

MOLECULAR STRUCTURE OF SOME TELLURIUM COMPOUNDS DETERMINED BY MAGNETIC METHOD

BY S. S. DHARMATTI

(Chemical Laboratories, Royal Institute of Science, Bombay)

Received June 7, 1940

(Communicated by Dr. Mata Prasad, D.Sc., F.I.C., F.A.Sc.)

THE structures of some of the selenium compounds obtained by the use of the Langevin equation and Slater's and Angus's methods for the calculation of $\Sigma \bar{r}^2$ are given in the previous paper.¹ In this investigation an attempt has been made to discuss the constitution of some tellurium compounds. Tellurium belongs to the same group of elements as S and Se and the constitution of their compounds may throw light on the constitution of the compounds of tellurium. The Guoy balance and the method of working described in the previous paper were used in this investigation. The magnetic susceptibilities of the compounds investigated are given in Table I.

TABLE I

Substance	Molecular formula	$\chi_a \times 10^6$	$\chi_m \times 10^6$
Tellurious acid	H_2TeO_3	-0.1956	- 34.89
Tellurium dichloride	$Te Cl_2$	-0.4760	- 94.45
Tellurium dibromide	$Te Br_2$	-0.3701	-106.20
Telluric acid	$H_2TeO_4, 2 H_2O$	-0.2508	- 57.55
Dimethyl tellurium diiodide . . .	$(CH_3)_2 TeI_2$	-0.3535	-145.40
Dimethyl tellurium dichloride	$(CH_3)_2 TeCl_2$	-0.4047	- 92.43

All substances except dimethyl tellurium diiodide and dimethyl tellurium dichloride were obtained either from Kahlbaum or from Theoder Schuchardt and were of extra pure quality. The author is thankful to Miss K. D. Gavankar, M.Sc., Analyst, Royal Institute of Science, for preparing the two substances in this laboratory.

Dimethyl tellurium diiodide $(CH_3)_2 TeI_2$.—Amorphous tellurium (25 g.) and methyl iodide (55 g.) were kept in a hard glass bulb on a water-bath

¹ Proc. Ind. Acad. Sci., (A), 1940, 12, 185.

at 80° for about 48 hours. It was then cooled and the substance was extracted with chloroform from which it was obtained as red crystals,² m.p. = 125°–26°; standard value 127°. The density of the crystals was found to be 2.651. gm./c.c.

Dimethyl tellurium dichloride ($CH_3)_2TeCl_2$.—To dimethyl tellurium diiodide (about 5 g.) concentrated aqueous ammonia was added drop by drop till the red salt was transformed entirely into a pasty greyish white mass. The precipitate was dissolved in water with one or two drops of ammonia and an aqueous solution [50 c.c. of the solution containing 12.14 g. of $AgNO_3$ and just sufficient quantity of NH_4OH to redissolve the precipitate of $Ag(OH)$] was added to it. The mixture was boiled and filtered and the filtrate was evaporated till no smell of ammonia was detected. Then it was diluted and any silver iodide present was removed. The excess of silver nitrate was removed by the repeated addition of HBr. The remaining solution was evaporated to about 100 c.c. and was treated with HCl until no further precipitation took place. The dichloride thus obtained was purified by crystallisation from alcohol (m.p. = 93°–94°; literature = 92°).

Discussion of Results

The values of $\sum \bar{r}^2$ and the ionic susceptibilities for Te in various valency states, calculated according to Slater's and Angus's methods as well as with the slight changes mentioned in the previous paper, are given in Table II.

