

Synthesis and Characterization of Novel Nickel Complexes Containing Tetrathiafulvalene Units

Daocheng Xia^{*1,2}, Wancheng Li³, Zhaoqi Fan², Daopeng Xia⁴, Yuchun Chang³, Lifeng Liu⁵, Chuanhui Cheng², Shukun Yu³, Qinglong Bai², Xu Wang⁶ and Guotong Du^{1,2}

¹College of Chemistry, Yuncheng University, Shanxi, Yuncheng, 044000, China; ²State Key Laboratory of Materials Modification by Laser, Ion and Electron Beams, Dalian University of Technology, Dalian 116023, China; ³State Key Laboratory on Integrated Optoelectronics, Jilin University, Changchun 130012, China; ⁴Yongji Experimental Second Middle School, Jilin, Yongji, 132200, China; ⁵Yongji Fourth Middle School, Jilin, Yongji, 132200, China; ⁶State Key Laboratory for Supramolecular Structure and Materials, Jilin University, Changchun 130012, China

Abstract: The synthesis, structure and electrical properties of two novel nickel complexes containing tetrathiafulvalene units were reported. These complexes were purified and isolated with chromatographic separation. Their structures were characterized by Elemental Analysis (EA), ICP-AES, IR, ¹H NMR and UV/Vis spectra. Their electrochemical properties were studied by cyclic voltammetry in DMF solution, and electrical conductivities of the complexes were measured. The electrical properties indicate that these novel nickel complexes are semiconductors.

Keywords: Synthesis, cyclic voltammetry, semiconductor.

1. INTRODUCTION

Tetrathiafulvalene (TTF) and its analogues were prepared as strong electron -donor compounds for the development of electrically conducting materials [1]. While, the first organic molecule based superconductor was prepared from TTF analogue which was called tetramethyltetraselenafulvalene (TMTSF) in 1979. The topics of organic metals complexes have been reviewed by many authors over the decades [2, 3].

The strategies for direct coordination of transition metal ions to the core of TTF derivatives had been developed. The two main methods involve either covalent attachment of appropriate metal ion binding groups such as pyridine, phosphine or crown ether groups or the formation of dithiolate coordination compounds with peripheral sulfur atoms [4-12].

Metal-bisdithiolates are often used as building blocks for conductors either acting as simply as counter-anions. Ferrocene [(Cp₂Fe)ⁿ⁺] and (Bu₄N)ⁿ⁺ are frequently used as counter-cations in TTFs [13, 14]. The synthesis and electrical characterization of the novel nickel coordination compounds with (Cp₂Fe)ⁿ⁺ and (Bu₄N)ⁿ⁺ radical cations were presented in this article.

2. EXPERIMENTAL

2.1. Instruments and Materials

2.1.1. Instruments

Melting points were obtained on a Gallenkamp apparatus. IR was measured by Nicolet 10DX-FT IR spectrometer

(NIGAOLY, USA), KBr (pellet). High-resolution ¹H NMR spectrometer was recorded on a Bruker AV 500 spectrometer unless otherwise stated. UV/Vis was recording Spectrophotometer (SHIMADZU, Japan). Mass was measured by Kratos MALDI-TOF mass spectrometer (SHIMADZU, Japan). Elemental analyses were performed on a Flash EA1112 Elemental Analyzer (Thermo Quest, Italy) PHMK and ICP-AES/1000 (PERKIN ELMER, USA). The solution redox properties of the compounds were investigated by cyclic voltammetry (CV). The electrical conductivity was measured by the four-probe method.

2.1.2. Materials

Methanol (99.5%), ethanol (99.7%), CH₂Cl₂ (99.9%), MgSO₄ (99%), Bu₄NBr (99%). Other chemicals and analytical solutions were purchased from market and without further purification.

