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Crystal Structures of Tetramethylammonium Dihalocyanoselenates(II)

STURLE BJØRNEVÅG, PETTER U. GAHRE, SVERRE HAUGE and OLAV VIKANE *

Department of Chemistry, University of Bergen, N-5000 Bergen, Norway

Tetramethylammonium dichlorocyanoselenate-(II), $(CH_3)_4NSeCl_2CN$, and the bromo analog, $(CH_3)_4NSeBr_2CN$, have been prepared by reacting tetramethylammonium selenocyanate with phenylselenenyl chloride and phenylselenenyl bromide, respectively. The crystals of the dichloride and the dibromide are isomorphous, space group $P\bar{4}2_1m$ (No 113), $Z=2$. The dichloro compound has the cell dimensions, $a=b=9.229(1)$ and $c=6.023(1)$ Å, and the dibromo compound, $a=b=9.453(1)$ and $c=6.131(1)$ Å.

In the two complexes, the selenium atom has a T-shape coordination with a symmetric halogen–selenium–halogen sequence. The Se–Cl bond length is 2.425(2) and the Se–Br is 2.575(1) Å. The halogen–selenium–halogen angle is 174.91(7)° in the dichloro and 176.28(7)° in the dibromo compound. In *trans* position to the Se–C bond, the selenium atom has a close contact to a nitrogen atom in an adjacent anion. The distances are 3.059(7) and 3.172(15) Å.

In the CNDO calculations, the variation of the energy of $SeCl_2CN^-$ and $SeBr_2CN^-$ with the carbon–selenium–halogen angle, has been calculated. The minimum energy geometries found are in excellent agreement with results from X-ray analyses.

Tetraalkylammonium dihalocyanoselenate(II) salts have been synthesized by Wynne and Golen[1] from selenocyanate and bromine or sulfuryl dichloride. They discussed the infrared and Raman spectra of the compounds. From analysis and comparison with the spectra and the crystal structure of potassium triselenocyanate hemihydrate, they concluded that all these structures should be similar. The coordination at the central selenium atom in the triselenocyanate ion is T-shaped. The bonding system can be described as consisting of a 2c–2e bond and a 3c–4e bond. Carbon is bonded with a 2c–2e bond and at right angle to this bond the two terminal and the central selenium atoms make a linear 3c–4e bonding system. The bonds are based on 4*p* orbitals of the central atom. The present work, determination of the crystal structure and a CNDO calculation, is a part of an investigation of complexes of selenium involving linear ligand–selenium–ligand sequence.

EXPERIMENTAL

In the present work, tetramethylammonium dihalocyanoselenate(II) was prepared from tetramethylammonium selenocyanate by reaction with phenylselenenyl halide in acetic acid anhydride:

$$Me_4NSeCN + 2PhSeX = PhSeSePh + Me_4NSeX_2CN$$

Tetramethylammonium dichlorocyanoselenate(II). 5 mmol (0.895 g) of Me_4NSeCN was dissolved in 30 ml acetic acid anhydride. The solution was filtered and 10 mmol (1.92 g) of PhSeCl dissolved in 20 ml acetic acid anhydride was added under stirring. When 75 % of the phenylselenenyl chloride had been added, the solution became brighter and at the end the solution was coloured clear orange. After one

* Present address: Rogaland Regional College, N-4001 Stavanger, Norway.

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Table 1. Crystal data and refinement characteristics.

	Me_4NSeCl_2CN	Me_4NSeBr_2CN
$a=b$ (Å)	9.229(1)	9.453(1)
c (Å)	6.023(1)	6.131(1)
V (Å^3)	513.0	548.0
M	250.03	338.94
Space group	$P\bar{4}2_1m$(No 113)	$P\bar{4}2_1m$(113)
Z	2	2
λMo$K\alpha$ (Å)	0.71073	0.71073
D_x (g cm^{-3})	1.62	2.05
D_{obs} (g cm^{-3})	1.60	2.05
μ (cm^{-1})	43.9	113.6
T (K)	293	293
F(000)	248	320
$\sin\theta/\lambda$ range (Å^{-1})	0–0.827	0–0.827
Scan width (°)	(1.0+0.35 tgθ)	(1.0+0.35 tgθ)
No. of refl.	755	804
No. of refl.>2$\sigma(F)$	518	371
Crystal dimensions, approx. (mm^3)	0.3×0.14×0.14	0.27×0.13×0.13
$R(F)$	0.038	0.035
$R_w(F)$	0.044	0.042
Goodness of fit	1.49	1.48
Difference Fourier, max (e Å^{-3})	0.3	0.3
Extinction coeff.	$1.6\cdot10^{-6}$	$2.7\cdot10^{-7}$
Variables	31	31

