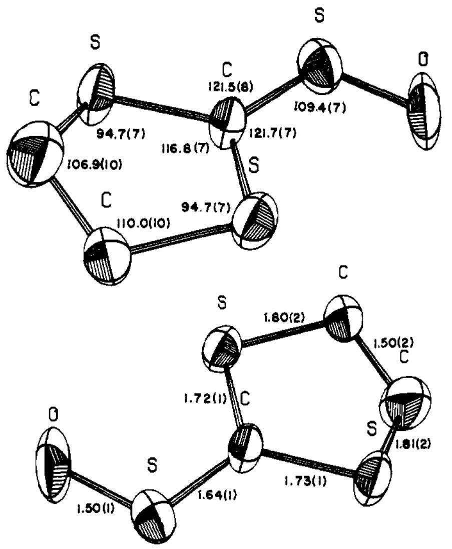

Figure 1. An ORTEP plot of the two molecules in a unit cell, looking approximately down *b*. Bond distances are in ångströms, bond angles in degrees, and thermal ellipsoids enclose 50% probability.

by oxidation of the corresponding thiocarbonyl compound, the only evidence regarding the geometry of this grouping appears to be that obtained by King and Durst,[2] who obtained two interconvertible forms of oxythiobenzoyl chloride and presumed them to be *cis,trans* isomers. We wish to report the results of a crystal structure analysis on ethylene trithiocarbonate oxide[3] which provides the first experimental values for bond parameters in a substance with the thiocarbonyl oxide grouping.

The crystals were grown from ethanol–pentane solution, mounted quickly, and sprayed immediately with Teflon to retard the otherwise very rapid oxidation. Pertinent crystal data are: space group $P\bar{1}$; $a = 7.20$ (1), $b = 5.41$ (1), and $c = 8.16$ (1) Å; $\alpha = 102.7°$ (3), $\beta = 100.0°$ (3), and $\gamma = 73.3°$ (3); $Z = 2$. The intensities of 770 independent reflections were estimated visually from Cu Kα photographs around all three axes. The three sulfur atoms were located from the three-dimensional Patterson map, and the first Fourier map revealed the carbons and oxygen. Refinement, first isotropic and then anisotropic, gave an *R* of 12.7.

Bond distances and angles are shown in Figure 1 on an ORTEP plot showing the contents of a unit cell. The C–S–O angle of 109.4° (7) is consistent with the use of (a) atomic orbitals by this sulfur, with the expected 90° angle expanded by 19° due to electrostatic repulsion between the oxygen and adjacent ring sulfur, or (b) sp^2 hybridization by the sulfur, with the optimum 120° angle contracted by 11° due to electrostatic repulsion between the oxygen and the unshared pair on sulfur. The hybridization of this sulfur is probably similar to that in sulfur dioxide, whose O–S–O angle of 119.0–119.5° (5)[4,5] suggests sp^2 hybridization with 1° distortion but can be rationalized in terms of atomic orbitals with 29° distortion.

The oxygen is 0.25 Å out of the plane formed by the three sulfurs and the carbon among them, presumably due to repulsion between the oxygen and the adjacent ring sulfur. The nonplanarity observed in the ring is expected since it relieves eclipsing of the two methylene groups.

The sulfur–oxygen bond length of 1.495 (11) Å compares with values of 1.4321 (5) Å for SO_2[4] and 1.47 (3) Å for dimethyl sulfoxide.[6] The amount of double bond character in the exocyclic carbon–sulfur bond can be estimated from its observed length to be 90%.[7]

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R. B. Bates, G. A. Wolfe
Department of Chemistry
University of Arizona, Tucson, Arizona 85721

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The Te_4^{2+} Cation

Sir:

Very recently Bjerrum and Smith[1] have shown that in Te–$TeCl_4$ melts with a mole ratio of 7 or greater a tellurium species with the formal oxidation state of $+\frac{1}{2}$ is formed. They formulate this species as the polymeric cation Te_{2n}^{n+} which they believe to be the Te_4^{2+} cation. We recently reported that selenium can be oxidized to the Se_8^{2+} and Se_4^{2+} cations in solution in various highly acidic media, *e.g.*, H_2SO_4, $H_2S_2O_7$, and HSO_3F.[2] We have been investigating the colored solutions that are formed by sulfur and tellurium in these same media, and we now report our evidence for the formation of the Te_4^{2+} cation.