2.2. Synthesis of Compounds

2.2.1. Synthesis of Compound 1-3

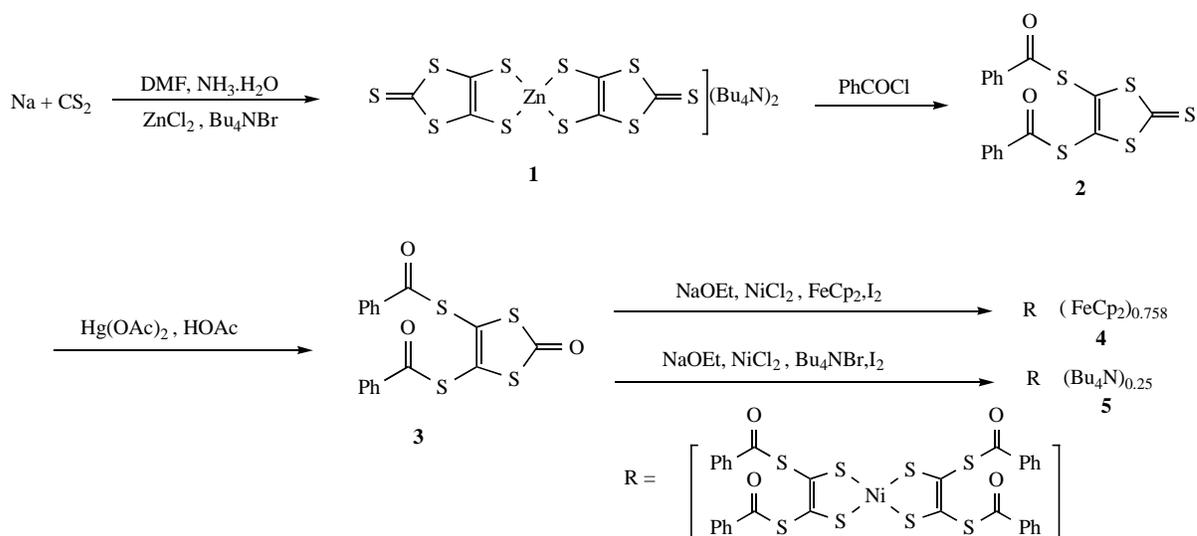
Synthesis of compounds **1-3** was described in the literatures [15, 16], the synthesis of novel nickel complexes containing TTF is carried out following the synthetic procedures depicted in Scheme 1.

2.2.2. Synthesis of Complexes

2.2.2.1. Complex 4

Compound **3** (0.39 g, 1 mmol) was dissolved in 20 ml solution of sodium ethoxide (0.068 g, 1 mmol) under argon at room temperature. The solution turned to wine after stirred for 2 h, then changed to black after NiCl₂ (0.064 g, 0.5 mmol) and FeCp₂ (0.376 g, 2 mmol) were added, with the reaction mixture stirred for 5 h. Then proceeded with I₂. The resulting mixture was filtered, washed with methanol,

*Address correspondence to this author at the State Key Laboratory of Materials Modification by Laser, Ion and Electron Beams, Dalian University of Technology, Dalian 116023, China; Tel: +8641184707865; Fax: +8641184709304; E-mail: xiadaocheng@yahoo.com.cn



Scheme 1. Synthetic route of novel nickel coordination compounds.

CH_2Cl_2 and NaHCO_3 saturated solutions, and distilled water, dried with anhydrous MgSO_4 to yield the crude product. The purification was carried out over silica gel chromatography (eluent: CH_2Cl_2 - CH_3COOEt = 20: 80) to obtain complex 4 as a black solid in yield 46.22%, m.p. 302-306 °C. IR (neat) ν 1680, 1455, 1350, 1245, 888, 475, 404 cm^{-1} ; FAB-MS obsd 922.9, calcd exact mass 922.85, ^1H NMR (500 MHz, DMF) δ 7.98 -7.96 (m, 4 H, ArH), 7.65-7.62 (m, 4 H, ArH), 7.54 -7.44 (m, 4 H, ArH), 3.957 (s, 8 H, CpH); λ_{abs} 280.0, 370.0 nm; Anal.: Calc. for $\text{H}_{27.58} \text{C}_{39.58} \text{Fe}_{0.758} \text{NiO}_4 \text{S}_8$: C, 51.5; H, 2.99; Fe, 4.6; Ni, 6.4; O, 6.94; S, 20.8. Found: C, 51.9; H, 3.13; Fe, 3.9; Ni, 5.5; O, 7.2; S, 20.4.

