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Synthesis, Characterization, and X-Ray Crystallographic Structure of 1,3-Dimethyl-2(3*H*)-imidazoleselone

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ABSTRACT

The reaction of elemental Se with 1,3-dimethylimidazolium iodide in methanolic K_2CO_3 yields 1,3-dimethyl-2(3H)-imidazoleselone for which three addition products, two with bromine and one with iodomethane, have been synthesized and for which X-ray crystallographic analysis shows the structure to consist of a selenium-substituted planar heterocyclic ring with bond distances and angles significantly different from those noted for the previously reported sulfur analog [1,3-dimethyl-2(3H)-imidazolethione, dmit]. Crystal data: $C_5H_8N_2Se$, space group C mcm, $M = 175.03$, $a = 8.625(3)$, $b = 11.447(6)$, $c = 6.900(4)$ Å, $V = 681.24$ Å^3, $Z = 4$, $D_c = 1.707$ g cm^{-3}, $D_0 = 1.68$ g cm^{-3}, $\lambda = 0.71073$ Å (Mo-K_α), $\mu = 5.35$ mm^{-1}, $R = 0.034$, and $R_w = 0.031$.

INTRODUCTION

A great deal of synthetic and structural characterization work has been carried out with the 1-alkyl- and 1,3-dialkyl-2(3*H*)-2(3*H*)-imidazolethiones, such as the sulfur analog of **2**, 1,3-dimethyl-2(3*H*)-imidazolethione (*dmit*), which has been shown to be a versatile ligand in forming both transition metal [1–3] and main group [4–6] complexes, as well as to provide the electron-rich aromatic heterocyclic backbone allowing halogens and pseudohalogens to add oxidatively to sulfur, thus giving rise to unique trivalent carbene-stabilized complexes of S(II) [7]. The first reported stable crystalline carbene, 1,3-di-1-adamantyl-2(3*H*)-imidazolylidene, shares the same heterocyclic skeleton [8].

The selenium analog of *dmit*, viz. 1,3-dimethyl-2(3*H*)-imidazoleselone (**2**), has not been reported in the literature although the saturated heterocyclic analog of this selenourea is known and has been studied [9]. In order to investigate some of the donor properties of the heavier chalcones, we modified the procedure reported by Benac *et al.* [10] for the synthesis of *dmit* to produce **2** in ca. 70% yield.

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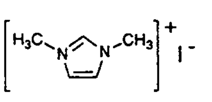

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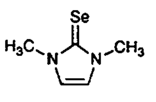

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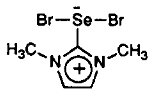

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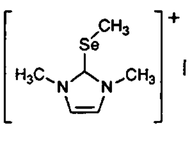

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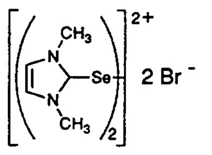

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Chemistry

Benac *et al.* had indicated that the selone and tellurone could be synthesized by the same procedure used for *dmit*, but the details were not included. We have yet to successfully synthesize the tellurone. A single crystal X-ray study was carried out as part of the characterization of **2**, and the results are reported subsequently. In addition, we have synthesized and characterized three new derivatives of **2** which are also reported subsequently.

EXPERIMENTAL

Chemicals

All chemicals were reagent grade and used as commercially obtained without further purification. 1,3-Dimethylimidazolium iodide (**1**) was synthesized as described later. Spectroscopic grade CD_3CN (Aldrich), $CDCl_3$ (MSD), and D_2O (MSD) were used as solvents to obtain the proton and ^{13}C NMR data. Electrical conductivity grade anhydrous CH_3CN (Fisher) was used as obtained without further purification for specific conductivity measurements. Highly purified deionized water (Continental) was also used for conductivity studies.

Analytical

Carbon, hydrogen, and nitrogen analyses were carried out by Atlantic Microlabs, Inc. Molecular weight data for **3** were obtained from Galbraith Laboratories, Inc.

Solution Studies

The specific conductivity for each of **2**, **3**, and **5** was measured in CH_3CN and for **4** in H_2O using a YSI Model 31 conductivity bridge equipped with a dip-type cell. Proton decoupled ^{13}C NMR (77.48 MHz) and proton NMR spectra were recorded on a 300 MHz GE Model QE-300 FT-NMR spectrometer. Proton and ^{13}C chemical shifts (δ) are reported relative to external tetramethylsilane.

