Communication

Charge-Transfer Adducts of Chalcogenourea Derivatives of *N*-Heterocyclic Carbenes with Iodine Monochloride

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Abstract: In this communication, we investigate the reaction between seleno- and thiourea, derived from *N*-heterocyclic carbenes, with the interhalogen iodine monochloride. The formation of all three products was confirmed by NMR spectroscopy, while single-crystal X-ray analyses were able to establish a charge-transfer coordination type, which showed a linear Se/S-I-Cl arrangement, for all adducts formed. Based on a detailed crystallographic analysis, we can deduce the zwitterionic character of these compounds.

Keywords: selenourea; thiourea; *N*-heterocyclic carbene; iodine monochloride

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1. Introduction

Over the last few years, *N*-heterocyclic carbene derivatives of group 16 elements have been subjected to significant interest in coordination chemistry and material science, as well as in the medicinal field [1–5]. In general, the electronic properties of organic compounds are intensified and altered by oxidative reactions using halogens X₂ (X = Br, I, Cl) or interhalogens XY (ICl, IBr) [6–8]. Previous reports in this field show that the stoichiometry of these molecules can differ in solution from the solid state [9]. Depending on the chalcogen donor E type (E = Se, S), the halogen X₂ or XY (X = Br, I, Cl; XY = ICl, IBr) source used, and the stoichiometry of the reaction, the geometry of the final compounds can vary between T-shaped (X-E-X) and charge transfer (CT) (E-X-Y) adducts, as well as ionic products featuring an E-E bridge [10–18]. To date, no report has clearly discerned the nature of the C-E bond. Devillanova et al. suggested a double-bond character between C and Se, based on the supposition that the molecule was stabilized by the Br-Se-Br moiety instead of the backbone [9–13]. However, Williams et al. proposed that these molecules have a zwitterionic character with a positive charge on the imidazol(in)ium ring and a negative charge on the dihalogen [19]. Juárez-Pérez et al. succeeded in the oxidation addition of interhalogens to seleno derivatives. To our knowledge, this is the only reported work resulting in T-shaped adducts, which feature linear, asymmetric I-Se-X moieties; this shows the low ability of the interhalogens to undergo an oxidation addition [20]. In our previous work, we have reported the synthesis of chalcogenourea derivatives of *N*-heterocyclic carbenes by deprotonation of their corresponding NHC salts, followed by the addition of chalcogens (Figure 1) [21]. Herein, we describe the reaction of seleno- and thiourea NHCs with iodine monochloride (ICl) to test the ability of ICl to undergo an oxidation addition with heavy donor molecules. Formation of the resulting products is confirmed by ¹H and ¹³C spectroscopy, and their molecular structures are revealed using single-crystal X-ray diffraction analysis.

Figure 1. Chemical structures of seleno- and thiourea NHCs used in this work.

2. Results and Discussion

Reaction of [E(NHCs)], illustrated in Figure 1, with 1.5 equiv. of ICl resulted in the clean formation of dark black powders in high yields (Scheme 1). These compounds were found to be stable under ambient conditions and were bench-stored for prolonged periods without any noticeable degradation. Here, ¹H and ¹³C-NMR spectroscopy was performed on all the compounds, as solutions in CDCl₃. After analyzing the NMR spectra and comparing them to their corresponding starting materials, we can confirm the formation of new compounds (see Supplementary Materials). Crystals, suitable for single-crystal X-ray diffraction analysis, were obtained for Compounds 4 and 6 by vapor diffusion of pentane in saturated solutions of the former compounds in DCM, while single crystals for Compound 5 were obtained by vapor diffusion of hexane into a saturated solution of this compound in chloroform. For each compound, multiple single crystals were screened to ensure the presence of only one type of crystal in the batches. The determined molecular structures are illustrated in Figure 2.

Scheme 1. Reaction of NHC-based chalcogenoureas with ICl.

