# Influence of Secondary Bonding on the Intradimer Distance of Trichloro(ethane-1,2-diolato-*O,O′*)tellurate(IV)†

**Markku R. Sundberg,**[a] **Rolf Uggla,**[a] **Tarja Laitalainen**[*,b] **and Jan Bergman**[*,c]
[a] *Department of Chemistry, Laboratory of Inorganic Chemistry, PO Box 6, FIN-00014, University of Helsinki, Finland*
[b] *Department of Chemistry, Laboratory of Organic Chemistry, PO Box 6, FIN-00014, University of Helsinki, Finland*
[c] *Department of Organic Chemistry, CNT, NOVUM, S-14157 Huddinge, Sweden*

The structure of ammonium trichloro(ethane-1,2-diolato-*O,O′*)tellurate(IV) was determined by single-crystal methods: monoclinic, space group $P2_1/c$ (no. 14), $a$ = 10.779(1), $b$ = 12.418(2), $c$ = 6.915(1) Å, $\beta$ = 108.65(1)°. The co-ordination around $Te^{IV}$ is distorted $\psi$ octahedral with one of the two oxygen atoms lying opposite to the lone pair of Te. Two identical anions form a dimeric unit *via* a centre of symmetry. A short Te–O intradimeric distance of 2.764(6) Å is about 0.84 Å shorter than the sum of the corresponding van der Waals radii. The structure is compared with that of the corresponding tetraphenylphosphonium salt where the intradimer distance is clearly longer. The size of the cation and the amount of intermolecular interactions seem to be decisive factors in secondary bonding between two anionic units. The electronic properties of the anions in the two salts were investigated by *ab initio* calculations and compared with those of the optimised structure of the corresponding monomeric anion. The positive charge of 1.36 electrons at Te is almost invariable. The main interaction within a dimeric unit in the ammonium salt is a donation of an electron pair from oxygen to the antibonding molecular orbital between Te–Cl in the neighbouring anion. The bond between Te and one of the equatorial Cl atoms (opposite to oxygen) is sensitive to dimerisation. The charge density, ionic nature of the bond and bond length increase when the degree of dimerisation increases, whereas the other two Te–Cl bonds are almost insensitive.

Interaction between $TeCl_4$ and ethane-1,2-diol in acetonitrile yields ammonium trichloro(ethane-1,2-diolato-*O,O′*)tellurate(IV) which exhibits immunomodulatory activity and also stimulates interleukin-2 production.[1–9] A few analogues have also been reported,[10] thus alkane-1,2-diols (*e.g.* butane-1,2-diol) generally work well whereas butane-2,3-diol and propane-1,3-diol failed to yield any analogues.

The structure of the compound was determined by single-crystal X-ray methods and published in a preliminary communication.[11] Later, the structure was published by Albeck *et al.*[3] but no *R* value and no deviations for the unit-cell parameters were given. There is also structural information for the corresponding tetraphenylphosphonium salt.[12]

Alcock[13] introduced the term 'secondary bonding' to describe the tendency in non-metallic compounds to form short intermolecular contacts. In general terms, a dative bond is supposed to be formed *via* a lone pair of an outer atom to an empty orbital on a central atom. The existence of the required lone pair was found experimentally in dimethyltellurium dichloride.[14] On the other hand, the presence of the lone pair of the central atom is said to prevent significant secondary bonding.[15] As far as we know, there has been no description of such bonding based upon *ab initio* calculations. In a recent article the use of natural bond order was suggested for analysis of secondary bonding.[16]

We report here our results for ammonium trichloro(ethane-1,2-diolato-*O,O′*)tellurate(IV). This compound is an uncommon example of dimer formation between two anions. The structural parameters within the asymmetric unit will be compared with those of the tetraphenylphosphonium analogue, where the intradimer distance is considerably longer. The bonding properties within a single anion and the dimeric units will be discussed based upon *ab initio* calculations and natural bond order analysis for all three moieties.

## Experimental

*Synthesis of Ammonium Trichloro*(*ethane*-1,2-*diolato*-O,O′)-*tellurate*(IV).—Ethane-1,2-diol (3.1 g, 50 mmol) was added to a solution of $TeCl_4$ (13.5 g, 50 mmol) in acetonitrile (45 cm$^3$) under dry $N_2$. The resulting solution was refluxed for 6 h and the crystals formed were collected after 24 h at 20 °C. Yield: 12.5 g (79%). Crystals suitable for X-ray analysis were obtained by recrystallisation from acetonitrile.