Solid-State Spectra

Infrared spectra were recorded by use of KBr pellets from 4000 to 400 cm^{-1} on a Mattson Galaxy 2020 Fourier transform infrared spectrophotometer (FTIR). Raman data were collected on powders from 4000 cm^{-1} to excitation line using a Bomen DA 3.02 FT-Raman spectrophotometer equipped with Nd-YAG laser (λ_{ox} = 1.064 μm). All values are reported in cm^{-1} ($\pm$4). Key: v—very, w—weak, m—medium, s—strong, br—broad, and sh—shoulder.

Synthesis

Due to extremely unpleasant odors of several of the reaction mixtures involved, most manipulations were carried out in a well-ventillated fume hood. Melting points (uncorrected) were obtained on a Fisher-Johns stage-type apparatus and reported in degrees Celsius.

1,3-Dimethyl-2(3H)-imidazoleselone (**2**)

In a 500 mL round bottom flask fitted with a magnetic stirrer were placed 75 mL of ethyl acetate, 5.4 g (66 mmol) of 1-methylimidazole (Aldrich), and 9.7 g (68 mmol) of CH_3I (Fisher). The mixture was allowed to stir at room temperature for ca. 30–40 minutes or until the white precipitate of **1** appeared. The ethyl acetate was then decanted and to the flask were added 75 mL of anhydrous methanol, 5.5 g (70 mmol) of gray Se (Alfa), and 7.6 g of K_2CO_3 (Baker). The flask was fitted with a reflux condenser, and the mixture was allowed to reflux for 24 hours. The solution was then hot-filtered through a Celite 545 pad and cooled overnight at 10°C. A total of 8.4 g (72%) of selone was obtained through successive concentration, cooling, and filtration of the reaction solution. Crystallographic grade crystals were obtained by recrystallization from water. White crystals, mp 203–204°C. Anal. (%) calcd for $C_5H_8N_2Se$: C, 34.30; H, 4.60; N, 16.00. Found: C, 34.24; H, 4.62; N, 15.97. ^1H NMR (300 MHz) δ (CD_3CN, $CDCl_3$) 3.57, 3.67 (s, 6H); 7.01, 6.82 (s, 2H). ^{13}C NMR (77.48 MHz) δ ($CDCl_3$) 36.6 (s), 119.2 (m), 154.9 (s). FTIR: 3146w, 3102s, 3032m, 2999w, 2951vw, 2922w, 2887vw, 1678w, 1570m, 1466s, 1435m, 1381s, 1319w,sh, 1234s, 1143s, 1084m, 997w, 887w, 739s, 650m, 470w. Raman: 2917s, 2861m, 1565m, 1443s, 1388s, 1144m, 1094m, 1021w, 844w, 743m, 623m.

An alternate method employing **1** in ethanolic NaHSe *via* the method of Klayman and Shine [11] gave **2** in less than 10% yield, and the S-methyl thiopseudourea of *dmit* (viz. 1,3-dimethyl-2-(methylthio)-2(3*H*)-imidazolylium iodide) yielded no isolable selenourea using the same method.

1,3-Dimethyl-2-(Se,Se-dibromoseleno)-2(3H)-imidazolylidene (**3**)

In a 100 mL round bottom flask fitted with a magnetic stirrer and chilled in an ice bath were placed

20 mL of dried [12] CH_2Cl_2 and 1.0 g of **2** (5.7 mmol). To this solution was added 0.92 g (5.7 mmol) of Br_2 (Fisher), the solution turning dark orange. The ice bath was removed and the solution allowed to stir at room temperature for 40 minutes. The solvent was then evaporated, and the remaining solid was recrystallized from CH_2Cl_2; 1.6 g of **3** (83%) was isolated. Large crystallographic grade crystals could be obtained by slow evaporation from CH_2Cl_2 or CH_3CN solution. Orange crystals, mp 236°C (sublimes). *Anal.* (%) calcd for $C_5H_8Br_2N_2Se$: C, 17.93; H, 2.41; N, 8.36. Found: C, 18.21; H, 2.44; N, 8.39. ^1H NMR (300 MHz) δ (CD_3CN) 3.94 (s, 6H), 7.45 (s, 2H). ^{13}C NMR (77.48 MHz) δ ($CDCl_3$) 38.5 (s), 122.9 (s). Λ_M (ca. 10^{-3}M in CH_3CN) 2.6 mhos cm^2 mol^{-1}. MW = 350. FTIR: 3146m, 3119s, 3096m,sh, 3050w, 3023w, 2943w, 2922vw, 2853w, 1709w, 1609w, 1561m, 1495s, 1460m, 1429s, 1402m, 1373w, 1337w, 1231s, 1157w, 1130w, 1094w, 1026w, 849w, 754s, 739s, 664s, 611w, 467m. Raman: 2938w, 1553m, 1442s, 1376s, 1160m, 1087m, 1033m, 857w, 740m, 616w.

