Crystal and Molecular Structure of Bis(*NN'*-dimethylformamidine) Disulphide Hexachlorotellurate †

By **Umberto Russo,** Istituto di Chimica Generale ed Inorganica, Università di Padova, Via Loredan 4, 35100 Padova, Italy
Giovanni Valle, Centro di Ricerca sui Biopolimeri del C.N.R., Via Marzolo 1, 35100 Padova, Italy
Sandro Calogero,* Laboratorio di Chimica e Tecnologia dei Radioelementi del C.N.R., Corso Stati Uniti, 35100 Padova, Italy

The structure of the title compound has been determined by *X*-ray analysis using direct methods. The compound crystallizes in the space group $Pna2_1$ with a = 13.874, b = 13.822, c = 9.914 Å, Z = 4, and R = 0.029 for 1 648 independent reflections. It consists of discrete $[(MeHN)_2CS]_2^{2+}$ and $TeCl_6^{2-}$ ions. The co-ordination of the Te atom is distorted octahedral with the Te–Cl distances ranging from 2.420 to 2.740 Å.

It is known that in reactions of thiourea derivatives with an oxidizing agent, one molecule of formamidine disulphide is formed for every two of thiourea present initially.[1-4] The oxidants may be chlorine, bromine, iodine, hydrogen peroxide, *etc.* or metals such as Ir^{IV}, Os^{VIII}, Te^{IV}, or Fe^{III}.[5] In the first case, the oxidation products were isolated and *X*-ray analyses performed,[6,7] but in the last case no oxidation product was separated and its existence in solution was deduced only by u.v. measurements.[1]

During our investigations on tellurium complexes with dimethylthiourea (dmtu) we obtained not only the complexes $[Te(dmtu)_4]Cl_2$ and $[Te(dmtu)_2Cl_2]$, but also a compound containing a S–S bond. The *X*-ray structural analysis of the latter shows that, even if the oxidation of the dmtu to disulphide results in the reduction of Te^{IV} to Te^{II}, the tellurium is still present in the solid only as $TeCl_6^{2-}$.

EXPERIMENTAL

The compound was prepared by mixing a solution containing TeO_2 (0.4 g, 2.5 mmol) dissolved in a few millilitres of concentrated HCl and a solution containing dmtu (1 g, 10 mmol) dissolved in methanol (*ca.* 5 cm³). After a few drops of the latter solution had been added to the former, an unexpected yellow solid was formed. It was immediately filtered off, washed, dried under vacuum, and recrystallized from methanol. The elemental analysis agrees with the formula $[(MeHN)_2CS]_2 \cdot TeCl_6$ (Found: C, 13.0; H, 2.9; Cl, 38.9; N, 10.2. $C_6H_{16}Cl_6N_4S_2Te$ requires C, 13.1; H, 2.9; Cl, 38.8; N, 10.2%).

The i.r. spectrum of the compound differs from those of the free ligand and of the $[Te(dmtu)_2Cl_2]$ complex, mainly in the positions of the ν(CN) and ν(CS) bands. The ν(CN) stretch is found at 1 560 cm⁻¹ for the free ligand, at 1 623 cm⁻¹ for $[Te(dmtu)_2Cl_2]$, and 1 642 cm⁻¹ for the title compound, and ν(CS) occurs at 722, 710, and 714 cm⁻¹ respectively.

Crystal Data. $C_6H_{16}Cl_6N_4S_2Te$, M = 548.66, Orthorhombic, a = 13.874(3), b = 13.822(4), c = 9.914(4) Å, D_m = 1.80 g cm⁻³ (by flotation), Z = 4, D_c = 1.80, U = 1 901.17 Å³, $F(000)$ = 1 064, space group $Pna2_1$, Mo-K_α radiation λ = 0.710 7 Å, μ = 39.57 cm⁻¹.

Intensity data were collected using a Philips PW 1100 four-circle diffractometer, in the range $4 \leqslant 2\theta \leqslant 50°$. Using the criterion $I \geqslant 3\sigma(I)$, 1 648 of the 1 785 recorded intensities were independent and observable. Lorentz and polarization corrections were applied.

