



REGULAR ARTICLE

# Synthesis, structure and solid-state electrical conductivity of bis(1,2-diphenylethylene-1,2-dithiolate)nickel(II)

ARGHYA DUTTA<sup>a</sup>, ARNAB CHATTERJEE<sup>a</sup>, KISHALAY BHAR<sup>b</sup>, ANINDITA BANERJEE<sup>c</sup> and RAJARSHI GHOSH<sup>a,\*</sup>

<sup>a</sup>Department of Chemistry, The University of Burdwan, Burdwan 713 104, West Bengal, India

<sup>b</sup>Department of Chemistry, School of Chemical Science and Pharmacy, Bandar Sindri 305 817, Rajasthan, India

<sup>c</sup>Department of Physics, The University of Burdwan, Burdwan 713 104, West Bengal, India

E-mail: rghosh@chem.buruniv.ac.in

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**Abstract.** One nickel(II)-dithiolene complex bis(1,2-diphenylethylene-1,2-dithiolate)nickel(II) has been synthesized and crystallographically characterized. The complex is square planar at its metal centre. The compound in its solid-state is found to conduct electricity at room temperature. Variation of conduction is also found on raising the temperature. Instead of a metal...metal orbital overlap, the electron density is expected here to pass through some other covalent and electrostatic bonds of the compound in solid-state resulting in electricity conduction.

**Keywords.** Ni(II) dithiolene complex; synthesis; X-ray structure; electricity conduction.

## 1. Introduction

Interest on metal dithiolene complexes has its root in the last few decades of the last century.<sup>1–3</sup> Early literature on this type of metal complexes are concerned particularly on the synthesis, structure and reactivity.<sup>1–3</sup> Later on, these were found to have its application in biology<sup>4,5</sup> and more importantly in material science.<sup>6–10</sup> In the latter area dithiolene complexes were found to be conducting,<sup>6,7</sup> catalytic,<sup>8</sup> non-linear optical,<sup>9</sup> near IR absorbing,<sup>10</sup> etc. The high electrical conductivity by pure metals is due to its enough overlap of atomic orbitals to produce the conduction path. In the case of molecular materials, the overlap of molecular orbitals is not sufficient enough for good electrical conductivity. Columnar stacking of molecules with larger atoms like chalcogens which makes the assembly well-packed by making interaction with next molecules in solid-state is found to be good.<sup>11</sup> Here the conductivity depends on the bandgap between the HOMO-based valence band and LUMO-based conduction band. Ni(II)-dithiolene complexes being square planar in geometry and having sulphur as coordinating

atoms in the ligand backbone are good candidates to conduct electricity.<sup>6</sup> In this present report, with a little modification, we have synthesized a previously reported nickel(II)-dithiolene complex bis(1,2-diphenylethylene-1,2-dithiolate)nickel(II)(1) by Ma *et al.*,<sup>12</sup> and characterized it X-ray crystallographically. The compound was previously shown<sup>12</sup> to be near IR absorbing. In our endeavour, we have found that the complex also conducts electricity semiconducting in its solid-state.

