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The Crystal Structure of *bis*-(NNN'N'-tetramethyl)-αα'-dithiobisformamidinium Hexachlorotellurate(IV): Possible Effects of Hydrogen Bondings on the Distortion of the Hexachlorotellurate(IV) Ion

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During our investigations on tellurium complexes with thiourea type ligands, we have obtained some compounds containing a S–S bond. In these compounds the tellurium is present at $TeCl_6^{2-}$ even if the oxidation of the thiourea derivatives to αα'-dithiobisformamidinium is produced by reduction of Te^{IV} to Te^{II} [1].

The crystal structures of compounds of type $[(RHN)_2CS]_2 \cdot TeCl_6$, where R = Me [1] or Et [2], consist of distorted octahedral $TeCl_6^{2-}$ and $[(RHN)_2CS]_2^{2+}$ ions. In these compounds the longest Te–Cl bonds involve Cl atoms partecipating to N–H····Cl hydrogen bondings [1, 2]. In order to obtain other information about the effects of hydrogen bondings on the co-ordination geometry of the tellurium atom, we have resolved the crystal structure of *bis*-(NNN'N'-tetramethyl)-αα'-dithiobis-formamidinium hexachlorotellurate(IV).

Experimental

Adapting methods previously reported [3], bis-(NNN'N'-tetramethyl)-αα'-dithiobis-formamidinium-dichloride was prepared adding H_2O_2 (0.1 g, 3 mmol) to a solution of tetramethylthiourea (tmthu) (0.7 g, 6 mmol) and HCl (10 mmol) in ethanol. The white

TABLE I. Bond Distances (A) and Angles (°) with the Estimated Standard Deviations in Parentheses.

a) *Bond Distances* (Å)			
Te(1)–Cl(1)	2.549(2)	Te(2)–Cl(4)	2.540(3)
Te(1)–Cl(2)	2.539(2)	Te(2)–Cl(5)	2.542(3)
Te(1)–Cl(3)	2.548(2)	Te(2)–Cl(6)	2.541(3)
S(1)–S(2)	2.050(3)		
S(1)–C(6)	1.776(10)	S(2)–C(1)	1.801(9)
C(6)–N(3)	1.333(12)	C(1)–N(1)	1.317(11)
N(3)–C(7)	1.486(13)	N(1)–C(2)	1.472(12)
N(3)–C(8)	1.474(13)	N(1)–C(3)	1.493(12)
C(6)–N(4)	1.331(13)	C(1)–N(2)	1.322(11)
N(4)–C(9)	1.479(14)	N(2)–C(4)	1.468(12)
N(4)–C(10)	1.477(14)	N(2)–C(5)	1.456(12)
b) *Bond angles* (°)			
Cl(1)–Te(1)–Cl(2)	89.5(1)	Cl(4)–Te(2)–Cl(5)	89.1(1)
Cl(2)–Te(1)–Cl(3)	88.4(1)	Cl(5)–Te(2)–Cl(6)	91,3(1)
Cl(1)–Te(1)–Cl(3)	89.8(1)	Cl(4)–Te(2)–Cl(6)	89.6(1)
S(1)–S(2)–C(1)	104.7(3)	S(2)–S(1)–C(6)	105.1(3)
S(2)–C(1)–N(1)	120.3(6)	S(1)–C(6)–N(3)	121.5(7)
C(1)–N(1)–C(2)	122.8(7)	C(6)–N(3)–C(7)	123.0(8)
C(2)–N(1)–C(3)	115.0(7)	C(7)–N(3)–C(8)	113.7(9)
C(1)–N(1)–C(3)	122.2(8)	C(6)–N(3)–C(8)	123.0(9)
N(1)–C(1)–N(2)	124.3(8)	N(3)–C(6)–N(4)	123.4(9)
C(1)–N(2)–C(4)	124.4(8)	C(6)–N(4)–C(9)	123.1(9)
C(4)–N(2)–C(5)	113.4(7)	C(9)–N(4)–C(10)	114.2(9)
C(1)–N(2)–C(5)	121.8(7)	C(6)–N(4)–C(10)	122.6(1.0)
N(2)–C(1)–S(2)	115.3(6)	N(4)–C(6)–S(1)	115.0(8)