Figure 2. Molecular structures of [(ICl)·Se(IPr^{Me})] (4), [(ICl)·S(IPr)] (5), and [(ICl)·S(SIMes)] (6) with atom-labeling scheme of all non-hydrogen atoms and thermal displacement ellipsoids drawn at the 50% probability level. Hydrogen atoms and all solvent molecules are omitted for clarity.

Compound 4 crystallized in the centrosymmetric monoclinic space group $P2_1/n$ with one [(ICl)·Se(IPr^{Me})] and one DCM solvent molecule in the asymmetric unit. The structure of Compound 4 resembles a typical 1:1 CT adduct with an approximately linear E-I-Cl arrangement, which shows a Se1-I1-Cl1 angle of $175.14(2)^\circ$, and with the E-I-Cl part almost perpendicular to the imidazole ring, which shows a N1-C1-Se1-I1 torsion angle of $89.4(2)^\circ$ (Figure 2). Intramolecular, non-classical hydrogen bonds are observed between the isopropyl C-H atoms and imidazole N-atoms [C12-H12...N2 = 2.51 Å; C15-H15...N2 = 2.42 Å; C24-H24...N1 = 2.40 Å; C27-H27...N1 = 2.50 Å], while C-H... π interactions are observed between the same isopropyl C-H atoms and the imidazole ring [C12-H12...Cg1 = 2.97 Å; C15-H15...Cg1 = 2.82 Å; C24-H24...Cg1 = 2.69 Å; Cg1 is the centroid of the C1-C3/N1-N2 ring].

In the crystal packing, intermolecular π - π interactions are present between both 2,6-diisopropylphenyl rings and their symmetry-equivalent rings with rather large centroid-centroid distances [Cg2...Cg3ⁱ = 4.8859(16) Å and Cg3...Cg2ⁱⁱ = 4.8858(16) Å; Cg2 is the centroid of the C6-C11 ring, Cg3 is the centroid of the C18-C23 ring; symmetry codes: (i) $3/2 - x, -1/2 + y, 3/2 - z$; (ii) $3/2 - x, 1/2 + y, 3/2 - z$] (Figure 3).

Compound 5 crystallized in the centrosymmetric monoclinic space group $P2_1/n$ with one [(ICl)·S(IPr)] molecule in the asymmetric unit. A solvent mask was applied to account for the solvent contribution of a highly disordered chloroform molecule. Analogous to Compound 4, the structure of Compound 5 shows the 1:1 CT adduct geometry with an approximately linear E-I-Cl arrangement perpendicular to the imidazole ring (S1-I1-Cl1 angle of $178.50(7)^\circ$; N1-C1-S1-I1 torsion angle of $86.6(6)^\circ$) (Figure 2). Analogous to Compound 4, intramolecular, non-classical hydrogen bonds are observed between the isopropyl C-H atoms and imidazole N-atoms [C10-H10...N1 = 2.40 Å; C13-H13...N1 = 2.49 Å; C22-H22...N2 = 2.47 Å; C25-H25...N2 = 2.38 Å], while intramolecular C-H... π interactions are observed between isopropyl C-H atoms and the imidazole ring [C10-H10...Cg1 = 2.74 Å; C25-H25...Cg1 = 2.67 Å; Cg1 is the centroid of the C1-C3/N1-N2 ring]. Here, one extra intermolecular C-H... π interaction is noticed between isopropyl C-H atoms and a symmetry-equivalent 2,6-diisopropylphenyl ring [C26-H26B...Cg3ⁱⁱⁱ = 2.74 Å; Cg3 is the centroid of the C16-C21 ring; symmetry code: (iii) $2 - x, 2 - y, 1 - z$].

Figure 3. Packing in the crystal structure of Compound **4**, viewed down the *a*-axis with indicated π - π interactions between both 2,6-diisopropylphenyl ring centroids and their symmetry-equivalents. Hydrogen atoms and solvent molecules are omitted for clarity.

