

Preliminary communication

ISOLATION AND CRYSTAL STRUCTURE OF AN UNUSUAL DITELLURIDE: BIS(*N,N*-DIMETHYLAMINOFORMYL) DITELLURIDE

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Summary

Solutions of disodium ditelluride in *N,N*-dimethylformamide (DMF) react with the solvent to give small yields of the unusual ditelluride, $[\text{Me}_2\text{NC(O)}]_2\text{Te}_2$. This molecule, which exhibits interesting photochemical behavior has been characterized and its crystal structure has been determined.

During the attempted synthesis of bis(*o*-nitrophenyl) ditelluride by the direct reaction between *o*-chloronitrobenzene and Na_2Te_2 in DMF, the expected product was not isolated. Instead, phenazine was isolated as the main reaction product. In attempting to understand the mechanism of this reduction it was decided to study the reaction between Na_2Te_2 and the solvent. This resulted in the isolation of this new compound with an unusual chemical structure and interesting photochemical properties.

Bis(dimethylaminoformyl) ditelluride. A solution of disodium ditelluride in DMF was prepared according to the method described by Sandman and co-workers [1]. The solution was stirred for 20 h, in the dark, under an atmosphere of argon or nitrogen. The solution was evaporated, at reduced pressure, to about 10% of its original volume, then it was extracted with ether, heated with charcoal and filtered. Slow evaporation of the solution caused the separation of long, gold-colored needles*. These were identified as bis(di-

**Crystal data.* Graphite monochromatized Mo- K_α radiation, λ 0.71073 Å; data collected by Molecular Structure Corp., College Station, Texas, CAD-4 diffractometer, gold prismatic crystal (0.20 × 0.15 × 0.20) mm³; monoclinic, $P2_1/c$, a 8.201(3), b 5.864(2), c 22.976(9) Å, β 91.26(3)° from 25 values of 2θ at t -105°C; 2103 measured intensities ($\theta/2\theta$) scan for which $I > 0.5\sigma(I)$, $\sigma^2(I) = \sigma_c^2 + (0.05I)^2$ and σ_c^2 is obtained from counting statistics; Lorentz, polarization corrections applied; empirical absorption corrections ($0.552 < T < 0.998$) and linear corrections for decomposition (3 standard reflections, maximum change = 12%) were made.

Supplementary material containing atomic coordinates and structure factors may be obtained from the authors upon request.

methylaminoformyl) ditelluride. Analysis. Found: C, 17.93; H, 2.97; N, 6.93. $C_6H_{12}N_2O_2Te_2$ calcd.: C, 18.04; H, 3.02; N, 7.01%. M.p. 127–129°C; low resolution mass spectrum: peak maximum at 402 with the isotope distribution pattern expected for two tellurium atoms. The mass spectrum is easily interpreted by peaks corresponding to the loss of one tellurium atom to give $[Me_2NC(O)]_2Te$, loss of the tellurium atom from the latter to give $[Me_2NC(O)]_2$, mass 144 followed by loss of CO to give $Me_2NC(O)NMe_2$, mass 116 which loses Me_2N to give Me_2NCO . A very intense $\nu(C=O)$ stretching frequency was observed in the IR spectrum at 1653 cm^{-1} .

Structure determination [2]. Patterson and electron density plots and weighted least-squares refinements (max shift ESD < 0.094) produced satisfactory values for coordinates and anisotropic temperature factors for Te, O, N, and C (Table 1), but also yielded disturbingly large R -values ($R_1 = \Sigma ||F_o - |F_c|| / \Sigma |F_o| = 0.091$ and $R_2 = [\Sigma \omega (|F_o| - |F_c|)^2 / \Sigma \omega |F_o|^2]^{1/2} = 0.086$) and four large maxima ($4.1\text{ e}/\text{\AA}^3$) and four large minima ($-3.3\text{ e}/\text{\AA}^3$) within 1 \AA of Te on the difference Fourier maps. Since the decline in the intensities of the check reflections indicated that decomposition had occurred during collection of the X-ray data, a limited set of the data acquired early in the run were analyzed. They yielded improved R -values but peaks and valleys near Te remained. Other refinements with all data were carried out in which scatterers were placed at the positions of the peaks in the difference Fourier maps and their occupancy varied (scattering factor = $f[\text{carbon}]$, $U = 0.05\text{ \AA}^2$, occupancy = 0.35, $R_2 = 0.081$). In addition, H-atom positions were chosen from difference maps and adjusted so that they were 1.0 \AA from their C-atom ($U = 0.05\text{ \AA}^2$, $R_2 = 0.078$). There were no significant changes in the molecular dimensions as a result of these changes in the model, so the values obtained originally for Te, O, N and C only have been given in the Tables and used for Fig. 1 and 2 [3].

