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Journal of Organometallic Chemistry 623 (2001) 87–94

Journal of Organometallic Chemistry

www.elsevier.nl/locate/jorganchem

Synthesis of some macrocycles/bicycles from bis(*o*-formylphenyl) selenide: X-ray crystal structure of bis(*o*-formylphenyl) selenide and the first 28-membered selenium containing macrocyclic ligand

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Received 4 July 2000; accepted 19 October 2000

Abstract

Bis(*o*-formylphenyl) selenide (**7**) was synthesized using the ortholithiation methodology. The reaction of *o*-lithiobenzaldehyde acetal (**5**) with $Se(dtc)_2$ (dtc = diethyldithiacarbamate) afforded bis(*o*-formylphenyl) selenide acetal (**6**) in good yield. The key starting material **7** was isolated as pale yellow solid upon refluxing **6** with concentrated HCl. The structure of **7** was solved in the monoclinic space group $P2/c$ with cell constants $a = 8.0170(6)$ Å, $b = 8.4514(6)$ Å and $c = 17.5289(12)$ Å, $Z = 4$. The condensation of **7** with diethylenetriamine yielded the novel macrocyclic ligand $[C_{36}H_{38}N_6Se_2]$ **8** via metal-free dimerization. Crystals of **8** are monoclinic, space group $C2/c$ with $a = 18.732(3)$ Å, $b = 8.6515(10)$ Å, $c = 22.590(3)$ Å and $Z = 4$. Hydrogenation of macrocycle **8** provided the corresponding saturated tetraazamacrocycle $[C_{36}H_{46}N_6Se_2]$ (**9**), protonation of which with HBr afforded $[C_{36}H_{52}N_6Se_2Br_6{\cdot}H_2O]$ (**10**). The two novel cryptands $[C_{54}H_{54}N_8Se_3]$ (**12**) and $[C_{54}H_{54}N_8Te_3]$ (**13**) were prepared from the reaction of tris(2-aminoethyl)amine (tren) and the chalcogenides (**7**) and bis(*o*-formylphenyl) telluride (**11**) respectively using cesium ion as the template.

Keywords: Macrocycle; Cryptands; Selenide; Selenaazamacrocycle; Polyamine; Tetrabromide salt

1. Introduction

The design and synthesis of Schiff-base macrocylic ligands for the selective coordination of metals has attracted considerable current interest [1]. There is a significant activity in the design and synthesis of Schiff base macrocyclic ligands incorporating additional donor atoms such as O (oxaaza) and S (thiaaza) [1]. Incorporation of the larger Se and Te would lead to a change in the size of the cage cavity and hence allow for some interesting coordination behaviour. In addition, the greater σ-donating ability of Se and Te would facilitate the complexation of a variety of metal ions. Surprisingly, there is a paucity of information in the literature concerning the heavier chalcogen (Se, Te) analogs, although some homoleptic selenoether macrocycles have been reported [2]. Also reports on the metal-ion complexes of the selenium macrocycles have mainly dealt with homoleptic selenoethers ligands such as 1,5,9,13-tetraselenacyclohexadecane ([16]aneSe_4) [3]. As part of our research into design and synthesis of novel heavier chalcogenaaza macrocycles, we recently reported the synthesis and complexation studies of the first telluraaza macrocyclic Schiff base [4].

To our knowledge, selenium has not been incorporated into a macrocyclic Schiff base. The closest example would be the nitro-capped cage with an N_3Se_3 donor set [5]. Other related polyselena macrocycles include; [6]aneSe_2 and [8]aneSe_4, the tetraselena-macrocycles [16]aneSe_4, [14]aneSe_4, [12]aneSe_4 and hexaselena-macrocycle [24]aneSe_6 [2a], the selenium containing cyclophane [2b], novel tetraselenide macrocycles [2c,d], cyclic polyselenoether, the selenium analogs [2e,f] of crown ethers, the host molecule containing the Se–Se bond [2g]. The diselena crown ether reported by Meunier et al. [2h], tetraselena crown ethers of three different sizes incorporating several oxygen atoms in the bridge [2i] are other notable examples.

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0022-328X/01/$ - see front matter
PII: S0022-328X(00)00830-5

In continuation of our work on selenium [6] and tellurium [4] containing macrocycles, we report in this paper the synthesis and coordination chemistry of a novel 28-membered selenium azamacrocyle (Se_2N_6 system) with more donor atoms and also the first example of a tellurium containing macrobicyclic ligand along with its selenium analog having E_3N_8 (E = Te, Se) donor sets.

