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Design and synthesis of organochalcogen (Se or Te) based multifunctional derivatives: structural determination and dynamic behavior of 2-chloro-4,6-bis(phenylselenoethylamino)-1,3,5-triazines

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Respectfully dedicated to Professor Ram Charan Mehrotra, University of Rajasthan, Jaipur, India, who passed away on July 11, 2004

Abstract—A novel class of multifunctional and multinucleate chalcogen (selenium and tellurium) containing derivatives (**1**–**10**) has been developed based on sequential chloride substitution of 2,4,6-trichloro-1,3,5-triazine with chalcogen-bearing amines. The structure of compound **1** has been determined in the solid state by X-ray crystallography.

There is continued interest in the rational design and synthesis of new organic donors with variable donor functionalities and their combinations with metals to build supramolecular structures.[1,2] Organic donors bearing variable donor functionalities such as O, S, N and P in their structural framework have been studied for several years and continue to be an area of active research for understanding the properties of donors that offer the opportunity to design metal complexes for specific purposes and applications.[3–5] The interplay between electronic and steric properties of a metal atom has long been recognized but predictions related to the behavior of organic donors remain difficult. The behavior of selenium in organic species remains uncertain. Studies of given systems are required before one could arrive at conclusions about reactivity and applications. The presence of selenium in a given structural motif of an organochalcogen species has a significant influence on the final structure of a complex, especially with polydentate systems, where it influences the size, shape, symmetry and the orientation of the donor groups. For these reasons, we report herein the design and synthesis of novel multifunctional organochalcogen donors with the aim of examining and study the structures of derived species displaying new topologies and perhaps new properties. The present systems are based on 1,3,5-triazines that have been functionalized at the 2,4,6-positions with flexible organochalcogen-containing species. Various 2,4,6-trisubstituted 1,3,5-triazine derivatives (e.g., amino, alkyl, aryl, alkoxy/aryloxy, arylseleno/telluro and halides) are synthetically available and have been prepared from 2,4,6-trichloro-1,3,5-triazine (cyanuric chloride) by successive displacement of the chlorine atoms by different nucleophiles.[6] We describe herein a synthetic protocol for flexible 'hexa-host' type molecules, which can be derived by the reaction of ligand (L) with 2,4,6-trichloro-1,3,5-triazine under mild conditions. The reaction in refluxing acetonitrile solution gave disubstituted derivatives (**1**–**5**) as the major (80–85%) products and trisubstituted derivatives (**6**–**10**) as the minor (5–10%).[7] Attempts to alter the reaction conditions in order to produce (**1**–**5**) or (**6**–**10**) as the sole species failed. Disubstituted derivatives (**1**–**5**) once isolated react further with one

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equivalent of their respective ligand (L) to give the desired symmetrical tripods (**6**–**10**) in yields of 30–50% (Scheme 1).

