First molecular and electronic structure determination of the dicationic salt of 1,11-(methanoselenomethano)-5*H*,7*H*-dibenzo[*b,g*][1.5]diselenocin by X-ray crystallographic analysis and *ab initio* calculation

Tsukasa Nakahodo, Ohgi Takahashi, Ernst Horn and Naomichi Furukawa*

Tsukuba Advanced Research Alliance Center, Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305, Japan

The X-ray crystallographic analysis of the dication salt of 1,11-(methanoselenomethano)-5*H*,7*H*-dibenzo[*b*,*g*][1,5]-diselenocin shows that the dication has a selenium atom in a trigonal-bipyramidal bonding environment; an *ab initio* calculation carried out for the dication revealed that the positive charge is exclusively carried by the three selenium atoms.

Recently, we have reported the synthesis of a selenium-bridged diselenametacyclophane, 1,11-(methanoselenomethano)-5*H*,7*H*-dibenzo[*b*,*g*][1,5]diselenocin **1** and the isolation of its dicationic salt. We also reported the interconvertible redox structural changes resulting from the multicenter chalcogenide interaction between **1** and its dicationic salt as observed by NMR spectra.[1] However, until recently we could not obtain any structural data of the dicationic salt, because of the difficulty of obtaining suitable single crystals. After several recrystallization attempts using different counter anions, we obtained suitable crystals for a detailed X-ray structural analysis, and thus the structure of the dication was determined. Furthermore, the electronic structure of the dication was elucidated by an *ab initio* molecular orbital calculation.

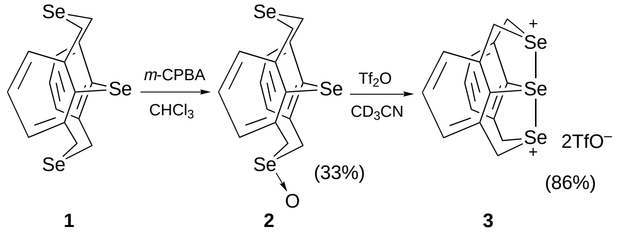
It is of particular interest that a conformational change of the selenoxide **2** occurred in the reaction of **2** with trifluoromethanesulfonic anhydride and triflic anhydride [$(CF_3SO_2)_2O$, Tf_2O]; *i.e.*, treatment of **2** with Tf_2O (1 equiv.) in anhydrous $CHCl_3$ under an Ar atmosphere at room temp. resulted in the formation of the dicationic salt **3** (86%) (Scheme 1).†

The crystal structure of dicationic salt **3** was determined by single-crystal X-ray crystallographic analysis (Fig. 1).‡

The X-ray analysis clearly reveals that in the solid state the conformation of **3** is a distorted boat–boat form fixed by the three-center transannular bond between the three selenium atoms.

Although, normally in case of **1** and **2** the chair conformer has been shown to be more stable and rigid than the boat conformer.[1,2] The respective Se···Se distances, 2.645(2) and 2.556(2) Å for Se(1)···Se(2) and Se(2)···Se(3), are longer than the normal Se–Se single bond (2.34 Å) found in diselenides.[3] The Se(1)–Se(2)–Se(3) bond angle of 170.21 (6)° is almost linear, and the C_{eq}–Se(2)–C_{eq} bond angle is 95.6(4)°. Thus, the bonding configuration about the seleniun atom is a distorted trigonal-bipyramidal structure with two apical Se–Se bonds, two equatorial Se–C bonds, and the lone-pair electrons occupying the third equatorial position. These structural features are consistent with a selenurane structure.[4]

In order to understand the electronic structure of the dication, we carried out an *ab initio* RHF calculation using the $3\text{-}21G^{(*)}$ basis set.[5] The geometry was optimized with a C_2 symmetry constraint, and the optimized C_2 structure which is shown in Fig. 2 was confirmed to be a true minimum by a vibrational analysis. The calculated structure is in reasonably agreement with the X-ray determined structure.