2. Experimental

Bis(*o*-formylphenyl) telluride [4a], $Se(dtc)_2$ [7] and $Pd(COD)Cl_2$ [8] were prepared by reported procedures. Air sensitive reactions were carried out under an inert atmosphere. Solvents were purified by standard techniques and were freshly distilled prior to use. Diethylenetriamine was reagent grade and was distilled prior to use. Tris(2-aminoethyl)amine (Aldrich) was used as received. Melting points were recorded in capillary tubes and are uncorrected. IR spectra were recorded as KBr pellets on a Nicolet Impact 400 FTIR spectrometer (4000–400 cm^{-1}). ^1H- (299.94 MHz), ^{13}C- (75.42 MHz), and ^{77}Se-NMR (57.22 MHz) NMR spectra were recorded on a Varian VXR 300S spectrometer at the indicated frequencies. Chemical shifts cited were referenced to TMS (^1H, ^{13}C) as internal, Me_2Se (^{77}Se) as external reference. Elemental analyses were performed on a Carlo-Erba model 1106 elemental analyzer. Mass spectra were recorded at room temperature (r.t.) on a JEOL D-300 (EI/CI) mass spectrometer. Fast atom bombardment (FAB) mass spectra were recorded at r.t. on a JEOL SX 102 DA-6000 mass spectrometer/data system using xenon (6 kV, 10 mV) as the bombarding gas. The acceleration voltage was 10 kV and *m*-nitrobenzyl alcohol was used as the matrix with positive-ion detection. In case of isotopic patterns the value given is for the most intense peak.

2.1. Preparation of bis(o-formylphenyl) selenide acetal (6)

To a solution of ethylene acetal of *o*-bromobenzaldehyde (4.7 g, 20.5 mol) in dry ether (100 ml) taken in a three-necked (250 ml) flask fitted with rubber septum and nitrogen gas inlet was added dropwise with stirring a 1.6 M solution of *n*-butyllithium (14 ml, 22.4 mmol) over a period of 5 min at r.t. The mixture was stirred for additional 5 min to get a cloudy white slurry. Then $Se(dtc)_2$ (3.86g, 10.3 mmol) was added under a brisk flow of nitrogen in small portions. After stirring for 1 h at r.t. the solution was poured into ice water (500 ml) and extracted with diethyl ether (3 × 50 ml). The ether solution was dried over anhydrous sodium sulfate and concentrated in vacuo. The residue was kept aside overnight to get colorless crystals of bis(*o*-formylphenyl) selenide acetal (**6**). Yield = 2.6g (68%); m.p.: 130–132°C; Anal. Found: C, 57.65; H, 4.54; $C_{18}H_{18}O_4Se$ Calc.: C, 57.30; H, 4.81%; ^1H-NMR ($CDCl_3$): δ 7.63–7.16 (m, 8H, aromatic-H), 6.14 (s, 2H, Ar–C<u>H</u>), 4.77–4.02 (m, 8H, OC<u>H</u>$_2$–C<u>H</u>$_2$O); ^{13}C-NMR ($CDCl_3$): δ 138.53, 134.71, 131.78, 130.04, 127.61, 126.90 (aromatic-C), 103.11 (Ar–<u>C</u>HO$_2$), 65.45 (O<u>C</u>H$_2$–<u>C</u>H$_2$O); ^{77}Se--NMR ($CDCl_3$): δ 321.

2.2. Preparation of bis(o-formylphenyl) selenide (7)

Bis(*o*-formylphenyl) selenide acetal (2.12 g, 5.63 mmol) in CCl_4 (10 ml) and methanol (30 ml) mixture was refluxed with HCl (6 N, 2.2 ml) for 2 h. To this water (10 ml) was added and the reaction mixture was further refluxed for 5 min. After cooling, the mixture was washed with water (3 × 25 ml). The organic layer was separated and dried over sodium sulfate. The excess of CCl_4 was distilled off and the product was precipitated out as pale yellow solid after keeping for overnight. Yield = 1.2 g (74%); m.p.: 124–126°C [lit. 127°C]; IR (KBr): 1706 cm^{-1}; Anal. Found: C, 59.05; H, 3.46; $C_{14}H_{10}O_2Se$ Calc.: C, 58.15; H, 3.49%; ^1H-NMR ($CDCl_3$): δ 8.01–7.27 (m, 8H, aromatic-H), 10.28 (s, 2H, aldehydic-H); ^{13}C-NMR ($CDCl_3$): δ 193.48 (Ar–<u>C</u>HO), 136.06, 135.81, 134.93, 134.63, 132.75, 128.28 (aromatic-C); ^{77}Se-NMR ($CDCl_3$): δ 393.