In the crystal packing, intermolecular π - π interactions are present between both 2,6-diisopropylphenyl rings and their symmetry-equivalent rings, with one significantly smaller and two larger centroid-centroid distances [$\text{Cg}2 \cdots \text{Cg}2^{\text{i}} = 4.093(4) \text{ \AA}$; $\text{Cg}2 \cdots \text{Cg}3^{\text{ii}} = 5.236(4) \text{ \AA}$; $\text{Cg}3 \cdots \text{Cg}3^{\text{iii}} = 5.617(4) \text{ \AA}$; $\text{Cg}2$ is the centroid of the C4-C9 ring, $\text{Cg}3$ is the centroid of the C16-C21 ring; symmetry codes: (i) $2 - x, 1 - y, 1 - z$; (ii) $1/2 + x, 3/2 - y, 1/2 + z$; (iii) $2 - x, 2 - y, 1 - z$] (Figure 4).

Compound **6** crystallized in the centrosymmetric monoclinic space group $P2_1/c$ with one [(ICI)·S(SIMes)] and half of a solvent DCM molecule (on the two-fold axes) in the asymmetric unit. Analogous to Compounds **4** and **5**, the structure of Compound **6** shows the 1:1 CT adduct geometry with an approximately linear E-I-Cl arrangement, although the E-I-Cl part is now significantly angled with respect to the imidazole ring (S1-I1-Cl1 angle of $178.72(4)^\circ$; N1-C1-S1-I1 torsion angle of $136.3(3)^\circ$) (Figure 2). In comparison to Compounds **4** and **5**, only one intramolecular, non-classical hydrogen bond is observed between the isopropyl C-H atoms and imidazole N-atoms [$\text{C}21\text{-H}21\text{A} \cdots \text{N}2 = 2.55 \text{ \AA}$], while no intramolecular C-H $\cdots\pi$ interactions are observed at all. However, analogous to Compound **5**, an intermolecular C-H $\cdots\pi$ interaction is noticed between methyl C-H atoms and a symmetry-equivalent mesityl ring [$\text{C}11\text{-H}11\text{B} \cdots \text{Cg}2^{\text{i}} = 2.80 \text{ \AA}$; $\text{Cg}2$ is the centroid of the C4-C9 ring; symmetry code: (i) $1 - x, y, 3/2 - z$].

Figure 4. Packing in the crystal structure of Compound 5 viewed down the a-axis with the shortest π - π interactions (4.089(5) Å) indicated, i.e., between 2,6-diisopropylphenyl ring centroids and their symmetry-equivalents. Hydrogen atoms and solvent molecules are omitted for clarity.

In the crystal packing, intermolecular π - π interactions are present between both 2,6-diisopropylphenyl rings and their symmetry-equivalent rings, with one significantly smaller, similar interaction as for Compound 5, and three larger centroid-centroid distances [$\text{Cg2}\cdots\text{Cg2}^{\text{i}} = 4.396(3)$ Å; $\text{Cg2}\cdots\text{Cg2}^{\text{ii}} = 5.525(3)$ Å; $\text{Cg2}\cdots\text{Cg2}^{\text{iii}} = 5.506(3)$ Å; $\text{Cg3}\cdots\text{Cg3}^{\text{iv}} = 5.778(3)$ Å; Cg2 is the centroid of the C4-C9 ring, Cg3 is the centroid of the C13-C18 ring; symmetry codes: (i) $1 - x, Y, 3/2 - z$; (ii) $1 - x, 1 - y, 1 - z$; (iii) $1 - x, 2 - y, 1 - z$; (iv) $2 - x, 1 - y, 1 - z$] (Figure 5).

Figure 5. Packing in the crystal structure of Compound 6 viewed down the b-axis with the shortest π - π interactions (4.396(3) Å) indicated, i.e., between mesityl ring centroids and their symmetry-equivalents. Hydrogen atoms and solvent molecules are omitted for clarity.