Scheme 1

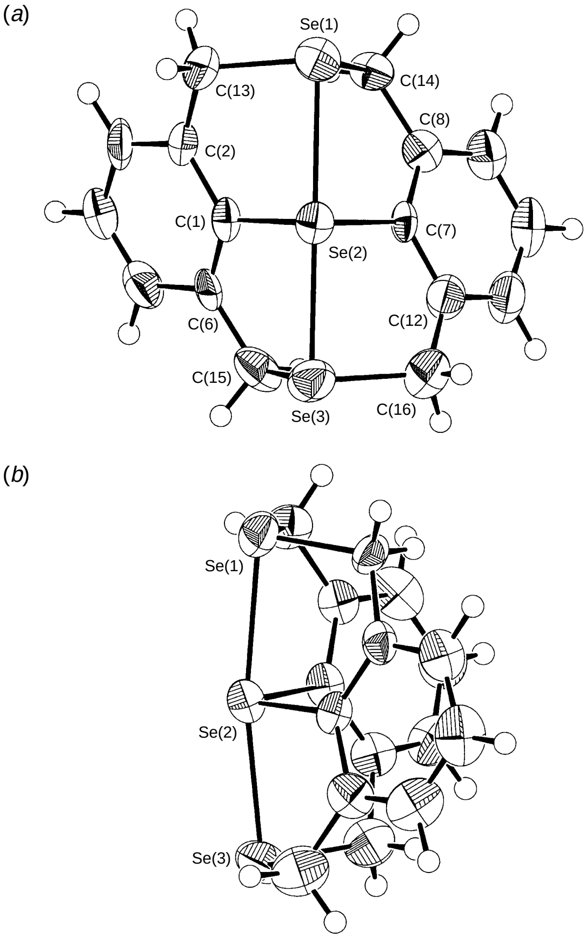


Fig. 1 Crystal structure of dication **3**. (*a*) View from above. (*b*) Side-on view. For clarity, triflate anions are omitted. Selected bond lengths (Å) and angles (°) (X-ray): Se(1)–Se(2) 2.645(2), Se(2)–Se(3) 2.556(2), Se(1)–C(13) 1.96(1), Se(2)–C(1) 1.93(1), Se(2)–C(7) 1.962(10), Se(3)–C(15) 1.93(1), C(1)–C(2) 1.42(1), C(1)–C(6) 1.39(1), C(2)–C(13) 1.49(2), C(6)–C(15) 1.51(2); Se(1)–Se(2)–Se(3) 170.21(6), C(1)–Se(2)–C(7) 95.6(4), Se(1)–Se(2)–C(1) 86.5(3), Se(3)–Se(2)–C(1) 86.8(3), Se(2)–C(1)–C(2) 119.5(8), Se(2)–C(1)–C(6) 119.9(8), C(2)–C(1)–C(6) 120(1), C(1)–C(2)–C(13) 121.5(10), C(1)–C(6)–C(15) 122(1), Ce(1)–C(13)–C(2) 113.0(8), Se(3)–C(15)–C(6) 112.0(9).

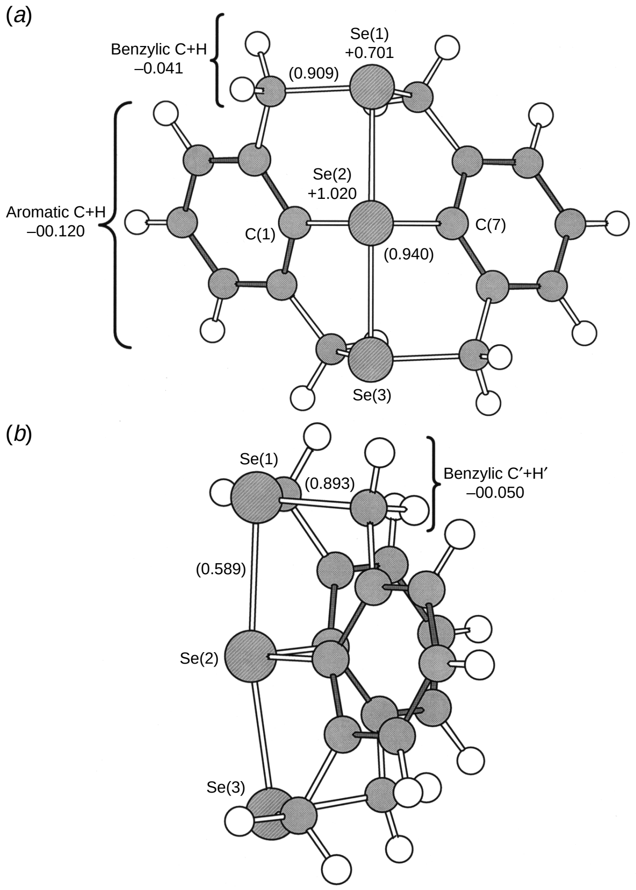


Fig. 2 The RHF/3-21G$^{(*)}$ optimized structure (C_2) of the dication. (*a*) View from above. (*b*) Side-on view. Charge distribution and bond orders (in parentheses) are also shown. Selected bond lengths (Å) and angles (°): Se(1)–Se(2) 2.537, Se(2)–C(1) 1.931; Se(1)–Se(2)–Se(3) 170.2, C(1)–Se(2)–C(7) 98.0, Se(1)–Se(2)–C(1) 86.8, Se(3)–Se(2)–C(1) 86.8.

The charge distribution obtained by natural population analysis (NPA)[6] is shown in Fig. 2. The charge on the central Se atom is +1.020 and those of the apical Se atoms are +0.701, which indicates that the +2 charge is exclusively carried by the three Se atoms. It is surprising that the positive charge is not delocalized onto the benzene rings at all; the rings are slightly negatively charged. The Mulliken bond order of the Se–Se bonds was calculated to be 0.589, while that of the equatorial Se–C bonds was 0.940. The central Se atom carries a more positive charge than the two apical Se atoms, indicating that the two apical Se–Se bonds are highly polarized as in the neutral hypervalent molecules having a three-center-four-electron (3c–4e) bond. The 4d orbital population of the central Se atom is 0.039, which is small and comparable with those of the apical Se atoms (0.026). Thus, the 4d orbitals of the central Se atom are not significantly involved in the 3c–4e bond which is in accordance with the current view of hypervalent molecules.[7] In the 3c–4e model by Rundle[8] and Musher[9] the HOMO (-16.1 eV) and LUMO (-6.4 eV) correspond to the non-bonding and antibonding orbitals respectively, though the HOMO is largely delocalized onto the benzene rings as a result of an interaction between the Se–Se–Se non-bonding orbital and the HOMOs of the benzene rings.