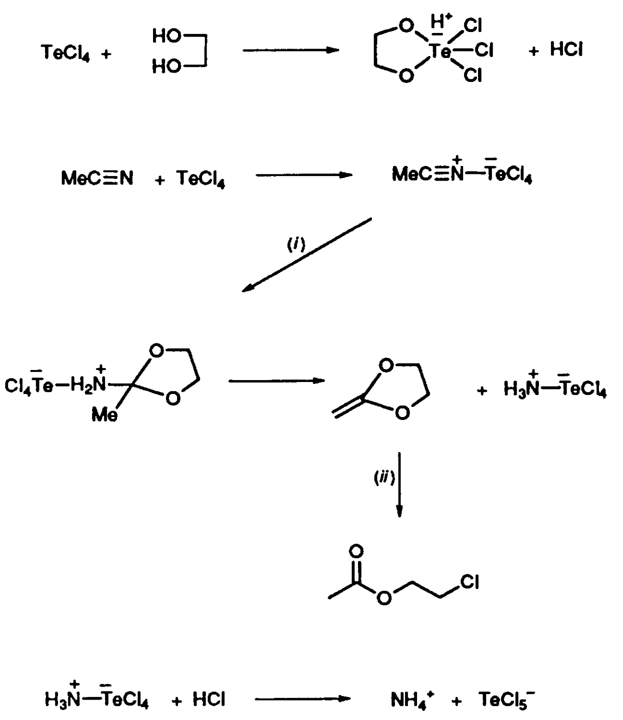
*Crystallography.—Crystal data.* $[NH_4][TeCl_3(C_2H_4O_2)]$, $M_r$ = 312.05, monoclinic, space group $P2_1/c$ (no. 14), $a$ = 10.779(1), $b$ = 12.418(2), $c$ = 6.915(1) Å, $\beta$ = 108.65(1)°, $U$ = 877.0(2) Å$^3$ (by least-squares refinement of diffractometer angles for 25 independent well centred reflections in the 2θ range 23.2–39.1°, $\lambda$ = 0.710 69 Å), $Z$ = 4, $D_c$ = 2.36 g cm$^{-3}$, $T$ = 296(1) K. Colourless prisms. Crystal dimensions 0.25 × 0.29 × 0.35 mm, $\mu$(Mo-K$\alpha$) = 43.6 cm$^{-1}$.

*Data collection and processing.* Nicolet P3 diffractometer, ω scan mode, variable scan speed 2.0–20.0° min$^{-1}$, graphite-monochromated Mo-K$\alpha$ radiation, 2340 unique reflections measured ($3 \leqslant 2\theta \leqslant 57°$), experimental absorption correction, giving 1982 independent reflections with $F > 4\sigma(F_o)$. No decay, but Lorentz and polarisation corrections were made.

*Structure analysis and refinement.* Direct methods followed by Fourier-difference techniques. Full-matrix least-squares refinement with all non-hydrogen atoms anisotropic and the

---

† *Supplementary data available* (No. SUP 57034, 10 pp.): natural localised molecular orbital analysis. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.



Scheme 1 A hypothetical mechanism for the formation of $[NH_4][TeCl_3(C_2H_4O_2)]$. (*i*) $HOCH_2CH_2OH$; (*ii*) HCl

**Table 1** Atomic coordinates for the non-hydrogen atoms and their standard deviations for ammonium trichloro(ethane-1,2-diolato-*O*,*O*′)-tellurate(IV)

| Atom | *X*/*a* | *Y*/*b* | *Z*/*c* |
|---|---|---|---|
| Te(1) | 0.186 42(4) | 0.047 48(3) | 0.049 63(6) |
| O(2) | 0.304 6(4) | −0.037 0(4) | −0.051 8(7) |
| O(1) | 0.056 3(5) | −0.058 4(4) | −0.104 2(8) |
| Cl(3) | 0.144 0(2) | 0.160 9(2) | −0.260 6(3) |
| Cl(2) | 0.253 1(2) | −0.077 8(2) | 0.354 3(3) |
| Cl(1) | 0.423 3(2) | 0.144 4(1) | 0.215 9(3) |
| C(1) | 0.104 2(8) | −0.122 9(7) | −0.238(1) |
| C(2) | 0.246 9(7) | −0.139 2(6) | −0.138(1) |
| N(1) | 0.439 9(6) | 0.097 6(5) | 0.711(1) |

**Table 2** Bond lengths (Å) and angles (°) of the non-hydrogen atoms with their standard deviations for ammonium trichloro(ethane-1,2-diolato-*O*,*O*′)tellurate(IV), the tetraphenylphosphonium salt and the anion optimised by *ab initio* methods. The original numbering scheme for the phosphonium salt was altered to correspond to that of the ammonium analogue