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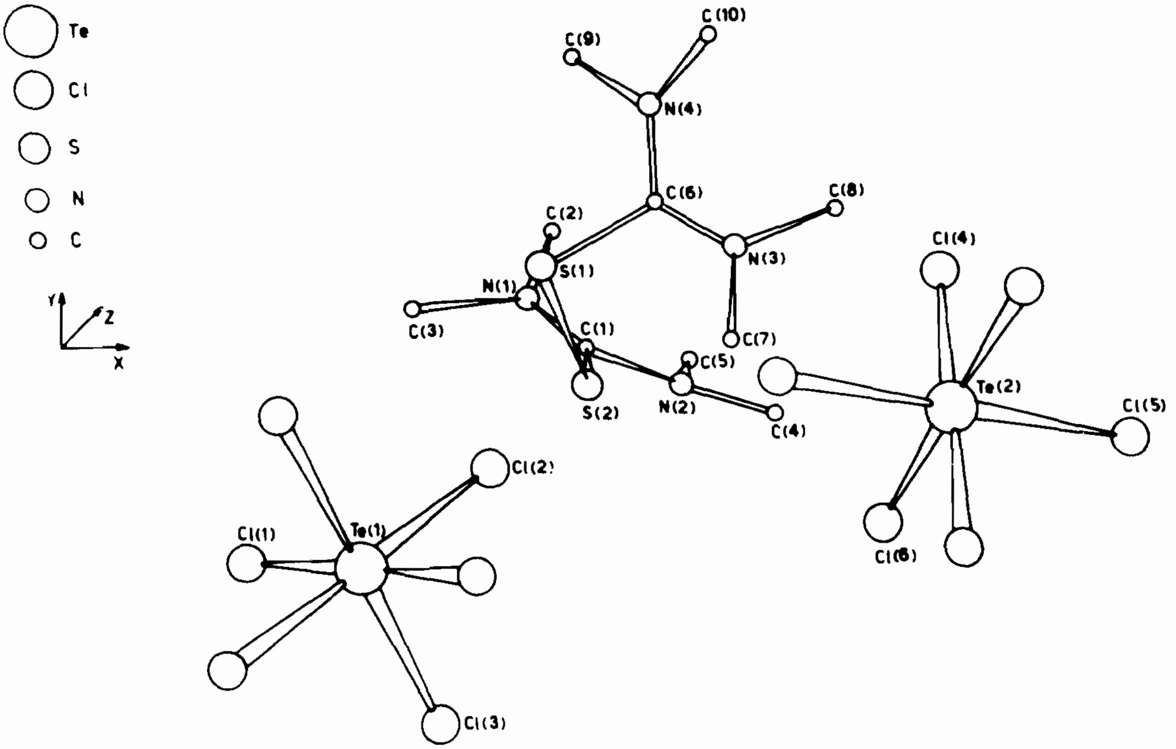

Fig. 1. Perspective view of $[(Me_2N)_2CS]_2 \cdot TeCl_6$ with the atom numbering scheme. Both the tellurium atoms are in special position 1 with occupancy 0.5.

solid so obtained was dissolved in deionized water and mixed with a hydrochloric solution of the stoicheiometric quantity of TeO_2. By stirring, a yellow precipitate was obtained, which was recrystallized from ethanol. The elemental analysis agrees with the formula $[(Me_2N)_2CS]_2 \cdot TeCl_6$ ($C_{10}H_{24}N_4S_2Cl_6Te$ requires: C, 19.9; H, 4.0; N, 9.3; Cl, 35.2; found: C, 20.0; H, 3.9; N, 9.2; Cl, 34.9%).

The crystals are monoclinic with unit-cell dimensions a = 32.917(3), b = 8.222(2), c = 18.128(3) Å, β = 105.05(8)°; space group $C2/c$; Z = 8; F(000) = 2.384; D_c = 1.69, D_m = 1.68 (by flotation) g cm^{-3}; U = 4738(2) Å^3; M = 604.77. Intensity data were collected using a Philips PW 1100 four-circle diffractometer in the range $4 \leqslant 2\theta \leqslant 50°$ with Mo-Kα radiation, λ = 0.7107 Å, μ = 39.57 cm^{-1}. Using the criterion $I \geqslant 3\sigma(I)$, 2662 of the 2906 recorded intensities were independent and observable. Lorentz and polarization corrections were applied.

The structure was solved using the direct methods of Multan program [4] that showed the Te, Cl and S atoms. The C and N atoms were then located from a three-dimensional Fourier synthesis. A full-matrix least-squares refinement on F was computed minimizing the function $\Sigma w[|Fo|-|Fc|]^2$ (w = 1). The 'SHELX 76' system of programs [5] was used on a CDC Cyber 76 computer with the usual scattering factors [6]. All the non-hydrogen atoms were refined anisotropically; all the hydrogen atoms were calculated and not refined. The final conventional R factor was 0.038. Bond distances and angles are shown in Table I; a perspective view of the compound is shown in Fig. 1. The fractional atomic co-ordinates and the observed and calculated structure factors and anisotropic thermal parameters are available from the authors on request.

