

The Effect of Two Substituents on Different Organoselenides and Tellurides to Form New Charge-Transfer Complexes

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تأثير مجموعتين معوضتين على بعض مركبات السلينيوم والتلوريوم العضوية لتكون معقدات إنتقال شحنات جديدة

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تم تحضير العديد من مركبات السلينيوم والتلوريوم العضوية الجديدة وأضيف إليها مجموعتين معوضتين مختلفتين أحدهما دافعة والأخرى ساحبة للإلكترونات لدراسة تأثيرها الكيميائي عند تكون معقدات جديدة لاننتقال الشحنات مع مركبات عضوية معروفة تعمل كمستقبلات للإلكترون. التحاليل الكيميائية والفيزيائية أكدت على تكون هذه المعقدات الجديدة كان عبر روابط كيميائية ضعيفة وأن تأثير المجموعتين المعوضتين المضافتين كما محدوداً على مثل هذا النوع من المعقدات الكيميائية.

Keywords: *Electron Donors, Benzoquinone, Complexes, Substituents, Organoselenides.*

ABSTRACT

Different organotellurides and selenides were prepared as electron donors and reacted with p-Benzoquinone (p-BQ) and m-Dinitrobenzene (m-DNB) as electron acceptors .

The resulted molecules were considered as new charge transfer complexes. The physical and analytical data proved that the addition of two different substituents on the electron donor molecules made no change on this type of weak interaction complexes.

1. Introduction

During the last few years interest has grown in the study of intramolecular compounds[1] and charge transfer (CT) interactions [2,3]. In fact interest in molecular charge transfer complexes, particularly those such as the strongly conducting black-polymorph of the complex of tetrathiafulvalenetetracyanoquinodimethane (TTF-TCNQ) [4] and the complex tetramethyltetraselenafulvalene-tetracyanoquinodimethane (TMTSF-TCNQ) [5] which show superconductivity at low temperature continues to be strong. The use of trinitrobenzene as an electron acceptor with phenoxtellurine (as an electron donor) has encouraged the researchers to look for other electron acceptors for the same purpose [6].

We have recently developed an interest in the role of charge transfer (CT) complexes formed by more simple organic derivatives [3], particularly of selenium and tellureum as electron donors[2]. The electron acceptors we have used in our study are p-Benzoquinone (p-BQ) and m-Dinitrobenzene(m-DNB) .

It has been concluded [7], that the charge transfer interaction is possible in these weak donor-acceptor combinations but can scarcely be the main intermolecular force to govern a molecular arrangement in a crystal.

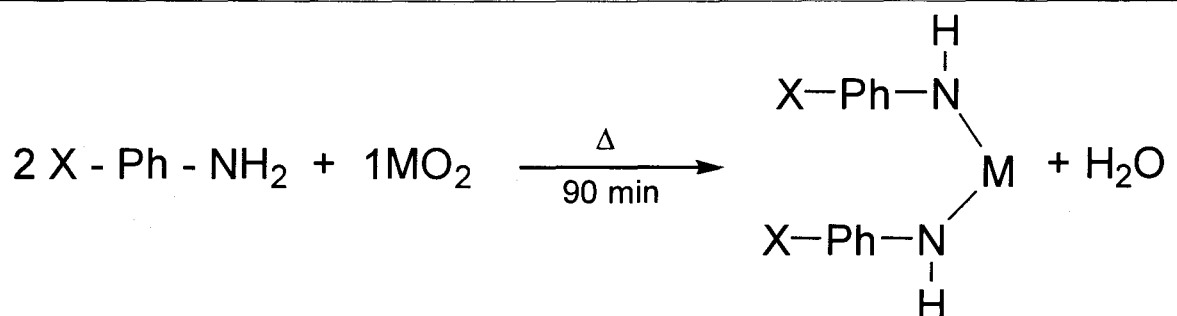
This paper is an extension of two previous pieces of work [2,3] in which we consider the effects of methoxy group(-MeO) and nitro group (-NO₂) substituents on the properties of the CT complexes.

2. Experimental

Synthesis of Organoselenium and -tellurium compounds

Preparation of compound No.1 (Table 1)

Selenium dioxide (4.44g, 0.04mol) was dissolved in dist. water (25 cm³) and treated with Aniline (5.76g, 0.08mol) in methanol (25cm³) . The mixture was boiled for 90 minutes, it was allowed to cool . The residue was recrystallised from ethanol to form redish brown crystals (m.p.95-96C) . The typical equation for these preparations are as follows:-



were: X = H, NO₂, CH₃O

M = Se, Te

where: X = H, NO₂, CH₃O

M = Se, Te

Synthesis of Charge Transfer Complexes

To a hot solution of the prepared donor compound (organoselenium or -tellurium) in acetonitrile solvent (25cm³) was added the acceptor compound in the same solvent (25cm³) (2:1), The mixture was stirred and refluxed for 60 minutes, after which the volume was reduced. On cooling to room temperature, small dark coloured crystals of the complex were deposited.

3. Results and Discussion

The obtained correct analytical data (C%, H%, N%) analysis in Table 1 agree with the suggested new prepared compounds and complexes. All the complexes were found to be stable in air for several months. The melting points for the Benzoquinone (BQ) complexes are higher than that of the m-Dinitrobenzen (m-DNB) complexes. Similar observation been noted for BQ and DNB complexes in previous studies [2,3].

It has been reported [8], that the introduction of electron-donating groups into the benzen ring will increase the π -basicity of the donors in general. This will lead to a red-shift in the CT absorption spectrum.