2.3. Synthesis of bis(diphenylselenide)BISDIEN Schiff base (8)

A solution of bis(*o*-formylphenyl) selenide (0.15 g, 0.5 mmol) in acetonitrile (100 ml) was added to a stirred solution of diethylenetriamine (0.052 g, 0.5 mmol) in CH_3CN (100 ml) over a period of 1 h. The mixture was stirred overnight and the precipitated white powder was filtered off, washed with acetonitrile and recrystallized from $CHCl_3/CH_3CN$: Yield = 0.16g (84%); m.p. 172–174°C; IR (KBr): 1639, 1584 cm^{-1}, ($\nu_{C=N}$ stretching); Anal Found: C, 60.88; H, 5.22; N, 11.88; $C_{36}H_{38}N_6Se_2$ Calc.: C, 60.67; H, 5.37; N, 11.79%; MS (FAB): m/z 713(M^+), 460, 358, 307, 289, 154, 136, 120, 107, 89, 63; ^{77}Se-NMR ($CDCl_3$): δ 387.9, 387.5, 335.6, 329.8, 328.5.

2.4. Synthesis of bis(diphenylselenide)BISDIEN (9)

To a suspension of **8** (0.29 g, 0.4 mmol) in ethanol $NaBH_4$ was added in excess in small portions and the reaction mixture was stirred for 3 h at r.t. Excess ethanol was removed under reduced pressure. To the residue, water (50 ml) was added and the product was extracted with dichloromethane. Yield = 0.17 g (61%); 185–187°C; IR (KBr): 3320 cm^{-1} (NH stretching), 1728, 1664 cm^{-1} (NH bending); Anal Found: C, 59.79;

H, 6.49; N, 11.38 $C_{36}H_{46}N_6Se_2$ Calc.: C, 60.00; H, 6.43; N, 11.66%; MS (FAB): m/z 723 (M^+), 635, 362, 259; ^{77}Se-NMR ($CDCl_3$): δ 328.

2.5. Synthesis of bis(diphenylselenide)BISDIEN hydrobromide salt (10)

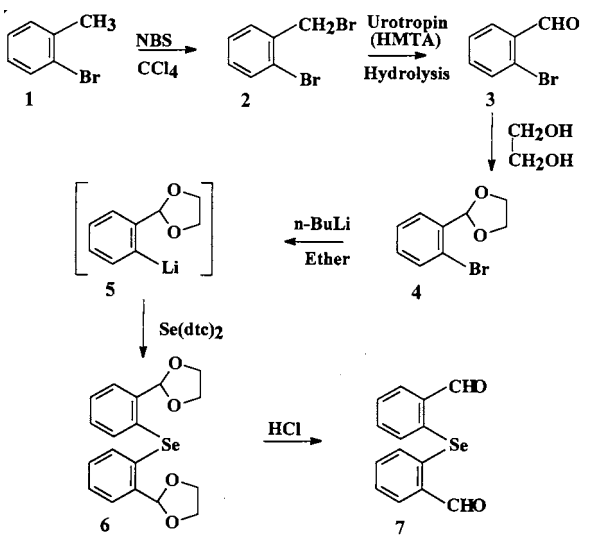
The crude reduced Schiff base (**9**) (0.36 g, 0.5 mmol) was treated with HBr (48%) and ethanol. The precipitated salt (**10**) was filtered off, washed with ethanol followed by ether. Yield = 0.48 g (80%); m.p. 278–280°C; IR(KBr): 1637–1578, 1446 cm^{-1} (NH bending); Anal Found: C, 34.84, H, 4.32, N, 6.53; $C_{36}H_{52}N_6Se_2Br_6.H_2O$ Calc.: C, 35.32, H, 4.45, N, 6.86%; MS (FAB): m/z 745 ($M^+ - 6Br^- + H_2O$), 723 ($M^+ - 6Br^-$), 587, 413, 176, 154, 136, 107, 91, 77; ^{77}Se-NMR ($CDCl_3$): δ 323.

2.6. General procedure for the synthesis of cryptands

The bis(*o*-formylphenyl) selenide/telluride (0.6 mmol) in methanol was added dropwise to the solution of tris(2-aminoethyl)amine (tren) (0.058 g, 0.4 mmol) and CsCl (0.034 g, 0.2 mmol) in methanol at r.t. over a period of 1 h. The mixture was allowed to stir for overnight and the yellow precipitate was filtered and washed with methanol.

2.6.1. Synthesis of 12

Yield = 0.19 g (90%); m.p. 218–220°C; IR (KBr): 1644 cm^{-1} ($\nu_{C=N}$ stretching); Anal Found: C, 61.48; H, 5.29; N, 10.76 $C_{54}H_{54}N_8Se_3$ Calc.: C, 61.66; H, 5.17; N, 10.65%; MS (FAB): m/z 1054 (M^+), 671, 534, 460, 401, 370, 307, 273, 258, 245, 226, 155, 120, 91, 65, 39, 31; ^{1}H-NMR ($CDCl_3$): δ 8.36 (s, 6H, CH=N), 7.82–7.11 (m, 24H, aromatic-H), 3.57 (t, C=N–C<u>H</u>$_2$, 12H), 2.76 (t, N–C<u>H</u>$_2$–CH_2–, 12H); ^{77}Se-NMR ($CDCl_3$): δ 397.



