

Synthesis, Spectral Characterization and Ligation of *N*-[2-(Phenylseleno)ethyl]phthalimide

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ABSTRACT

PhSe⁻Na⁺ generated *in situ* by reduction of PhSeSePh, with sodium borohydride on reaction with *N*-(2-bromoethyl)phthalimide in N₂ atmosphere results in the formation of *N*-[2-(phenylseleno)ethyl]phthalimide (**L**¹). The title compound has been characterized by elemental analysis, FT-IR, ¹H and ¹³C NMR techniques. The crystal structure of **L**¹ has been solved by direct methods and refined by full-matrix least squares. The ligand **L**¹ crystallize in the monoclinic space group. Selenium forms two Se-C linkages, one is due to Se-C_{alkyl} and the other one to Se-C_{aryl}. Further, the ligation reaction of **L**¹ with complex **1** is also explored whose identities are characterized by spectroscopic techniques.

Keywords: Phthalimide; Selenium; Monoclinic; Phenylseleno; Sodium Borohydride

1. Introduction

There is current interest in the chemistry of a variety of polydentate organochalcogen ligands due to their hemilabile nature, and the possibility of using their metal complexes as precursor for II-VI semiconductors [1-4]. The synthesis and characterization of *N*-{2-(4methoxyphenyl telluro) ethylphthalimide} [5], potentially [Te, N, O₂] type donor along with its palladium [5] and ruthenium complexes [6] were studied. Recently various bidentate heteroleptic ligands [7] containing donor groups (N, S and N, Se), have been prepared which offer opportunities in catalytic cycle of aryl bromides. In our previous study, we reported the synthesis, characterization, and crystal structure of the first example of selenium containing acetate salt (3-Phenylseleno) propylammonium acetate salt [8]. We have also reported the cleavage of **L**¹ in two different ways upon reaction with selected metal salts [8]. In continuation of our studies on (Te, N, O) and (N, S and N, Se) donors, we have synthesized a novel (Se, N, O) donors. **L**¹ was characterized by spectral and X-ray analysis.

2. Experimental

2.1. Materials

Diphenyl diselenide [9], was prepared according to the published method, *N*-(2-bromoethyl) phthalimide was

used as received from Aldrich. Selenium powder and sodium borohydride were purchased from CDH (India). All glassware were cleaned with acetone, followed by copious rinsing with distilled water before rinsing with distilled water before drying at 150°C in oven for a few hours.

2.2. Equipment

All reactions involving air sensitive compounds were performed under nitrogen atmosphere. The C, H and N analysis were carried out with an Elementar Vario EL III analyser. ¹H and ¹³C NMR spectra were recorded with a JEOL AL300 FT NMR spectrometer at 300 MHz and 75.45 MHz, respectively, in CDCl₃ and DMSO(d₆) as solvents (tetra methyl silane (TMS) as internal standard). IR spectra in the range of 4000 - 400 cm⁻¹ were recorded on a Shimadzu Prestige 21 FT-IR spectrometer as KBr pellets. The melting point was determined in open capillary are reported as such.

2.3. Ligand Synthesis

Synthesis *N*-[2-(phenylseleno)ethyl]phthalimide (**L**¹). To an aqueous THF solution (20 mL THF + 0.2 mL H₂O) of diphenyl diselenide (3.14 g, 10 mmol) and NaOH (0.80 g, 20 mmol) under N₂ atm, NaBH₄ (0.75 g, 20 mmol) was added in pinches. The yellow color of the diselenide darkened and then gradually faded to colorless. To this colorless solution, *N*-(2-bromoethyl)phthalimide [5.08

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gm, 20 mmol] in THF (20 mL) was added dropwise and the solution was stirred for 24 h at room temperature. It was hydrolyzed with 100 mL water and extracted into 200 mL chloroform, washed with 100 mL water and dried over anhydrous magnesium sulphate. The extract was concentrated to 5 mL under reduced pressure, then washed with diethyl ether to remove the precursor diphenyl diselenide, and kept overnight at room temperature. The resulting white precipitate was recrystallized with chloroform-diethyl ether mixture (1:2) and dried in vacuo. It was followed by crystallization with slow evaporation of a $\text{CHCl}_3/\text{MeOH}$ solution to yield a transparent crystals. Yield: 70% Mp: 120°C Found: C, 58.04; H, 3.99; N, 4.17; Se, 23.82; Calcd for $\text{C}_{16}\text{H}_{13}\text{NO}_2\text{Se}$ (MW: 331 g/mol); C, 58.19; H, 3.96; N, 4.24; Se, 23.90%. IR (KBr, cm^{-1}): 512 m, ν (Se-C_{alkyl}); 1170 s, ν (C-N); 1708 s, ν (C=O); $^1\text{H-NMR}$ (300 MHz, CDCl_3 , TMS): δH 7.81 - 7.21 (m, 9H, H-Ar), 3.19 (t, 2H, $3J_{\text{H-H}} = 6.3$ Hz, Se-CH₂), 4.00 (t, 2H, $3J_{\text{H-H}} = 7.2$ Hz, N-CH₂) ppm. $^{13}\text{C NMR}$ (75 MHz, CDCl_3 , TMS) δC , 24.82 (C₁₀, Se-CH₂); 38.29 (C₉, N-CH₂); 129.03 (C₁₁, Se_{ipso}); 168.04 (C₈, C=O), 127.11 (C₁₃), 123.27 (C₁₄), 129.13 (C₆), 132.00 (C₇), 132.72 (C₅), 133.94 (C₁₂).