2.2.2.2. Complex 5

Bu_4NBr instead of FeCp_2 to prepare coordination complex 5, yield 28.42%, black solid, m.p. 301-303 °C, IR (neat) ν 1679, 1453, 1365, 1348, 1245, 889, 402 cm^{-1} ; FAB-MS, obsd 842.8, calcd exact mass 842.42, ^1H NMR (500 MHz,

DMF) δ 7.966 -7.982 (m, 4 H, ArH), δ 7.66 -7.65 (m, 4 H, ArH), 7.44-7.55 (m, 4 H, ArH), 3.15-3.18 (m, 16 H, $-\text{CH}_2-$), 1.24-1.28 (m, 16 H), 1.29-1.33 (m, 16 H, $-\text{CH}_2-$), 0.95-0.92(s, 24 H, $-\text{CH}_3$); λ_{abs} 270.0, 310.0, 380.0 nm; Anal: Calc. for $\text{H}_{29} \text{C}_{36} \text{N}_{0.25} \text{NiO}_4 \text{S}_8$: C, 51.3; H, 3.4; N, 0.4; Ni, 7.1; O, 7.6; S, 22.8. Found: C, 51.6; H, 2.9; N, 0.8; Ni, 7.6; O, 8.1; S, 23.1.

2.3. Electrochemical Property

Cyclic voltammetry (CV) data were obtained from CHI610a Electrochemical Analyzer. Electrochemical data were recorded by a conventional three-electrode cell: a platinum disk (area 0.00502 cm^2) as the working electrode; a platinum wire as the counter electrode and an Ag/AgCl as the reference electrode. All oxidation potentials were determined under N_2 in DMF (0.01 mol/L). Measurements were carried out at a scan rate of 100 mV/s.

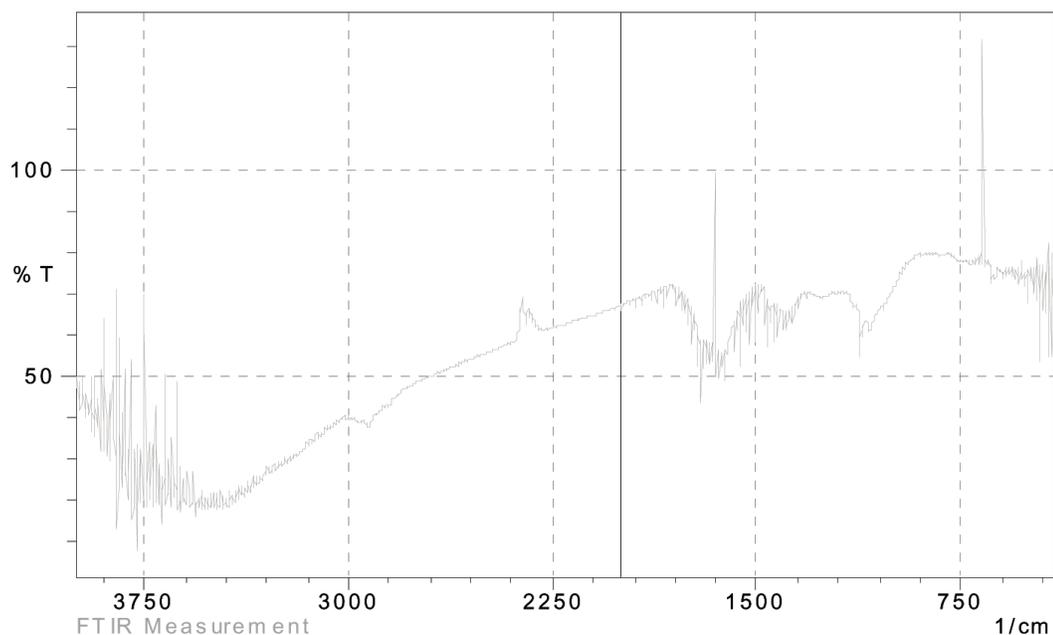


Fig. (1). IR spectrum of 4.