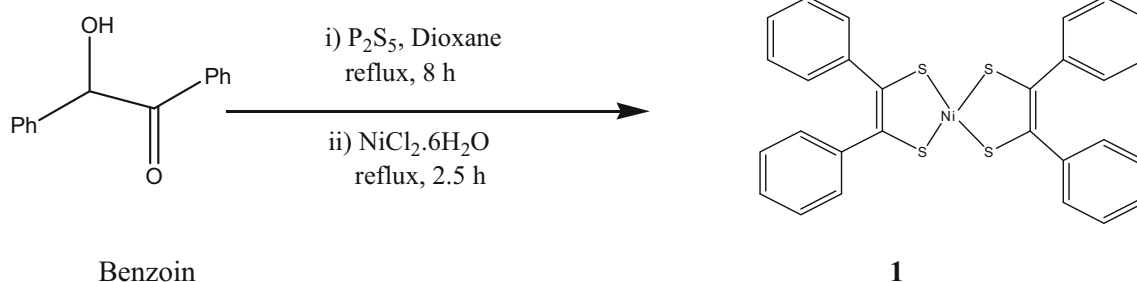
## 2. Experimental

### 2.1 Preparation of the complex 1

**2.1a Chemicals, solvents and starting materials:** High purity Benzoin (extra pure, 99%; SRL, India), phosphorus pentasulfide (99%; Sigma Aldrich, India), 1,4-dioxane (extra pure AR, 99.5%; SRL, India) and all other solvents were purchased from the respective companies and used as received. Solvents were dried according to standard procedure and distilled prior to use.

\*For correspondence

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**Scheme 1.** The synthesis of bis(1,2-diphenylethylene-1,2-dithiolate)nickel(II) (**1**).

**2.1b Synthesis of **1**:** **1** was synthesized (Scheme 1) using a reported method<sup>12</sup> with a little modification. Benzoin (4.24 g, 20 mmol) was refluxed with P<sub>2</sub>S<sub>5</sub> (8 g, 36 mmol) in 50 mL of dry dioxane for 8 h. During this period, the thiophosphoric ester of dithiobenzoin was formed. After 8 h of reflux, the hot reaction mixture was filtered to remove excess P<sub>2</sub>S<sub>5</sub> and a solution of NiCl<sub>2</sub>·6H<sub>2</sub>O (1.16 g, 4.9 mmol) in 8 mL of distilled water was added to it and refluxed for 2.5 h and cooled by ice-water bath for 18 h. A deep greenish crude complex was formed and collected by filtration, washed with a little amount of water, ether, alcohol and dioxane. It was then dried to give the crude complex. Purification was conducted by recrystallization from dichloromethane to afford greenish-black crystals. Yield: 1.30 g (12%). IR (KBr, cm<sup>-1</sup>): 1357, 1136, 1026, 880, 746, 696; UV-Vis (nm): 269, 314, 593.

## 2.2 Physical measurements

IR (KBr discs, 4000–500 cm<sup>-1</sup>) and UV-Vis spectra were recorded on Shimadzu IR Prestige spectrometer and Shimadzu UV-Vis 2450 spectrophotometer, respectively. Electrical conductivity was measured in the Keithley 2400 source meter. The molecular orbital calculation was done using the GAUSSIAN 05 software package.

## 2.3 X-ray diffraction

Single crystal X-ray crystallographic analysis of **1** was carried out on a Bruker SMART APEX II CCD diffractometer using Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ), Diffraction data were collected at 296 K and was identified as P 2<sub>1</sub>/n space group. Crystal data and refinement details are listed in Table 1. The structure was solved by direct methods, and the structure solution and refinement were based on  $|F|^2$ .

## 3. Results and Discussion

### 3.1 Synthesis and formulation

**1** was synthesized (Scheme 1) using a reported method<sup>12</sup> with a little modification. The reaction

mixture of benzoin and phosphorus pentasulphide after refluxing for eight hours was filtered to remove excess phosphorus pentasulphide. To this mixture aqueous solution of nickel(II) chloride hexahydrate was gradually added and this final mixture was further refluxed for some hours. In our method, the reaction time was to some extent reduced in comparison to reported literature.<sup>12</sup> After this, the mixture was ice-cooled and green coloured crystals were formed from this. This was recrystallized from dichloromethane to get good quality X-ray grade single crystals.