2.4. Complex Synthesis

Synthesis of [(HgCl₂ (L¹))] (1). A mixture of L¹ (0.331 gm, 1 mmol) and mercuric chloride (0.271 g, 1 mmol) in methanol 5 mL was stirred at room temperature for 5 hr. The resultant white precipitate was filtered, washed with petroleum ether and dried in vacuo. It was recrystallized with a methanol:chloroform (9:1) mixture. Yield: 82% Mp: 90°C Found: C, 31.84; H, 2.14; N, 2.36; Se, 13.04; Calcd for $\text{C}_{16}\text{H}_{13}\text{NO}_2\text{SeHgCl}_2$: C, 32.05; H, 2.17; N, 2.33; Se, 13.02%. IR (KBr, cm^{-1}): 501 m, ν (Se-C_{alkyl}); 1153 s, ν (C-N); 1708 s, ν (C=O); $^1\text{H NMR}$ (300 MHz, DMSO (d₆), TMS): δH , 7.74 - 7.82 (m, 9H), 3.81 (t, 2H, $3J_{\text{H-H}} = 4.5$ Hz, Se-CH₂), 4.22 (t, 2H, $3J_{\text{H-H}} = 6$ Hz, N-CH₂) ppm. $^{13}\text{C NMR}$ (75 MHz, DMSO (d₆), TMS): δC , 25.24 (C₁₀, Se-CH₂); 39.45 (C₉, N-CH₂); 129.17 (C₁₁, Se_{ipso}); 167.46 (C₈, C=O), 126.63 (C₁₃), 123.27 (C₁₄), 129.17 (C₆), 131.39 (C₇), 132.10 (C₅), 134.27 (C₁₂) ppm.

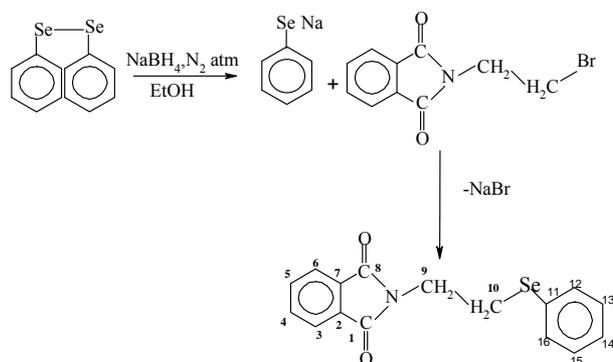
3. Crystal Structure Analysis

X-ray data for *N*-[2-(phenylseleno)ethyl]phthalimide were collected with an Oxford Diffraction Gemini R CCD area detector using CrysAlisPro software and graphite-monochromated MoK α ($\lambda = 0.71073$ Å) at 200 (2) K. The size of crystal used for data collection was $0.55 \times 0.35 \times 0.12$ mm³. The structure was solved by direct methods using SHELXS97 [10] and all of the non-hydrogen atoms were refined anisotropically by full matrix least-squares on F² using SHELXL97 [10]. The hydrogen atoms were placed in their calculated positions and included in the refine-

ment using the riding model. An absorption correction was performed using CrysAlis RED and all calculations were performed using SHELXTL [11].