| | | | |
|---|---|---|---|
| Te(1)–O(1) | 1.968(5) | 1.973(4) | 1.953 |
| Te(1)–O(2) | 1.946(5) | 1.919(3) | 1.957 |
| Te(1)–Cl(1) | 2.722(2) | 2.590(1) | 2.368 |
| Te(1)–Cl(2) | 2.531(2) | 2.524(2) | 2.375 |
| Te(1)–Cl(3) | 2.483(2) | 2.495(1) | 2.368 |
| O(1)–C(1) | 1.440(11) | 1.428(7) | 1.423 |
| O(2)–C(2) | 1.454(8) | 1.436(6) | 1.423 |
| C(1)–C(2) | 1.484(11) | 1.475(8) | 1.557 |
| | | | |
| O(1)–Te(1)–O(2) | 83.2(2) | 84.12(13) | 83.99 |
| O(1)–Te(1)–Cl(1) | 159.0(2) | 165.90(11) | 161.00 |
| O(1)–Te(1)–Cl(2) | 90.2(2) | 89.60(11) | 88.13 |
| O(1)–Te(1)–Cl(3) | 90.5(2) | 89.36(11) | 87.97 |
| O(2)–Te(1)–Cl(1) | 75.93(13) | 82.13(9) | 77.00 |
| O(2)–Te(1)–Cl(2) | 85.68(15) | 86.73(9) | 82.24 |
| O(2)–Te(1)–Cl(3) | 87.43(15) | 87.43(9) | 81.77 |
| Cl(1)–Te(1)–Cl(2) | 86.68(6) | 92.70(5) | 89.66 |
| Cl(1)–Te(1)–Cl(3) | 90.17(6) | 86.94(4) | 88.94 |
| Cl(2)–Te(1)–Cl(3) | 172.93(8) | 174.15(5) | 163.86 |
| Te(1)–O(1)–C(1) | 112.3(4) | 111.5(3) | 114.22 |
| Te(1)–O(2)–C(2) | 112.0(4) | 110.7(3) | 113.50 |
| O(1)–C(1)–C(2) | 107.7(6) | 108.3(4) | 108.99 |
| O(2)–C(2)–C(1) | 108.5(6) | 109.6(4) | 109.45 |

chelate ring hydrogens in their calculated positions. The positions of the hydrogen atoms of the ammonium cation were not found from a Fourier-difference map. The weighting scheme $w = 1/[\sigma^2(F_o)]$ with $F_o$ from counting statistics gave satisfactory agreement analyses. Final *R* and *R*′ values were both 0.038. Neutral atom scattering factors and correction factors for anomalous scattering were those included in the program package. The calculations were carried out with XTAL software.[17]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Ab initio *Calculations*.—The calculations were carried out at the STO-3G* level by use of the GAUSSIAN 92 program package,[18] which was installed on a CONVEX C3840 and CRAY-XMP super computer. The basis set includes single first polarisation functions (p on H, d on the heavier elements). The electronic charges and the bonding properties were analysed with the help of the NBO program, which is a subprogram[19] in GAUSSIAN 92. The atomic coordinates for the dimeric unit obtained from the X-ray study and ref. 12 were used as input. The structure of the trichloro(ethane-1,2-diolato-*O*,*O*′)tellurate(IV) anion was optimised at the same level of theory. Since the calculated IR spectrum of the optimised monomer does not have any imaginary frequencies the geometry is considered to represent the true minimum.

## Results and Discussion

*Synthesis*.—Obviously acetonitrile serves as the nitrogen source for the formation of the ammonium ion in this compound. Albeck *et al.*[3] have tried to account for this remarkable transformation by assuming that ethane-1,2-diol is transformed into $HOCH_2CH_2Cl$, which will react with acetonitrile forming the iminoester $H_3C(C{=}NH)OCH_2CH_2Cl$. The iminoester then reacts with water and HCl forming the ammonium ion. This view was considered to be supported by the identification of 2-chloroethyl acetate in the reaction mixture. We have now reinterpreted the mechanism as outlined in Scheme 1. The unstable HCl scavenger[20] 2-methylene-1,3-dioxolane could be detected by gas chromatography–mass spectrometry. The indicated formation of a nitrilium ion complex is hypothetical but it should be remembered that $TeCl_4$ is a powerful catalyst in cyclopolymerisation of nitriles.[21]

*Crystal Structure*.—The positional and geometrical parameters are given in Tables 1 and 2, respectively. The dimeric unit is depicted in Fig. 1. The structure consists of ammonium cations and trichloro(ethane-1,2-diolato-*O*,*O*′)tellurate(IV) anions. Two neighbouring anions form dimers with a crystallographic centre of symmetry between the molecules. The dimers form layers connected by interlayer ammonium cations (Fig. 2).

In the corresponding tetraphenylphosphonium salt the packing is essentially different; in the present compound the density is clearly higher, $D_c = 2.36$ g cm$^{-3}$ (*cf.* 1.63 g cm$^{-3}$). Moreover, the shortest intradimer distance between Te(1) and O(1) was 3.485(3) Å, whereas in the present compound it is 2.764(6) Å. The overall configuration of the dimer in the two compounds is very similar, however. The short intermolecular distances with the angles referring to possible secondary bonding have been deposited (SUP 57034).