Based on these crystal structures, it is clear that changing the organic framework between these three molecules and the donor type (Se or S) does not affect their coordination behavior to ICl, yielding the 1:1 CT adduct geometry in all cases. On the one hand, after coordination of ICl, lengthening of the I-Cl bond in all the compounds (2.6903(7) Å for Compound 4, 2.742(2) Å for Compound 5, and 2.5970(13) Å for Compound 6) can be noticed, as compared to the same bond in the ICl molecule in gaseous state (ca. 2.32 Å) [22]. This elongation results from the donation of electron density from the chalcogen (Se or S) into the σ^* low occupied molecular orbital of ICl. On the other hand, elongation of the C-E bond distances in all structures is encountered (from 1.827(5) to 1.880(2) Å for Compound 4, 1.670 to 1.726(7) Å for Compound 5 and 1.656 to 1.728(4) Å for Compound 6), along with shortening of the C-N bonds, in comparison to the uncoordinated ligands. Selected bond lengths and angles are listed in Table 1. It should be noted that other NHC-based CT compounds have been previously obtained from the reaction of *N*-methylbenzothiazole-2(3H)-thione/selone with ICl, accompanied by the same observation of an elongation of C-Se and I-Cl bonds, compared to the corresponding free molecules [13]. Based on the data presented herein, we can suggest a single-bond character for the C-E bond, as well as a double-bond character for the C-N bonds. Thus, we can deduce the zwitterionic character of these compounds; the E-I-Cl moiety is negatively charged, while the positive charge is delocalized on the nitrogen atoms of the heterocyclic ring.

Table 1. Selected bond lengths (Å) and angles (°) for the reported structures of [(ICl)·Se(IPr^{Me})] (4), [(ICl)·S(IPr)] (5) and [(ICl)·S(SIMes)] (6), and the NHC-based seleno- and thioureas [Se(IPr^{Me})] (1), [S(IPr)] (2) and [S(SIMes)] (3).

Structure	C ₁ -E ₁	E ₁ -I ₁	I ₁ -Cl ₁	C ₁ -E ₁ -I ₁	E-I ₁ -Cl ₁
[(ICl)·Se(IPr ^{Me})] (4)	1.880(2)	2.6516(3)	2.6903(7)	101.63(8)	175.143(18)
[(ICl)·S(IPr)] (5)	1.726(7)	2.545(2)	2.742(2)	101.3(2)	178.50(6)
[(ICl)·S(SIMes)] (6)	1.728(4)	2.6034(11)	2.5970(13)	103.91(15)	178.71(4)
[Se(IPr ^{Me})] ^a (1)	1.827(5)	-	-	-	-
[S(IPr)] ^b (2)	1.670(3)	-	-	-	-
[S(SIMes)] ^c (3)	1.666(2)	-	-	-	-

^a CCDC 1,997,590 [20]; ^b CCDC 1,000,479 [23]; ^c CCDC 282,503 [24].

3. Materials and Methods

Chalcogenourea NHCs were synthesized according to a previously published procedure [21].

NMR spectra were acquired on a Bruker AV3-400 (Billerica, MA, USA) spectrometer equipped with a liquid nitrogen cryoprobe or a Bruker AV400 spectrometer with a BBFO-z-ATMA probe; ¹H-NMR spectra were referenced to residual solvent signals and ¹³C{¹H} DEPT Q-NMR spectra to the deuterated solvent signal, while chemical shifts are reported in ppm.

X-ray intensity data were collected at 100 K on a Rigaku Oxford Diffraction Supernova Dual Source (Cu at zero) diffractometer (Rigaku Corporation, Tokyo, Japan), equipped with an Atlas CCD detector using ω scans and Cu K α (λ = 1.54184 Å) radiation. The images were interpreted and integrated with the program CrysAlisPro 1.171.40.67a [25]. Using Olex2 the structures were solved by direct methods using the ShelXT structure solution program and refined by full-matrix least squares on F² using the ShelXL program package [26–28]. Non-hydrogen atoms were anisotropically refined, and the hydrogen atoms in the riding mode with isotropic temperature factors were fixed at 1.2 times U(eq) of the parent atoms (1.5 times for methyl groups).