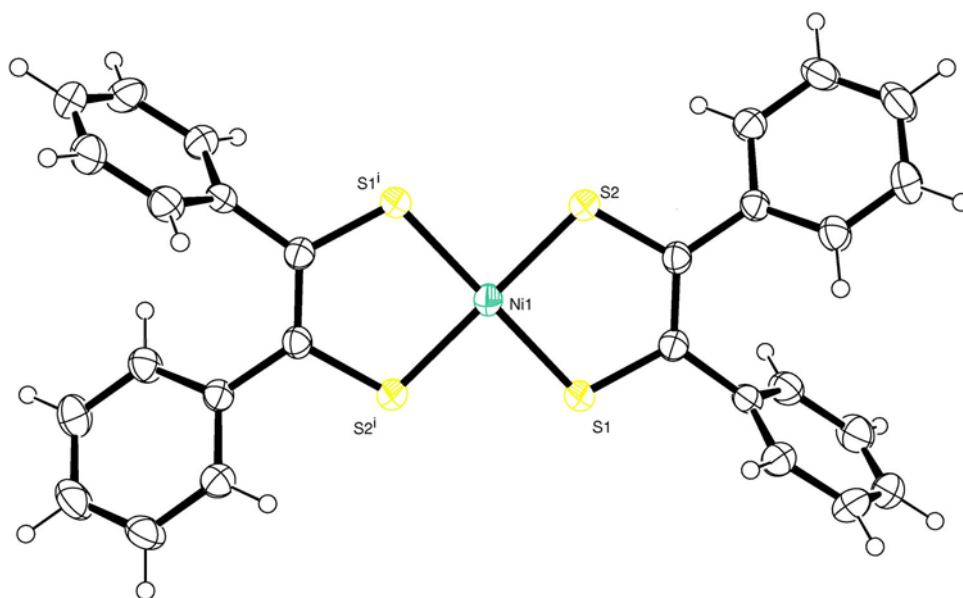
### 3.2 X-ray structure

Single crystal X-ray diffraction data (Table 1) were obtained for **1** to get its molecular structure (Figure 1). From bond angle bond distance data (Table 2) it can be found that Ni(II) is in square planar geometry. The four S-Ni-S bond angles are around 90° and the Ni-S bonds are of equal value (2.1187 Å).

The square planar molecules of **1** are stacked to each other *via* strong intermolecular C-H $\cdots$  $\pi$  interactions [C3-H3 $\cdots$ Cg(4): 2.84 Å, C3 $\cdots$ Cg(4): 3.650(6)Å, C3-H3 $\cdots$ Cg(4): 147°, symmetry code: 1 + x, y, z; Cg(4): C9-C10-C11-C12-C13-C14] and weak C-H $\cdots$ S hydrogen bonds [C14-H14 $\cdots$ S1: 3.185 Å, C14-H14 $\cdots$ S1: 108.80°, symmetry code: x - 1, y, z] forming 1D layer along crystallographic *a*-axis (Figure 2). The Ni $\cdots$ Ni separation is equal to the length of the *a*-axis 5.9428(4)Å. Each 1D layer is further stabilised through intramolecular C-H $\cdots$  $\pi$  interactions [C10-H10 $\cdots$ Cg(3): 2.92 Å, C10 $\cdots$ Cg(3): 3.557(6)Å, C10-H10 $\cdots$ Cg(3): 127°, symmetry code: x, y, z; Cg(3): C2-C3-C4-C5-C6-C7] and weak C-H $\cdots$ S hydrogen bonds [C14-H14 $\cdots$ S2: 2.731 Å, C14-H14 $\cdots$ S2: 102.37°] (Figure 2). These 1D layers are oriented in ABAB $\cdots$ fashion throughout the whole crystal lattice (Figure 3). The AA $\cdots$ /BB $\cdots$  layers are connected to each other through intermolecular  $\pi$ - $\pi$  stacking [Cg(4)-Cg(4) distance: 3.856(3)Å, dihedral angle: 0°,