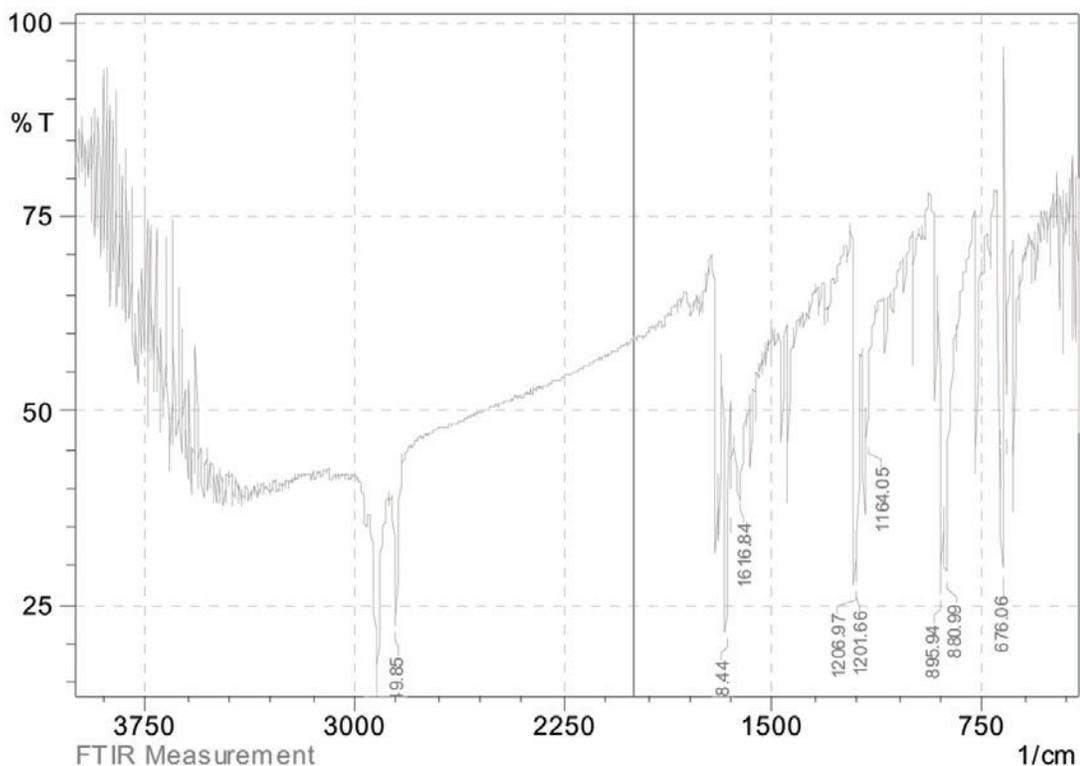


Fig. (2). IR spectrum of 5.

2.4. Electrical Conductivity

The electrical conductivity with compressed pellets was measured by the four-probe method. Electrical contacts were achieved with gold paste. The temperature changed from room temperature to 25 K in liquid nitrogen.

3. RESULTS AND DISCUSSION

3.1. Synthesis

As shown in Fig. (1), 3000 cm^{-1} , 1650 cm^{-1} , 1550 cm^{-1} is attributed to Ar; 1680.00 cm^{-1} is attributed to $\nu_{\text{C=O}}$;

1455.34 cm^{-1} and 1350.45 cm^{-1} is attributed to $\nu_{\text{C=C}}$; 888.97 cm^{-1} is attributed to $\nu_{\text{C-S}}$; $1050\text{-}1065\text{ cm}^{-1}$; $750\text{-}800\text{ cm}^{-1}$ is attributed to $\nu_{\text{S-C-S}}$.

As shown in Fig. (2), 3000.55 cm^{-1} , 1654 cm^{-1} , 1550 cm^{-1} is attributed to Ar; 1679.70 cm^{-1} is attributed to $\nu_{\text{C=O}}$; 2965 cm^{-1} , 2878 cm^{-1} is attributed to ν_{CH_3} ; 2925 cm^{-1} ; 2859 cm^{-1} is attributed to ν_{CH_2} ; 1453.04 cm^{-1} and 1348.65 cm^{-1} is attributed to $\nu_{\text{C=C}}$; 1365.84 cm^{-1} is attributed to $\nu_{\text{C-N}}$; 1245.84 cm^{-1} is attributed to $\nu_{\text{C-O-C}}$; 402.50 cm^{-1} is attributed to $\nu_{\text{Ni-S}}$; 889.10 cm^{-1} is attributed to $\nu_{\text{C-S}}$; $1050\text{-}1065\text{ cm}^{-1}$; $750\text{-}800\text{ cm}^{-1}$ is attributed to $\nu_{\text{S-C-S}}$.

