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## Synthesis and Study of Charge-transfer Complexes for 5,6-dimethyl-2,1,3-benzoselenadiazole

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### Abstract

The synthesis of new solid charge-transfer (CT) complexes using 5,6-dimethyl-2,1,3-benzoselenadiazoles as donors with 1,4-naphthaquinone; 1,8-dihydroxyanthraquinone, 2-hydroxy-1,4-naphthaquinone and 2,3-dichloro-4,5-dicyano-p-benzoquinone (DDQ) as acceptor are reported. These complexes are characterized by elemental analysis, IR, UV-V, and <sup>1</sup>HNMR spectroscopic data. Solid conductivity for 1, 2 and 3 compounds reveal that they are not conductors. The calculated HOMO is largely localized on the selenadiazoles fragment, while the calculated LUMO of the studied molecule is seen to be substantially localized along the C–C axis of the conjugated system.

*Keywords:* Charge transfer complexes; Dimethylbenzoselenadiazoles; Naphthaquinone; Dihydroxyanthraquinone; Hydroxynaphthaquinone; Dichlorodicyanobenzoquinone (DDQ); Semi-empirical (PM3) methods.

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### 1. Introduction

It is well known that the most reactions in the preparation of selenadiazole are based on the reaction between diamine and SeO<sub>2</sub> [1-3]. This very reproducible reaction has been used for absorption or spectroscopic detection of small amounts of selenium in chemical or natural media [4]. Charge-transfer complexes of selenadiazoles have been synthesized and spectroscopically characterized [5-10]. Recently there has been considerable interest in the studies on the charge-transfer complexes of 5, 6-dimethyl-2, 1, 3-benzoselenadiazole with tetracyano-p-quinodimethane (TCNQ), tetrachloro-p-benzoquinone (TCQ) and tetracyanoethylene (TCNE) [6] which act as electron acceptors. Physical studies of these new complexes are reported.

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The aim of present work is to synthesize some new charge-transfer complexes of 5,6-dimethylbenzo[c] [1, 2, 5] selenadiazole as an electron donor with 1,4-naphthaquinone; 2,7-dihydroxy-1,2,3,4-tetrahydroanthracene-9,10-dione, 2-hydroxynaphthalene-1,4-dione and 4,5-dichloro-3,6-dioxocyclohexa-1,4-diene-1,2-dicarbonitrile (DDQ) as  $\pi$ -acceptors.  $^1\text{H}$ NMR, UV-V and IR spectroscopic studies of compounds, are used to deduce the structure and new electrical behavior of these new compounds.

## **2. Experimental**

### **2.1. Synthesis of 5, 6-dimethyl-2, 1, 3-benzoselenadiazole**

To the solution of 4, 5-dimethyl 1, 2-diaminobenzene (2.72 g, 1mmol) in ethanol (30 ml) was added a solution of selenium dioxide (2.22 gm, 2 mmol) in ethanol (30 ml). The mixture was refluxed for (90) min. and cooled to room temperature to afford brown crystals. The product was washed with hot ethanol for several times dried in vacuum, m.p 138-140 °C.

### **2.2. Charge-transfer complexes**

A common procedure was used for the preparation of charge-transfer complexes [5]. To a solution of 2 mmol of selenadiazole compound in acetonitrile (30 ml) was added a solution of 2 mmol of quinone in acetonitrile 30 ml. The reaction mixture was refluxed for 3 hrs and the solvent was removed by rotary evaporator to give colored crystals. The product was washed with small amounts of acetonitrile and dried in vacuum.

### **2.3. Physical measurements**

IR spectra as KBr discs in the range (200-4000)  $\text{cm}^{-1}$  were recorded on a Pye-Unicam SP3-300s IR spectrometer. Electronic spectra were recorded on a Pye-Unicam SP8-100 spectrophotometer in DMSO solution.  $^1\text{H}$ NMR spectra in DMSO- $d_6$  were recorded on Joel EX-90 FT using TMS as an internal standard [8]. Melting point was measured on Gallenkamp melting point apparatus and is uncorrected. The carbon hydrogen and nitrogen analyses were carried out with Perkin-Elmer240M elemental analyzer.