The dimensions of the molecule differ slightly from those expected for conventional bonds. In particular, the bonds from C(1), C(2) to Te(1), Te(2) are long and the bond between Te(1) and Te(2) is short. The short Te—Te

TABLE 1

FRACTIONAL COORDINATES AND EQUIVALENT ISOTROPIC TEMPERATURE FACTORS (\AA^2) FOR NON-H ATOMS $U = \frac{1}{3} \Sigma_i \Sigma_j U_{ij} a_i^* a_j^* (a_i \cdot a_j)$

	x/a	y/b	z/c	U
Te(1)	0.59842(12)	0.17053(21)	0.69599(4)	0.03040
Te(2)	0.47306(12)	0.49541(19)	0.62737(4)	0.02809
O(1)	0.87659(135)	0.30160(249)	0.62141(46)	0.04863
O(2)	0.41907(134)	0.04839(168)	0.56777(46)	0.03321
N(1)	0.93274(141)	-0.01978(233)	0.67257(51)	0.03076
N(2)	0.29346(139)	0.33448(234)	0.51778(46)	0.02726
C(1)	0.83706(163)	0.16097(267)	0.65575(53)	0.02385
C(2)	0.38440(163)	0.24342(237)	0.56173(61)	0.02495
C(3)	1.09889(240)	-0.03193(410)	0.64598(92)	0.06488
C(4)	0.88345(231)	-0.20165(360)	0.71174(84)	0.05874
C(5)	0.22206(167)	0.17364(278)	0.47386(57)	0.02783
C(6)	0.23504(213)	0.56890(274)	0.51691(67)	0.03643

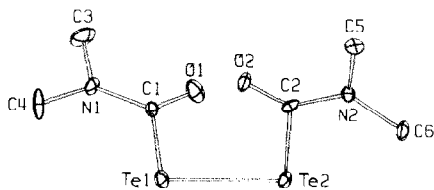


Fig. 1. ORTEP [3] drawing of $C_6H_{12}N_2O_2Te_2$ (H-atoms not shown).

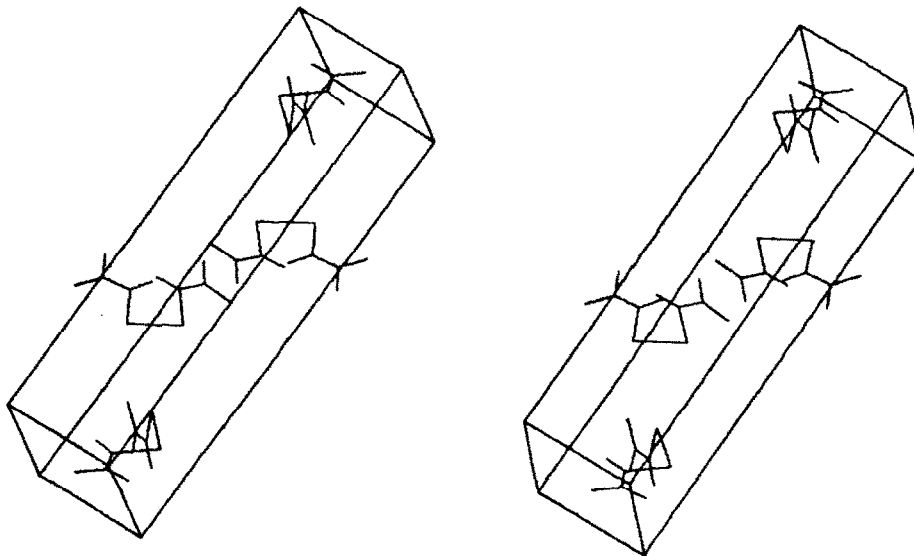


Fig. 2. Packing diagram of $C_6H_{12}N_2O_2Te_2$.