**Table 1.** Crystal data and structure refinement parameters for **1**.

Parameters	<b>1</b>
Empirical formula	C <sub>28</sub> H <sub>20</sub> S <sub>4</sub> Ni
Formula weight	543.39
Temperature (K)	296(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P 2 <sub>1</sub> /n
a (Å)	5.9428(4)
b (Å)	11.0892(8)
c (Å)	18.5997(14)
V (Å <sup>3</sup> )	1224.63(15)
Z	2
D <sub>calc</sub> [g/cc]	1.474
F(000)	560.0
θ range for data collection (°)	3.558 to 24.985
Reflections collected	16932
h/k/l	– 7/7, – 13/13, – 22/22
Independent reflections [R(int) = 0.0745]	2130
Completeness to θ	99.7%
Goodness-of-fit on F <sup>2</sup>	1.177
Final R indices [I > 2σ(I)]	R <sub>1</sub> = 0.0493, wR <sub>2</sub> = 0.1528;
R indices (all data)	R <sub>1</sub> = 0.0643, wR <sub>2</sub> = 0.1617;
Largest diff. peak and hole (e Å <sup>-3</sup> )	1.006 and – 0.665

**Figure 1.** ORTEP of **1** with 40% ellipsoid probability.

slippage: 0.967 Å, symmetry code:  $-1 - x, 1 - y, 1 - z$ ] while AB... layers are involved in intermolecular C-H... $\pi$  interactions [C11-H11...Cg(3): 2.79 Å, C11...Cg(3): 3.717(5)Å, C11-H11...Cg(3): 172°, symmetry code:  $-1/2 - x, 1/2 + y, 1/2 - z$ ] as shown in Figure 4.

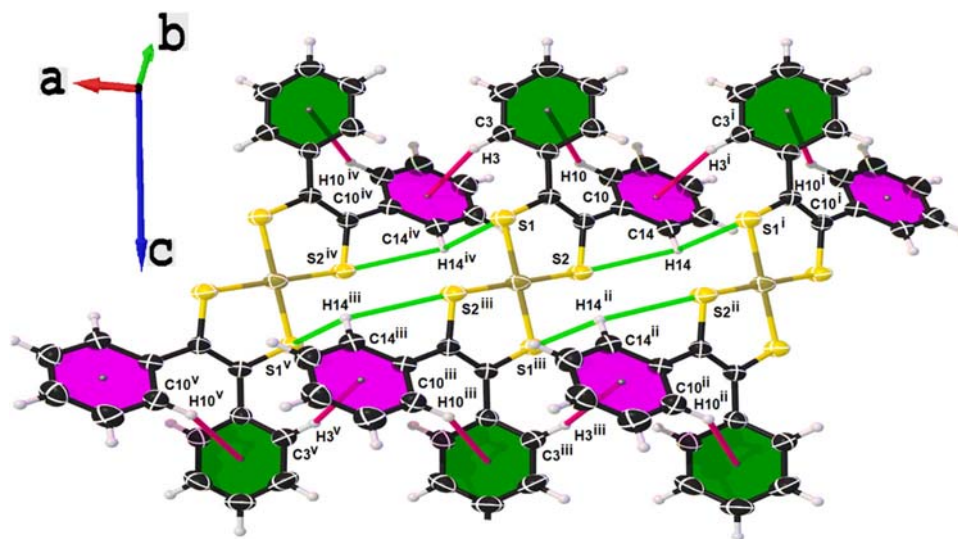
### 3.3 Electrical conductivity of **1** and MO calculation

On the application of electrical potential **1** (with sample pellet thickness 0.08 cm and diameter 1.3 cm) was found to conduct electricity ( $9.47 \times 10^{-6} \text{ Scm}^{-1}$

