

Formation of Usual and Bridging Complexes Using Organoselenium and -Tellurium Compounds

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تكوين معقدات اعتيادية وجسرية باستخدام مركبات السيلينيوم والتلوريوم العضوية

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في هذا البحث تم الحصول على معقدات جديدة اعتيادية عن طريق تفاعل انتقال الشحنات ما بين الهاليدات من بعض مركبات السيلينيوم والتلوريوم العضوية وبين عناصر السيلينيوم والتلوريوم الموجودة في مركبات عضوية أخرى. أما المعقدات الأخرى التي تم تحضيرها فكانت عبارة عن مركبات عضوية للسيلينيوم والتلوريوم عبر جسور من كلوريد البلاتين الذي يربط بين الجانبين. لقد أثبتت تحاليل العناصر للمعقدات الجديدة وبعض الدراسات الفيزيائية الأخرى صحة تكوين هذه المركبات وإمكانية الحصول عليها مختبرياً.

Keywords: *Heterocyclic Compounds, Charge Transfer, bridging Complexes, Elemental Analysis, Chloroform.*

ABSTRACT

The reactions of 1,3-benzoselenadiazole with some diiodo selenium and tellurium heterocyclic compounds have led to the formation of charge transfer complexes. From the same reactions but in the presence of K_2PtCl_4 new types of selenium and tellurium complexes via a bridge of $PtCl_2$ molecules were obtained. The analytical data confirm the formation of the new complexes and their UV-VIS and IR spectra are discussed.

1. Introduction

Organoselenium and -tellurium charge-transfer (CT) complexes with some halides have previously been reported [1,2]. However, only few examples of coordinative organoselenium and -tellurium bridging ligands with PtCl_2 moiety are known [3-5].

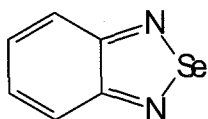
The present paper reports the charge-transfer spectra of some unusual organoselenium and -tellurium compounds with iodides and chlorides. The present work leads to the synthesis of a new type of PtCl_2 bridged selenium and tellurium complexes.

2. Experimental

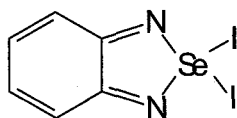
The synthesis of the following known selenium and tellurium heterocyclic compounds were carried out by literature procedures.

The elemental analyses (CHN) for the prepared compounds and complexes were carried out using a Carlo Erba (CHNS) EA 1108 elemental analyzer. IR absorption spectra were recorded as KBr pellets on a Mattson 5000 FTIR spectrophotometer. The UV-VIS spectra were recorded for solutions in 1 cm path way quartz cells with a pye-Unicam PU-8800 spectrophotometer.

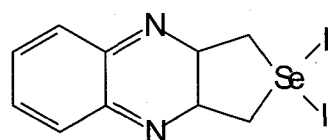
- (1) 2,1,3- benzoselenadiazole [6],



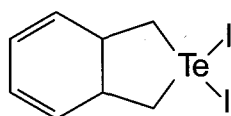
- (2) 1,1- diiodo- 2,1,3- benzoselenadiazole [6],



- (3) 1,1- diiodo- 3,4- quinoxalino- 1- selenacyclopentane [7],



- (4) 1,1- diiodo- 1,3- dihydro- 2,2- telluraindene [8],

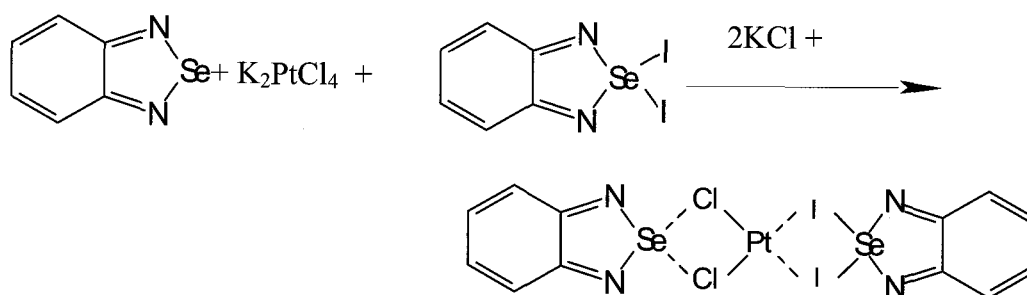


Charge transfer complexes:

A general procedure was used and only a representative one is given below. 2,1,3-Benzoselenadiazole (1) (0.18g, 1m mol) in chloroform (25 ml) was added to a solution of 1,1-diiodo-2,1,3-benzoselenadiazole (2) (0.44g, 1m mol) in chloroform (25 ml). The mixture was stirred under reflux for 1 hour, and its volume reduced to 20 ml to give reddish crystals (m.p. 80-82°C).