TABLE 2

INTERATOMIC DISTANCES (Å) AND ANGLES (°) WITH e.s.d.'s IN PARENTHESES

Te(1)—Te(2)	2.665(2)		
Te(1)—C(1)	2.184(13)	Te(2)—C(2)	2.222(14)
C(1)—O(1)	1.191(19)	C(2)—O(2)	1.186(17)
C(1)—N(1)	1.369(19)	C(2)—N(2)	1.352(18)
N(1)—C(3)	1.507(23)	N(2)—C(5)	1.492(19)
N(1)—C(4)	1.458(24)	N(2)—C(6)	1.456(21)
Te(1)...O(1)	2.984(11)	Te(2)...O(2)	2.986(10)
Te(1)...O(2)	3.341(11)	Te(2)...O(1)	3.505(12)
Te(1)...N(1)	3.019(12)	Te(2)...N(2)	3.039(11)
Te(2)—Te(1)—C(1)	96.1(4)	Te(1)—Te(2)—C(2)	92.4(4)
Te(1)—C(1)—O(1)	121.5(11)	Te(2)—C(2)—O(2)	119.2(10)
Te(1)—C(1)—N(1)	114.4(9)	Te(2)—C(2)—N(2)	114.3(10)
O(1)—C(1)—N(1)	124.1(13)	O(2)—C(2)—N(2)	126.5(14)
C(1)—N(1)—C(3)	116.1(14)	C(2)—N(2)—C(5)	117.2(13)
C(1)—N(1)—C(4)	125.1(13)	C(2)—N(2)—C(6)	124.0(12)
C(3)—N(1)—C(4)	118.7(14)	C(5)—N(2)—C(6)	117.6(11)

bond distance merits some discussion. For comparison, (Te—Te) distances from recent X-ray structure determinations of diaryl ditellurides [4–6] vary from 2.680(1) to 2.712(2) Å, (Te—C) from 2.08(1) to 2.16(1) Å. Similar values were found for the non-planar tellurium containing heterocycle, *cis*-3,5-dibenzylidene-1,2,4-tritellurole [7], (Te—Te) 2.710 Å, (Te—C) 2.117(5), 2.122(4) Å, while shorter (Te—Te) values were observed in the strained planar heterocycle, 5,6:11,12-bis(ditelluro)tetracene [1,8], 2.673(3), 2.680(1) Å and in the inorganic cations, Te_4^{2+} [9] and Te_6^{4+} [10], (Te—Te) 2.662(3) to 2.694(5) Å, along with other, much longer (Te—Te) distances, 3.062(2) to 3.148(6) Å, in the latter unit.

The errors estimated are probably too small because of decomposition, but the dimensional changes make the molecule seem ready to decompose into the fragments CO, Te_2 and $\text{N}(\text{CH}_3)_2$ or $\text{OCN}(\text{CH}_3)_2$. The units (Te(1), O(1), N(1), C(1)) and (Te(2), O(2), N(2), C(2)) are twisted 90.3° from each other. There are no unusual intermolecular contacts (Te \cdots Te 4.188 Å).

Prior to the determination of this structure, our experience has been that when extensive decomposition occurs before, or during, the collection of X-ray data from Te or Se compounds that there is a general lack of agreement between calculated and observed structure factors. However, the appearance of such large maxima and minima in this structure seemed unusual to us and suggested that photodecomposition under X-rays was not accompanied by long distance migration of Te in this material at -105°C . This observation suggested the following exploratory experiments which could be performed in a reproducible manner.

1. Exposure of the compound to ultraviolet radiation (Engelhard Hanovia model 30620; 5780 Å (1.5 watts), 5461 Å (1.5 watts), 3660 Å (1.82 watts), 3130 Å (1.30 watts), 3025 Å (0.57 watt)) is accompanied by the deposition of tellurium, but the compound is stable to ordinary light.

2. A solution of the compound in ether was prepared and a filter paper was immersed in the solution, removed and allowed to dry. The impregnated paper was exposed imagewise with ultraviolet radiation. The exposed portion turned black (deposition of tellurium) and a sharply defined image remained on the unexposed portion previously occupied by the metal object.

3. When the experiment described in (2) was performed at Dry-Ice or lower temperatures, no deposition of tellurium was noted. When the exposed paper was allowed to come to room temperature, black tellurium deposited in the exposed portion and the protected portion appeared as a well-defined image of the object.

These observations suggest that a photochemical decomposition occurs at low temperatures, but the Te atoms do not migrate from the unit cells in which they are generated unless the temperature is sufficiently high. This means that at lower temperatures a record of the decomposition at the molecular level is produced and stored. At higher temperatures this is followed by the formation of Te crystallites as a result of the greater ease of atomic migration.

The study of carbonyl ditellurides is being investigated at present in our laboratories.

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