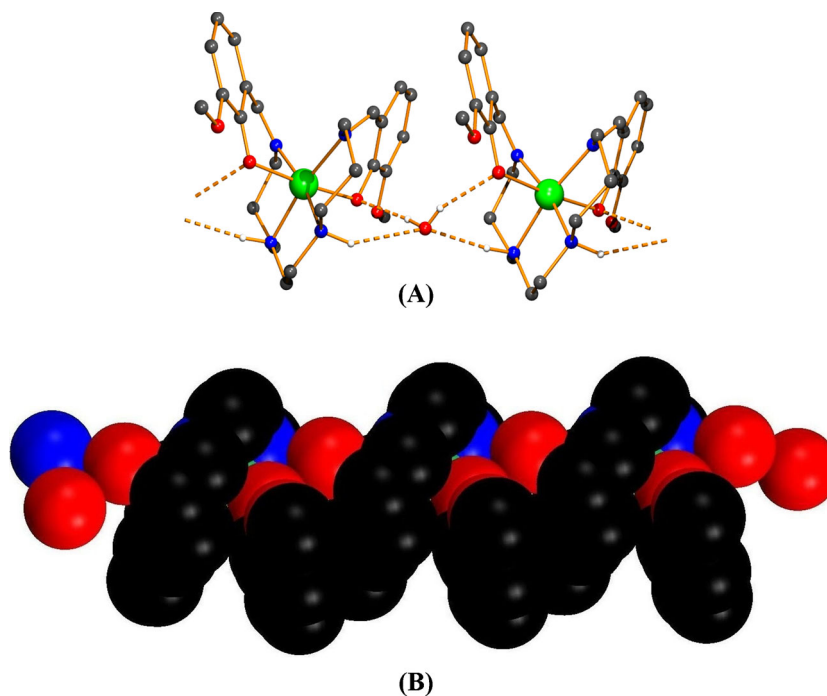


Figure 3. (a) The quasi 1D chain through bifurcated H-bonding interaction in complex **1**. (b) Space-filling model showing Spiral binding of complex **1** through H-bonding. N1-H1...O1S: H1...O1S = 2.11(4) Å, N1-H1 = 0.92(4) Å, N1...O1S = 3.022(4) Å, \angle N1-H1...O1S = 173(3)°; O1S-H40...O3: H40...O3 = 2.11(3) Å, O1S-H40 = 0.78(3) Å, O1S...O3 = 2.848(4) Å, \angle O1S-H40...O3 = 160(3)°; N3-H45...O1S: H45...O1S = 2.45(4) Å, N3-H45 = 0.98(4) Å, N3...O1S = 3.323(4) Å, \angle N3-H45...O1S = 148(3)°; O1S-H55...O1: H55...O1 = 1.97(4) Å, O1S-H55 = 0.87(4) Å, O1S...O1 = 2.817(3) Å, \angle O1S-H55...O1 = 2.817(3)°.

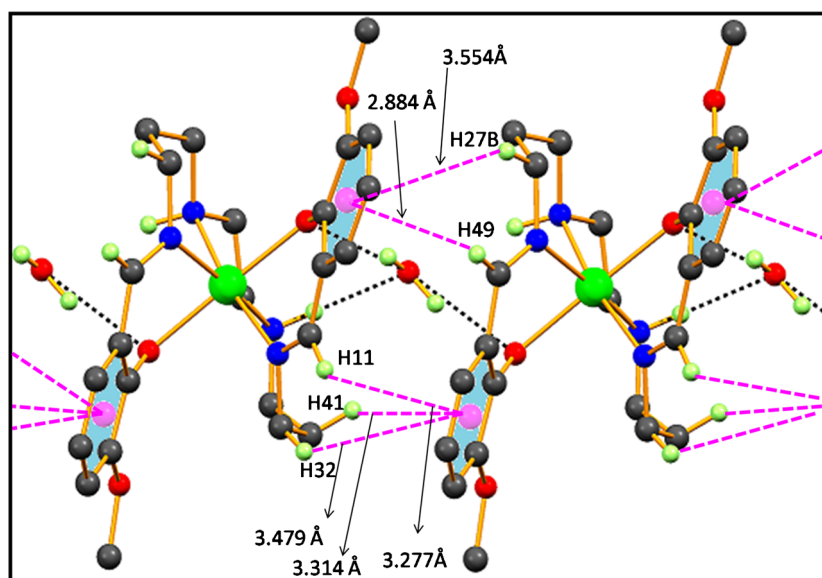


Figure 4. The one dimensional CH...pi(phenyl) interactions (dotted lines in magenta colors) and supramolecular H-bonding (dotted lines in black colors) are observed in complex **1**.

Table 3. C-H... π Interaction for Complexes **1** and **2**.

interaction	atoms	distances H...Cg (Å)	\angle C-H...Cg (°)	distances C(H)...Cg(Å)
Complex 1				
C-H... π (phenyl)	C(26)-H(49)...Cg (1)	2.884	132.55	3.582
C-H... π (phenyl)	C(27)-H(27B)...Cg(1)	3.554	134.83	4.294
C-H... π (phenyl)	C(11)-H(11)...Cg(2)	3.277	108.44	3.679
C-H... π (phenyl)	C(29)-H(32)...Cg(2)	3.479	118.01	3.999
C-H... π (phenyl)	C(30)-H(41)...Cg(2)	3.314	131.19	4.040
Complex 2				
C-H... π (phenyl)	C(10)-H(10B)...Cg(3)	3.441	100.65	3.744
C-H... π (phenyl)	C(9)-H(9A)...Cg(3)	3.265	129.49	3.953

Cg (1) = C15 C14 C100 C13 C12 C17 and Cg (2) = C18 C19 C20 C21 C1 C2 denotes for complex **1**, Cg (3) = C3 C13 C4 C5 C6 C7 denotes for complex **2**.