Scheme 1.

2.6.2. Synthesis of 13

Yield = 0.19g (79%); m.p. 222–224°C; IR (KBr): 1636 cm^{-1} ($\nu_{C=N}$ stretching); Anal Found: C, 53.93; H, 4.45: N, 9.47 $C_{54}H_{54}N_8Te_3$ Calc.: C, 54.15; H, 4.54; N, 9.35%; MS (FAB): m/z 1195 (M^+), 663, 490, 418, 320, 287, 232; ^{1}H-NMR ($CDCl_3$): δ 8.40 (s, 6H, C<u>H</u>=N), 7.99–7.05 (m, 24H, aromatic-H), 3.52 (t, C=N–C<u>H</u>$_2$, 12H), 2.69 (t, N–C<u>H</u>$_2$–CH_2, 12H).

3. Results and discussion

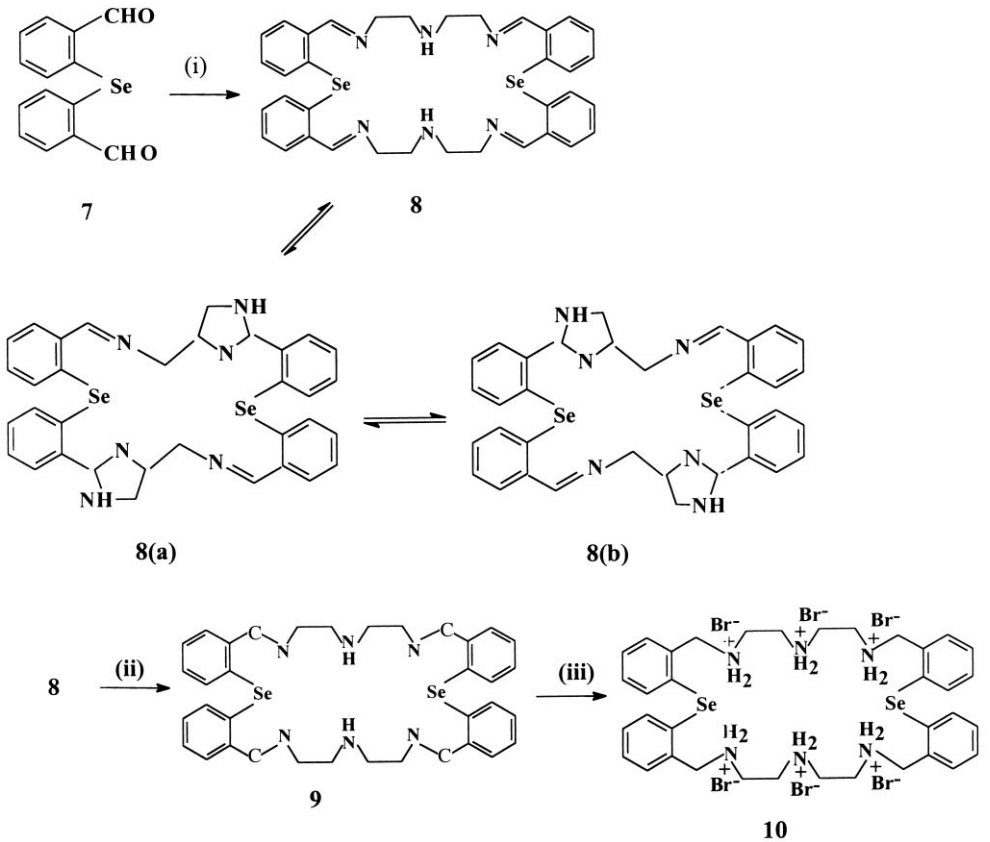
For the preparation of the selenium containing precursor bis(*o*-formylphenyl) selenide (**7**), easily available and inexpensive *o*-bromotoluene (**1**) was used as the starting material.

o-Bromobenzaldehyde (**3**) was prepared following the reported procedure (Scheme 1) [9].