TABLE II

Diamagnetic susceptibilities of Te in various valency states calculated from various methods

Valency states	$\sum \bar{r}^2$ calculated by Slater's method	$\chi \times 10^6$ calculated by Slater's method	$\sum \bar{r}^2$ calculated by modification in Slater's method	$\chi \times 10^6$ calculated by modification in Slater's method using constant 0.790 instead of 0.807	$\sum \bar{r}^2$ calculated by Angus's method	$\chi \times 10^6$ calculated by Angus's method	$\sum \bar{r}^2$ calculated by modification in Angus's method	$\chi \times 10^6$ calculated by modification in Angus's method and using constant 0.790 instead of 0.807
Te divalent ..	66.19	–53.43	45.66	–36.08	66.36	–53.30	56.08	–44.30
Te tetravalent	39.01	–31.49	30.28	–23.92	38.85	–31.35	30.10	–23.78
Te hexavalent	22.08	–17.81	19.71	–15.57	21.92	–17.69	19.53	–15.43

These values were employed to calculate the magnetic susceptibilities and have been designated with the same symbols as given in the previous paper (*loc. cit.*).

Tellurious Acid (H_2TeO_3).—Like sulphurous and selenious acids there are two possibilities for its constitution: $O = Te \begin{cases} OH \\ | \\ OH \end{cases}$ (I) and $O \begin{cases} \diagup \\ \diagdown \end{cases} Te \begin{cases} OH \\ | \\ H \end{cases}$ (II). The experimental and calculated values for tellurious acid, on the basis of Pascal's value for O (-3.36×10^{-6}), are given under A of the Table III.

TABLE III

Constitution	A		B	
	Symmetrical $O = Te \begin{cases} OH \\ \\ OH \end{cases}$ $-\chi \times 10^6$ (I)	Unsymmetrical $O \begin{cases} \diagup \\ \diagdown \end{cases} Te \begin{cases} OH \\ \\ H \end{cases}$ $-\chi \times 10^6$ (II)	Symmetrical $O = Te \begin{cases} OH \\ \\ OH \end{cases}$ $-\chi \times 10^6$ (I)	Unsymmetrical $O \begin{cases} \diagup \\ \diagdown \end{cases} Te \begin{cases} OH \\ \\ H \end{cases}$ $-\chi \times 10^6$ (II)
$(\chi_a)_1$ $(\chi_m)_1$	0.2813 49.93	0.1978 35.12	0.3364 59.72	0.3089 54.70
$(\chi_a)_2$ $(\chi_m)_2$	0.2386 42.36	0.1852 32.88	0.2938 52.15	0.2955 52.46
$(\chi_a)_3$ $(\chi_m)_3$	0.2805 49.79	0.1972 35.00	0.3357 59.58	0.3075 54.58
$(\chi_a)_4$ $(\chi_m)_4$	0.2373 42.12	0.1844 32.74	0.2930 52.01	0.2947 52.32
$(\chi_a)_E$ $(\chi_m)_E$..	0.1966 34.89
$(\chi_a)_{O_1}$ $(\chi_m)_{O_1}$..	0.1900 33.72
$(\chi_a)_{O_2}$ $(\chi_m)_{O_2}$..	0.2027 35.97
$(\chi_a)_{O_3}$ $(\chi_m)_{O_3}$..	0.1897 33.68

O_1 Refers to the values obtained by S. Meyer (Mellor's *Inorganic Chemistry*, 11, 73).

O_2 Refers to the values calculated from Bragg's data by Bhatnagar and Luther (*J. Ind. Chem. Soc.*, 1929, 3, 30).

O_3 Refers to values calculated as an electronic isomer by Bhatnagar and Dhawan, also by Bhatnagar and Mathur (*Phil. Mag.*, 1928, 5, 536; 1928, 6, 217).

The calculated values for the constitution II agree well with the experimental values thus confirming that the constitution $O \begin{cases} \diagup \\ \diagdown \end{cases} Te \begin{cases} OH \\ | \\ H \end{cases}$ for the tellurious acid is similar to that of the selenious acid. This is to be expected from the similarity in the behaviour of selenium and tellurium and their

compounds. It should, however, be noted that in the calculation of the molecular susceptibilities of selenious acid Slater's value for O (-13.15×10^{-6}) was used. Calculations made with this value in the case of tellurious acid are shown under B of the above table. No value thus calculated agrees with the experimental value showing thereby that Pascal's value alone can be employed in this case. The reason for this peculiarity may be found in the fact that the binding between oxygen and tellurium may be stronger than that between oxygen and selenium, for, lower diamagnetic value of oxygen is admissible in the calculation of the susceptibility of tellurious acid.