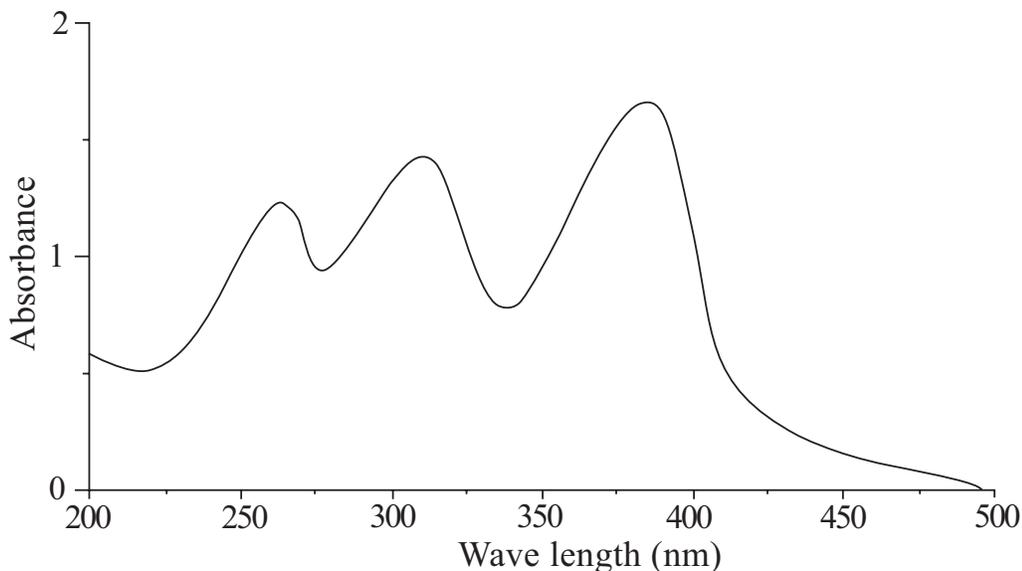


Fig. (3). UV spectrum of 5.