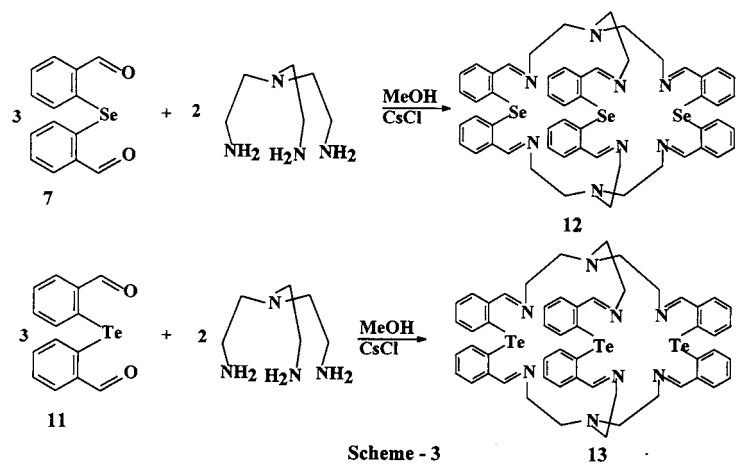
n-Butyllithium was added to *o*-bromobenzaldehyde acetal (**4**) in ether at room temperature as reported by Piette and Renson [10] and stirred for 15 min to get *o*-lithiobenzaldehyde acetal (**5**) as a cloudy white slurry. Subsequently $Se(dtc)_2$ was added and the reaction mixture stirred for 1 h at room temperature. The reaction mixture was extracted with ether. On evaporation of the solvent, bis(*o*-formylphenyl) selenide acetal (**6**) separated out as a white solid in 68% yield. Deprotection of the aldehydic group was performed by refluxing the acetal with concentrated HCl and bis(aldehyde) **7** was found as pale yellow solid in 74% yield. Interestingly Syper et al. [11] have reported the isolation of bis(*o*-formylphenyl) selenide as a by-product in 6% yield while preparing bis(*o*-formylphenyl) diselenide by reacting lithium diselenide with *o*-chlorobenzaldehyde. They have characterized **7** by IR and ^{1}H-NMR study only.

The novel 28-membered macrocycle **8** was obtained by the condensation of bis(*o*-formylphenyl) selenide and diethylenetriamine in acetonitrile in the absence of any templating cation and was isolated in good yield (Scheme 2). Secondary intramolecular Se···N co-ordination (vide infra) plays an important role in the formation of the macrocycle by reducing the unfavourable lone pair–lone pair interaction between nitrogen atoms in the ring. The ligand is fairly soluble in $CHCl_3$ and CH_2Cl_2 but insoluble in polar solvent like MeOH and $(CH_3)_2SO$; it could be recrystallized from $CHCl_3$/MeCN (1:1). Reduction with $NaBH_4$ in ethanol under reflux conditions afforded **9** in good yield. The protonated derivative **10** was obtained in quantitative yield by treatment of **9** with 48% hydrobromic acid.

The two macrocyclic cryptands (**12**, **13**) could be conveniently synthesized from [2 + 3] condensation of tris(2-aminoethyl)amine (tren) with bis(2-formylphenyl) chalcogenides (**7** and **11** [4a]) at room temperature using cesium ions as the template in methanol in 90 and 79% yield, respectively (Scheme 3). Isolation of crystals



Scheme 2. (i) $NH_2CH_2CH_2NHCH_2CH_2NH_2$, MeCN, room temperature; (ii) $NaBH_4$, EtOH, reflux; (iii) 48% HBr, EtOH.



Scheme 3.

suitable for X-ray analysis has so far proved elusive. Also, due to poor solubility of **12** and **13** in common organic solvents, all attempts towards coordination of **12** and **13** with common metal ions or reduction with $NaBH_4$/methanol/ethanol and $LiAlH_4$/THF have proved futile.

These compounds were characterized by elemental analysis, IR, NMR (^1H, ^{13}C and ^{77}Se) and mass spectroscopic studies. That the macrocyclization had occurred was evidenced by the presence of an imine band in the IR and the absence of carbonyl and amine stretching frequencies, together with the absence of a –C(H)=O proton in the ^1H-NMR spectra of the ligand **8**. The ν(C=O) frequency for the selenide **7** was observed at 1706 cm^{-1}. The ν(C=N) vibrational frequency of the macrocycle **8** was observed at 1639 cm^{-1} and its mass spectrum showed the molecular ion peak at m/z 713 as base peak. The ^1H-NMR spectra of **6–9**, **12** and