Table 2. Atomic coordinates for Me_4NSeCl_2CN and Me_4SeBr_2CN in fractions of cell edges and isotopic equivalent thermal parameter, Beq, defined as $4/3[a^2B(1.1)+\cdots ab\cos\gamma\, B(1.2)+\cdots]$. Standard deviations from least squares are given in parentheses.

	x	y	z	B_{eq}
$[SeCl_2CN]^-$				
Se	1/2	0	0.11776(7)	3.37(4)
Cl	0.68561(7)	0.18561(7)	0.09980(5)	3.82(8)
C1	1/2	0	−0.19164(8)	3.3(3)
N1	1/2	0	−0.37491(6)	5.5(5)
$[Me_4N]^+$				
C2	0	0	1/2	3.0(3)
N2	0.06570(2)	0.11429(9)	0.35112(9)	4.6(3)
$[SeBr_2CN]^-$				
Se	1/2	0	0.10695(4)	3.32(5)
Br	0.69250(6)	0.19250(6)	0.09329(2)	4.23(8)
C1	1/2	0	−0.19924(7)	3.7(7)
N1	1/2	0	−0.37605(3)	6.1(10)
$[Me_4N]^+$				
C2	0	0	1/2	3.4(6)
N2	0.06879(4)	0.10939(8)	0.35815(6)	5.1(4)

hour, the solution was filtered and the light yellow precipitate was washed with ether and dried. Yield of Me_4NSeCl_2CN, 0.69 g or 56 % based on the amount of selenocyanate employed.

To get crystals suitable for X-ray investigation, some of the precipitate was dissolved in the mother liquor at room temperature. The solution was set aside for 12 h at 4 °C. Two types of crystals deposited, yellow-green needles of PhSeSePh and short light yellow prisms formed as pyramids in both ends. The crystals were filtered off, washed with dried ether which dissolved the diselenide, and dried in vacuum. The crystals of Me_4NSeCl_2CN were hygroscopic.

Tetramethylammonium dibromocyanoselenate(II), Me_4NSeBr_2CN, was prepared from Me_4NSeCN and PhSeBr, in the same way as described for the dichloro salt. Yield from 5 mmol (0.895 g) of Me_4SeCN and 10 mmol (2.36 g) of PhSeBr was 0.80 g or 54.5 %. The crystals were hygroscopic, orange prisms elongated along the *a* axis.

CRYSTAL DATA

Since the crystals were hygroscopic, they were mounted in glass tubes.

Collection of X-ray data was done by means of an Enraf-Nonius CAD-4 diffractometer with graphite monochromatized Mo$K\alpha$ radiation. Unit cell parameters were determined from setting angles of 25 reflections, using least squares analysis. The reflection data were collected by $\Delta\omega$-scan and the variation of three standard reflections was used for scaling of the data. The variation of the standard reflections was within five per cent during the collection periods. The data were corrected for Lorentz and polarization, absorption, extinction and anomalous dispersion effects.

The crystal structures were solved by Patterson and Fourier methods and refined by full-matrix least-squares, minimizing the function $\Sigma w(F_o - KF_c)^2$ where K is a scale factor and $w = 1/\sigma^2(F_o)$.

For further details about data collection and computer programs used, we refer to a previous paper.[3] Crystal data and refinement characteristics are given in Table 1.