The structure was solved by direct methods using the Multan program [8] which showed the positions of the Te, Cl, and S atoms, and the C and N atoms were located from a three-dimensional Fourier synthesis. A full-matrix least-squares refinement on F was computed minimizing the function $\Sigma w(|F_o| - |F_c|)^2$ ($w = 1$). The SHELX 76 system of programs [9] was used on a CDC Cyber 76 computer, together with the usual scattering factors.[10] All the non-hydrogen atoms were refined anisotropically; the hydrogen atoms were located from a difference-Fourier map and then included in the last refinement cycle. The final conventional R value was 0.029. The final atomic co-ordinates with their standard deviations are listed in Table 1, bond distances and angles, uncorrected for changes due to thermal vibration, in Table 2. Observed and calculated structure factors and anisotropic thermal parameters are listed in Supplementary Publication No. SUP 22813 (14 pp.).‡ The molecular configuration of the molecule is shown in the Figure, together with the atom-numbering scheme.

Iterative extended-Hückel molecular-orbital calculations were carried out, within the framework of the all-valence approximation, using the program in ref. 11. Previous approximations [12-14] and the crystallographic data of the present compound were employed. The calculations for the $TeCl_6^{2-}$ anion and the disulphide cation were performed separately to limit the number of atomic wavefunctions.

---

† $N^1N^2N^3N^4$-Tetramethyl-α,α'-dithiobisformamidinium hexachlorotellurate(IV).

‡ For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

TABLE 1

Final fractional atomic co-ordinates, with estimated standard deviations in parentheses, for $[(MeHN)_2CS]_2\cdot TeCl_6$

Atom	x/a	y/b	z/c
Te	0.738 5(0)	0.467 4(0)	0.250 0(0)
Cl(1)	0.891 5(2)	0.479 4(2)	0.400 3(4)
Cl(2)	0.802 5(2)	0.311 9(2)	0.130 3(3)
Cl(3)	0.823 7(3)	0.565 1(2)	0.086 2(3)
Cl(4)	0.659 1(2)	0.355 1(3)	0.448 7(4)
Cl(5)	0.595 1(2)	0.460 6(3)	0.103 4(5)
Cl(6)	0.678 2(3)	0.615 8(2)	0.359 7(4)
S(1)	0.786 9(2)	0.417 9(2)	0.793 9(3)
S(2)	0.916 5(2)	0.357 9(2)	0.829 7(3)
N(1)	0.903 9(7)	0.568 7(7)	0.731 0(13)
N(2)	0.740 6(6)	0.591 2(6)	0.706 1(9)
N(3)	0.879 5(10)	0.283 5(8)	0.583 5(12)
N(4)	1.019 0(8)	0.239 6(8)	0.686 4(12)
C(1)	0.816 2(7)	0.536 3(7)	0.535 7(14)
C(2)	0.640 1(10)	0.557 2(11)	0.705 8(17)
C(3)	0.928 4(12)	0.665 3(11)	0.681 2(19)
C(4)	0.937 9(9)	0.287 9(7)	0.682 0(12)
C(5)	0.895 5(23)	0.224 7(19)	0.463 9(22)
C(6)	1.084 6(19)	0.238 5(20)	0.800 0(26)
H(N1)	0.947(9)	0.545(11)	0.775(20)
H(N2)	0.753(13)	0.676(12)	0.643(19)
H(N3)	0.845(7)	0.307(7)	0.585(12)
H(N4)	1.047(13)	0.203(13)	0.608(21)
H(21)	0.618(11)	0.552(11)	0.796(20)
H(22)	0.617(9)	0.498(8)	0.642(12)
H(23)	0.589(9)	0.632(8)	0.680(13)
H(31)	0.902(9)	0.677(9)	0.586(14)
H(32)	0.913(10)	0.699(10)	0.750(20)
H(33)	1.005(16)	0.681(16)	0.664(26)
H(51)	0.900(13)	0.189(11)	0.483(20)
H(52)	0.852(9)	0.232(10)	0.430(15)
H(53)	0.984(13)	0.242(13)	0.431(19)
H(61)	1.020(13)	0.212(12)	0.917(19)
H(62)	1.107(13)	0.211(13)	0.800(26)
H(63)	1.080(12)	0.280(10)	0.822(17)