Large cations are known to prevent dimerisation or polymerisation.[23] The reason for this is not yet clear. However,

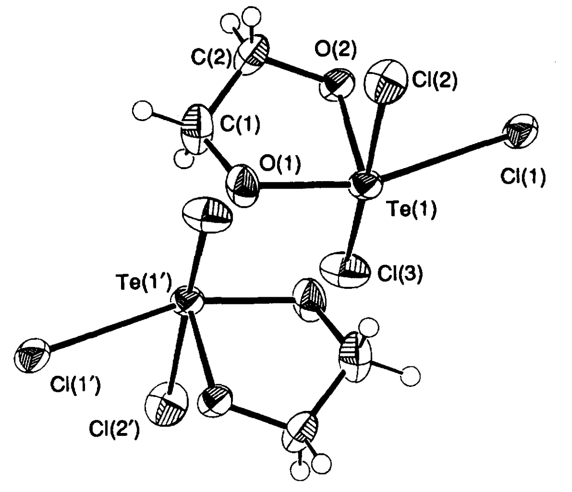


**Fig. 1** An ORTEP[22] drawing showing the labelling of the non-hydrogen atoms in ammonium trichloro(ethane-1,2-diolato-*O*,*O*′)-tellurate(IV). The thermal ellipsoids for the non-hydrogen atoms are drawn at the 50% probability level. Primed atoms are related to unprimed ones by the crystallographic centre of symmetry lying between the molecules

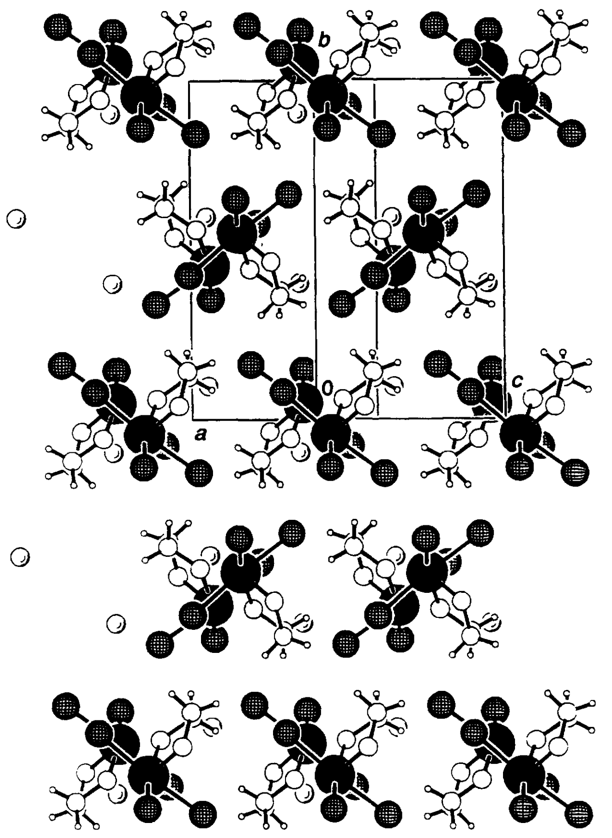


**Fig. 2** Packing of the dimeric units

it seems that also here the cation size is a decisive factor. Although anions normally repel each other, the intradimer distances are fairly short in our compound. Obviously the dimer formation is charge dependent. The positive part (tellurium) is very likely attracting the negative part of a neighbouring anion and thus the overall configuration will be the same. Moreover, the ability of an ammonium cation to form hydrogen bonds is far more extensive than that of a tetraphenylphosphonium cation. Accordingly, it will very likely lessen the overall charge of the anion and thus permit the anions to get nearer to each other. It should be noted that Cl(1) especially is the atom which is favoured upon hydrogen-bond formation. Accordingly, we suggest that intermolecular interactions play an important role in dimer formation or secondary bonding in general.

The co-ordination around $Te^{IV}$ is distorted square pyramidal or ψ octahedral. The equatorial plane consists of three chlorine atoms and one of the two oxygens of the ethanediolate anion. As usual for this kind of tellurium compound, the central tellurium atom is displaced from the plane, 0.1965(13) Å away from the apical O(2) atom. This is very clearly seen also in the Cl(1)–Te(1)–O(1) angle [159.0(2)°].

The puckering parameters[24] for the five-membered chelate ring are $Q = 0.366$ Å and $\varphi = 90.85°$. The latter indicates that the ring displays an almost pure twist conformation. The carbon atoms C(1) and C(2) deviate by 0.284(11) and −0.302(10) Å, respectively, from the Te(1), O(1) and O(2) plane. The dimer formation does not seem to affect the puckering parameters, because the corresponding values for the tetraphenylphosphonium salt are $Q = 0.357$ Å and $\varphi = 89.48°$.