Since the space group is non-centrosymmetric and the scattering factors were corrected for anomalous dispersion, it was possible to deter-

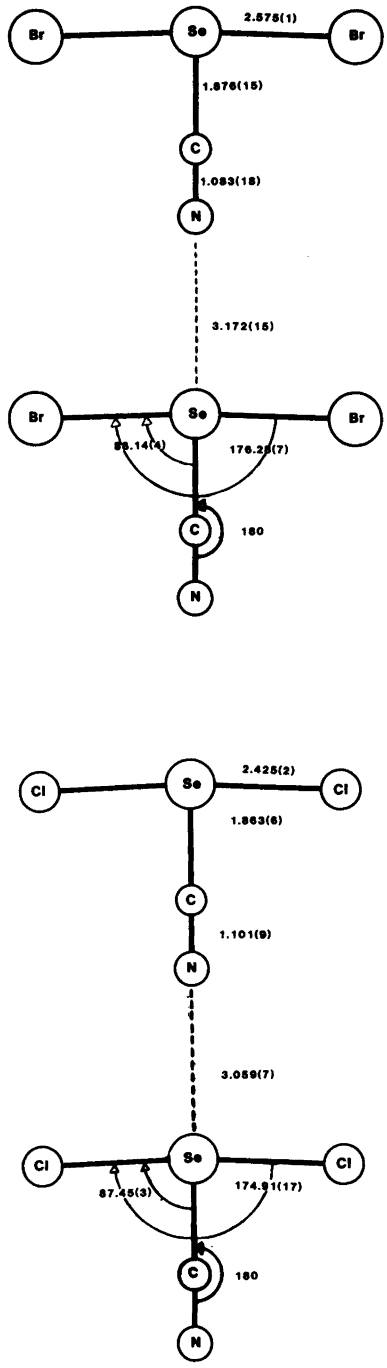

Fig. 1. The dihalocyanoselenate(II) ions as crystallized with tetramethylammonium cation. Bond lengths (Å) and angles (°). Standard deviations are given in parentheses.

mine the absolute configuration. The signs of the *z*-coordinates for all atoms were changed and the structures were refined to convergence. The final *R*-value for the dichloro compound increased from 0.038 to 0.052 and for the dibromo compound from 0.035 to 0.039. The significance of the difference between the two solutions was tested by Hamiltons *R*-factor test.[4] For both structures, the test is in great favour of the coordinates originally chosen.

Tables of thermal parameters and of structure factors are available from the authors on request.

RESULTS

Bond lengths and angles in the selenium complex ions, based on the coordinates in Table 2, are shown on Fig. 1. The selenium atom is primary three coordinated, being bonded to a carbon atom and two halogen atoms in a T-shape, with the halogen atoms in *trans* positions. The four atoms are, due to space group symmetry, exactly co-planar. The halogen–selenium–halogen sequence is almost linear. The angle is 174.91(7)° in the dichloro and 176.28(7)° in the dibromo compound. Due to mirror symmetry, the two selenium–halogen bonds are equal, 2.425(2) Å in the dichloro compound and 2.575(1) Å in the dibromo compound. Taking the covalent radii of Se, Br and Cl to be 1.16, 1.14 and 0.99 Å, respectively, the bond lengths found, in both complexes are 0.28 Å longer than a single covalent bond. A similar Br–Se–Br sequence is found in the crystals of dibromo(tetramethylthiourea)selenium(II)[5] where the angle is 174.70(10)° and the Se–Br distances are 2.569(3) and 2.620(3) Å. The bromine with the longest distance to selenium is also engaged in an intermolecular contact, 3.34 Å, to selenium in an adjacent anion. Complexes of divalent selenium with linear three-centre systems have also been found with selenocyanate or selenourea as ligands. In six compounds[6] with nearly symmetric three-centre systems the mean value of the Se–Se bond lengths in each compound is in the range 2.649–2.668 Å. The mean bond lengths is 0.34 Å longer than the single covalent bond. It seems that in such complexes, halogen has relatively shorter bonding to selenium than ligands with selenium as complexing atom.