Physicochemical and spectral (IR, ^{1}H, ^{13}C, ^{77}Se NMR, FAB and ES-MS) studies revealed the formation of disubstituted and trisubstituted species (**1**–**10**). In solution, disubstituted derivatives (**1**–**5**) showed two sets of signals of equal intensity in their respective ^{1}H, ^{13}C and ^{77}Se NMR spectra. The spectra did not change even when the temperature was decreased to 213 K or at elevated temperatures. No change in the multiplicity of these derivatives were observed even when the ^{1}H, ^{13}C, ^{77}Se NMR spectra were observed in coordinating solvents such as DMSO-d_6 or CF$_3$COOD. Species (**6**–**10**) displayed signals for organochalcogen species substituted at the 2,4,6-positions of 1,3,5-triazine ring with the expected multiplicities in their respective ^{1}H and ^{13}C NMR spectra and were found to be consistent with the formation of symmetrical structures. The ES-MS data for **1**–**5** showed the expected molecular ion peaks. Information regarding their associative phenomena was observed for a saturated solution of the complexes in their molecular weight determinations. A definitive assignment of the structures of compounds **1**–**5** was performed by X-ray structure determination of compound **1**. Single crystal X-ray diffraction studies of 2-chloro-4,6-bis(phenylselenoethylamino)-1,3,5-triazine **1** revealed that the molecule crystallizes in a triclinic, *P-1*, space group with two molecules per unit cell. A perspective view of the molecular structure and crystal packing is given in Figure 1a and b. The molecule is oriented in such a way that both arms of each substituted –N(CH$_2$CH$_2$SePh)$_2$ groups point to the opposite side of each other. As a result one pair of arms comes closer to each other with a Se(1B)···Se(1C) separation of 4.919 Å while the other pair are farther from each other with a Se(1A)···Se(1D) separation of 11.466 Å thus providing a very open conformation. The exocyclic C(2)–N(1Y) and C(3)–N(1X) bonds are 1.350(4) and 1.345(5) Å, respectively, being shorter than the other C–N bonds [C(1A)–N(1Y) 1.473(5) and C(1C)–N(1X) 1.480(4) Å] originating from N(1X) and N(1Y).[8] Also, the sum of the bond angles around N(1X) and N(1Y) are 360° signifying sp^2 hybridized nitrogens. The increased double bond character of the exocyclic C–N bonds resulting from conjugation of the lone pair of the amino nitrogen with the electron deficient triazine ring restrict the rotation about the triazine-N$_3$C$_3$-(CH$_2$CH$_2$SePh)$_2$ bonds. If we consider that restricted rotation[9a] is the possible cause for further splitting of the NMR signals then an identical spectral pattern could also be expected for its sulfur analogue [2-chloro-4,6-bis(2-thiopyridylethylamine)-1,3,5-triazine]. However, the spectral pattern of the sulfur analogue represented a symmetrical structure although its crystal structure gave a clear indication of restricted rotation due to the increased double bond character of the exocyclic C–N bonds.[9b] The structural parameters clearly indicate that both sulfur atoms are in identical environments in the

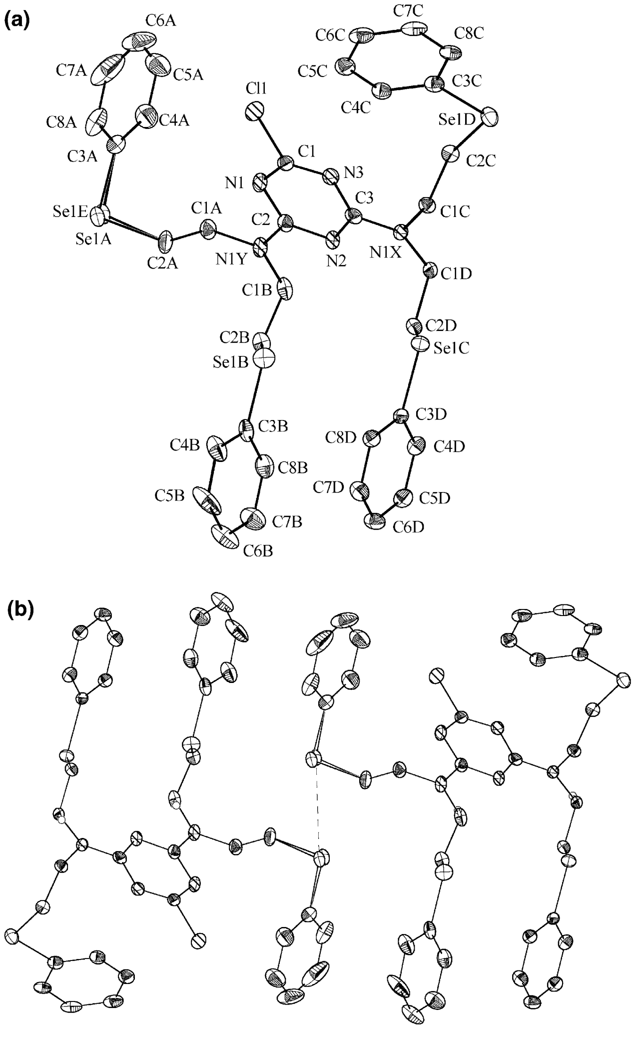
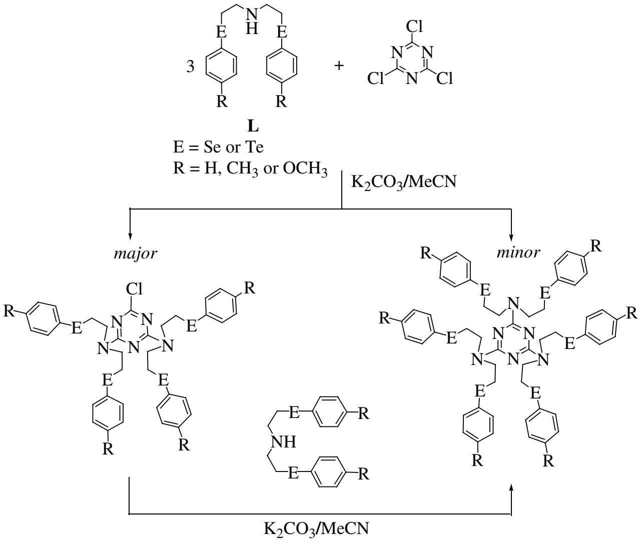