4. Results and Discussion

The reaction given in **Scheme 1** produce *N*-[2-(phenylseleno)ethyl]phthalimide (L¹), which remain stable under ambient conditions for 2 - 3 months. It is soluble in ethanol, methanol, chloroform and dichloromethane. It was characterized by elemental analysis, IR, ^1H , ^{13}C NMR and single crystal structure. In the IR spectra of L¹ due to presence of electronegative selenium, band of amide group is shifted to higher wavenumber 1708 cm^{-1} in comparison to the precursor *N*-[2-(bromo) ethyl] phthalimide at 1681 cm^{-1} . The bands at 1170 and 512 cm^{-1} are attributed to ν (C-N) and ν (Se-CH₂). The ^1H and ^{13}C NMR spectra of L¹ display the expected resonances and peak multiplicities. 1:1 heterobimetallic adducts of L¹ with HgCl₂ was obtained by stirring a mixture of the two components in methanol: chloroform mixture (1:1) at r.t. (**Scheme 2**). Complex 1 remains stable under ambient conditions for 2 - 3 months. It is soluble in ethanol, methanol, chloroform and dichloromethane. It was characterized by elemental analysis, FAB mass IR, ^1H NMR and ^{13}C NMR. FAB mass spectrum of complex 1 confirms its monomeric character and the presence of a 1:1 metal:ligand stoichiometry in the compound. The molecular ion peak [M + H] is observed at m/z 604 with a very low intensity. The base peak at m/z 174 corresponds to [L¹-SePh]. The peaks at m/z 533 [MH-2Cl] and m/z 254 [L¹-Ph] are observed with low intensity whereas the peaks at m/z 568 [MH-Cl] and 331 [L¹] observed with abundance. In the IR spectra of complex 1, the absorption due to ν (C-N) and ν (Se-CH₂) are shifted to lower frequency and appear at 1153 and 501 cm^{-1} re-



Scheme 1. Preparation of *N*-[2-(phenylseleno)ethyl]phthalimide (L¹).



Scheme 2. Preparation of complexes 1.

spectively. The absorption due to ν (C=O) remain almost unaffected, indicating that L^1 in complex **1** is coordinated through N and Se. The ^1H and ^{13}C NMR spectra of complex **1** are normal. In d_{10} system, coordination shifts in the NMR spectra is found to be insignificant [8]. In ^1H NMR spectrum of complex **1** the downfield shift of Se-CH₂ and N-CH₂ signals clearly establishes the coordination through Se and N to the metal atom. In the ^{13}C $\{^1\text{H}\}$ NMR spectra of complex **1**, the deshielding of Se-CH₂ and N-CH₂ signals by 0.42 and 1.16 ppm respectively with respect to those of free ligand L^1 , also argues for the coordination of the selenium and the nitrogen atom to the metal ion. Thus, the IR and NMR data shows that the ligand L^1 ligates through (Se, N) in a bidentate mode [12-14] to the metal salt and support from previous work, the following most possible structure has been proposed on the presumption that geometry of complex **1** is tetrahedral (**Figure 1**)

The molecular and that of the unit cell, as determined by X-ray diffraction on a single crystal of *N*-[2-(phenylseleno)ethyl]phthalimide, are shown in **Figures 2** and **3**. It may act as a (Se, N) donor easily and perhaps (Se, N, O) donor also in bimetallic complexes. L^1 crystallizes in the

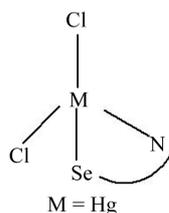


Figure 1. Proposed structure of complex **1**.

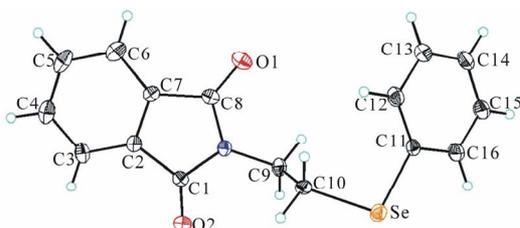


Figure 2. The molecular structure of the complex, $\text{C}_{16}\text{H}_{13}\text{NO}_2\text{Se}$, showing the atom numbering scheme and 30% probability displacement ellipsoids. Symmetry transformations used to generate equivalent atoms.

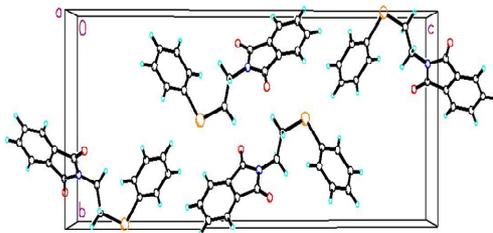


Figure 3. The molecular packing for $\text{C}_{16}\text{H}_{13}\text{NO}_2\text{Se}$, viewed down the axis.

monoclinic space group P 21/n with unit cell parameters $a = 5.0586$ (5), $b = 10.1316$ (8), $c = 27.050$ (5), Å = 93.250 (11)°, $Z = 4$. Crystal and experimental data for L^1 are listed in **Table 1**. Bond lengths and bond angles are all within expected ranges, (see **Table 2**). In the present compound selenium is regarded as in oxidation state +2. The length of the C-Se bonds, 1.919 (3) and 1.952 (3)

Table 1. Crystal data and structure refinement for *N*-[2-(phenylseleno)ethyl]phthalimide.