2,2′-Diselenobis[1,3-dimethyl-2(3H)-imidazolylium] dibromide (4)

This compound was synthesized in a manner similar to that described for **3**, except that 0.46 g (2.9 mmol) of Br_2 was used. A yellow precipitate of **4** was isolated upon evaporation of the solvent, and recrystallization from ethanol gave 1.2 g of the product (80%). Yellow crystals, mp 265–267°C. *Anal.* (%) calcd for $C_5H_8BrN_2Se$: C, 23.55; H, 3.16; N, 10.98. Found: C, 23.63; H, 3.21; N, 10.89. ^1H NMR (300 MHz) δ (D_2O) 3.75 (s, 6H), 7.77 (s, 2H); Λ_M (ca. 10^{-3}M in H_2O) 268 mhos cm^2 mol^{-1}. FTIR: 3134w, 3106m, sh, 3073s, 3047s, 2944w, 2870vw, 2805vw, 2743vw, 1742w, 1562m, 1496s, 1458vw, 1439w, 1420m, 1391w, 1339w, 1244s, 1163m, 1096m, 1026mw, 876w, 775s, 737m, 656m, 613w, 469w. Raman: 2938w, 1561w, 1376s, 1164m, 1098w, 1029w, 874vw, 740w, 665w, 616w.

1,3-Dimethyl-2-(methylseleno)-2(3H)-imidazolylium iodide (5)

In a 125 mL erlenmeyer flask fitted with a magnetic stirrer were placed 0.46 g (2.6 mmol) of a crude sample of **2** and 40 mL of CH_3I. A white precipitate of **5** appeared immediately. The solution was allowed to stir while CH_3I was evaporated under a hood with a stream of dry N_2. Recrystallization from ethanol yielded 0.46 g of **5** (55%). The low yield may be attributed to the use of crude starting material. Pale yellow crystals, mp 183°C (sublimes). Anal. (%) calcd for $C_6H_{11}IN_2Se$: C, 22.73; H, 3.50; N, 8.84. Found: C, 22.87; H, 3.44; N, 8.91. ^1H NMR (300 MHz) δ (CD_3CN) 2.36 (s, 3H), 3.90 (s, 6H), 7.52 (s, 2H); Λ_M (ca. 10^{-3}M in H_2O) 114 mhos cm^2 mol^{-1}. FTIR: 3071s, 3043s, 3001w, 2945vw, 2918vw, 1661m, 1568m, 1497s, 1466m, 1465m, 1427m, 1408m, 1344m, 1269m, 1246s, 1163w, 1099m, 1028m, 918s, 789s, 741w, 656s, 615w. The Raman spectrum was obscured by fluorescence.

X-ray Crystallographic Data

Suitable crystals of **2** were mounted on a glass fiber using epoxy cement such that the longest crystal dimension was approximately parallel to the fiber axis. Unit cell parameters were determined on a Syntex $P2_1$ four circle diffractometer equipped with a graphite monochrometer (Bragg 2θ angle = 12.2°) using MoK_α (λ = 0.71069 Å) radiation at a takeoff angle of 6.75°. Fifteen reflections were machine centered and used in least-squares refinement of the lattice parameters. Omega scans of several low 2θ angle reflections gave peak widths at half-height of less than 0.24 Å, indicating a satisfactory mosaic spread for the crystal examined. Axial photographs were used to determine the space group, with zero and upper level intensity data being examined for systematic absences in the usual fashion.

Intensity data were collected using ω scans with X-ray source and monochromator settings identical to those used for determination of the unit cell parameters. A variable scan rate of 3.91 to 29.3° min^{-1} was used, and a scan width of 1.0° was sufficient to collect all the peak intensity. Stationary background counts were measured at the beginning and at the end of each scan, with a total background-to-scan time ratio of 1.0. No significant fluctuations were observed in the intensities of three standard reflections measured every 100 reflections. Intensities were calculated from the total scan count and background counts by the usual relationship.

The intensities were assigned standard deviations in the usual manner, and intensity data are summarized in Table 1. Reflections were collected in a complete quadrant ($\pm h$ $+k$ $+1$) out to 2θ = 50°. Reflections were accepted as statistically above background on the basis that F was greater than $2.5\sigma(F)$. Lorentz and polarization corrections were made in the usual way. A psi-zero correction was made for absorption.