Figure 1. (a) Crystal structure of 2-chloro-4,6-bis(phenylselenoethylamino)-1,3,5-triazine **1**. (b) Crystal packing of 2-chloro-4,6-bis(phenylselenoethylamino)-1,3,5-triazine **1**.



(E = Se, R = H) **1** (83%);
(E = Se, R = OCH$_3$) **2** (85%);
(E = Se, R = CH$_3$) **3** (82%);
(E = Te, R = H) **4** (84%);
(E = Te, R = OCH$_3$) **5** (85%)

(E = Se, R = H) **6** (40%);
(E = Se, R = OCH$_3$) **7** (50%);
(E = Se, R = CH$_3$) **8** (37%);
(E = Te, R = H) **9** (35%);
(E = Te, R = OCH$_3$) **10** (40%)

Scheme 1.

solid state, as a result expected multiplicity was observed in solution (at room temperature) despite restricted rotation. The noticeable feature in the X-ray structure of compound **1** was the unusual Se–C (aliphatic) and Se–C (aromatic) bonds, suggesting that at least two different selenium environments are present in the solid state. The presence of two signals of equal intensity in the ^{77}Se NMR spectrum of compound **1** not only confirms the two different environments for selenium atoms but also suggests that the molecule is retaining its solid-state structure in solution. However, there are no close *intramolecular* or *intermolecular* contacts between selenium atoms or selenium and heteroatoms. Thus the presence of two magnetically non-equivalent environments due to the selenium atoms is responsible for the observed multiplicities in the ^{1}H, ^{13}C and ^{77}Se NMR spectra and significantly influences the resultant structure. Nevertheless, trisubstituted species (**6–10**) showed the expected multiplicities in their respective ^{1}H, ^{13}C and ^{77}Se NMR spectra, undoubtedly indicating that these molecules have a symmetrical structure.

Although there are a few organochalcogen donors, both acyclic and cyclic in nature, with higher denticity, and their metal complexes are well known, a working methodology for creating *extended-reach structures* using heavier chalcogens has not been formulated. The compounds prepared in the present study (**1–5** and **6–10**) are both polydentate and polynucleating and may have future applicability in creating *extended-reach structures*. Further investigations on the structural aspects and elaboration of these donor systems are currently underway and will be published in due course.