The selenocyanate groups lie in two mirror planes and are therefore exactly linear. There is no significant difference between the two Se–C bond lengths 1.876(15), 1.863(6) and the single covalent Se–C_{sp} bond length, 1.847 Å, which is the sum of the single covalent radii of selenium, 1.16 Å, and of *sp*-hybridized carbon, 0,687 Å.[7] The C–N bond lengths, 1.083(18) and 1.101(9) Å, are shorter than the C–N triple bond length, 1.150 Å, given by Pauling[8] or the value given by Britton,[9] 1.158±0.002 Å, for a C–N distance in C-bonded cyanide. The weighted average bond length from several crystal structures of selenocyanate compounds is 1.141(4) Å.[6]

In *trans* position to the Se–C bond, the selenium atom has a short contact to a selenocyanate nitrogen in an adjacent anion. The contact makes the anion polymeric with an

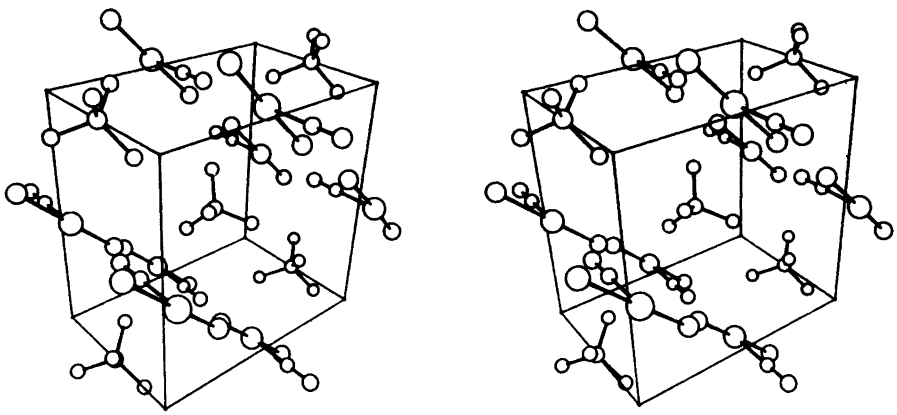

Fig. 2. Packing in the unit cell of Me_4NSeCl_2CN.

Table 3. Orbital exponents and bonding parameters used in CNDO/2 calculations.

Atom	ζ_s	ζ_p	$-1/2[I_s+A_s]$	$-1/2[I_p+A_p]$	$-\beta_A^o$
Se	1.8780^{12}	1.8780^{12}	16.315^{12}	7.100^{12}	16.00^{12}
Br	2.6382^{14}	2.2570^{14}	18.285^{13}	8.400^{13}	21.46^{13}
Cl	2.3561^{14}	2.0387^{14}	19.880^{15}	8.780^{15}	22.33^{16}
C	1.6083^{14}	1.5679^{14}	14.960^{15}	5.810^{15}	21.00^{16}
N	1.0237^{14}	1.9170^{14}	20.360^{15}	8.110^{15}	25.00^{16}

infinite linear ···N–C–Se···N–C–Se··· chain. The Se···N distance is 3.059(7) in the dichloro compound and 3.172(15) Å in the dibromo compound. The van der Waals Se···N distance can be taken to be 3.30 Å. If the Se···N contact is included, then the coordination around the selenium atom is distorted square planar. The bonding may then be described as consisting of two 3c–4e systems, one symmetric halogen–selenium–halogen system and one highly asymmetric carbon–selenium–nitrogen system.