Solution and Refinement of the Structure

Computations were performed using the standard programs [13], and they were carried out on the CDC Cyber 74 System. For structure factor calculations, the scattering factors were taken from the *International Tables for X-Ray Crystallography* [14]. The agreement factors are defined in the conventional way. In all least-squares refinements, the quantity minimized has been previously defined [15]. The weighting scheme based on counting sta-

TABLE 1 Data Collection and Processing Parameters

Molecular formula	$C_5H_8N_2Se$
Molecular weight	175.03
Unit cell parameters	
	a = 8.625(3) Å
	b = 11.447(6) Å
	c = 6.900(4) Å
	V = 681.24 $Å^3$
	Z = 4
	$F(000)$ = 344
λ(Mo-K_α)	0.71073 Å
μ(Mo-K_α)	5.35 mm^{-1}
Temperature	294 K
Density (calcd)	1.707 g/cm^3
Density (obsd)	1.68 g/cm^3 (flotation CCl_4/CH_2Br_2)
Space group	C mcm
Crystal size	0.24 × 0.20 × 0.10 mm
Unique data measured	351
Observed data with $\lvert F_0 \rvert > 2.5\sigma \lvert F_0 \rvert$	270
Conventional R	0.034
Weighted R	0.031
Goodness of fit	1.736
Res. electron density	−0.460/+0.520 $e/Å^3$
Maximum shift/error ratio final cycle	<0.000

tistics is also as previously defined for the calculation of R_w and in least-squares refinement [15].

The structure was solved using a Patterson map. Hydrogen atoms were not added. Final calculated values for R and R_w, as well as other crystallographic data, are summarized in Table 1. Interatomic distances and angles are presented in Figure 1. Final thermal parameters and a list of calculated and observed structure factor tables are available [16].

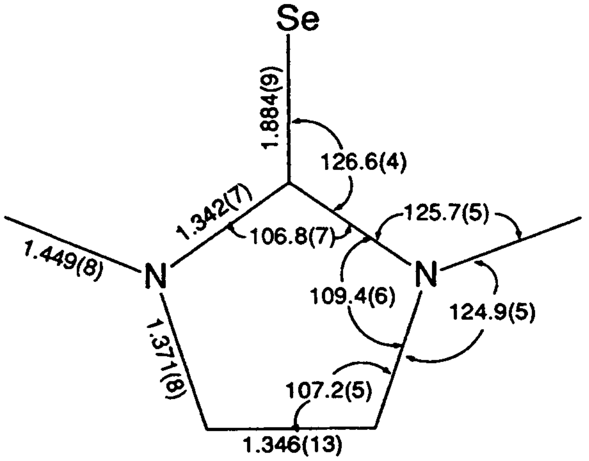

FIGURE 1 Bond distances (Å) and angles (°) for **2**. Estimated standard deviations given in parentheses.

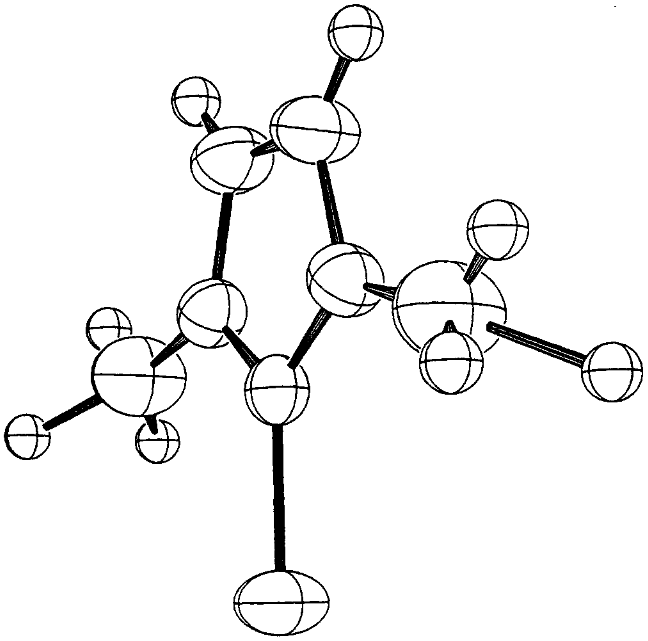

FIGURE 2 ORTEP drawing of **2** showing the planarity of the ring. Thermal ellipsoids drawn at 50% probability level.

