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Synthesis and characterization of N,N-methylphenylthiocarbamoyliminoarylselenides and -tellurides

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ABSTRACT

N-[N',N'-Methylphenylamino(thiocarbonyl)]benzimidoyl chloride (1) reacts with *in situ*-prepared arylselenolates or aryltellurolates under formation of the first representatives of the corresponding iminoselenides or -tellurides. The products are air-stable solids, which have been studied spectroscopically and by single-crystal X-ray diffraction.

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N-[N',N'-(Dialkylamino(thiocarbonyl)]benzimidoyl chlorides (1) are versatile building blocks for the synthesis of bi-, tri- and tetradentate ligand systems. Reactions with amines give the corresponding benzamidines **2**, which form stable complexes with a large number of transition metals [1–11].



Only less is reported about reactions of **1** with chalcogenolates. An early report describes the formation of the methylester **2a**, -thioester **2b** and -selenoester **2c** of the diethylamino derivative [12]. The former two compounds have been used for the complexation of thiophilic metal ions such as Ag^+ and Hg^{2+} [13,14]. The selenium derivative, however, is described as an instable solid, which slowly decomposes, even when stored at low temperatures [12].

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The use of arylchalcogene building blocks instead of the methyl substituted ones increases the stability of the products. Thus, compounds **3** and **4** can be obtained in good yields from one-pot reactions of **1** (R = Me, Ph), the corresponding diselenides or ditellurides and NaBH₄ in ethanol [15] as deep yellow or orange-red solids. They are stable as solids as well as in solution and can be obtained in crystalline form after recrystallization from toluene.

The ¹H NMR spectra support the structure of products. It is interesting to note that for the protons of the methylphenylamino residues only one single methyl signal is observed. This is in contrast to the spectra of corresponding thiocarbamoylbenzamidines, where hindered rotation around the C–NR₂ bonds doubles the NMR signal of the respective residues [3–11]. Obviously, the compounds under study possess located C–N double, while delocated π -systems are found in the nitrogen derivatives. The ⁷⁷Se and ¹²⁵Te resonances at 440 ppm (**3a**), 596 ppm (**4a**) and 799 ppm (**4b**) appear in the expected ranges for aromatic organoselenium(II) and -tellurium(II) compounds [16,17]. ESI mass spectra of the compounds show the molecular ion peaks of the compounds and give some evidence for

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Fig. 1. Ellipsoid representation of the molecular structure of 3a [20].

dimerization in the gas phase by the formation of cluster ions of the composition of $[M_2 + K]^+$ or $[M_2 + Na]^+$.

Single crystal X-ray diffraction studies confirm the composition of the title compounds [18]. Fig. 1 displays the molecular structure of 3a. Selected bond lengths are summarized in Table 1. The X-ray diffraction results clearly confirm the conclusions from the spectroscopic studies and the formation of the target compound. The arylselenolate unit has replaced the chlorine atom of 1 in a straightforward reaction. The resulting selenoester has Z configuration with respect to the C10-N1 bond. This bond of 1.274(3) Å is clearly shorter than the other carbon-nitrogen bonds in 3a and can be assigned to a double bond. Nevertheless, some delocalization of π electron density can be deduced for the C17-N1 and C17-N2 bonds. This delocalization, however, is small compared with the situation in the corresponding thiocarbamoylbenzamidines. There, an almost ideal bond length equalization is found for the C-N bonds, which also includes the bond to the dialkylamino groups [3–11]. The lower extend of such delocalization of electron density in the title compounds also explains the fact that no hindered rotation around the C17-N2 bonds is observed in the NMR spectra of the compounds 3a, 4a and 4b.

The thiourea moiety of **3a** has the expected planar structure and, in accordance with the almost located N1=C10 double bond, the sulfur atom is not in plane with the selenium atom. The corresponding Se1-C10-N1-C17 torsion angle is around 55°.

