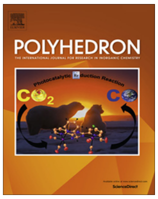
Polyhedron 79 (2014) 284–290

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly



Thiocarbamoylbenzimidophenylselenide and -telluride and their reactions with metal ions

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ARTICLE INFO

Article history:
Received 6 March 2014
Accepted 7 May 2014
Available online 15 May 2014

Keywords:
Iminochalcogenides
Selenium
Tellurium
Mercury
Palladium

ABSTRACT

Thiocarbamoylbenzimidophenylselenide and -telluride have been prepared from *N*-[*N*′,*N*′-methylphenylamino(thiocarbonyl)]benzimidoyl chloride and the *in situ*-prepared phenylselenolate or -tellurolate, and their structures have been determined by X-ray diffraction. The air-stable compounds react with metal ions such as $HgCl_2$, $PdCl_2$ or $Pd(acetate)_2$ under cleavage of their C═N or C–Se/Te bonds. The decomposition fragments react with the transition metal ions under formation of stable products such as $[HgCl(SePh)]_\infty$, (3-methylphenylamino-5-phenyl-1,2,4-dithiazolium)$_2$[HgCl$_4$], [Pd(MePhbtu)$_2$] (HMePhbtu = *N*-methyl-*N*-phenyl-N′-benzoylthiourea) or [Pd(MePhtu)$_4$]Cl$_2$ (MePhtu = *N*-methyl-*N*-phenylthiourea). The products have been isolated in crystalline form and characterized spectroscopically and by X-ray structure analysis.

1. Introduction

N-[*N*′,*N*′-(Dialkylamino(thiocarbonyl)]benzamidines (**I**) are versatile ligand systems, which form stable complexes with a large number of transition metals. Bi-, tri- and tetradentate ligands of this type can readily be prepared from the corresponding benzimidoyl chlorides and amines [1–6]. Corresponding sulfur compounds (**II**) are formed when benzimidoyl chlorides react with thiols (Chart 1) [7,8], and recently we have extended this synthetic route for some selenium and tellurium derivatives (**III** and **IV**, Se: R^3 = mesityl, Te: R^3 = mesityl, 4-methoxyphenyl) [9].

Since the products are crystalline solids and much more stable than a previously reported methylselenium derivative [10], we decided to extend this chemistry by the synthesis of some more representatives and to conduct reactions of the potential *S,Se* and *S,Te* ligands with metal ions. Here, we present synthesis and structures of the phenyl derivatives **IIIa** and **IVa** (R^3 = phenyl) as well as their reactions with mercury(II) and palladium(II) salts.

2. Results and discussion

2.1. Synthesis and structures of the iminochalcogenides

Thiocarbamoylbenzimidophenylselenide (**IIIa**) and the corresponding -telluride (**IVa**) can be obtained following the general procedure for substituted derivatives from the benzimidoyl chloride **I**, the diphenyldichalcogenides and $NaBH_4$ in ethanol (Scheme 1). The syntheses can be performed in one-pot reactions and the products are obtained as yellow (E = Se) or orange-red (E = Te) crystalline solids. They are readily soluble in solvents such as CH_2Cl_2, $CHCl_3$ or toluene. Single crystals for X-ray diffraction were obtained from $CHCl_3$ solutions.

Compounds **IIIa** and **IVa** have been characterized by spectroscopic and crystallographic methods. Proton NMR spectra confirm the composition of the compounds. Unlike the situation in the corresponding thiocarbamoylbenzamidines (compounds **I**, Chart 1), where two sets of signals of the NR_2 groups appear as the result of a hindered rotation around the C–NR_2 bonds [3–6], in the spectra of the selenium and tellurium derivatives under study only each one signal is observed for the CH_3 group. This is a strong hint for almost localized double bonds in **IIIa** and **IVa** as has also been observed earlier for other Se and Te derivatives [9]. The ^{77}Se resonance for **IIIa** at 541 ppm and the ^{125}Te signal for **IVa** at 785 ppm are observed in ranges, which are typical for aromatic selenides or tellurides [11,12]. EI$^+$ Mass spectra show intense signals for the molecular ions and additionally evidence for diselenide or