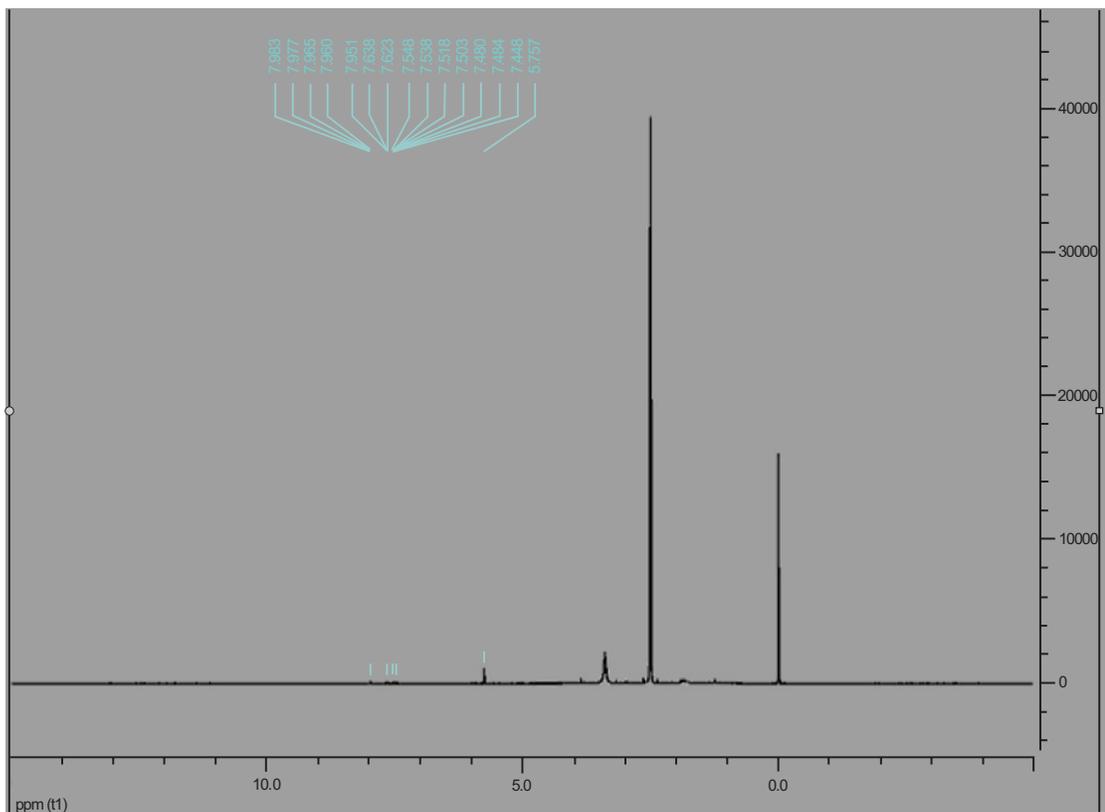


Fig. (4). ^1H NMR spectrum of 4.

As shown in Fig. (3), 270 nm is attributed to π - π between Ar and C=O, 310 nm is attributed to large conjugate of π - π , 380 nm is attributed to Ni-S.

As shown in Fig. (4), 27, 7.983-7.965 ppm (m), 7.623-7.651 ppm(m), 7.448-7.549 ppm (m) is attributed to Ar-H.

3.000ppm is attributed to solvent. 3.957 ppm (s) is attributed to Cp- H.

As shown in Fig. (5), 7.966-7.982 ppm (m), 7.622-7.652 ppm (m), 7.445-7.549 ppm (m), is attributed to Ar-H. 3.147-3.177 ppm (m) is attributed to -CH-H of Bu, 1.290-1.333

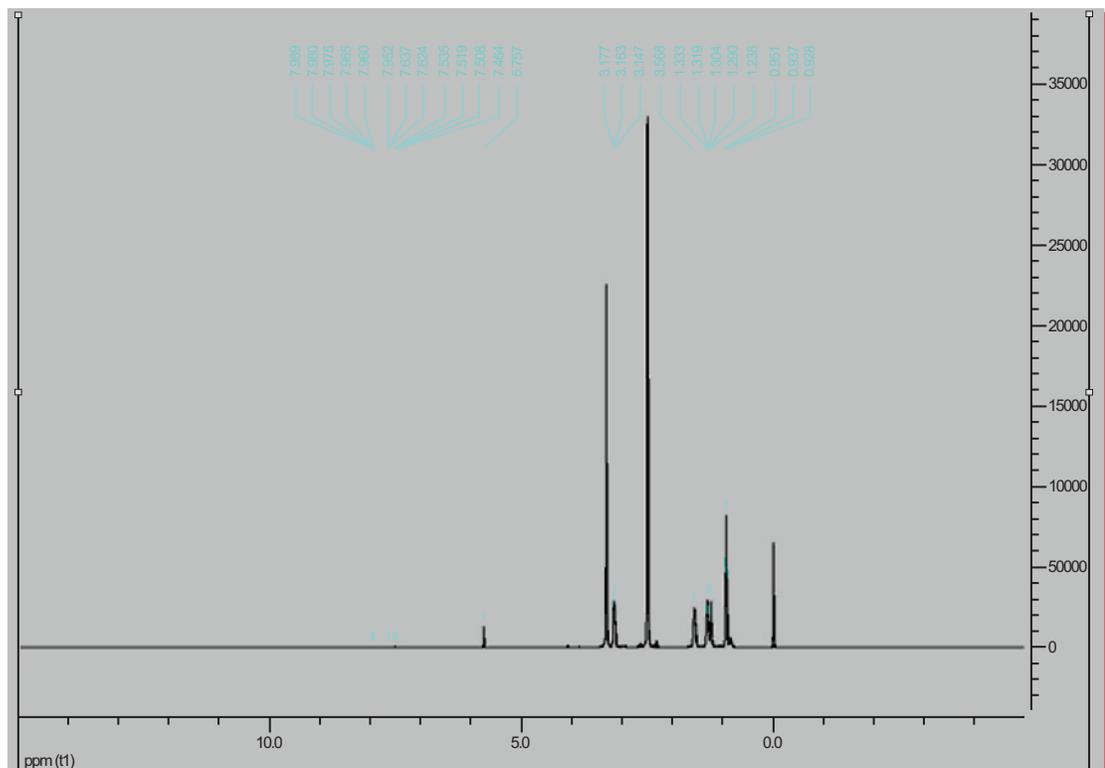


Fig. (5). ^1H NMR spectrum of 5.