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References and notes

1. (a) Schalley, C. A.; Lützen, A.; Albrecht, M. *Chem. Eur. J.* **2004**, *10*, 1072–1080; (b) Ruben, M.; Rojo, J.; Romero-Salguero, F. J.; Uppadine, L. H.; Lehn, J.-M. *Angew. Chem., Int. Ed.* **2004**, *43*, 3644–3662; (c) Hartshorn, C. M.; Steel, P. *J. Chem. Commun.* **1997**, 541–542; (d) Cotton, F. A.; Lin, C.; Murillo, C. A. *Acc. Chem. Res.* **2004**, *34*, 759–771; (e) Eschbaumer, C.; Schubert, U. S. *Angew. Chem., Int. Ed.* **2001**, *41*, 2892–2926; (f) Selby, H. D.; Roland, B. K.; Zheng, Z. *Acc. Chem. Res.* **2003**, *36*, 933–944; (g) Fujita, M.; Umemoto, K.; Yoshizawa, M.; Fujita, N.; Kusukawa, T.; Kumar, B. *Chem. Commun.* **2001**, 509–518; (h) Seel, C.; Vögtle, F. *Angew. Chem., Int. Ed.* **1992**, *31*, 528–549.
2. (a) Brunsveld, L.; Folmer, B. J. B.; Meijer, E. W.; Sijbesma, R. P. *Chem. Rev.* **2001**, *101*, 4071–4097; (b) Cotton, F. A.; Lin, C.; Murillo, C. A. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 4810–4813; (c) Kuehl, C. J.; Kryschenko, Y. K.; Radhakrishnan, U.; Seidel, S. R.; Huang, S. D.; Stang, P. J. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 4932–4936; (d) Barboiu, M.; Lehn, J.-M. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 5201–5206; (e) Oxtoby, N. S.; Blake, A. J.; Champness, N. R.; Wilson, C. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 4905–4910; (f) Goshe, A. J.; Steele, I. M.; Ceccarelli, C.; Rheingold, A. L.; Bosnich, B. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 4823–4829.
3. (a) Ohkita, M.; Kawano, M.; Suzuki, T.; Tsuji, T. *Chem. Commun.* **2002**, 3054–3055; (b) Schuster, D. I.; Rosenthal, J.; MacMahon, S.; Jarowski, P. D.; Alabi, C. A.; Guldi, D. M. *Chem. Commun.* **2002**, 2538–2539; (c) Hong, M.; Zhao, Y.; Su, W.; Cao, R.; Fujita, M.; Zhou, Z.; Chan, A. S. C. *J. Am. Chem. Soc.* **2000**, *122*, 4819–4820; (d) Bielejewska, A. G.; Marjo, C. E.; Prins, L. J.; Timmerman, P.; de Jong, F.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **2001**, *123*, 7518–7533; (e) Prins, L. J.; Jolliffe, K. A.; Hulst, R.; Timmerman, P.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **2000**, *122*, 3617–3627; (f) Prins, L. J.; Neuteboom, E. E.; Paraschiv, V.; Crego-Calama, M.; Timmerman, P.; Reinhoudt, D. N. *J. Org. Chem.* **2002**, *67*, 4808–4820; (g) Vodak, D. T.; Kim, K.; Iordanidis, L.; Rasmussen, P. G.; Matzger, A. J.; Yaghi, O. M. *Chem. Eur. J.* **2003**, *9*, 4197–4201.
4. (a) Gamez, P.; Hoog, P. D.; Roubeau, O.; Lutz, M.; Driessen, A. L.; Spek, A. L.; Reedijk, J. *Chem. Commun.* **2002**, 1488–1489; (b) Blake, A. J.; Brooks, N. R.; Champness, N. R.; Cooke, P. A.; Deveson, A. M.; Fenske, D.; Hubberstey, P.; Li, W.-S.; Schröder, M. *J. Chem. Soc., Dalton Trans.* **1999**, 2103–2110.
5. (a) Liu, H. K.; Sun, W.-Y.; Ma, D.-J.; Yu, K.-B.; Tang, W.-X. *Chem. Commun.* **2000**, 591–592; (b) Sasa, M.; Tanaka, K.; Bu, X.; Shiro, M.; Shionoya, M. *J. Am. Chem. Soc.* **2001**, *123*, 10750–10751; (c) Pike, R. D.; Borne, B. D.; Maeyer, J. T.; Rheingold, A. L. *Inorg. Chem.* **2002**, *41*, 631–633; (d) Carrión, M. C.; Guerrero, A.; Jalón, F. A.; Manzano, B. R.; de la Hoz, A.; Claramunt, R. M.; Milata, V.; Elguero, J. *Inorg. Chem.* **2003**, *41*, 885–895.
6. (a) Milton, M. D.; Kumar, N.; Sokhi, S. S.; Singh, S.; Singh, J. D. *Tetrahedron Lett.* **2004**, *45*, 6453–6455; (b) Kumar, N.; Milton, M. D.; Singh, J. D. *Tetrahedron Lett.* **2004**, *45*, 6611–6613.
7. To a solution of $[NH\{(CH_2)_2SeC_6H_4{-}CH_3\text{-}p\}_2]$ (1.23 g, 3 mmol) in anhydrous acetonitrile (30 mL) was added a solution of 2,4,6-trichloro-1,3,5-triazine (0.184 g, 1 mmol) in acetonitrile (25 mL) in the presence of anhydrous K_2CO_3 (1 g) under an atmosphere of dry dinitrogen and the reaction mixture was refluxed. The progress of the reaction, which usually takes ~8–10 h for completion, was monitored by TLC. After completion, the reaction mixture was filtered while hot and the solid mass collected was washed twice with hot acetonitrile. The combined filtrates were concentrated to dryness under reduced pressure to give a viscous liquid. The crude products were purified by column chromatography using neutral alumina (grade 1) and by elution with hexane/ethyl acetate (90:10) to give trisubstituted product **8** (0.14 g, 15%) and disubstituted product **3** (1.11 g, 82%) as yellow viscous masses. Elemental analysis for $C_{39}H_{44}ClN_5Se_4$ **3**: calcd: C, 50.15; H, 4.75; N, 7.50%. Found: C, 49.76; H, 4.64; N, 7.24%; *m*/*z* (FAB-MS): 938 (M^+); ν_{max}/cm^{-1} (KBr pellets) 1585 ν(C=N) 1057 ν(C–Cl); ^{1}H NMR ($CDCl_3$, 300 MHz): 7.35–7.23 (dd, 8H, *J*(HH) both 7 Hz, phenyl), 6.99–6.91 (dd, 8H, *J*(HH) both 7 Hz, phenyl), 3.63–3.49 (dt, 8H, *J*(HH) both 7.5 Hz, N–CH_2), 2.94–2.79 (dt, 8H, *J*(HH) both 8 Hz, Se–CH_2), 2.22 {two peaks (merged), 12H, –CH_3} ppm; $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 75 MHz): 169.0, 164.2, 137.2,