The bond lengths from the central $Te^{IV}$ to the three surrounding chlorine atoms are clearly different from each other (Table 2). The Cl(1) atom lies farther away than the other two chlorine atoms, for which the bond lengths are near to the mean value of 2.52(3) Å calculated for 22 compounds.[25] This is in sharp contrast with the phosphonium salt, where the Te(1)–Cl(1) distance was 2.590(1) Å. The authors proposed that the short bond reflects a very slight *trans* effect in the anion. This in turn would be caused by the relatively small Cl(1)–Te(1)–O(1) angle of 165.90(11)° in their compound. The present value is 159.0(2)° and yet the Te(1)–Cl(1) bond is longer, 2.722(2) Å. In the optimised monomeric unit the Cl(1)–Te(1)–O(1) angle is similar, 161.00°. However, the Te(1)–Cl(1) bond is significantly shorter, 2.368 Å. There is also a clear elongation in the Te(1)–O(2) bond, when the asymmetric units get closer. In the optimised structure the bond is longer than in the structures in the solid phases, 1.957 Å. The major changes occur clearly in the O(1)–Te(1)–Cl(1) direction of the ψ octahedron, whereas the Cl(2)–Te(1)–Cl(3) direction remains almost intact. No doubt the different packing with closer dimer contacts may well explain the differences. Since the dimer is very sensitive to changes, we may not be certain whether the differences in the unit-cell parameters between our determination and that in ref. 3 may be due to different phases. The differences in the bond lengths are discussed later in connection with the *ab initio* calculations.

Ab initio *Studies*.—The natural charges calculated for a dimeric unit in the present compound, the tetraphenylphosphonium salt and the optimised monomeric anion are shown in Table 3. The tellurium atom carries a clear positive charge, which is almost independent of the degree of dimerisation. The negative charge of the anion resides on the surrounding donor atoms. The difference in Te(1)–Cl(1) bond length in the present compound, the tetraphenylphosphonium salt and in the optimised anion is reflected in the charge densities at the Cl(1) atom. When the degree of dimerisation increases the charge density at Cl(1) also increases. In contrast, the charge densities at atoms Cl(2) and Cl(3) change very little. The negative charges at the oxygen atoms also change, but the correlation is not clear.

The molecular orbitals are listed in Table 4. The bonds to the central tellurium atom are clearly stronger for the optimised monomeric anion than for the dimerised anions in the solid state. Also the lone pairs of the chlorine atoms have the same characteristics. It is clearly seen that the occupancies of the molecular orbitals consisting of the atomic orbitals of tellurium deviate from the ideal value of two electrons. The corresponding antibonding orbitals have significant amounts of electrons. No three-centre orbitals were found in the analysis.

The bond between Te(1) and Cl(1) is clearly the weakest. Again there is a correlation between the bond lengths and the energy of a Te–Cl bond: the bond becomes weaker upon dimerisation. Two of the three lone pairs of the Cl(1) seem to be the highest-occupied molecular orbitals. The occupancy of the antibonding orbital between Te(1) and O(2) (*ipso* to the lone pair of Te) clearly diminishes upon dimerisation. The opposite behaviour is seen for the antibonding orbital between Te(1)–Cl(2) and Te(1)–Cl(3).

**Table 3** Summary of natural population analysis. The values in the other unit of the dimer are identical

| | Natural charge | | |
|---|---|---|---|
| Atom | This work | Ref. 3 | Optimised monomer |
| Te(1) | 1.368 48 | 1.362 38 | 1.353 93 |
| O(1) | −0.418 40 | −0.409 53 | −0.473 54 |
| O(2) | −0.416 96 | −0.430 24 | −0.462 53 |
| Cl(1) | −0.649 24 | −0.596 90 | −0.524 64 |
| Cl(2) | −0.552 82 | −0.550 00 | −0.532 45 |
| Cl(3) | −0.534 43 | −0.542 66 | −0.526 14 |
| C(1) | 0.032 33 | 0.002 34 | 0.065 50 |
| C(2) | 0.028 88 | 0.016 10 | 0.064 27 |
| H(11) | 0.038 72 | 0.036 73 | 0.005 73 |
| H(12) | 0.036 45 | 0.036 30 | 0.009 27 |
| H(21) | 0.028 63 | 0.042 51 | 0.011 74 |
| H(22) | 0.038 35 | 0.032 50 | 0.008 86 |

To evaluate the interactions between the anions a second-order perturbation theory analysis of a Fock matrix in the natural bond order basis was carried out. The results are shown in Table 5. The main interaction is clearly between a lone pair of atom O(1) and the antibonding orbital between Te(1) and Cl(1) in the neighbouring anion. No significant interactions were found for the tetraphenylphosphonium salt. The position of the tellurium inert electron pair is clearly pointing in a direction with the minimum amount of interaction with a neighbouring molecule (Fig. 3). This is in accord with the Alcock thesis.[13] Moreover, the lone pair of atom O(1) is pointing towards the bond Te(1)–Cl(1).