The molecular structure of the tellurium analogue **4a** is very similar to that of **3a**. Therefore, no extra figure is given for this structure. Selected bond lengths and angles are contained in Table 1 and the atomic labeling scheme has been adopted from the selenium compound. No significant differences of bond lengths and angles are observed as a consequence of the replacement of selenium by the heavier chalcogen.

Table 1

Sel	ected	bond	lengths	(A)	and	angles	(°).	
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	3a	4a	4b
S1-C17	1.665 (1)	1.645 (6)	1.676 (4)
C24-N2	1.469 (4)	1.457 (7)	1.461 (8)
C18-N2	1.434 (4)	1.441 (7)	1.436 (5)
C17-N2	1.338 (4)	1.366 (7)	1.384 (5)
C17-N1	1.397 (3)	1.404 (6)	1.373 (5)
N1-C10	1.274 (3)	1.285 (6)	1.284 (4)
C10-Se1/Te1	1.927 (3)	2.152 (5)	2.142 (3)
Se1/Te1-C1	1.942 (3)	2.134 (5)	2.118 (3)
C1-Se1/Te1-C10	102.5 (1)	95.4 (2)	95.3 (1)
Se1/Te1-C10-N1	122.0 (2)	122.0 (3)	121.8 (3)
N1-C17-S1	122.3 (2)	123.0 (4)	122.1 (3)
N1-C17-N2	112.8 (2)	112.0 (5)	113.2 (4)
S1-C17-N2	124.4 (2)	124.7 (4)	124.5 (3)
S1-C17-N1-C10	54.97 (1)	46.23 (1)	60.11 (1)



Fig. 2. Ellipsoid representations of two molecules of **4b**, which are arranged in a pseudo-dimeric fashion by inversion symmetry [20].

Fig. 2 displays the molecular structure of the 4-methoxy-substituted compound **4b**. All general structural features of **3a** and **3b** are also found in this iminotelluride. The main difference between the two tellurium compounds is the Te1–C10–N1–C17 torsion angle, which is larger by about 15° for **4b**. This may have to do with the smaller steric stress around the tellurium atom and causes another arrangement of the molecules in the solid state structure. Each two of the molecules of **4b** are arranged to pseudo-dimers via weak long-distance interactions between the tellurium and sulfur atoms. The corresponding distance is 3.698(1) Å, which is within the sum of the van der Waals radii of tellurium and sulfur. Secondary interactions between tellurium and halogen or sulfur atoms are not unusual and represent common features in the structural chemistry of organotellurium (II) compounds [21–23]. In the present case, such interactions have a significant influence on the crystallization behavior of the tellurium compound.

In future studies, the title compounds will be tested as ligands in transition metal complexes and precursors for the synthesis of selenium- and tellurium-containing heterocycles. Another potential field of application, which is widely unexplored up to now, is the use of organoselenium and -tellurium compounds for pharmaceutical purposes [24]. Some vinyltellurium derivatives have recently been found to possess considerable anti-oxidant activity, which implies a potential against excitotoxic agents [25,26]. The iminoselenides and -tellurides **3** and **4** can be regarded as nitrogen analogues of such active compounds.

Appendix A. Supplementary material

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.inoche.2012.10.021.