Tellurium dissolves slowly in cold sulfuric acid or fluorosulfuric acid to produce a red solution. With oleum the reaction is more rapid, and on warming the red oleum solution a color change to orange and finally to yellow occurs. A yellow-orange color is also produced on adding persulfate to the red sulfuric acid solution or peroxydisulfuryl difluoride to the fluorosulfuric acid solution. In the reaction of tellurium with the pure solvents, sulfur dioxide is produced in all three cases. The colored tellurium species are, therefore, positive oxidation states of tellurium, the yellow species being a higher oxidation state than the red.

The absorption spectra of tellurium in fluorosulfuric acid under different conditions show clearly the existence of two distinct species. In Figure 1, curve A was obtained from the reaction of tellurium with pure fluorosulfuric acid after removal of the sulfur dioxide produced in the reaction. This red species has an intense absorption maximum at 510 mμ and a shoulder between 400 and 450 mμ. This spectrum is almost identical with that reported by Bjerrum and Smith[1] for their Te_{2n}^{n+} species and is quite similar to that previously reported

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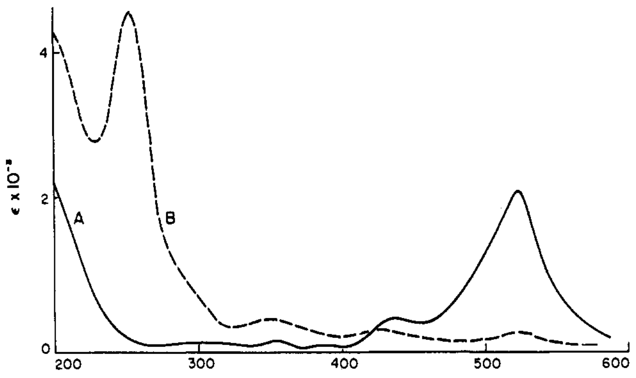

Figure 1.

for Se_4^{2+}. Curve **B** was obtained from a 2:1 Te:$S_2O_6F_2$ mixture in fluorosulfuric acid and shows an intense absorption at 250 mμ with two weak maxima at 360 and 420 mμ. This spectrum also contains a very weak 510-mμ peak, which we have never been able completely to eliminate from the yellow solutions.

Conductometric and cryoscopic measurements were carried out on red solutions produced by the reaction of tellurium with pure fluorosulfuric acid. Values of γ, the number of fluorosulfate ions produced by one atom of tellurium, were calculated by comparison with the conductivity of potassium fluorosulfate. At both temperatures studied, γ was essentially constant over the concentration range studied and had values of 0.69 ± 0.02 at 25° and 0.72 ± 0.01 at −86.4°. A value of 1.71 for ν, the number of particles produced per atom of tellurium, was obtained from the cryoscopic results.

For the formation of polyatomic cations of general formula Te_n^{x+}, the reaction is

$$n\mathrm{Te} + 2x\mathrm{HSO_3F} = \mathrm{Te}_n^{x+} + \frac{x}{2}\,\mathrm{SO_2} + \frac{x}{2}\,\mathrm{HF} + \frac{x}{2}\,\mathrm{H_3O^+} + \frac{3x}{2}\,\mathrm{SO_3F^-} \qquad (1)$$