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http://dx.doi.org/10.1016/j.poly.2014.05.018
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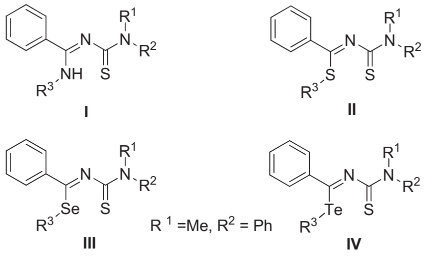
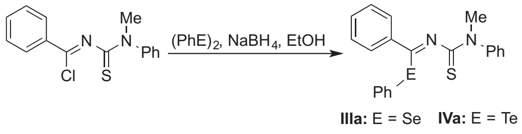


Chart 1. *N*, *S*, *Se*, *Te*-Substituted thiocarbamoylbenzimides.



Scheme 1. Formation of the thiocarbamoylbenzimidophenylchalcogenides used in this study.

ditelluride formation in the gas phase as is indicated by the appearance of corresponding $[M-M+Na]^+$ peaks.

Ellipsoid representations of the molecular structures of **IIIa** and **IVa** are depicted in Fig. 1. Selected bond lengths and angles are summarized in Table 1. All main structural features of the molecular structures of the two compounds fit with those described for their mesityl and 4-methoxyphenyl derivatives [9]. The N1–C10 bonds of 1.274(3) and 1.271(4) Å are clearly shorter than the other carbon–nitrogen bonds and can be regarded as double bonds. Nevertheless, some delocalization of π electron density may be concluded from the values of the C17–N1 and C17–N2 bond lengths. This delocalization, however, is small compared with the situation in the corresponding thiocarbamoylbenzamidines. There, an almost ideal bond length equalization is found for all C–N bonds, which also includes the bond to the dialkylamino groups [1–6]. The lower extent of such delocalization of electron density in the selenium and tellurium compounds under study also explains the fact that no hindered rotation around the C17–N2 bonds is observed in the NMR spectra of the compounds **IIIa** and **IVa**. In a recent study, aggregation of each two iminotelluride molecules by “long range” Te–S interactions (3.698(1) Å) were detected in the solid state structure of the corresponding p-methoxy derivative [9]. Such interactions, which are most probably caused by crystal packing effects, are not present neither in compound **IVa** of the present study nor in the corresponding mesityl derivative [9].

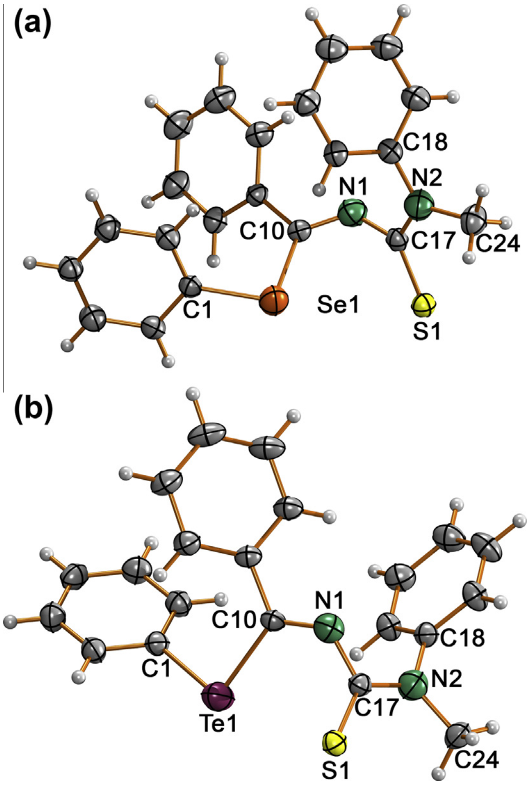


Fig. 1. Ellipsoid representation [57] of (a) compound **IIIa** and (b) compound **IVa**. Thermal ellipsoids represent 50 per cent probability.