Although the counter ions were not included in the *ab initio* calculation, the calculated structure is in good agreement with the X-ray structure. We think that the electrostatic factor is dominant in the dication–counter ions interaction. It should be noted that the positive charge is exclusively carried by the three Se atoms in the absence of the counter ions; a further accumulation of the positive charge induced by the counter ions is not expected.

We also calculated the two-center dication (boat–chair form). The optimized structure (C_s symmetry) is 27.6 kcal mol^{-1} (1 cal = 4.184 J) higher in energy than the three-center dication; the Se$^+$–Se$^+$ bond length were calculated to be 2.329 Å. The large energy gap between the two-center (boat–chair) and three-center (boat–boat) dications confirms that the dication always assumes a boat–boat form regardless of the environment in which it exists.

In summary, the hypervalent bonding structure of the dication salt of 1,11-(methanoselenomethano)-5*H*,7*H*-dibenzo[*b*,*g*][1,5]diselenocin **1** has been revealed by X-ray crystallographic analysis and *ab initio* calculation. Moreover, it has been shown that the positive charge is exclusively carried by the three Se atoms.

Further studies on related compounds are currently in progress.

This work was supported in part by the Ministry of Education, Science, Sports and Culture of Japan (Grant No. 07404035), and the Fund of Tsukuba Advanced Research Alliance (TARA) project (University of Tsukuba).

Footnotes and References

* E-mail: fuwukawa@staff.chem.tsukuba.ac.jp

† *Physical and spectroscopic data* for **3**: mp 226–228 °C (decomp.); ^{1}H NMR (CD$_3$CN) δ 4.60, 5.10 (ABq, *J* 15.7 Hz, 8 H), 7.51 (d, *J* 7.70 Hz, ArH, 2 H) and 7.75 (t, *J* 7.70 Hz, ArH, 2 H); ^{13}C NMR (CD$_3$CN) δ 39.7, 131.8, 132.5, 134.9 and 141.5; ^{77}Se NMR δ 517.9 (SeCH$_2$Ar, 2 Se) and 837.8 (SeAr, 1 Se) (relative to Me$_2$Se); Anal. Calc. for $C_{18}H_{14}F_6O_6S_2Se_3$: C, 29.16; H, 1.90. Found: C, 29.11; H, 1.82%.

‡ *Crystal data* for the selenurane dication salt **3**: crystals of $C_{18}H_{14}F_6O_6S_2Se_3$ are monoclinic, space group $P2_1/c$ (no. 14), a = 11.639(3), b = 10.170(3), c = 20.576(4) Å, β = 105.87(2)°, U = 2342.9(10) Å^3, Z = 4, D_c = 2.101 g cm^{-3}, Mo-Kα radiation (λ = 0.710 69 Å) from a Rigaku AFC7R diffractometer, 2166 reflections with $I > 2.00\sigma(I)$. The data were corrected for Lorentz and polarization effects, a linear decay (10.90%) and crystal absorption (DIFABS,[10] transmission factors ranging from 0.3275 to 1.0000). The structure was solved by direct methods and refined by a full-matrix least-squares method using the teXsan[11] crystallographic software package. The final residuals are R = 0.049 and R_w = 0.053. CCDC 182/542.

1 H. Fujihara, H. Mima, T. Erata and N. Furukawa, *J. Am. Chem. Soc.*, 1992, **114**, 3117.
2 H. Fujihara, N. Oi, R. Akaishi, T. Kawai and N. Furukawa, *Heterocycles*, 1989, **29**, 441.
3 *The Chemistry of Organic Selenium and Tellurium Compounds*, ed. S. Patai and Z. Rappoport, Wiley, New York, vol. 1 and 2, 1986 and 1988.
4 H. Fujihara, T. Nakahodo and N. Furukawa, *Chem. Commun.*, 1996, 311.
5 The calculation was carried out on a HP 735/125 workstation using Spartan 3. 1 (Wavefunction Inc.).
6 A. E. Reed, R. B. Weinstock and F. Weinhold, *J. Chem. Phys.*, 1985, **83**, 735.
7 A. E. Reed and P. v. R. Schleyer, *J. Am. Chem. Soc.*, 1990, **112**, 1434.
8 R. E. Rundle, *J. Am. Chem. Soc.*, 1963, **85**, 112.
9 J. I. Musher, *Angew. Chem., Int. Ed. Engl.*, 1969, **8**, 54.
10 DIFABS An empirical absorption correction program: N. Waker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.
11 teXsan: Crystal Structure Analysis Package, Molecular structure Corp. The Woodlands, TX, 1985, 1992.

Received in Cambridge, UK, 24th June 1997; 7/04431C