Similarly compound 1 was treated with compound 3 and 4. The elemental analysis (Table 1) confirmed the formation of the new complexes in each case.

The formation of the new type of PtCl₂ bridged complexes resulted from of the treatment of compounds 1,2,3 and 4 with potassium tetrachloro platinate (II). The analytical data were obtained for the new complexes (Table 1) as suggested in the chemical equation of compound 1 with K₂PtCl₄ and compound 2 (as an example) could be as follows:



3. Results and Discussion

The mixtures of electron donors and electron acceptors in solution often exhibit a new absorption band, which is not shown by each component separately. This band is attributed to the presence of a donor-acceptor complex. In such mixtures the transition is referred to a charge-transfer (CT) transition and in general is broad and structureless [9]. The optical density of the band is proportional to both iodine and hydrocarbon concentrations when they are involved.

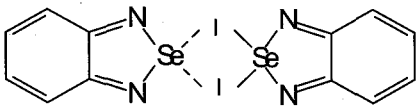
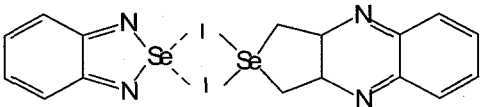
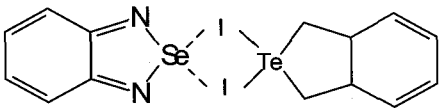
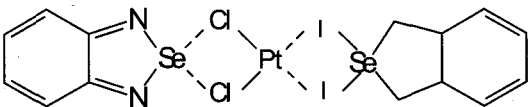
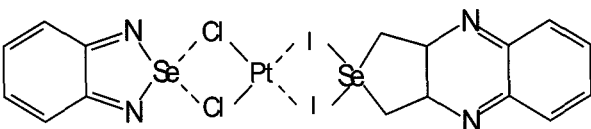
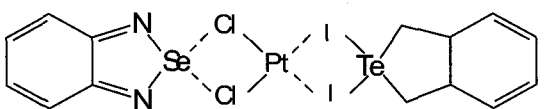
The UV spectra revealed (Table 2) a slight bathochromic shift ($\pi \rightarrow \pi^*$) and some variation in the intensity (e.g. complexes no. 6,8,9 and 10).

The absorptions of complexes (5-7) differ from these of their components (1-4) [9-11]. The increase in the intensity of the peaks accompanied by blue-shift is in agreement with the formation of new complexes via the charge-transfer of M-X. A clear shift has also been found in complexes (8-10) from these of complexes (5-7) (Table 2), which could be explained as a result of the platinum atom bridge.

No strong shift in the IR absorption was observed in the region 850-800 cm⁻¹ characteristic of complexes (5-7) in comparison to that of the starting compounds (1-4) because of the structural similarity. In the case of the new platinum complexes (8-10), we know that the usual Pt-Cl stretching is around 290 cm⁻¹ [12-13]. Here, in Table 2 we found the following:

1. A clear chemical shift in the absorption of ν (Pt-X) between 330 and 385 cm⁻¹.
2. An observable alteration in the band of (Pt-X) from the single split of (Pt-Cl) to a double split band of (I-Pt-Cl). These findings may confirm the formation of the new bridging complexes.

Table 1: Physical and analytical data for CT complexes and the new type of Platinum complexes.

No	Compound	Colour (M.P. °C)	Yield (%)	C%	H%	N%
5		Reddish (80-82)	90	23.2 C 23.3 F	1.3 C 1.1 F	9.0 C 9.3 F
6		Deep Yellow (88-90)	85	25.9 C 25.2 F	1.9 C 1.7 F	8.6 C 8.9 F
7		Brown- Red (78-80)	90	25.1 C 25.9 F	1.8 C 1.2 F	4.2 C 4.8 F
8		Brown (>220)	80	16.3 C 17.1 F	0.9 C 0.5 F	6.3 C 6.9 F
9		Brownish (>220)	75	18.9 C 17.9 F	1.3 C 1.0 F	6.1 C 6.8 F
10		Dark Brown (>220)	75	18.0 C 18.8 F	1.3 C 1.0 F	3.0 C 3.8 F

C = Calculated, F = Found.

Table 2: UV-VIS and IR data for the new prepared complexes.

Comp. No.	UV-VIS λ_{\max} (nm) (DMSO)	IR ν (Pt-X) (cm^{-1})
5	320	-
6	201, 228, 234, 321	-
7	214, 322	-
8	301	385, 335
9	302	378, 355
10	301	375, 330

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