International Critical Tables give for tellurious acid $\chi_a = -0.24 \times 10^{-6}$ or $\chi_m = -42.60 \times 10^{-6}$. These values agree neither with the calculated ones nor with those experimentally found by the author and other workers and need correction.

Tellurium dichloride ($TeCl_2$).—Tellurium does not form monochloride of the type Te_2Cl_2 . This behaviour is unlike selenium and sulphur which yield compounds of the type Se_2Cl_2 and S_2Cl_2 . Therefore dichloride was chosen for investigation. This compound is very unstable and the decomposition begins even when the tube is being filled up. Hence great precautions were taken to fill the tube and the observations were taken as quickly as possible. The results obtained experimentally and those calculated

for the constitution $Te \begin{array}{l} \diagup \\ Cl \\ \diagdown \\ Cl \end{array}$ are given below:

TABLE IV

Constitution	$Te \begin{array}{l} \diagup \\ Cl \\ \diagdown \\ Cl \end{array}$ $-\chi \times 10^6$
$(\chi_a)_1$	0.4928
$(\chi_m)_1$	97.83
$(\chi_a)_2$	0.4057
$(\chi_m)_2$	80.48
$(\chi_a)_3$	0.4925
$(\chi_m)_3$	97.70
$(\chi_a)_4$	0.4471
$(\chi_m)_4$	88.70
$(\chi_a)_E$	0.4760
$(\chi_m)_E$	94.45

The calculated values are slightly different from the experimental one but in view of the experimental difficulties mentioned above, the results obtained may be taken to be in good agreement with the theory.

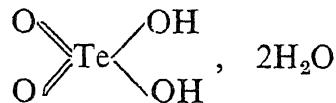
Tellurium dibromide ($TeBr_2$).—This compound also, like $TeCl_2$, is an unstable one. With all the necessary care taken in the measurement it cannot be said that the experimental value is the susceptibility of the pure compound.

TABLE V

Constitution	Te Br Br $-\chi \times 10^6$
$(X_a)_1$	0.4121
$(X_m)_1$	118.43
$(X_a)_2$	0.3515
$(X_m)_2$	101.08
$(X_a)_3$	0.4117
$(X_m)_3$	118.30
$(X_a)_4$	0.3804
$(X_m)_4$	109.30
$(X_a)_E$	0.3701
$(X_m)_E$	106.20

The observed discrepancy between the calculated and the experimental values may be due to the unstable nature of the compound. In both the dichlorides and dibromides, the divalent tellurium tends to undergo self-oxidation and reduction, forming a solid solution of the element in the tetrachloride and tetrabromide.³ Further both of them are hygroscopic and the water absorbed by them from the atmosphere, causes decomposition into the tetrahalide and free tellurium.⁴

Telluric acid (H_2TeO_4 , 2 H_2O).—There is no possibility of any other constitution for this acid (with molecules of water distinct from the anhydrous acid) except the graphic formula,

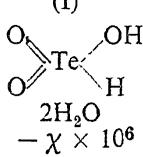
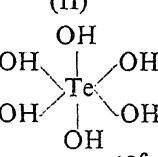


³ Darmiens, *Ann. Chim.*, 1923, 19, 44.

⁴ Brauner, *Monatsh.*, 1889, 10, 411.

Since it is a hydrated salt, it will be interesting to see how far the law of additivity applies to this case. The calculated and observed values are given under A of Table VI.