RESULTS AND DISCUSSION

The crystal structure consists of discrete $[(MeHN)_2CS]_2^{2+}$ and $TeCl_6^{2-}$ ions. The Te atom is octahedrally surrounded by six Cl atoms, but the co-ordination polyhedron is somewhat distorted: the bond angles Cl–Te–Cl deviate from the ideal value by up to 5° and the bond lengths range from 2.420 to 2.740 Å. These deviations are also evident in the least-squares planes (I)–(III) of Table 3. So far as we know, this is the first example of a distorted TeX_6^{2-} octahedron: in fact, the *X*-ray data for $Cs_2[TeBr_6]$, $[NH_4]_2[TeBr_6]$,[15] $K_2[TeBr_6]$,[16] and $K_2[TeI_6]$ [17] and the Mössbauer data for $Cs_2[TeCl_6]$ [18] point to undistorted structures. Iterative extended-Hückel calculations on the $TeCl_6^{2-}$ anion indicate the electronic configuration $5s^{1.40}5p^{1.05}4d^{9.98}$ for the tellurium atom and charges ranging from −0.87 up to −0.99 electron units for the Cl atoms.

TABLE 2

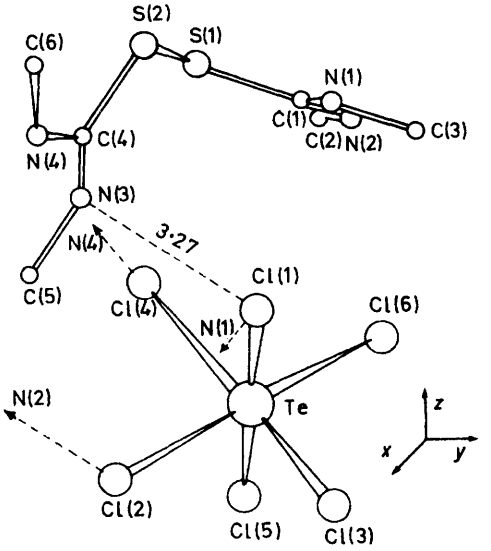
Bond distances (Å) and angles (°) for $[(MeHN)_2CS]_2\cdot TeCl_6$ with estimated standard deviations in parentheses

(*a*) Distances

Te–Cl(1)	2.598(3)	Te–Cl(4)	2.740(3)
Te–Cl(2)	2.611(3)	Te–Cl(5)	2.466(4)
Te–Cl(3)	2.420(3)	Te–Cl(6)	2.468(3)
S(1)–S(2)	2.012(4)		
S(1)–C(1)	1.782(11)	S(2)–C(4)	1.799(12)
C(1)–N(1)	1.297(12)	C(4)–N(3)	1.270(17)
N(1)–C(3)	1.465(17)	N(3)–C(5)	1.454(23)
C(1)–N(2)	1.328(13)	C(4)–N(4)	1.309(15)
N(2)–C(2)	1.471(15)	N(4)–C(6)	1.448(25)

(*b*) Angles

Cl(1)–Te–Cl(2)	92.0(1)	Cl(1)–Te–Cl(4)	87.3(1)
Cl(2)–Te–Cl(3)	89.3(1)	Cl(1)–Te–Cl(5)	178.2(1)
Cl(3)–Te–Cl(4)	174.3(1)	Cl(1)–Te–Cl(3)	87.2(1)
Cl(4)–Te–Cl(5)	94.4(1)	Cl(2)–Te–Cl(6)	179.1(1)
S(2)–S(1)–C(1)	103.4(3)	S(1)–S(2)–C(4)	103.2(4)
S(1)–C(1)–N(1)	122.9(8)	S(2)–C(4)–N(3)	123.5(9)
C(1)–N(1)–C(3)	123.0(1.1)	C(4)–N(3)–C(5)	123.8(1.6)
N(1)–C(1)–N(2)	122.4(1.0)	N(3)–C(4)–N(4)	123.3(1.2)
C(2)–N(2)–C(1)	124.5(1.0)	C(6)–N(4)–C(4)	124.9(1.4)
N(2)–C(1)–S(1)	114.6(7)	N(4)–C(4)–S(2)	113.1(1.0)