The dimensions of the tetramethylammonium

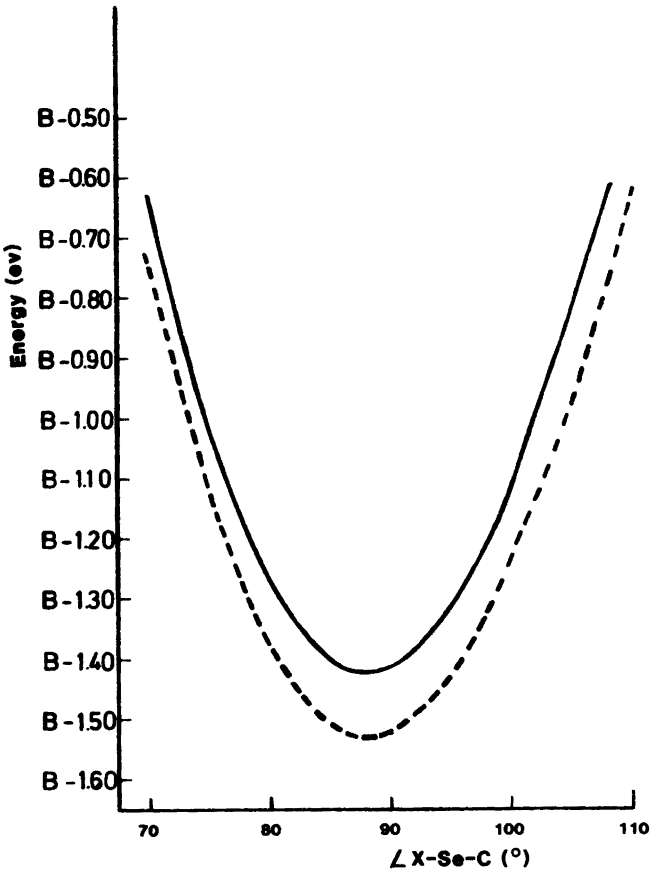

Fig. 3. Plot of CNDO/2 total energy against X–Se–C angle in $SeCl_2CN^-$ (– – –, $B=-1659.00$ eV) and $SeBr_2CN^-$ (——, $B=-1550.00$ eV).

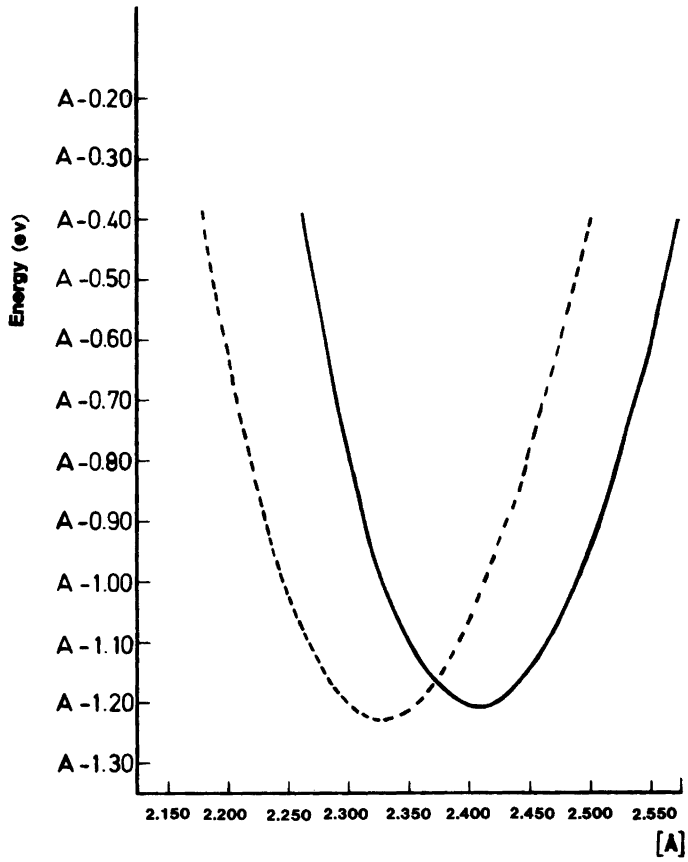

Fig. 4. Plot of CNDO/2 total energy against X–Se bond length in $SeCl_2CN^-$ (– – –, $A = -1659.60$ eV) and $SeBr_2CN^-$ (——, $A = -1551.00$ eV).

cation are in the dichloro compound: N–C=1.511(4) Å with the C–N–C angles 107.1(4) and 110.7(2)°. In the dibromo compound N–C=1.500(7) Å and the C–N–C angles 109.0(6) and 109.7(3)°. The shortest methyl carbon–halogen distance is 3.466(4) Å.

Table 4. Gross atomic charges from the CNDO/2 calculations.