13 were recorded in $CDCl_3$. A singlet at 6.14 ppm corresponding to Ar–CH protons and multiplets at 4.40 ppm for OCH_2–CH_2O protons were observed in the ^{1}H-NMR spectrum of **6**. For the compound **7** a singlet for the aldehydic protons was observed at 10.28 ppm. The ^{1}H-NMR spectra of **8–10** were complex. In particular though the macrocycle **8** gave satisfactory elemental analysis and mass spectral data, its ^{1}H-NMR and ^{77}Se-NMR spectra were complex. The ^{77}Se-NMR displayed several signals. This is probably due to a ring contraction of the macrocyclic cavity of the Schiff base, often leading to the stabilization of metal-free ligands. This generally, occurs when there is a group such as NH or OH available for addition to the imine bond. The attack of the amine function (NH) to the imine group of the open Schiff base macrocycle **8** results in a decrease of the ring size (28–22) and formation of isomers **8a** and **8b** [12]. Also, formation of the 10-Se-3 selane (vide infra) system by intramolecular N→Se coordination might lead to a different environment for the two selenium atoms in **8**, **8a** and **8b.** In the case of compound **9** the disappearance of the ν(C=N) absorption in IR confirmed the reduction of the CH=N bond. For the macrocyclic polyamine ligand the molecular ion peak was observed as a base peak at m/z 723. The ^{77}Se-NMR spectrum shows a single peak at 328 ppm, which confirmed the identical environment around both the selenium atoms. No molecular ion peak was observed for **10**. But the highest recorded peak at m/z 745 was equivalent to [**10**·H_2O–$6Br^-$]. The preliminary identification of the macrobicyclic ligand was established from IR spectra. The IR spectra of **12** and **13** do not show any peaks corresponding to the amino and carbonyl groups. The medium intensity band at 1644 and 1636 cm^{-1} for **12** and **13** were assignable to the ν(C=N) stretching frequency. The azomethine proton signal for the Schiff base **12** and **13** were observed at 8.36 and 8.40 ppm, respectively. The ^{77}Se-NMR shows a single signal for **12** at 397 ppm and thus implies the similar environment around both the selenium atoms. The ^{125}Te-NMR of **13** could not be recorded due to its poor solubility. In the case of cryptand **12**, the molecular ion peak at m/z 1054 was observed as the base peak (Fig. 1). For the cryptand **13** a low intensity peak was observed for the molecular ion peak at m/z 1195.

3.1. Crystal structure of compound 7

An ORTEP view of **7** is shown in Fig. 2. The selected bond angles and distances are given in Table 1. The crystal structure involves packing of four molecules in the unit cell. The bond configuration around the Se atom is V shaped and the angle C(1A)–Se–C(1B) is 97.84(9)°. The Se–C(1A) and Se–C(1B) bond distances of 1.921(2) Å and 1.936(2) Å, respectively, are slightly longer than the sum of the Pauling covalent radii 1.91 Å. This value is also comparable to the Se–C bond distances in bis[2-(dimethylaminomethyl)phenyl] selenide [1.941(3) and 1.953(3) Å] [13]. The Se···O(1A) distance 2.806 Å is higher than the sum of the single bond covalent radii for selenium (1.17 Å) and oxygen (0.66 Å) but considerably shorter than the sum of the van der Waals radii 3.4 Å. This distance is higher than the Se···O bond distance in (phenylseleno)iminoquinone [2.476 Å] [14] but shorter than the Se···O(mean) distance (2.977 Å) in the diselenide bearing a methoxy substituent *ortho* to the selenium [15]. The other oxygen atom is away from the Se atom and thus not coordinated. The O(1A)–Se–C(1B) bond angle is 166.5° which means the O(1A)–Se bond is roughly *trans* to the Se–C(1B) bond. This may be due to the weak interaction between oxygen and selenium. The intermolecular Se···Se distance (4.141 Å) is slightly greater than the sum of the van der Waals radii of selenium atoms.

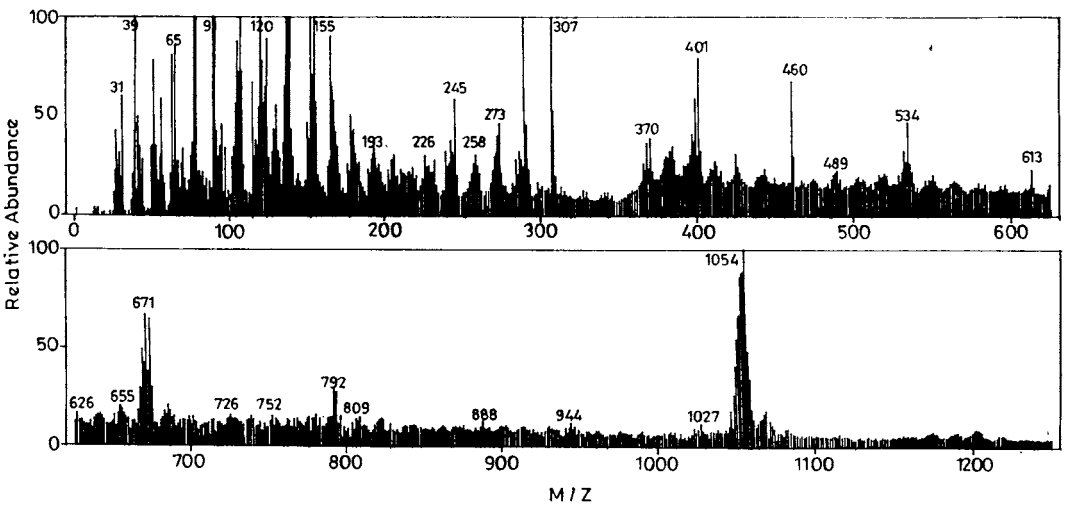


Fig. 1. FAB mass spectrum of **12**.