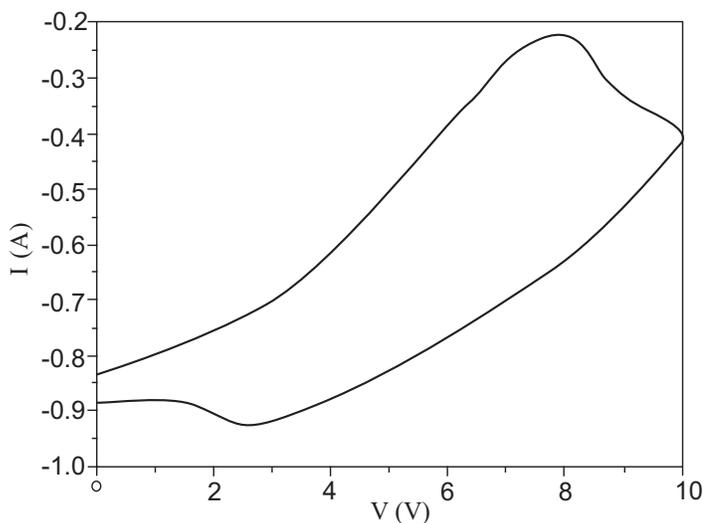


Fig. (6). Cyclic voltammety of compound 4.

ppm (m) is attributed to -CH-H of Bu, 1.236 ppm (m) is attributed to -CH-H of Bu, 0.951-0.923 ppm (m) is attributed to -CH₂-H of Bu.

3.2. Electrochemical Property

The electrochemical behavior of complexes 4 and 5 was investigated by cyclic voltammety in DMF solution, in which, the one reversible wave is clearly visible (see Figs. 6 and 7). The CV data are presented in Table 1.

Table 1. Cyclic Voltammety Data of Complexes

Complexes	E _{red1/2} (v)	E _{ox1/2} (v)	ΔE _P (v)
4	-0.934	-0.228	0.706
5	-0.209	-0.030	0.179

The charge-transfer between the nickel coordination compounds and dithiolate ligand is only one step because there is only a set of redox peak which is shown in Table 1 and Figs. (6) and (7). A single oxidation peak is observed from the complexes, it indicates that the TTF unit in com-

plexes is completely absent of interaction and independently oxidized to remove one electron with equal potential in DMF solvent. This is the reason that the mono-anionic species of complex were difficult to be isolated [17].

From above data, it can be seen that complex 4 with cation group FeCp₂⁺ exhibits much higher oxidation potential than that complex 5 with group Bu₄N⁺. This is attributed to the rich electron property of the FeCp₂⁺ [18, 19].

3.3. Electrical Conductivity

Room temperature Conductance data of complexes are presented in Table 2.

Table 2. Room Temperature (300 k) Conductance Data of Complexes

Complexes 4, 5
Conductance (s/cm) 6.7×10 ⁻³ 1.3×10 ⁻³

The temperature dependence of resistance for coordination compounds is shown in Figs. (8) and (9).

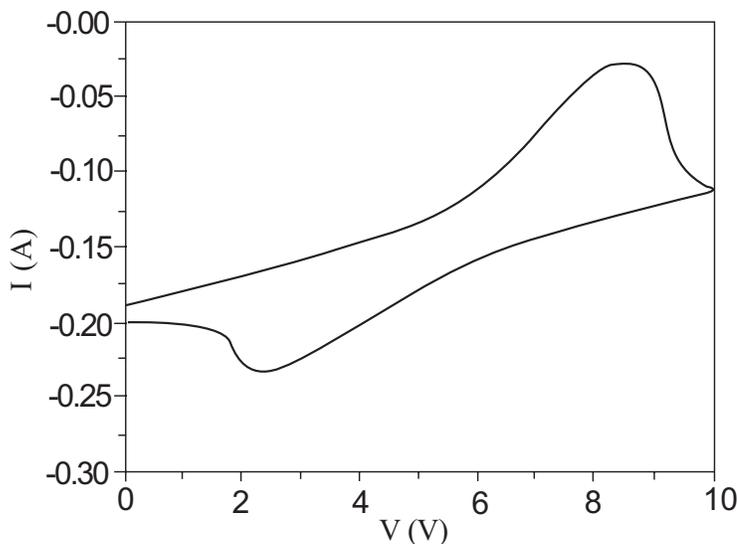


Fig. (7). Cyclic voltammety of compound 5.