**Table 5** Interdimer interactions from unit 1 to unit 2. The threshold value for listing is 0.99 kcal mol$^{-1}$.[a] The corresponding values for the interactions from unit 2 to unit 1 have identical values. The primed atoms refer to the neighbouring unit

| Donor NBO (*i*) | Acceptor NBO (*j*) | $E(2)$/ kcal mol$^{-1}$ |
|---|---|---|
| LP(1) O(1) | 157. RY*(3) Te(1′)[b] | 0.99 |
| LP(1) O(1) | 185. BD*(1) Te(1′)–O(1′) | 1.20 |
| LP(1) O(1) | 187. BD*(1) Te(1′)–Cl(1′) | 3.01 |

[a] cal = 4.184 J. [b] Empty Rydberg orbital.

**Table 4** Natural bond orbitals for ammonium trichloro(ethane-1,2-diolato-*O*,*O*′)tellurate(IV), the tetraphenylphosphonium salt and for the optimised monomer

| | Occupancy, energy/$E_\mathrm{h}$[a] | | |
|---|---|---|---|
| NBO (*i*)[b] | This work | Ref. 12 | Optimised monomer |
| BD(1) Te(1)–O(1) | 1.835 75, −0.325 28 | 1.843 19, −0.299 32 | 1.846 81, −0.398 83 |
| BD(1) Te(1)–O(2) | 1.778 36, −0.320 40 | 1.783 46, −0.344 10 | 1.770 83, −0.357 68 |
| BD(1) Te(1)–Cl(1) | 1.917 93, −0.077 43 | 1.908 94, −0.118 15 | 1.900 26, −0.292 45 |
| BD(1) Te(1)–Cl(2) | 1.884 36, −0.148 24 | 1.885 36, −0.139 57 | 1.887 26, −0.292 93 |
| BD(1) Te(1)–Cl(3) | 1.882 01, −0.172 34 | 1.882 54, −0.159 46 | 1.886 03, −0.297 60 |
| BD(1) O(1)–C(1) | 1.976 73, −0.566 80 | 1.981 45, −0.555 29 | 1.981 70, −0.637 51 |
| BD(1) O(2)–C(2) | 1.978 02, −0.558 13 | 1.978 69, −0.582 55 | 1.981 16, −0.632 51 |
| BD(1) C(1)–C(2) | 1.995 01, −0.531 80 | 1.995 95, −0.531 85 | 1.990 97, −0.536 30 |
| BD(1) C(1)–H(11) | 1.991 18, −0.520 43 | 1.991 30, −0.544 41 | 1.992 57, −0.524 47 |
| BD(1) C(1)–H(12) | 1.995 22, −0.515 89 | 1.995 66, −0.540 73 | 1.994 58, −0.517 74 |
| BD(1) C(2)–H(21) | 1.991 52, −0.530 95 | 1.995 56, −0.549 50 | 1.994 64, −0.514 26 |
| BD(1) C(2)–H(22) | 1.995 31, −0.519 40 | 1.991 76, −0.558 27 | 1.992 11, −0.520 97 |
| LP(1) Te(1) | 1.993 59, −0.271 79 | 1.993 43, −0.250 47 | 1.995 52, −0.327 47 |
| LP(1) O(1) | 1.972 28, −0.668 60 | 1.987 82, −0.640 64 | 1.984 32, −0.687 92 |
| LP(2) O(1) | 1.928 49, −0.159 28 | 1.928 45, −0.130 80 | 1.923 87, −0.201 45 |
| LP(1) O(2) | 1.988 08, −0.660 88 | 1.986 08, −0.647 53 | 1.985 47, −0.695 16 |
| LP(2) O(2) | 1.932 76, −0.159 75 | 1.928 91, −0.162 29 | 1.935 95, −0.200 16 |
| LP(1) Cl(1) | 1.999 94, −0.594 81 | 1.999 86, −0.618 23 | 1.999 63, −0.742 91 |
| LP(2) Cl(1) | 1.996 27, −0.048 78 | 1.994 33, −0.073 36 | 1.989 83, −0.184 46 |
| LP(3) Cl(1) | 1.992 62, −0.048 01 | 1.988 42, −0.071 02 | 1.979 79, −0.183 21 |
| LP(1) Cl(2) | 1.999 83, −0.642 95 | 1.999 82, −0.633 42 | 1.999 60, −0.748 48 |
| LP(2) Cl(2) | 1.992 17, −0.099 94 | 1.992 13, −0.087 85 | 1.989 62, −0.194 43 |
| LP(3) Cl(2) | 1.985 57, −0.093 89 | 1.984 89, −0.084 90 | 1.981 82, −0.192 13 |
| LP(1) Cl(3) | 1.999 80, −0.660 45 | 1.999 80, −0.647 73 | 1.999 62, −0.751 77 |
| LP(2) Cl(3) | 1.991 18, −0.113 01 | 1.991 67, −0.100 90 | 1.989 83, −0.196 10 |
| LP(3) Cl(3) | 1.981 86, −0.108 41 | 1.985 83, −0.098 14 | 1.981 84, −0.194 96 |
| BD*(1) Te(1)–O(1) | 0.136 86, 0.825 47 | 0.134 09, 0.850 63 | 0.146 86, 0.799 33 |
| BD*(1) Te(1)–O(2) | 0.150 94, 0.896 69 | 0.154 63, 0.919 57 | 0.170 29, 0.868 97 |
| BD*(1) Te(1)–Cl(1) | 0.203 65, 0.611 52 | 0.181 68, 0.654 09 | 0.161 55, 0.639 10 |
| BD*(1) Te(1)–Cl(2) | 0.180 86, 0.677 41 | 0.182 72, 0.686 40 | 0.172 56, 0.653 93 |
| BD*(1) Te(1)–Cl(3) | 0.175 08, 0.684 89 | 0.177 34, 0.694 64 | 0.168 28, 0.656 98 |
| BD*(1) O(1)–C(1) | 0.022 95, 0.821 80 | 0.020 40, 0.852 84 | 0.021 65, 0.796 15 |
| BD*(1) O(2)–C(2) | 0.023 18, 0.800 56 | 0.021 96, 0.818 25 | 0.020 85, 0.798 18 |
| BD*(1) C(1)–C(2) | 0.027 33, 0.894 44 | 0.030 31, 0.906 16 | 0.041 49, 0.769 54 |
| BD*(1) C(1)–H(11) | 0.014 11, 0.997 87 | 0.013 90, 1.071 34 | 0.019 53, 0.828 11 |
| BD*(1) C(1)–H(12) | 0.016 60, 0.999 54 | 0.016 36, 1.075 58 | 0.023 15, 0.830 72 |
| BD*(1) C(2)–H(21) | 0.013 19, 0.991 54 | 0.015 42, 1.067 07 | 0.023 72, 0.834 89 |
| BD*(1) C(2)–H(22) | 0.016 24, 0.997 31 | 0.013 07, 1.057 33 | 0.018 69, 0.832 31 |