TABLE VI

Constitution	A	B
	(I)  $-\chi \times 10^6$	(II)  $-\chi \times 10^6$
$(\chi_a)_1$	0.2855	0.2747
$(\chi_m)_1$	65.53	63.05
$(\chi_a)_2$	0.2757	0.2650
$(\chi_m)_2$	63.29	60.81
$(\chi_a)_3$	0.2850	0.2743
$(\chi_m)_3$	65.41	62.93
$(\chi_a)_4$	0.2751	0.2643
$(\chi_m)_4$	63.15	60.67
$(\chi_a)_E$	0.2508	0.2508
$(\chi_m)_E$	57.55	57.55

It is seen from the above that the calculated values are higher than the experimental ones. Gutbier⁵ considers that both molecules of water in the hydrate $H_2TeO_4 \cdot 2H_2O$ are constitutional so that the formula for telluric acid would be H_6TeO_6 or $Te(OH)_6$ and the constitutional formula can be written as



The magnetic susceptibilities of telluric acid for the above constitution were calculated and are given under B of the above table.

Even with the molecular constitution (II), the calculated values are higher than the observed ones, although they are a little lower than those

⁵ Mellor's *Inorganic Chemistry*, 11, 85.

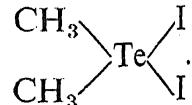
calculated for (I). The experimentally determined value appears to be in line with the view of Ray Choudhary⁶ who determined the magnetic susceptibility of a number of salts in the hydrated and anhydrous state and found that for a large number of substances investigated, the observed value for the hydrate is less than the calculated value. He also showed that the deviation from the additivity law is more prominent in cases where the heat of hydration is large. As a quantitative estimation he found that in the case of salts whose heats of hydration lie in the vicinity of 20 calories, the observed values of magnetic susceptibility are about 20 per cent. lower than the values calculated from the anhydrous salts. Though much importance cannot be attached to the quantitative nature of the change, the results on telluric acid support Ray Choudhary's general conclusions.

Varadachari⁷ measured the diamagnetic susceptibilities of a number of crystalline inorganic salts. In the case of sodium sulphate⁸ he found that the magnetic susceptibility of the hydrated salt undergoes no change when the salt is rendered anhydrous and he, therefore, suggested that the binding of the water molecules with the sulphate is very loose. It appears probable that the lowering in the observed value of telluric acid is due to the strong binding of the water molecules with oxygen ions. This conclusion is in agreement with the representation of the molecular constitution of the acid as $\text{Te}(\text{OH})_6$.

International Critical Tables give the diamagnetic susceptibility χ_a for anhydrous telluric acid as -0.43×10^{-6} and $\chi_m = -98.69 \times 10^{-6}$. These values are very different from the calculated and the experimental ones and need correction.

Dimethyl tellurium diiodide $(\text{CH}_3)_2\text{TeI}_2$.—Pascal's additivity law is based mostly on his extensive results obtained from organic compounds, which have covalent bindings and as such his susceptibility constants fit in well in inorganic compounds involving covalent linkages, though complete agreement is not found as can be seen from the foregoing discussions. The study of some organo-inorganic compounds of tellurium was, therefore, undertaken. $(\text{CH}_3)_2\text{TeI}_2$ was selected because the nature of its covalency has been dis-

cussed at length by Lowry⁹ and its graphic formula is fixed as



⁶ *Zeit. Phys.*, 1932, 77, 271.

⁷ *Annamalai University Journal*, 1935, 4, 73.

⁸ *Proc. Ind. Acad. Sci.*, 1935, 2, 161.

⁹ *Soc. Chim. Belg.*, 1931, 91.

For the calculation of its susceptibility the value for iodine is taken as -45.6×10^{-6} .¹⁰ The values for CH_3 calculated from different compounds are different, as shown below:-

Value for CH_3 from	CH_3Cl	9.86×10^{-6}
" "	CH_3Br	12.78×10^{-6}
" "	CH_3I	11.58×10^{-6}
" "	CH_3OH	16.14×10^{-6}

Consequently all the values for CH_3 were used, together with different values for tetravalent tellurium, to calculate the susceptibility of $(\text{CH}_3)_2\text{TeI}_2$.