RESULTS AND DISCUSSION

The reaction of elemental Se with **1** in methanolic K_2CO_3 yields **2** in approximately 70% yield or better. The selone is a stable, white, relatively odorless crystalline solid which is very soluble in most nonpolar solvents and, to a lesser extent, in ethanol and water. The X-ray diffraction analysis of **2** reveals a structure similar to that noted by Ansell *et al.* for *dmit* [17]. Figure 1 shows bond angles and distances for the planar heterocyclic ring structure of **2**, and Figure 2 is a perspective showing the planarity of the ring. The principle significant structural feature of **2** is the more nearly equal C–N and C–C bond distances about the imidazole ring. By comparison, in *dmit*, the C(thionyl)–N, C(ethylenic)–N, and C=C distances are 1.35 Å, 1.41 Å, and 1.31 Å, respectively. The authors concluded that, based on bond distances within the ring, the electronic structure would best be represented by a resonance hybrid of structures **a** and **b** shown in Figure 3b. Further support for this conclusion came from the C–S distance, which was observed to be intermediate between average single and double bond values [17]. The ring distances observed for **2**, however, tend to support a more delocalized structure, as depicted by Figure 3c. Proton NMR spectra in two different solvents also support the more aromatic nature of the ring in **2**, with greater downfield shifts (δ 7.01, 6.82) relative to *dmit* noted for the olefinic protons (cf. δ 6.69 in CH_3CN and 6.67 in $CDCl_3$ for *dmit* [18]). Further support for the electronic configuration shown in Figure 3c is

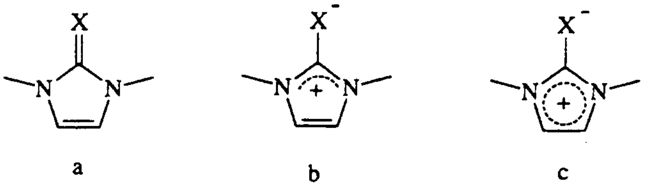

FIGURE 3 (a)–(c) Possible electronic structural configurations for 2(3*H*)-imidazolechalcones. X = S, Se.

seen in the C–Se bond distance of 1.884 Å, which is significantly longer than that noted for an isolated double bond, such as in CSe_2 (1.698 Å) [19], and much closer to a single bond distance of 1.94 Å, as estimated by the sum of the covalent radii[20] and as seen in cationic selenoether adducts of $C_5H_5Fe(CO)_2$ (1.924 Å and 1.942 Å) [21].

Three derivatives of **2** were also isolated. These included two addition products with bromine (**3**,**4**) and one with iodomethane (**5**). The bromine products are synthesized by controlled stoichiometric additions of Br_2 in CH_2Cl_2 to **2** in a manner similar to that described by Arduengo and Burgess [7]. With 1:1 molar proportions of Br_2 to **2**, large air-stable sublimable orange crystals of 1,3-dimethyl-2-(Se,Se-dibromoseleno)-2(3*H*)-imidazolylidene (**3**) appeared upon evaporation of the solvent. With half as much bromine in molar proportion, yellow crystals of 2,2′-diseleno*bis*[1,3-dimethyl-2(3*H*)-imidazolylium] dibromide (**4**) precipitated immediately from CH_2Cl_2. The proposed structures of **3** and **4** are based on composition, conductivity, spectral data, and structural results observed by Arduengo and Burgess for the bromine addition products of *dmit* mentioned previously [7]. Of particular interest is **3** which, based on the sulfur analog results, may be a trivalent selenurane adduct or, viewed another way, a carbene-stabilized Se(II) bromide complex. Se(II) halides have been stabilized by other ligands, such as 1,1,3,3-tetramethylthiourea [22] and triphenylphosphine [23], while the hypervalent selenium halide adducts of tetramethylselenourea [24] and a very interesting 1,2,3-triselenetan-4-(Se,Se-dibromoselone) [25] have been structurally characterized. A single-crystal X-ray study is currently underway for **3** to confirm the structure and compare it to the compounds noted earlier.

Refluxing **2** in pure iodomethane yielded the Se-methyl adduct, 1,3-dimethyl-2-(methylseleno)-2(3*H*)-imidazolylium iodide (**5**). Analogous S-methyl derivatives, sometimes referred to as thiopseudoureas, have been isolated and characterized by reactions of *dmit* with iodomethane and trimethyloxonium hexachloroantimonate (V) [26,27].

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