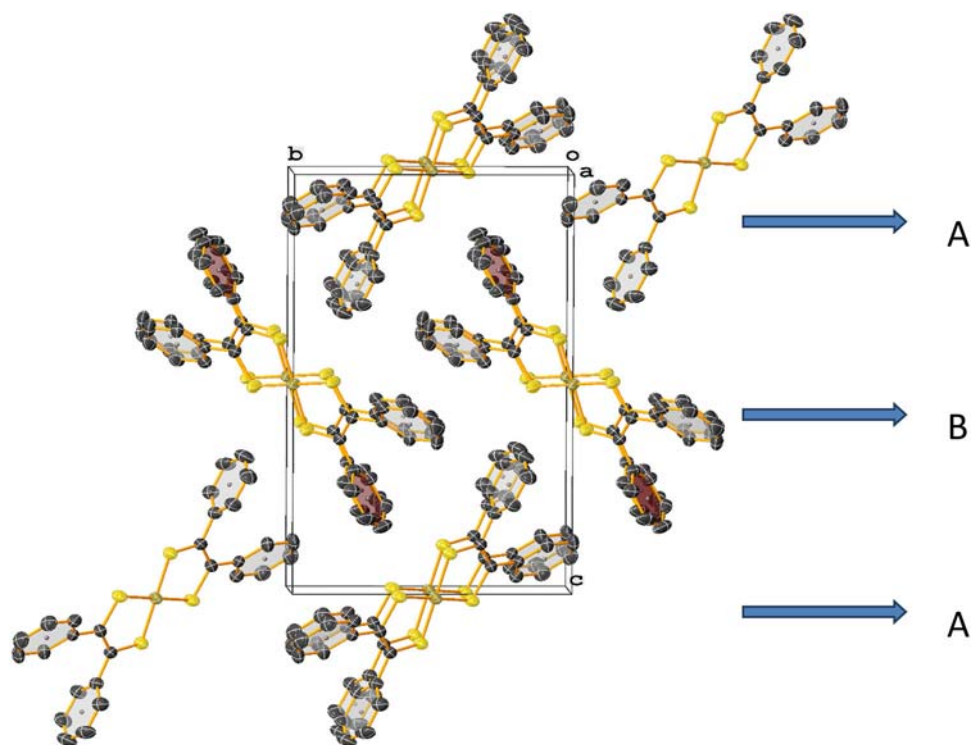
**Table 2.** Bond angle-bond distance parameter for 1.

Bond angles		Bond distances	
S(1)-Ni(1)-S(2)	91.04(4)°	Ni(1)-S(1)	2.1187(11)Å
S(2)-Ni(1)-S(2)	180.0°	Ni(1)-S(2)	2.1187(11)Å

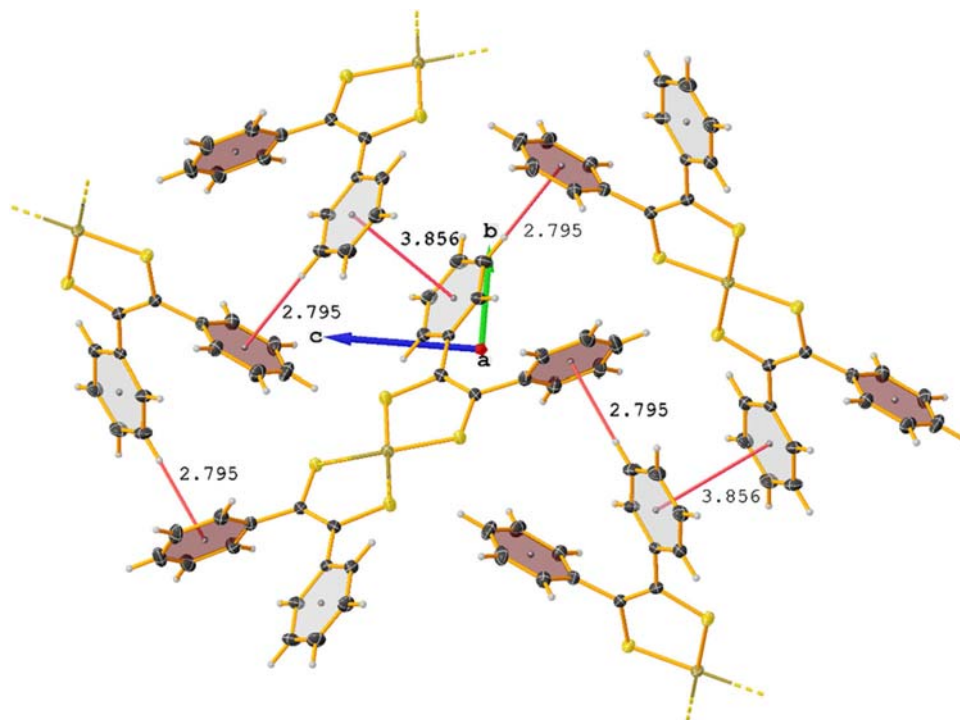
at 288 K) in solid-state. The electrical current-voltage plot (Figure 5) reveals that the current was of Ohmic type. Interestingly, on varying temperature and keeping the voltage in between  $-5$  to  $+5$  V (by using Keithley 2400 source meter) the molecules behave like semiconducting materials (Figure 6). The conductivity