Results and Discussion

The crystal structure consists of discrete $[(Me_2N)_2CS]_2^{2+}$ and $TeCl_6^{2-}$ ions. The cation presents a S–S single bond with a length of 2.050 Å and a mean S–S–C angle of 104.9°. Both the values are a little larger than the previously reported ones [1, 2]. The bond lengths S(1)–C(2), 1.776 Å, and S(2)–C(1), 1.801 Å, correspond to nearly single bonds. The thiourea groups are nearly planar with a dihedral angle of 77.1° instead of 87.3° found in the dimethyl [1] and 88.9° in diethyl $\alpha\alpha'$-dithiobisformamidinium [2]. It is interesting to compare the strucure of the cation $[(Me_2N)_2CS]_2^{2+}$ with those of $[(MeHN)_2CS]_2^{2+}$ and $[(EtHN)_2CS]_2^{2+}$. A remarkable packing may be observed from Table II in all these cations which lose their twofold symmetry axis perpendicular to the S–S bond [7] and lower their

TABLE II. Comparison of Some Contact Distances, less than 3.35 Å, between Correspondent Atoms.

	$[(Me_2N)_2CS]_2^{2+}$ [a]	$[(MeHN)_2CS]_2^{2+}$ [b]	$[(EtHN)_2CS]_2^{2+}$ [b]
S(1)–C(7)	3.13	–	2.92
S(1)–C(9)	2.98	2.87	–
S(2)–C(3)	3.11	2.94	2.93
S(2)–C(4)	3.02	–	–
N(1)–C(5)	2.89	–	2.87
N(2)–C(2)	2.93	2.81	–
N(3)–C(10)	2.91	–	2.89
N(4)–C(8)	2.95	2.80	–
S(1)–N(1)	3.32	3.08	3.09
S(2)–N(3)	3.33	3.08	3.07
C(3)–S(1)	3.31	–	–
C(7)–S(2)	3.26	–	–
C(2)–C(5)	2.96	–	–
C(8)–C(10)	2.99	–	–

[a] *Cf.* Figure for the atom numbering scheme. [b] *Cf.* Refs. 1 and 2.

symmetry. This packing may be due to the π-delocalization along the N–C–N systems which decrease the C–N distances in the thioureic moieties (mean 1.326 Å) if compared with that of the free tmthu (1.37 Å) [8]. This bond length shortening may be deducted also from the IR spectra: in fact, in the title compound the ν(CN) stretching frequency presents a shift to higher wavenumber of 103 cm^{-1} respect to the free tmthu, and this feature is typical of the other two cations too (82 and 68 cm^{-1} respectively).

The octahedral geometry around the tellurium atom is practically undistorted (*cf.* Table I). This feature agrees with the results obtained by X-ray, ^{125}Te and ^{125}I Mössbauer and far IR measurements on compounds with general formula M_2TeX_6 (M = NH_4, Me_4N, K, Rb or Cs; X = Cl, Br, or I) [9–15] and has been explained assuming a contraction toward the tellurium nucleus of the stereochemically inactive 5s^2 non-bonding electrons [12].

On the contrary, the crystal structures of $[(RHN)_2CS]_2\cdot TeCl_6$, where R = Me [1] or Et [2], show a distortion around the tellurium atom. To explain this distortion we have considered their hydrogen bonding system. In compounds with undistorted TeX_6^{2-} hydrogen bondings either are not present, as in the title compound and in the above reported M_2TeX_6 compounds, or form a symmetric net around the halogen atoms, as in the hexabromotellurate of DL-α-Ammonio-n-butyric acid [17]. On the other hand, all compounds with distorted TeX_6^{2-} ions possess asymmetric hydrogen bondings: four are present in $[(MeHN)_2CS]_2\cdot TeCl_6$ [1], two in $[(EtHN)_2CS]_2\cdot TeCl_6$ [2], three in the hexabromotellurate of protonated disuccinamide monohydrate [16]. It is also interesting to note that, in the distorted anions, the longest Te–X bonds correspond to halogen atoms involved in hydrogen bondings and that the collinear Te–X bonds are always the shortest.

In conclusion, even if it is necessary to have more experimental evidence, the data so far obtained seem to show that the environment of a metal centre may be influenced also by groups that are far from it, *via* hydrogen bondings.

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