[a] $E_\mathrm{h}$ = 2625.5 kJ mol$^{-1}$. [b] Bonding (BD) and antibonding (BD*) two-centre bond and lone-pair (LP) orbitals; the index *i* refers to the number of bonds between any two atoms.

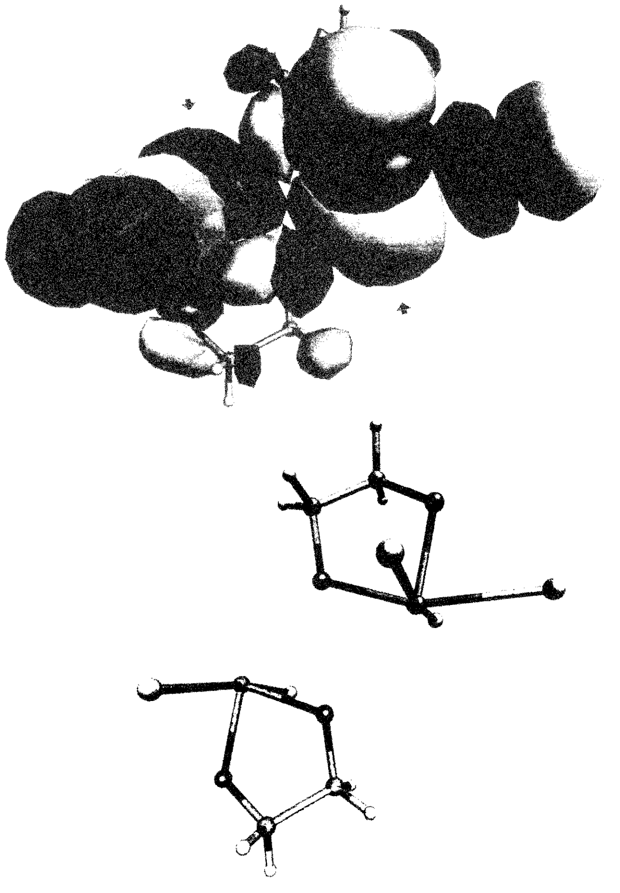


**Fig.** 3 The trichloro(ethane-1,2-diolato-*O,O'*)tellurate(IV) dimer (below) and its highest occupied molecular orbital (HOMO) seen from the same direction (above). In the HOMO the lone pair of each tellurium (marked by arrows) is pointing to a 'free' direction, whereas the lone pair of atom O(1) is pointing towards the Te(1)–Cl(1) bond of the neighbouring unit

Natural localised molecular orbital (NLMO) analysis was carried out to evaluate the 'purity' of the molecular orbitals. The results are given in SUP 57034. There is a small contribution from the tellurium atom of the neighbouring anion, distributed between the fragment containing the atoms Te(1), O(1), O(2) and Cl(1) (and even the O–C bonds). However, this effect decreases markedly when the distance between the anions increases, as seen from the values calculated for the tetraphenylphosphonium salt.