2, there is strong H-bonding interaction between H atom on N2 (imine nitrogen) and O3 (non-coordinated NO₃⁻) atom and extended in 1D fashion. Details of H-bonding interactions are shown in figure **3** for **1** figure **S4** for **2**.

On the other hand, the packing of the molecules in both complexes **1** and **2** is controlled by CH... π as well as by H-bonding interactions between two neighboring complex units to give compact 1D supramolecular architectures. In complex **1**, five types of CH... π (phenyl) interactions are prevalent (figure **4**). Among them, three CH... π interactions are established between two methylenic and one azomethine H-atoms of one complex with the centroid of the phenyl ring of its neighboring complex. Similarly, two CH... π interactions are established between one methylenic and one azomethine H atoms and the centroid of the phenyl ring of other complex. These two centroids belong to two different neighboring complexes. These CH... π interactions fall in the range 2.884 – 3.554 Å. Details of CH... π interactions are given in table **3**. In complex **2**, only two types of CH-pi interactions are present (figure **S5**), they are established between methylenic H atoms (H10B and H9A) and neighboring phenyl ring of Schiff base with distances 3.441 Å and 3.265 Å.

3.2 UV-vis spectra of complexes **1** and **2**

The electronic spectra of complexes **1** and **2** were recorded in MeCN (figure **5**). The electronic transition appears at ~373 nm with molar extinction coefficients (ϵ) 3280 dm³ mol⁻¹ cm⁻¹ for complex **1**. In case of complex **2** there are two electronic transitions that appear at 633 and 402 nm with ϵ values 392 and 7540 dm³ mol⁻¹ cm⁻¹, respectively. The bands at longer wavelengths may be attributed to the d-d transitions for complex **2** (633 nm) but no d-d transition

is observed in complex **1**. The bands at shorter wavelengths (373 and 402 nm) are due to ligand to metal (L→M) charge-transfer transitions.

3.3 BVS calculation

Bond valence sum (BVS) method is very frequently used to examine the nature of coordination and oxidation state of the central metal atom using the crystallographic data in coordination complexes as well as in many biological molecules. The most successfully used empirical equation is:

$$\sum s_{ij} = \sum \exp(r_o - r_{ij})/0.37$$

Where r_o is a parameter characteristic of the bond and r_{ij} is the crystallographically obtained bond distances.

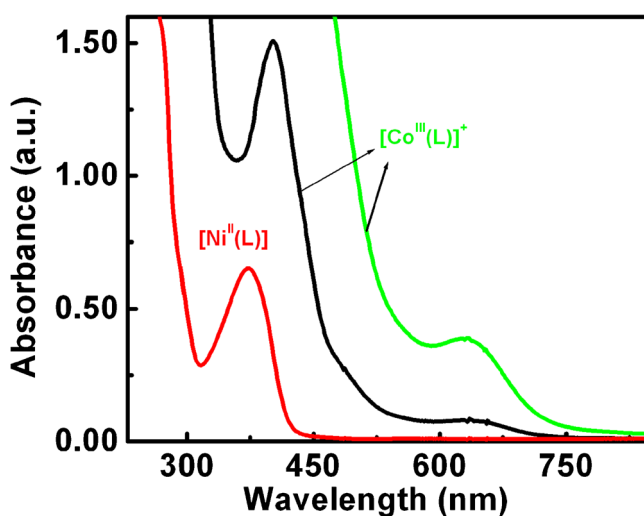


Figure 5. UV-vis spectra of complexes **1** and **2** in MeCN. [c] = 1.0 × 10⁻³ M for d-d bands at longer wavelengths (633 nm, green line) for complex **2** and [c] = 1.0 × 10⁻⁵ M for LMCT bands at shorter wavelengths (373 nm, red line for **1** and 402 nm, black line for **2**).

Σs_{ij} represents the charge on the central metal atom. BVS values¹³ are: Ni^{II}-O = 1.670 Å, Ni^{II}-N = 1.647 Å. The BVS of Ni was calculated to be 2.07 (table S1a) which unequivocally establishes the +2 oxidation state of the central Ni atom in complex **1**. Similarly BVS values are: Co^{III}-O = 1.79 Å, Co^{III}-N = 1.68 Å^{29,30} and calculated BVS value of Co is 3.35 (table S1b) which again establishes the +3 oxidation state for the central cobalt atom in complex **2**.

4. Conclusion

In conclusion, two mononuclear complexes of a hexacoordinating Schiff base ligand with N₄O₂ donor atoms have showed helical twist topology. Both complexes exhibit strong H-bonding and CH $\cdots\pi$ (phenyl) interactions that fall in the range 2.884–3.554 Å for complex **1** and 3.265–3.441 Å for **2** to generate 1D chain. The bond valence sum (BVS) calculations clearly indicate that Co is in +3 oxidation state in complex **2** while Ni is in +2 oxidation state in **1**.

Supplementary Information

The electronic Supplementary Information can be seen at www.ias.ac.in/chemsci.

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