Perspective view of $[(MeHN)_2CS]_2\cdot TeCl_6$ showing the atom-numbering scheme and possible hydrogen bonds

TABLE 3

Least-squares planes in the form $PX + QY + RZ = S$ with the deviations (Å) from the planes in square brackets

	P	Q	R	S
Plane (I)	0.4578	0.5613	−0.6895	6.6374
[Te * −0.0291, Cl(1) 0.0100, Cl(2) −0.0100, Cl(5) 0.0106, Cl(6) −0.0107]				
Plane (II)	−0.3638	0.8236	0.4352	2.6678
[Te * 0.0044, Cl(1) 0.0181, Cl(3) −0.0190, Cl(4) −0.0163, Cl(5) 0.0173]				
Plane (III)	0.8301	0.0388	0.5563	10.1924
[Te * −0.0585, Cl(2) −0.0656, Cl(3) 0.0716, Cl(4) 0.0623, Cl(6) −0.0684]				
Plane (IV): S(1), N(1), and N(2)	−0.0547	0.3280	0.9431	8.7202
[C(1) * −0.0281, C(2) * −0.0886, C(3) * −0.0388, C(6) * −0.2261, S(2) * −0.0375]				
Plane (V): S(2), N(3), and N(4)	−0.0784	0.9232	−0.3761	0.4765
[C(4) * −0.3631, C(5) * −0.3153, C(6) * −0.5233, S(1) * 1.0394]				

* Atom not used in the plane calculations.

The cation has a S–S single bond (2.010 Å) and a mean S–S–C angle of 103.3°, in good agreement with previously reported values for the compounds $[(H_2N)_2CS]_2X_2$ (X = Cl,[6] 2.017 and 103.9; X = Br,[7] 2.044 and 104.0; X = I,[7] 2.044 Å and 98.7°). The bond lengths S(1)–C(1) and

S(2)–C(4) correspond approximately to single bonds (*cf.* Table 2). The thiourea groups are all nearly planar [*cf.* least-squares planes (IV) and (V) of Table **3**] with a dihedral angle of 87.3°. The bond lengths C(1)–N [1.288(14) and 1.326(13) Å] and C(4)–N [1.267(23) and 1.308(16) Å] are within experimental error and show, as previously reported,[6] a remarkable π delocalization along the N–C–N systems. This is consistent with the C(1) and C(4) bond angles which are close to those of a carbon atom with trigonal hybridization. The following charges were calculated for the atoms of the cation: C(1), 0.11; C(4), 0.12; N(1), –0.05; N(2), –0.05; N(3), –0.05; N(4), –0.05; S(1), 0.68; and S(2), 0.67 electron units.

TABLE 4

Most significant van der Waals interactions (Å)

Cl(1) · · · N(1^{I}) *	3.38	Cl(5) · · · C(2^{VI})	3.43
Cl(1) · · · N(3)*	3.27	Cl(6) · · · C(4^{V})	3.37
Cl(2) · · · N(2^{II}) *	3.20	Cl(6) · · · N(2)	3.56
Cl(4) · · · N(4^{III}) *	3.33	Cl(6) · · · C(2)	3.56
Cl(2) · · · S(2^{IV})	3.43	Cl(1) · · · C(5)	3.58
Cl(3) · · · C(1^{IV})	3.50	Cl(1) · · · N(1)	3.50
Cl(3) · · · S(1^{IV})	3.58	Cl(1) · · · C(1)	3.57
Cl(4) · · · N(3)	3.49	Cl(1) · · · S(2^{I})	3.56

Symmetry code: I $2 - x, 1 - y, z - \frac{1}{2}$; II $\frac{3}{2} - x, y - \frac{1}{2}, z - \frac{1}{2}$; III $-x - \frac{1}{2}, \frac{1}{2} - y, z$; IV $x, y, z - 1$; V $\frac{3}{2} - x, \frac{1}{2} + y, z - \frac{1}{2}$; VI $1 - x, 1 - y, z - \frac{1}{2}$.