Table 1
Selected bond lengths (Å) and angles (deg) in **IIIa** (E = Se) and **IVa** (E = Te).

	IIIa		**IVa**	
S1–C17/C24–N2	1.663(3)	1.467(4)	1.673(3)	1.460(4)
C18–N2/C17–N2	1.434(3)	1.338(3)	1.447(4)	1.340(4)
C17–N1/N1–C10	1.386(3)	1.274(3)	1.397(4)	1.271(4)
E1–C1/E1–C10	1.919(2)	1.927(2)	2.122(3)	2.141(3)
C1–E1–C10/E1–C10–N1	100.5(1)	121.0(2)	96.7(1)	121.6(2)
N1–C17–S1/N1–C17–N2	121.5(2)	113.0(2)	121.3(2)	113.3(2)
S1–C17–N2	125.2(2)		125.1(2)	

Compounds **IIIa** and **IVa** are perfectly stable as solids or in solution. No decomposition could be detected during recrystallization procedures from $CHCl_3$ or toluene or prolonged heating in alcohol in air. However, reactions even with metal ions, which have a high affinity for ‘soft’ donor atoms such as Se or Te, result in decomposition of the iminochalcogenides. Thus, we were only able to isolate complexes with decomposition or hydrolysis products from reactions of **IIIa** with $HgCl_2$ and **IVa** with palladium salts.

2.2. $[Hg(SePh)Cl]_\infty$ (**V**) and $\{Me,PhNC(S)NC(Ph)S\}_2[HgCl_4]$ (**VI**)

Reactions of **IIIa** with $HgCl_2$ in methanol do not result in the formation of *S*,*Se* chelates. A metal-driven decomposition of the iminoselenide was observed even at room temperature and two mercury complexes with the decomposition products could be isolated in crystalline form: the polymeric $[Hg(SePh)Cl]_\infty$ (**V**) and tetrachloromercurate(II) as 3-methylphenylamino-5-phenyl-1,2,4-dithiazolium salt (**VI**) (Scheme 2). The composition of these products strongly suggests a cleavage of the C10–Se bond as a consequence of a nucleophilic attack. Such a behavior is not completely unexpected with regard to some reactions of the similar diethylthiocarbamoyliminothianes with $[ReOCl_4]^-$, which also resulted in a C–S bond cleavage [8]. The increased instability of the chalcogeno derivatives **II**, **III** and **IV** compared to their thiocarbamoylbenzamidine analogues (**I**) is most probably caused by their lesser degree of electron delocalization within the C–N bonds, which results in almost localized C10–N1 double bonds.

The polymeric product $[Hg(SePh)Cl]_\infty$ (**V**) contains the released phenylselenolate building blocks in a bridging mode between each two mercury ions forming infinite chains along the crystallographic *c* axis. Fig. 2a depicts the structure of this coordination polymer. These chains are connected by chlorido ligands, which finally gives a regular three-dimensional network. The Hg–Se and Hg–Se′ bonds of 2.622(1) and 2.542(1) Å are almost equal, while some differences are observed for the Hg–Cl distances (Hg–Cl: 2.485(2) Å and Hg–Cl″: 2.720(2) Å). The coordination polyhedron around the mercury atom is a strongly distorted tetrahedra with ‘tetrahedral’ angles between 93.86(6)° (Cl–Hg–Cl″) and 130.86(5)° (Cl–Hg–Se’). Subunits of the polymeric compound under study can also be described as a 8-membered metallacycle containing four mercury atoms together with each two selenium and chlorine atoms (Fig. 2a).