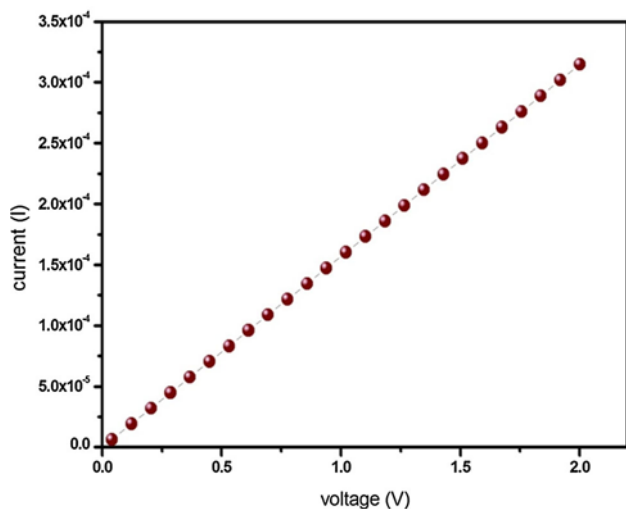
**Figure 2.** A view of 1D layer structure (A or B) along crystallographic  $a$ -axis involving intra- and intermolecular C-H $\cdots$  $\pi$  interactions (pink line) and weak C-H $\cdots$ S hydrogen bonds (green line). [pink plane: Cg(4): C9-C10-C11-C12-C13-C14 and green plane: Cg(3): C2-C3-C4-C5-C6-C7].



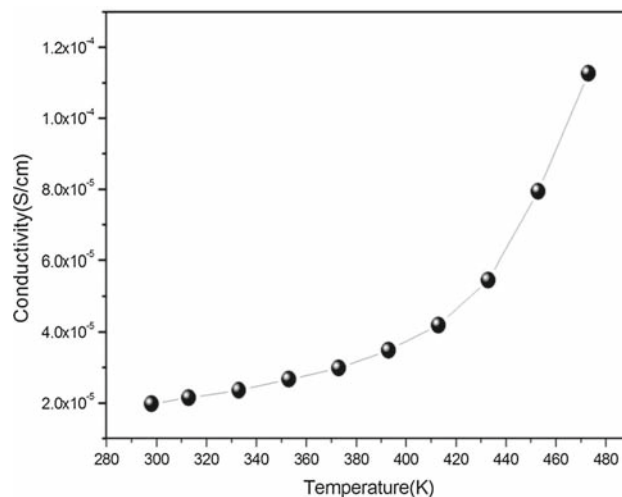
**Figure 3.** A view of ABAB... the orientation of 1D layer structures in the crystal lattice.