* Possible hydrogen bond.

The possible hydrogen bonds and other intermolecular contacts shorter than 3.6 Å are listed in Table 4. The crystal packing is essentially determined by N–H · · · Cl hydrogen bonds (*cf.* Figure) whose lengths are in the usual range, 3.20—3.37 Å.[19] It is interesting that the strong interactions between the two ions provoke a lowering of their symmetry. In fact, the anion is quite distorted from the ideal structure found in other compounds,[15-17] because the Cl(1), Cl(2), and Cl(4) atoms, all involved in hydrogen bonding, yield the longest Te–Cl bonds. On the other hand, the cation loses the two-fold symmetry axis perpendicular to the S–S bond[6] on adapting itself to the huge anion.

We acknowledge the stimulating interest of Professor G. Tagliavini and the partial support from CNR.

[9/2022 *Received*, 31*st December*, 1979]

REFERENCES

[1] H. N. Po, H. Eran, Y. Kim, and J. E. Byrd, *Inorg. Chem.*, 1979, **18**, 197.

[2] M. Hoffmann and J. O. Edwards, *Inorg. Chem.*, 1977, **16**, 3333 and refs. therein.

[3] Z. Amjad and A. McAuley, *Inorg. Chim. Acta*, 1977, **25**, 127.

[4] F. Cristiani and A. Diaz, *Inorg. Chim. Acta*, 1977, **24**, L7.

[5] U. Russo, S. Calogero, N. Burriesci, and M. Petrera, *J. Inorg. Nuclear Chem.*, 1979, **41**, 25.

[6] A. C. Villa, A. G. Manfredotti, M. Nardelli, and M. E. V. Tani, *Acta Cryst.*, 1972, **B28**, 356.

[7] O. Foss, J. Johnsen, and O. Tvedten, *Acta Chem. Scand.*, 1958, **12**, 1782 and refs. therein.

[8] G. Germain, P. Main, and M. M. Woolfson, *Acta Cryst.*, 1971, **A27**, 368.

[9] G. Sheldrick, SHELX 76 System of Programs, University of Cambridge, 1976.

[10] 'International Tables for *X*-Ray Crystallography,' 2nd edn., Kynoch Press, Birmingham, 1974, vol. 4, p. 99.

[11] S. Calogero, U. Russo, and A. Del Prà, *J.C.S. Dalton*, 1980, 646.

[12] R. Hoffmann, *J. Chem. Phys.*, 1963, **39**, 1397.

[13] A. Coker, T. Lee, and T. P. Das, *Phys. Rev. B*, 1976, **13**, 55.

[14] F. P. Colonna, G. Distefano, V. Galasso, K. J. Irgolic, C. E. King, and G. C. Pappalardo, *J. Organometallic Chem.*, 1978, **146**, 235.

[15] A. K. Das and I. D. Brown, *Canad. J. Chem.*, 1966, **44**, 939.

[16] I. D. Brown, *Canad. J. Chem.*, 1964, **42**, 2758.

[17] S. Syoyama, K. Osaki, and S. Kusanagi, *Inorg. Nuclear Chem. Letters*, 1972, **8**, 181.

[18] T. C. Gibb, R. Greatrex, N. N. Greenwood, and A. C. Sarma, *J. Chem. Soc.* (*A*), 1970, 212.

[19] S. C. Nyburg, '*X*-Ray Analysis of Organic Structures,' Academic Press, New York, 1961, p. 306.