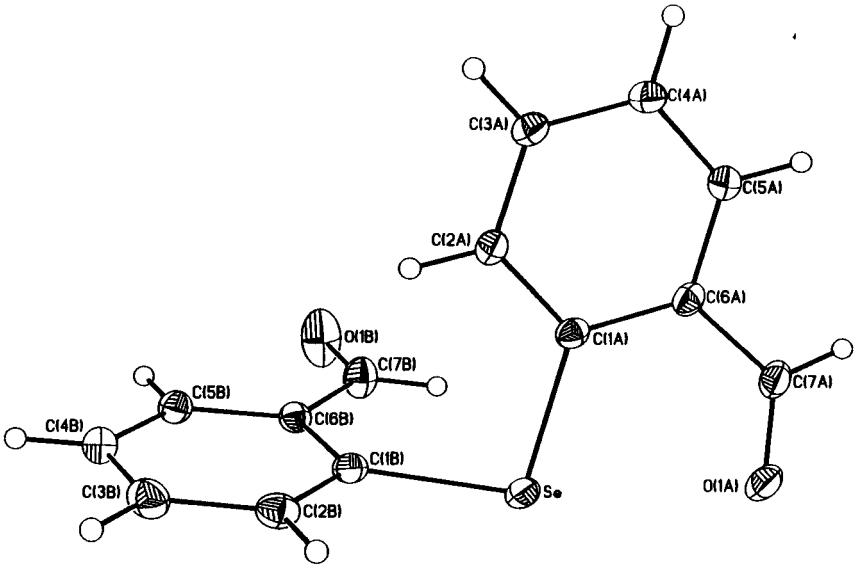


Fig. 2. Crystal structure of **7**.

3.2. Crystal structure of compound *8*

X-ray diffraction determinations of **8** show that the compound crystallizes in a centrosymmetric space group $C2/c$ and there are four molecular units in the unit cell. A selection of bond lengths and bond angles is given in Tables 2 and 3 in accordance with the numbering system given in Fig. 3. The structure shows that this macrocycle has a 28-membered cavity.

The Se–C(1B) distance (1.931(3) Å) is slightly higher than the sum of the Pauling single bond covalent radii for selenium (1.17 Å) and sp^2 hybridized carbon (0.74 Å). This bond distance can be comparable to the Se(2A)–C(12A) bond length (1.933(8) Å) in 1-(methylselanyl)-8-(phenylselanyl)naphthalene [16]. However, the Se–C(1A) bond distance (1.949(3) Å) is longer than Se–C(1B) distance. This may be due to the fact that Se–C(1A) is *trans* to the weakly coordinated nitrogen atom. In this case, out of the four nitrogens of the azomethine groups, only two are coordinating to the selenium atoms as the other two are away from the selenium atoms. The solid-state geometry of the molecule indicates the presence of only one attractive Se···N interaction per selenium atom, i.e. it corresponds to the structure of 10-Se-3 selane. The geometry around the selenium atom is T-shaped. The intramolecular Se···N(1BA) distance of 2.814 Å is remarkably shorter than the sum of the van der Waals radii (3.5 Å) of the two elements. The transannular Se···Se(A) distance (4.177 Å) is slightly longer than the sum of van der Waals radii (4 Å). Deviation of N(1BA) from the C(1A)–Se–C(1BA) plane is 0.1882°. The C(1B)–Se(1)–C(1A) angle for this macrocycle is 97.54(13)°.

4. Conclusions

The key starting material bis(*o*-formylphenyl)selenide was prepared by using ortholithiation methodology. [2 + 2] Cyclocondensation of the bis(aldehyde) with diethylenetriamine afforded the novel selenaaza macrocyclic ligand. Reduction of this Schiff base with an

Table 1
Significant bond lengths (Å) and angles (°) for **7**

Se–C(1A)	1.921(2)	Se–C(1B)	1.936(2)
O(1A)–C(7A)	1.209(3)	O(1B)–C(7B)	1.200(3)
Se–O(1A)	2.806	C(1A)–Se–C(1B)	97.84(9)
C(2A)–C(1A)–Se	121.20(17)	C(6A)–C(1A)–Se	120.28(15)
C(2B)–C(1B)–Se	118.95(16)	C(6B)–C(1B)–Se	121.63(17)
O(1B)–C(7B)–C(6B)	124.6(3)	O(1A)–C(7A)–C(6A)	124.8(2)