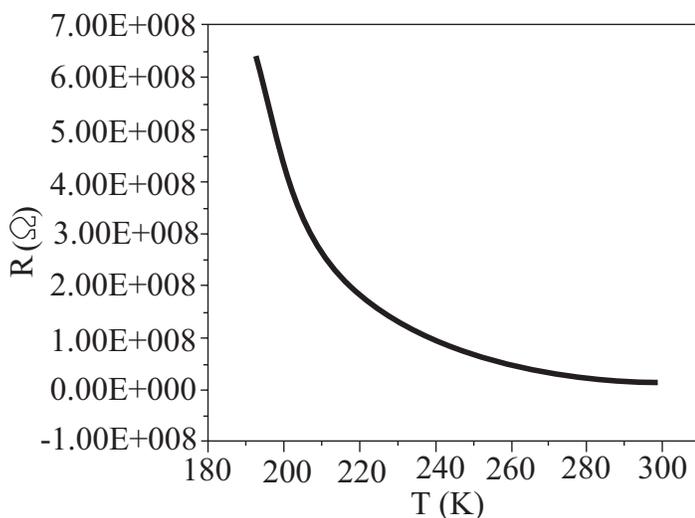


Fig. (8). R--T curve of 4.

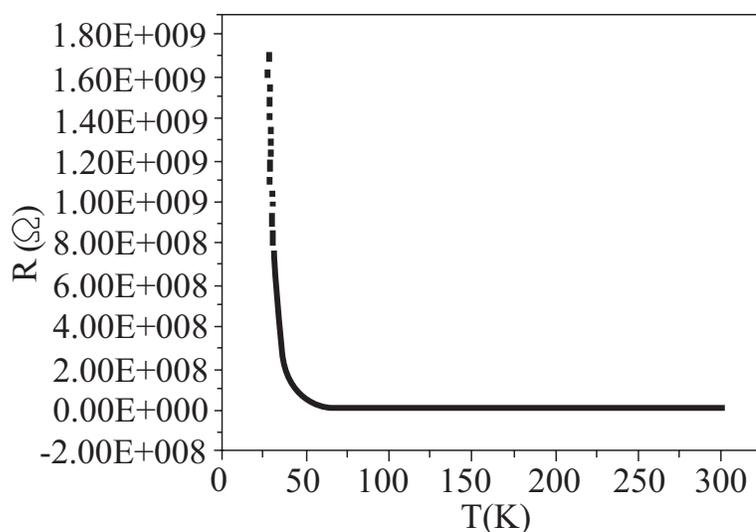


Fig. (9). R--T curve of 5.

Along with temperature increased, the electrical conductivity changed to decrease, as shown in Figs. (8 and 9). The electrical conductivity study of the nickel salts demonstrates that they are all semiconductors. For the Ni atom is in an approximately tetrahedral environment, with two coordinating dithiolate ligands, and density of electronic cloud in molecule is decreased by benzol which is withdraw-electron radical group, electrons of π band can not well translate in molecule, leading to lower conductivity [17].

The room temperature (300 K) conductivity is 2.6×10^{-3} (s/cm), which is the maximum value of conductivity for FeCp_2^+ radical cation salts which oxidate value is 0.832. Ferrocene is a rich electron molecule with a single iron atom between two quasi-aromatic cyclopentadienyl-rings. A possible explanation might be the easier participation of the aromatic FeCp_2^+ moiety in the charge delocalization than the non-aromatic Bu_4N^+ units of the molecules [18, 19].

4. CONCLUSIONS

The complexes structures were fully characterized by EA, ICP-AES, IR, ^1H NMR and UV/Vis spectra. Their electrochemical properties were studied by cyclic voltammetry in

DMF solution. In this paper, along with temperature increased, the electrical conductivity changed to decrease. The two novel nickel complexes were proved to be semiconductors. The room temperature conductivity of compound 4 is higher than compound 5, because of the easier participation of the aromatic FeCp_2^+ moiety in the charge delocalization than the non-aromatic Bu_4N^+ units of the molecules.

5. ACKNOWLEDGEMENTS

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