Crystal data for Compound 4. C₃₀H₄₂Cl₃IN₂Se, *M* = 742.87, monoclinic, space group *P*2₁/n (No. 14), *a* = 9.74100(10) Å, *b* = 16.92180(10) Å, *c* = 19.8068(2) Å, β = 97.3990(10)°, *V* = 3237.67(5) Å³, *Z* = 4, *T* = 100 K, ρ_{calc} = 1.524 g cm^{−3}, μ (Cu-K α) = 11.489 mm^{−1}, *F*(000) = 1496, 30,992 reflections measured, 6440 unique (*R*_{int} = 0.0456), which were used in all calculations. The final *R*1 was 0.0284 (*I* > 2 σ (*I*)), and *wR*2 was 0.0697 (all data).

Crystal data for Compound 5. $C_{28}H_{37}Cl_4IN_2S$, $M = 702.35$, monoclinic, space group $P2_1/n$ (No. 14), $a = 10.5912(5)$ Å, $b = 18.7089(6)$ Å, $c = 16.0710(6)$ Å, $\beta = 102.093(4)^\circ$, $V = 3113.8(2)$ Å³, $Z = 4$, $T = 100$ K, $\rho_{\text{calc}} = 1.498$ g cm^{−3}, $\mu(\text{Cu-K}\alpha) = 12.013$ mm^{−1}, $F(000) = 1424$, 23,270 reflections measured, 6214 unique ($R_{\text{int}} = 0.1084$), which were used in all calculations. The final $R1$ was 0.0628 ($I > 2\sigma(I)$), and $wR2$ was 0.1758 (all data). A solvent mask was applied using Olex2 [26] to account for a disordered solvent contribution; 228 electrons were found in a volume of 572 Å³ in one void per unit cell. This is consistent with the presence of one CHCl_3 molecule per asymmetric unit, which accounts for 232 electrons per unit cell and is consistent with the crystallization conditions.

Crystal data for Compound 6. $C_{43}H_{54}Cl_4I_2N_4S_2$, $M = 1086.62$, monoclinic, space group $P2_1/c$ (No. 14), $a = 20.8949(4)$ Å, $b = 8.23050(10)$ Å, $c = 13.9891(2)$ Å, $\beta = 99.642(2)^\circ$, $V = 2371.80(7)$ Å³, $Z = 2$, $T = 100$ K, $\rho_{\text{calc}} = 1.522$ g cm^{−3}, $\mu(\text{Cu-K}\alpha) = 13.567$ mm^{−1}, $F(000) = 1092$, 23,053 reflections measured, 4732 unique ($R_{\text{int}} = 0.0646$), which were used in all calculations. The final $R1$ was 0.0411 ($I > 2\sigma(I)$), and $wR2$ was 0.1144 (all data).

4. Conclusions

To investigate the adduct types from the reaction of NHC-based chalcogenoureas with an interhalogen, we have reacted three seleno- and thiourea compounds with ICl . The crystal structures of these compounds show that the oxidation of the chalcogen does not occur and, therefore, does not result in a T-shaped moiety formation. Instead, the obtained structures exhibit a charge-transfer character with the coordination showing a nearly linear E-I-Cl arrangement, almost perpendicular to the NHC heterocyclic ring. The type of the donor molecule did not affect the geometry of the synthesized compounds for the three selected NHC molecules studied.

Supplementary Materials: The following are available online: Experimental section, NMR spectra for chloro-iodo-chalcogenoureas, ¹H-NMR spectra of the new compounds compared with the starting materials, Crystallographic data. CCDC 2131177–2131179 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

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