**Figure 4.** Intermolecular  $\pi$ - $\pi$  stacking and C-H... $\pi$  interactions connecting A and B layers.



**Figure 5.** Electrical current vs voltage plot of **1**.



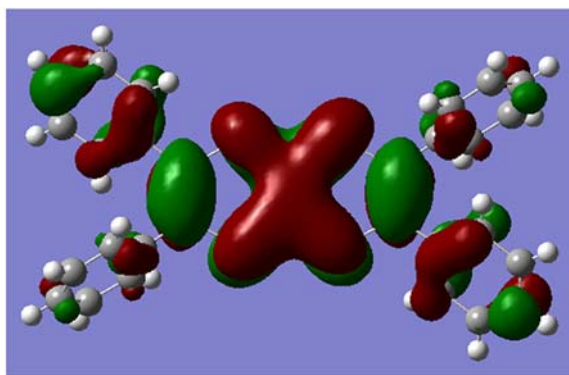
**Figure 6.** Conductivity at  $-5$  to  $+5$  V with varying temperature.

varies from  $1.96 \times 10^{-5} \text{ S cm}^{-1}$  (298 K) to  $1.12 \times 10^{-4} \text{ S cm}^{-1}$  (470 K).

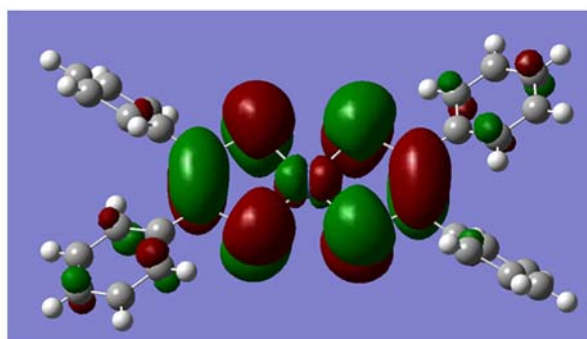
Molecular Orbital calculation (using the B3LYP level and 6-31G basis set of GAUSSIAN 05 software package) shows that the nickel centre is rich in electron density (Figure 7(i)) and it may be assumed that this centre is responsible for electron passage to show the electrical conductivity. The LUMO of the molecule is found to be ligand centric (Figure 7(ii)).

In most of the square planar well-stacked platinum complexes, the reason for electrical conductivity is well understood.<sup>13</sup> The close proximity of Pt...Pt centres in their complexes is suggestive of sufficient overlap between  $d_{z^2}$  orbitals which forms the path to conduct electrons resulting electrical current.<sup>13</sup> Few square planar Ni(II)-dithiolene complexes (Ni being the element in the same group of the periodic table (Group 10) with Pt) are there in literature which are found to conduct electricity.<sup>6</sup> But to the best of our





(i)



(ii)

**Figure 7.** (i) HOMO (metal centric) and (ii) LUMO (ligand centric) diagram.

effort, no report was found explaining the mechanism of this electrical conduction. In our case, the sufficiently long Ni...Ni distance (5.9428(4)Å) is not favorable to suppose any orbital overlap between the metal centres. Despite, the reason for electrical conduction may be thought of as the passage of electron density from one Ni(II) centre to next Ni(II) centre through the ligand covalent and electrostatic bonds (through Ni1 to S2 to H14 to S1<sup>i</sup> to next Ni centre, Figure 2). Travelling of electron density through several atoms (hence facing higher resistance) may be the reason for lower conductivity value of **1** in comparison to some other reports.<sup>6</sup>

#### 4. Conclusions

In conclusion, it may be stated that the Ni(II)-dithiolene complex (**1**) was synthesized using little modification of the previously reported method<sup>12</sup> and X-ray crystallographically characterized. The compound, as like other Ni(II)-dithiolene compounds,<sup>6</sup> are conducting electricity at room temperature in solid-state. On raising the temperature, the compound is found to behave like a semiconductor. The mechanism of this

electrical conduction is tried to be understood from the molecular orbital calculations and solid-state packing diagrams. Considering all these, **1** may be a good addition to the coordination molecules which shows electrical conductivity in solid-state.

#### Supplementary Information (SI)

Supplementary figures S1–S2 are available at [www.ias.ac.in/chemsci](http://www.ias.ac.in/chemsci).

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