Table 2
Significant bond lengths (Å) and angles (°) for **8**

Se–C(1B) # 1	1.931(3)	N(1A)–C(7A)	1.258(4)
Se–C(1A)	1.949(3)	N(1A)–C(8A)	1.460(5)
N(2)–C(9B)	1.461(4)	N(2)–C(9A)	1.463(4)
N(1B)–C(7B)	1.260(4)	N(1B)–C(8B)	1.458(4)
C(1B)–Se # 1	1.931(3)		
C(1B) # 1–Se–C(1A)	97.54(13)	C(7A)–N(1A)–C(8A)	117.8(3)
C(9B)–N(2)–C(9A)	112.3(3)	C(2A)–C(1A)–Se	117.7(2)
C(6A)–C(1A)–Se	122.3(2)	C(7B)–N(1B)–C(8B)	117.3(3)
N(1A)–C(7A)–C(6A)	123.0(3)	N(1A)–C(8A)–C(9A)	111.0(3)
N(2)–C(9A)–C(8A)	110.8(3)	N(2)–C(9B)–C(8B)	112.2(3)
C(2B)–C(1B)–Se # 1	121.1(2)	C(6B)–C(1B)–Se # 1	119.9(2)
N(1B)–C(7B)–C(6B)	124.2(3)	N(1B)–C(8B)–C(9B)	112.2(3)

Table 3
Crystal data and structure refinement for **7** and **8**

	7	**8**
Empirical formula	$C_{14}H_{10}O_2Se$	$C_{36}H_{38}N_6Se_2$
Fw	289.18	712.64
Crystal system	Monoclinic	Monoclinic
Space group	$P2/c$	$C2/c$
Unit cell dimensions		
a (Å)	8.0170(6)	18.732(3)
b (Å)	8.4514(6)	8.6515(10)
c (Å)	17.5289(12)	22.590(3)
α (°)	90	90
β (°)	93.6860(10)	113.376(8)
γ (°)	90	90
V (Å^3)	1185.21(15)	3360.5(8)
Z	4	4
D_{calc} (Mg m^{-3})	1.621	1.409
Temperature (K)	208(2)	293(2)
λ (Å)	0.71073	0.71073
Absorption coefficient (mm^{-1})	3.153	2.235
Observed reflections [$I>2\sigma$]	2898	3815
Final $R(F)$ [$I>2\sigma$] [a]	0.0298	0.0416
$wR(F^2)$ indices [$I>2\sigma$]	0.0641	0.0899
Data/restraints/parameters	2898/0/164	3813/0/221
Goodness-of-fit on F^2	1.030	1.038

[a] Definitions: $R(F_0)=\Sigma||F_0|-|F_c||/\Sigma|F_0|$ and $wR(F_0^2)=\{\Sigma[w(F_0^2-F_c^2)^2]/\Sigma[w(F_c^2)^2\}^{1/2}$.

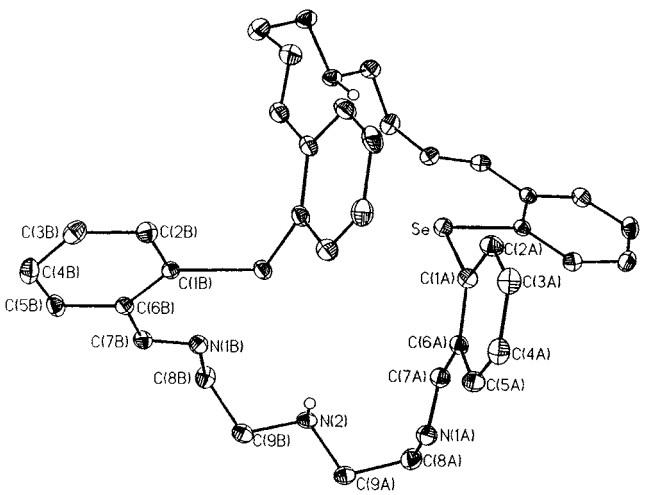


Fig. 3. Crystal structure of **8**.

excess of $NaBH_4$ in ethanol under reflux conditions afforded the tetraamino derivative as a white solid. The tetraamino derivative upon reaction with 48% HBr afforded the protonated derivative. [2 + 3] Condensation of chalcogenides with tris(2-aminoethyl)amine in the presence of cesium metal ion yielded the novel selenium/tellurium cryptands.

5. Supplementary material

Crystallographic data for H-atom coordinates, anisotropic thermal parameters and full listings of bond lengths and bond angles for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Acknowledgements

We are grateful to the Department of Science and Technology (DST), New Delhi and Board of Research in Nuclear Sciences (BRNS), Department of Atomic Energy, Bombay for funding this work. Additional help from the Regional Sophisticated Instrumentation centre (RSIC), Indian Institute of Technology (IIT), Bombay for the 300 MHz NMR spectroscopy, RSIC, CDRI Lucknow for the mass recording facility and Tata Institute of Fundamental Research (TIFR), Bombay for the 500 MHz NMR spectroscopy is gratefully acknowledged. R.J.B. wishes to acknowledge the DOD-ONR program for funds to upgrade the diffractometer.

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