### **2.4. Conductivity measurements**

A sample of the CT complexes was compressed into a disc of 10 mm diameter and 1mm thickness. Two aluminum electrodes were deposited on the disc by evaporation under reduced pressure ( $10^{-6}$  torr). Copper wires were attached by silver paint. The induced currents at different applied voltages were measured at room temperature to establish the characteristics of the studied complexes (I-IV) [5-8].

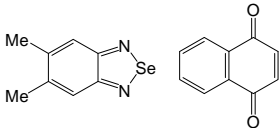
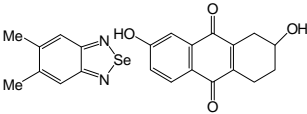
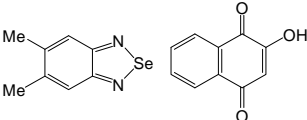
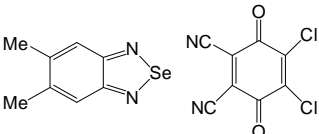
### 2.5. Computational method

Semi-empirical methods are done on HYPERCHEM program version 7.5 [11] running on a windows XP workstation with a Pentium IV PC. The HOMO and LUMO of the studied complexes were done by performing semi-empirical methods. Semi-empirical self-consistent field molecular orbital (SCF-MO) method at PM3 level [12] within the restricted Hartree–Fock (RHF) [13] formalism has been considered. Geometry optimization is carried out by using a conjugate gradient method (Polak–Ribiere algorithm) [14]. The SCF convergency is set to 0.001 kcal mol<sup>-1</sup>, while the RMS gradient is set to 0.001 kcal/(Å mol) in the calculations.

### 3. Results and Discussions

The reaction of 5, 6-dimethyl-2, 1, 3-benzoselenadiazole as donor with 1,4-naphthaquinone; 2-hydroxynaphthalene-1,4-dione; 1,8-dihydroxy anthraquinone and DDQ as an acceptors in acetonitrile solution gives solid complexes 1:1 stoichiometry. Table 1 shows the analytical and physical properties of these complexes.

Table 1. Analytical and physical properties of CT-complexes (I-IV).

No.	Complex	m.p. (oC)	Colour	CHN Analyses		
				C (calc.)	H (calc.)	N (calc.)
I		99-101	Yellow	58.51 (59.27)	3.7 (3.2)	7.5 (6.9)
II		124-126	Orange	58.53 (59.29)	3.54 (3.27)	6.2 (6.7)
III		130	Dark - yellow	56.13 (56.11)	3.61 (3.66)	7.26 (7.27)
IV		90-92	Red	43.82 (43.86)	1.83 (1.84)	12.78 (12.79)

The IR spectra of (CT) complexes are compared with the spectra of their components; the spectra of (CT) complexes are similar to the superposition of the spectra of the donors and acceptors. There is a shift in frequency [8] and some alteration in the intensity, indicating the molecular association. The degree of charge-transfer of complexes was monitored by examination of  $\nu_{C=O}$  for quinones and  $\nu_{(CO)}$  and  $\nu_{(CN)}$  in DDQ [6, 15] complex. Slight changes in the  $\nu_{(CO)}$  presumably is caused by charge-transfer (Table 2). Charge-transfer complex of DDQ shows (C≡N) stretching vibration at 2220 [6, 15, 16] compared with normal value of (C≡N) vibration ( $2230\text{ cm}^{-1}$ ) in the free DDQ.

The UV-visible spectra were recorded for 200-750 nm. There are two types of electronic transitions, viz.,  $n-\pi^*$  and the transitions. The second transition is absorption.

The electronic spectral data of 1, 2 and 3 complexes are in DMSO solvent (Table 2). The electronic spectra of CT complexes show complexity, arising from overlapping between  $n-\pi^*$  and  $\pi-\pi^*$  transitions (Fig. 1).

Table 2. Electronic, IR data for the new CT complexes (I-IV).

Comp.	$\lambda_{\text{max}}$ (UV-vis) (nm)	IR (cm-1)			
		$\nu(CO)$	$\nu(C=N)$	$\nu C=C$	$\nu(C\equiv N)$
I	235, 246, 252, 330, 340	1655	1580	1500	
II	228, 254, 275, 286, 356, 424, 462	1660	1620	1500	
III	238, 244, 250, 274, 282, 330, 342	1640	1580	1500	
IV	358, 338, 420	1675	1550	1500	2220

In general the  $n-\pi^*$  transitions undergo a considerable blue shift upon formation of CT complexes. This change can be attributed to the formation of complexes and the deviation of electron cloud around selenium atom. The electron donors, the quinones, decrease the  $n-\pi^*$  and  $\pi-\pi^*$  conjugate effect in chromophoric group and increase the energy needed for the  $n-\pi^*$  and  $\pi-\pi^*$  transitions [17-20], resulting shifting in the absorption band toward shorter wave length.