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- [15] Synthesis of 3 and 4: the corresponding diaryldiselenide or -ditellurides (0.2 mmol) were dissolved in 10 mL of dry ethanol and treated with NaBH₄ (15 mg, 0.4 mmol) under an atmosphere of dry argon. The resulting colorless solutions were added dropwise to stirred suspensions of 1 (115 mg, 0.4 mmol) in 5 mL of dry ethanol. The color immediately changed to deep yellow (3a and 4b) or orange red (4a) and yellow or orange red precipitates deposited within 2 h. The solids were filtered off and recrystallized from toluene.3a: yellow, crystalline solid. Yield: 125 mg (69 %). Elemental analysis: calc. for C24H24N2SSe: C, tained solid refer the respective form of th 772 (vs), 727 (vs), 694 (vs), 667 (m), 640 (s), 598 (m), 550 (s), 529 (w), 467 (w). ESI+MS (m/z): 943 $[M_2+K]^+$, 927 $[M_2+Na]^+$, 491 $[M+K]^+$, 475 $[M+Na]^+$, 453 $[M+H]^+$. High resolution MS of $[M+Na]^+$, which is the base peak of the spectrum: calc.: 475.0723, Found: 475.0733. ¹H NMR (CDCl₃, ppm): 2.13 (s, 3H, CH₃); 2.25 (s, 6H, CH₃); 3.83 (s, 3H, CH₃); 6.69–7.45 (m, 12H, CH_{arom}). ⁷⁷Se NMR (CDCl₃, ppm): 440.**4a**: orange-red, crystalline solid. Yield: 136 mg (68 %). Elemental analysis: calc. for C₂₄H₂₄N₂STe: C, 57.64; H, 4.84; N, 5.60; S, 6.41 %. Found: C, 57.29; H, 4.69; N, 5.30; S, 6.51%. IR (KBr, $\nu_{\rm max}\,{\rm in}\,{\rm cm}^{-1}$): 3015 (w), 2965 (w), 2914 (w), 1596 (s), 1558 (vs), 1491 (s), 1458 (s), 1444 (s), 1371 (vs), 1315 (m), 1294 (s), 1285 (s), 1229 (m), 1179 (m), 1152 (s), 1111 (s), 1074 (m), 1022 (m), 1001 (w), 1255 (5), 1225 (11), 1179 (11), 1132 (5), 1111 (5), 1074 (11), 1022 (11), 1051 (11), 916 (10), 895 (s), 848 (m), 837 (m), 762 (s), 727 (vs), 698 (s), 690 (vs), 663 (m), 637 (s), 584 (m), 569 (m), 550 (m), 457 (w). ESI + MS (m/z); 541 [M + K]+, 525 [M + Na]⁺, 503 [M + H]⁺. ¹H NMR (CDCl₃, ppm): 2.12 (s, 3H, CH₃); 2.39 (s, 6H, CH₃); 3.86 (s, 3H, CH₃); 6.69–7.46 (m, 12H, CH_{arom}). ¹²⁵ Te NMR (CDCl₃, ppm): 2.12 (s, 3H, CH₃); 2.39 (s, 6H, CH₃); 3.86 (s, 3H, CH₃); $\frac{1}{2}$; $\frac{1}{2$ 596.4b: deep yellow, crystalline solid. Yield: 129 mg (66 %). Elemental analysis: calc. for $C_{22}H_{20}N_2OSTe$: C, 54.14; H, 4.13; N, 5.74; S, 6.57%. Found: C, 54.30; H, 4.12; N, 5.67; S, 6.62%. IR (KBr, ν_{max} in cm⁻¹): 3026 (w), 2991 (w), 2931 (w), 2829 (w), 1589 (vs), 1487 (vs), 1442 (vs), 1375 (vs), 1285 (vs), 1244(vs), 1175 (vs), 1152 (vs), 1107 (s), 1065 (m), 1033 (s), 1001 (m), 972 (w), 920 (w), 887 (s),

818 (s), 768 (m), 725 (s), 692 (m), 635 (m), 586 (m), 565 (w), 546 (m), 513 (m), 818 (s), 768 (m), 725 (s), 692 (m), 635 (m), 586 (m), 560 (w), 546 (m), 513 (m), 487 (w). ESI+MS (m/z): 1015 $[M_2+K]^+$, 999 $[M_2+Na]^+$, 529 $[M+K]^+$, 513 $[M+Na]^+$ 491 $[M+H]^+$. ¹H NMR (CDCI₃, ppm): 3.68 (s, 3H, CH₃); 3.84 (s, 3H, CH₃); 6.50–7.51 (m, 14H, CH_{arom}). ¹²⁵Te NMR (CDCI₃, ppm): 799. [16] M. Lardon, J. Am. Chem. Soc. 92 (1970) 5063.

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