136.5, 133.5, 133.0, 131.8, 129.9, 125.7, 125.5, 122.0, 48.8, 48.5, 25.8, 24.1 ppm; ^{77}Se NMR {$CDCl_3$, 57.3 MHz (relative to Me_2Se)} 285.6 and 279.9 ppm. Elemental analysis for $C_{57}H_{66}N_6Se_6$ **8**: calcd: C, 52.30; H, 5.08; N, 6.42%. Found: C, 52.14; H, 4.87; N, 6.23%; *m/z* (FAB-MS): 1314 (M^+); v_{max}/cm^{-1} (KBr pellets) 1582 v(C═N); ^{1}H NMR ($CDCl_3$, 300 MHz): 7.26 (d, 12H, *J*(HH) 7 Hz, phenyl), 6.89 (d, 12H, *J*(HH) 7 Hz, phenyl), 3.48 (t, 12H, *J*(HH) 7.5 Hz, N–CH_2), 2.84 (t, 12H, *J*(HH) 8 Hz, Se–CH_2), 2.20 (s, 18H, –CH_3) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): 164.8,137.3, 133.2, 130.5, 125.7, 21.2, 48.6. 26.7 ppm; ^{77}Se NMR {$CDCl_3$, 57.3 MHz (relative to Me_2Se)} 282.32 ppm.

8. *Selected bond lengths* (Å) *and angles* (°): Se(1A)–C(2A) 1.948(4), Se(1A)–C(3A) 1.958(4), Se(1E)–C(3A) 1.810(7), Se(1E)–C(2A) 2.030(8), Se(1B)–C(3B) 1.916(4), Se(1B)–C(2B) 1.955(3), Se(1C)–C(3D) 1.919(3), Se(1C)–C(2D) 1.953(3), Se(1D)–C(3C) 1.923(3), Se(1D)–C(2C) 1.939(3), N(1)–C(1) 1.311(4), N(1)–C(2) 1.366(4), N(2)–C(2) 1.341(5), N(2)–C(3) 1.334(4), N(3)–C(1) 1.317(5), N(3)–C(3) 1.363(4), C(3)–N(1X) 1.345(5), C(2)–N(1Y) 1.350(4); C(1)–N(1)–C(2) 112.4(3), C(3)–N(2)–C(2) 115.2(3), C(1)–N(3)–C(3) 111.9(3), N(1)–C(1)–N(3) 130.3(3), N(2)–C(2)–N(1) 124.6(3), N(2)–C(3)–N(3) 125.4(3). Crystallographic data for compound **1** have been deposited at the Cambridge Crystallographic Data Centre, CCDC No 245033. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (+44 1223 336408; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).
9. (a) Díaz-Ortiz, A.; Elguero, J.; Foces-Foces, C.; de la Hoz, A.; Moreno, A.; Moreno, S.; Sánchez-Migallón, A.; Valiente, G. *Org. Biomol. Chem.* **2003**, *1*, 4451–4457; (b) Milton, M. D.; Sokhi, S. S.; Singh, J. D.; Butcher, R. J., unpublished results.