In our study we have used a donating group (-MeO) as well as a withdrawing group (-NO₂) as substituents of the (-H) in every prepared compound (Table 1) for the sake of comparison.

Usually the m-dinitrobenzen (m-DNB) appeared at ν (1300-1375 and ν 1500-1575) cm⁻¹, while the p-benzoquinone (p-BQ) appeared at ν (1500, 1620 and 1680-1850 cm⁻¹). The infra-red spectra of the DNB complexes (No.3,6,9,11,14 and 15) were virtually the superposition of the spectra of the individual components (Table 2). Also there is no clear shift of ν (CO) with the BQ complexes, despite all of the following considerations [2,9]:

1. The organo tellurides usually offers CT complexes more clear than that of the organo selenides,
2. The ionisation potential of tellurium and selenium are quite low which ease the CT operation, and,
3. We found a clear splitting of the band 1540 cm⁻¹ in complex No.3 (Table 2).

This implies an extremely weak CT interaction, and could be in line with results previously obtained for the 1,3-dihydro-2-telluraindene- DNB complex [2,9].

The electronic absorption spectra for the CT complexes were measured in acetonitrile solution.

In the present study, the obtained results (Table 2) are quite similar to that of previous studies on BQ and DNB complexes [2,3]. It has been assumed that, since all the BQ and DNB complexes absorb at the same region of visible spectrum due to a certain transition. The transition is from the highest occupied molecular orbital on the donor to the lowest unoccupied molecular orbital on the acceptor (HOMO-LUMO) [2,3]. The idea, that this type of weak interaction is indeed sort of π - π charge transfer [10]. Since there is no hydrogen bond is possible between such molecules and π - π overlap is slight, so the arrangement of the molecules might be due to strong electrostatic interaction [7]. These judgments are in good agreement with the present obtained results (Table 2).

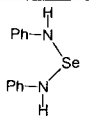


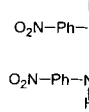


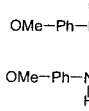


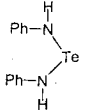
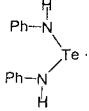
It has been pointed out [11], that the molar conductivity for charge transfer complexes is an indication for the electronic current movement in a solution when these complexes is dissolved. The rate of the conduction in any solution depends on the concentration, valency and speed of the ions.

Although Se and Te metals are available within the chemical content of the prepared electron donors, low values for molar conductivity has been obtained (Table 2). Since all the prepared complexes have same valency (II) for Se and Te, this could indicate little concentration dependence and implies weak com-

plexation. Random molar conductivity values were observed for both BQ and DNB complexes (Table 2), very similar to that of analogues study[3].

Finally, one can conclude that the addition of two different substituents (-OMe, -NO₂) to the organo selenide and telluride electron donors made no big change on the formation of new charge transfer complexes.

Table 1: Physical and analytical data for new compounds.

No	Compound	Colour (M.P..Q)	Yield (%)	C%		H%		N%	
				Calcd	Found	Calcd	Found	Calcd	Found
	p-BQ	Red (115)	—	—	—	—	—	—	—
	m-DNB	Yellow (85)	—	—	—	—	—	—	—
1		Redish Brown (95-96)	87	45.1	54.7	4.2	4.6	11.2	10.6
2		Brown (95-96)	75	58.4	58.2	4.8	4.3	7.1	7.5
3		Brown	85	49.6	50.1	4.3	3.9	13.6	13.0
4		Yellow (53-54)	70	40.1	40.8	3.3	2.8	16.1	15.9
5		Dark Brown (110-112)	65	46.8	47.3	5.0	4.6	11.5	12.2
6		Dark Brown (82-84)	68	41.1	41.5	3.1	2.7	15.9	16.1
7		Violet (98-100)	78	51.0	52.0	5.3	5.0	8.2	8.7
8		Dark Violet (93-94)	65	55.1	55.7	5.2	4.6	6.1	6.5
9		Violet (86-88)	75	48.2	48.9	3.8	4.0	11.9	11.4
10		Paye Yellow (190-192)	85	45.5	46.2	4.0	3.8	9.2	9.0
11		Redish Brown (74-76)	70	45.0	44.2	3.3	3.7	11.7	11.2

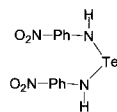
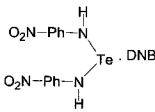
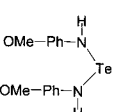
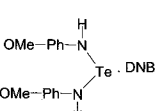
No	Compound	Colour	Yield	C%		H%		N%	
12		Yellow (130-132)	80	36.2	35.5	2.5	2.9	14.1	13.8
13		Greenish Yellow (74-76)	90	41.2	42.0	2.7	2.3	16.0	17.0
14		Brownish Red (66-68)	80	45.2	46.1	4.3	3.9	7.5	7.1
15		Brown (72-74)	75	44.4	44.1	3.3	3.5	10.4	10.6

Table 2: Infra Red, Electronic Absorption and Molar Conductivity Data

No	ν (Cm-1)		UV-VIS	Molar Conductivity
	(CO)	(C-NO)	λ Max (nm)	$\Omega^{-1} \text{ CM}^2 \text{ Mol}^{-1}$
2	1602,1612,1767		550	30.3
3		1300,1540	558	71.2
5	1634		510	11.18
6		1300,1505,1590	590	7.31
8	1631		595,610	56.7
9		1347,1537	570	16.0
11		1348,1528,1539	405	41.7
12				8.4
14		1318,1363,1371,1587	595	15.2
15		1301,1349,1512,1538	398	80.2

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