The present results indicate clearly that the Te–Cl bonds have very pronounced ionic character, as can be seen from the values given in Tables 3 and 4. Although no relativistic effects were included in the calculations we feel that the results obtained describe the essential electronic properties of the dimeric unit.

## Acknowledgements

Financial support from the Academy of Finland, the Neste Foundation, the Technology Development Centre and the University of Helsinki is gratefully acknowledged.

## References

1 B. Sredni, R. R. Caspi, A. Klein, Y. Kalechman, Y. Danzinger, M. Ben Ya'akov, T. Tamari, F. Shalit and M. Albeck, *Nature (London)*, 1987, **330**, 173.
2 B. Sredni, R. R. Caspi, S. Lustig, A. Klein, Y. Kalechman, Y. Danzinger, M. Ben Ya'akov, T. Tamari, F. Shalit and M. Albeck, *Nat. Immun. Cell Growth Regul.*, 1988, **7**, 163.
3 M. Albeck, T. Tamari and B. Sredni, *Synthesis*, 1988, **8**, 635.
4 M. Albeck and B. Sredni, *U.S. Pat.*, 4 764 462, 1987.
5 B. Sredni, M. Albeck, G. Kazimirsky and F. Shalit, *Int. J. Immunopharmacol.*, 1993, **14**, 613.
6 Y. Kalechman, I. Sotnik-Barkai, M. Albeck and B. Sredni, *Cancer Res.*, 1993, **53**, 1838.
7 L. Kozenitzky, M. David, B. Sredni, M. Albeck and B. Shohat, *Photodermatol. Photoimmunol. Photomed.*, 1992, **9**, 24.
8 A. Vonsover, S. Loya, B. Sredni, M. Albeck, T. Gotlieb-Stematsky, A. Tamar, H. Orly and A. Hizi, *AIDS Res. Hum. Retroviruses*, 1992, **8**, 613.
9 Y. Kalechman, I. Sotnik-Barkai, M. Albeck, G. Horwith, S. N. Sehagl and B. Sredni, *Cancer Res.*, 1991, **51**, 5614.
10 R. A. Zingaro, H. M. K. K. Pathirana, J. H. Reibenspies and E. A. Meyers, *Phosphorus, Sulfur Silicon Relat. Elem.*, 1991, **62**, 91.
11 R. Kivekäs, T. Laitalainen, M. R. Sundberg and J. Bergman, Symposium on Inorganic and Analytical Chemistry, Lappeenranta, *Proceedings* in Report 20, Technical University of Lappeenranta, 1988, pp. 42, 43.
12 K. Büscher, S. Heuer and B. Krebs, *Z. Naturforsch., Teil B*, 1981, **36**, 307.
13 N. W. Alcock, *Adv. Inorg. Chem. Radiochem.*, 1972, **15**, 1.
14 R. F. Ziolo and J. M. Troup, *J. Am. Chem. Soc.*, 1983, **105**, 229.
15 N. W. Alcock and W. D. Harrison, *J. Chem. Soc., Dalton Trans.*, 1983, 2015.
16 A. E. Masunov and P. M. Zorkii, *Zh. Strukt. Khim.*, 1992, **33**, 105.
17 S. R. Hall and J. M. Stewart (Editors), XTAL 3.0 User's Manual, Universities of Western Australia and Maryland, 1988.
18 M. J. Frisch, M. Head-Gordon, G. W. Trucks, J. B. Foresman, H. B. Schlegel, K. Raghavachari, M. A. Robb, J. S. Binkley, C. Gonzalez, D. J. Defrees, D. J. Fox, R. A. Whiteside, R. Seeger, C. F. Melius, J. Baker, R. L. Martin, L. R. Kahn, J. J. P. Stewart, S. Topiol and J. A. Pople, GAUSSIAN 92, Gaussian Inc., Pittsburgh, PA, 1992.
19 E. D. Glendening, A. E. Reed, J. E. Carpenter and F. Weinhold, NBO, Version 3.1, link 607 in GAUSSIAN 92, Gaussian Inc., Pittsburgh, PA, 1992.
20 S. E. Pamer, *U.S. Pat.*, 4 418 231, 1981.
21 J. Bergman, *Tetrahedron*, 1972, **28**, 3323.
22 C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.
23 M. R. Sundberg, R. Kivekäs, J. Ruiz, J. M. Moreno and E. Colacio, *Inorg. Chem.*, 1992, **31**, 1062.
24 D. Cremer and J. A. Pople, *J. Am. Chem. Soc.*, 1975, **97**, 1354.
25 F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1987, S1.

*Received* 25th *April* 1994; *Paper* 4/02429J