Empirical formula	$\text{C}_{16}\text{H}_{13}\text{NO}_2\text{Se}$	
Formula weight	330.23	
CCDC deposit No.	766004	
Temperature (K)	200 (2)	
Wavelength (Å)	0.71073	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	$a = 5.0586$ (5) Å	= 90°
	$b = 10.1316$ (8) Å	= 93.250 (11)°
	$c = 27.050$ (5) Å	= 90°.
Volume	1384.1 (3) Å ³	
Z	4	
Density (calculated)	1.585 Mg/m ³	
Absorption coefficient	2.713 mm ⁻¹	
Diffractometer/scan	Oxford Diffraction Gemini R	
	CCD detector $\omega/2\theta$	
F (000)	664	
Crystal size	0.55 × 0.35 × 0.12 mm ³	
Theta range for data collection	4.61° to 32.56°	
Index ranges	-7 ≤ h ≤ 7, -14 ≤ k ≤ 14, -36 ≤ l ≤ 39	
Reflections collected	12342	
Independent reflections	4560 [R (int) = 0.0680]	
Completeness to theta = 25.00°	98.8%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.65708	
Refinement method	Full-matrix least-squares on F ²	
Data/restraints/parameters	4560/0/181	
Goodness-of-fit on F ²	0.934	
Final R indices [I > 2 sigma (I)]	R1 = 0.0485, wR2 = 0.1092	
R indices (all data)	R1 = 0.1411, wR2 = 0.1513	
Largest diff. peak and hole	0.543 and -0.850 e ⁻ Å ⁻³	

Table 2. Bond lengths [Å] and angles [°] for *N*-[2-(phenylseleno)ethyl]phthalimide.

Bond lengths [Å]		Bond angles [°]	
Se-C(11)	1.919 (3)	C(11)-Se-C(10)	101.36 (14)
Se-C(10)	1.952 (3)	C(8)-N-C(1)	112.2 (3)
O(1)-C(8)	1.210 (4)	C(8)-N-C(9)	124.1 (3)
O(2)-C(1)	1.214 (4)	C(1)-N-C(9)	123.5 (3)
N-C(8)	1.384 (4)	O(2)-C(1)-N	124.7 (3)
N-C(1)	1.401 (4)	N-C(1)-C(2)	105.8 (3)
N-C(9)	1.466 (4)	O(1)-C(8)-N	125.4 (3)
C(1)-C(2)	1.476 (4)	N-C(8)-C(7)	105.9 (3)
C(7)-C(8)	1.493 (4)	N-C(9)-C(10)	112.5 (3)
C(9)-C(10)	1.512 (5)	C(16)-C(11)-C(12)	119.0 (3)
C(11)-C(16)	1.370 (5)	C(16)-C(11)-Se	117.0 (3)
C(11)-C(12)	1.380 (5)	C(12)-C(11)-Se	124.0 (3)
C(12)-C(13)	1.393 (5)	C(11)-C(12)-C(13)	119.6 (3)
C(13)-C(14)	1.366 (6)	C(14)-C(13)-C(12)	120.9 (4)
C(14)-C(15)	1.367 (6)	C(13)-C(14)-C(15)	119.1 (4)
C(15)-C(16)	1.381 (5)	C(14)-C(15)-C(16)	120.5 (4)
		C(11)-C(16)-C(15)	120.8 (4)

Å and the angle between these two bonds, C-Se-C are consistent [15]. The Se-C(Ar) bond distance is somewhat shorter than the Se-C(alkyl) distance as expected [16].

5. Conclusion

We have shown that NaBH₄ can be used as reduction system to generate an organochalcogen anion. This anion reacts in a SN₂ reaction on *N*-[2-bromoethyl]phthalimide to produce *N*-[2-(phenylseleno)ethyl]phthalimide (**L**¹) under mild conditions. These organochalcogen derivatives, **L**¹, was used to synthesize a metal complex **1**, from HgCl₂. **L**¹ act as a polydentate ligand containing oxygen or nitrogen as a hard donor. And chelate **1** was characterized as 1:1 complex by various spectroscopic techniques (IR, FAB mass, ¹H and ¹³C NMR).

6. Supplementary Material

For **L**¹, crystal data, structural information (geometric bond distances, bond and torsion angles; hydrogen bonding) & refinement data are provided. Crystallographic data (CIF) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre and allocated the deposition numbers CCDC 766004 for **L**¹. These data can be obtained, free of charge

via www.ccdc.cam.ac.uk/data_request/cif, by sending an e-mail to data_request@ccdc.cam.ac.uk, from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax; +44 1223 336033

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