$^1\text{H}$  NMR of complex (IV) in DMSO solvent shows a chemical shift at 2.3 ppm (singlet) for methylene group and at 7.55 for benzene ring of selenadiazole; while chemical shift at 2.5 ppm (singlet) belongs to DMSO solvent.

The conductivity for the solid I, II and III complexes shown in Table 3 reveals that these complexes are non conductors.

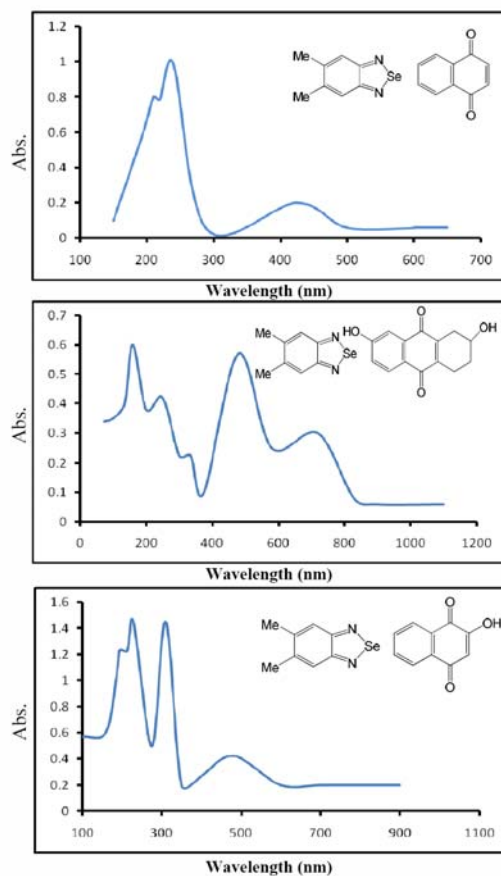


Fig. 1. The electronic spectra of complexes I-III.

Table 3. The Electrical conductivity of the solid complexes I to III.

V (volt)	I (nA) for comp. I	I (nA) for comp. II	I (nA) for comp. III
0	1	2	1
50	3	3	2
100	15	10	15
150	20	30	20
200	30	60	50
250	40	70	70
300	50	80	80
350	60	90	90
400	60	100	110
450	80	120	150
500	90	130	200

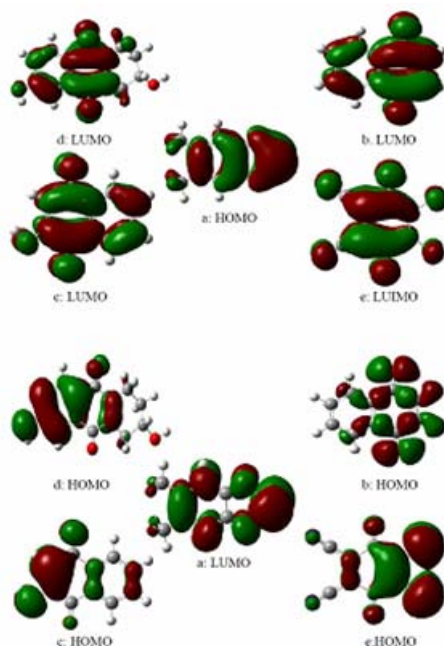


Fig. 2. Three dimensional pictures of HOMO and LOMO of the studied complexes. a: 5, 6-dimethyl-2, 1, 3-benzoselenadiazole; b: 1,4-naphthaquinone; c: 2-hydroxynaphthalene-1,4-dione; d: 1,8-dihydroxy anthraquinone; and e: DDQ.

The calculated frontier bonding molecular orbitals (MO) are shown in Fig. 2. The calculated HOMO is largely localized on the selenadiazoles fragment. The electronic character is also of interest with respect to its reactivity, especially towards nucleophilic agents. The calculated LUMO (electron acceptor orbital) of the studied complexes is seen to be substantially localized along the C–C axis of the conjugated system.

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