The equilibrium

$$\mathrm{H_3O^+} + \mathrm{SO_3F^-} \rightleftharpoons \mathrm{HF} + \mathrm{H_2SO_4} \qquad (2)$$

would affect the value of γ, but not the value of ν which would be $(1 + 3x)/n$. The equilibrium constant, K, for reaction 2 has the values 0.12 at 25°, 0.042 at 0°, and 0.031 at −78°.[3] The value at −86.4° has not been measured but in view of the above figures a value of 0.030 is reasonable. The relation between γ and the values of x and n is complicated, but it can be shown that

$$\gamma = \frac{x}{n}\{(K - 3.50) + (K^2 + 5K + 0.25)^{1/2}\}(2K - 2)^{-1}$$

Using the above values of K, $\gamma = 1.39x/n$ at 25° and $\gamma = 1.47x/n$ at −86.4°. The experimental γ values give $x/n = 0.495 \pm 0.015$ at 25° and 0.497 ± 0.007 at −86.4°. At both temperatures it is thus clear that $n = 2x$, and the red species contains tellurium in the $+{}^1/_2$ oxidation state. This corresponds to species such as Te_2^+, Te_4^{2+}, Te_6^{3+}, etc. The expected values of ν for the various species are shown below.

Ion:	Te_2^+	Te_4^{2+}	Te_6^{3+}	Te_8^{4+}	Te_{10}^{5+}
γ	2.00	1.75	1.67	1.62	1.60

The observed value of 1.71 agrees best with the formation of Te_4^{2+} or Te_6^{3+}. Measurement of the magnetic susceptibility of a concentrated red solution of tellurium in fluorosulfuric acid showed the solute to be diamagnetic with a susceptibility of -27×10^{-6} cgs units per g-atom of Te. Thus the species Te_6^{3+} can be ruled out as it would be expected to be paramagnetic.

The Raman spectrum of the red solution in fluorosulfuric acid showed two peaks which can be attributed to tellurium–tellurium bonds: a very strong peak at 219 cm⁻¹ and a very weak peak at 139 cm⁻¹. This spectrum is very similar to that of Se_4^{2+} which has a strong band at 327 cm⁻¹ and a very weak band at 188 cm⁻¹.[4] An as yet incomplete X-ray crystallographic investigation of the Se_4^{2+} cation in the compound $Se_4(HS_2O_7)_2$ has shown that Se_4^{2+} very probably has a square-planar structure.[5] The infrared and Raman spectra are also consistent with this structure. In view of the similarities between the absorption spectra and the Raman spectra of Te_4^{2+} and Se_4^{2+}, we propose a similar square-planar structure for Te_4^{2+}.

The reaction of tellurium with antimony pentafluoride gives rise to several compounds which are not easy to separate. There is certainly, however, a red compound containing the Te_4^{2+} cation and a yellow compound which appears to have the composition $TeSbF_6$ and in which tellurium is probably present in the +1 oxidation state. This appears to be the oxidation state of tellurium in the yellow solutions of tellurium in acid solvents. Our investigation of the nature of this species is not yet complete.

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J. Barr, R. J. Gillespie, R. Kapoor, G. P. Pez
Department of Chemistry
McMaster University, Hamilton, Ontario
Received September 16, 1968

Energy-Transfer Reactions of $N_2(A\,^3\Sigma_u^+)$I. Quenching and Emission by C_2N_2, SO_2, and Other Molecules

Sir:

In a previous paper[1] we described the production of a flow of metastable $N_2(A\,^3\Sigma_u^+;\ v' = 0, 1)$ molecules[2] in a mixture of argon and nitrogen at 1–5 torr pressure in the absence of other reactive species. This was confirmed by detection of the nitrogen (A–X) Vegard–Kaplan (V–K) bands in emission and by energy-transfer reactions with Hg, NO, and CO giving ($^3P_1$), ($A^2\Sigma^+$), and ($a^3\Pi$) emission, respectively. With the argon–nitrogen flow system we have now studied the reactions of $N_2[A\,^3\Sigma_u^+;\ v' = 0$ (142 kcal), 1 (146 kcal)] with oxygen, nitrous oxide, ethene, benzene, iodine, acetophenone, biacetyl, carbon disulfide, cyanogen, and sulfur dioxide. These reactions apparently proceed by collisional quenching with energy transfer from $N_2(A)$, and it appears that $N_2(A)$ can serve as a triplet sensitizer for the 142–146-kcal mole⁻¹ energy region which is at present inaccessible.[3]

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