Atom	$SeCNCl_2^-$	$SeCNBr_2$
Se	0.246	0.224
Cl(Br)	−0.543	−0.539
C	0.095	0.099
N	−0.255	−0.246

CNDO/2 CALCULATION

The bending of the symmetric halogen–selenium–halogen sequence is towards the selenocyanate carbon. It can be looked at as a result of lone pair repulsion. In the present work a theoretical calculation of the carbon–selenium–halogen bond angle has been done by use of a CNDO/2 program.[10–13] The program uses *s* and *p* Slater orbitals on all atoms. The parameters used in the calculations are given in Table 3. In the calculations, the bond lengths are from the X-ray analysis. The variation of the energy of $SeCl_2CN^-$ and $SeBr_2CN^-$ with the carbon–selenium–halogen angle is shown in Fig. 3. For the dichloro compound minimum energy is at an angle of 87.8° and for the dibromo compound at 88.0°. The results are in excellent

agreement with the results from the X-ray analysis. Fig. 4 shows how the energy of the two systems depends upon the selenium–halogen bond length. The carbon–selenium–halogen angle is fixed equal to the value found in the structure analysis. The equilibrium bond lengths are found at 2.324 for the dichloro and 2.405 Å for the dibromo compound, which are between observed bond lengths and single covalent bond lengths. The calculated gross atomic charge are given in Table 4. The selenium atom in the dichloro compound has greater positive charge than in the dibromo compound, due to greater electronegativity of chlorine.

The results of the calculations are in good agreement with other calculations on molecules with third row elements. Hase and Schweig[13] have done CNDO/2 calculations on hydrides of arsenic, germanium, selenium, and of interhalogen compounds. Bond angles reproduce well, but bond lengths deviate. The deviation between calculated and experimental bond lengths can be explained as resulting from errors introduced by neglecting the differential overlaps[10] which again are functions of the internuclear distances.

The CNDO/2 has been used with success to calculate the geometry of molecules, but one has to bear in mind that the method also has limitations. A demonstration of this occurs in the calculation of the interhalogen compounds AB_5,[14] where the calculation gave minimum energy for a trigonal bipyramidal geometry while the observed one is square pyramidal.

REFERENCES

1. Wynne, K. J. and Golen, J. *Inorg. Chem. 13* (1974) 185.
2. Hauge, S. and Sletten, J. *Acta Chem. Scand. 25* (1971) 3094.
3. Bjørnevåg, S. V. and Hauge, S. *Acta Chem. Scand. A 37* (1983) 235.
4. Hamilton, W. C. *Acta Cryst. 18* (1965) 502.
5. Wynne, K. J., Pearson, P. S., Newton, M. G. and Golen, J. *Inorg. Chem. 11* (1972) 1192.
6. Hauge, S. and Sletten, J. *Acta Chem. Scand. 25* (1971) 3094; Hauge, S. *Ibid. 25* (1971) 3103; *A 29* (1975) 163; Hauge, S., Opedal, D. and Årskog, J. *Ibid. A 29* (1975) 225; Hauge, S. *Ibid. A 33* (1979) 317.
7. Bastiansen, O. and Tretteberg, M. *Tetrahedron 17* (1962) 147.
8. Pauling, L. *The Nature of Chemical Bond,* 3rd Ed., Cornell University Press, Ithaca 1960.
9. Britton, D. *Perspectives Struct. Chem. 1* (1967) 109.
10. Pople, J. A., Santry, D. P. and Segal, G. A. *J. Chem. Phys. 43* (1965) 136.
11. Pople, J. A. and Segal, G. A. *J. Chem. Phys. 44* (1966) 3289.
12. Santry, D. P. and Segal, G. A. *J. Chem. Phys. 47* (1967) 158.
13. Hase, H. L. and Schweig, H. *Theor. Chim. Acta 31* (1973) 215.
14. Deb, B. M. and Coulson, C. A. *J. Chem. Soc. A* (1971) 958.
15. Clementi, E. and Raimondi, D. L. *J. Chem. Phys. 38* (1963) 2686.
16. Sichel, J. M. and Whitehead, M. A. *Theor. Chim. Acta 7* (1967) 32.
17. Siegbahn, K., Nordling, C., Johansson, G., Hedman, J., Heden, P. F., Hamrin, K., Gelius, U., Bergmark, T., Werme, L. O., Manne, R. and Baer, Y. *ESCA Applied to Free Molecules,* North-Holland, Amsterdam-London 1969, p. 180.

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