TABLE VII

	χ calculated using CH_3 values from CH_3OH $\times 10^6$	χ calculated using CH_3 values from CH_3Br $\times 10^6$	χ calculated using CH_3 values from CH_3Cl $\times 10^6$	χ calculated using CH_3 values from CH_3I $\times 10^6$
$(X_a)_1$	0.3768	0.3606	0.3461	0.3547
$(X_m)_1$	154.97	148.25	142.40	145.85
$(X_a)_2$	0.3581	0.3420	0.3277	0.3362
$(X_m)_2$	147.40	140.68	134.84	138.28
$(X_a)_3$	0.3762	0.3600	0.3459	0.3542
$(X_m)_3$	154.83	148.11	142.27	145.71
$(X_a)_4$	0.3580	0.3415	0.3275	0.3358
$(X_m)_4$	147.26	140.54	134.70	138.14
$(X_a)_E$	0.3535
$(X_m)_E$	145.40
$(X_a)_{E1}$	0.3600
$(X_m)_{E1}$	148.10
$(X_a)_{O1}$	0.3700
$(X_m)_{O1}$	152.20

O₁ Refers to values calculated by Bhatnagar and Lahiri (*Curr. Sci.*, 1932, 1, 380).

E₁ Refers to the experimental values of Bhatnagar and Lahiri (*loc. cit.*).

The above table clearly shows that the susceptibilities calculated by taking the value for CH_3 from CH_3I and the values of tetravalent tellurium according to Angus and Slater, are in very good agreement with the experimental values. The experimental value obtained by Bhatnagar and Lahiri¹¹ agrees very closely with that of the author. But their calculated value is rather high and may be due to the choice of the value of CH_3 which is large if

¹⁰ Stoner, *Magnetism and Matter*, p. 468.

¹¹ *Ibid.*

calculated from CH_3OH . The author's calculated values in column 1 of the table is very nearly the same as that calculated by Bhatnagar and Lahiri.

Dimethyl tellurium dichloride ($\text{CH}_3)_2\text{TeCl}_2$.—This is the second organo-inorganic compound of tellurium selected for investigation. The following table gives the various values of the susceptibilities calculated in the same manner as in the case of $(\text{CH}_3)_2\text{TeCl}_2$.

TABLE VIII

	χ calculated using CH_3 values from CH_3OH $- \chi \times 10^6$	χ calculated using CH_3 values from CH_3Br $- \chi \times 10^6$	χ calculated using CH_3 values from CH_3I $- \chi \times 10^6$	χ calculated using CH_3 values from CH_3Cl $- \chi \times 10^6$
$(\chi_a)_1$	0.4737	0.4443	0.4336	0.4186
$(\chi_m)_1$	108.17	101.45	99.95	95.61
$(\chi_a)_2$	0.4403	0.4111	0.4005	0.3855
$(\chi_m)_2$	100.60	93.93	91.48	88.04
$(\chi_a)_3$	0.4729	0.4434	0.4330	0.4179
$(\chi_m)_3$	108.03	101.32	98.91	95.47
$(\chi_a)_4$	0.4403	0.4104	0.3999	0.3849
$(\chi_m)_4$	100.46	93.74	91.34	87.90
$(\chi_a)_E$	0.4047
$(\chi_m)_E$	92.43
$(\chi_a)_{E1}$	0.42
$(\chi_m)_{E1}$	95.92
$(\chi_a)_{O1}$	0.47	
$(\chi_m)_{O1}$	107.40	

O_1 Refers to the values calculated by Bhatnagar and Lahiri (*loc. cit.*).

E_1 Refers to their experimental values.

It is seen here also that if Slater's and Angus's values for Te^{+++} are employed, the only calculated values which approach the experimental ones are those in which the value for CH_3 obtained from CH_3Cl is used. The calculated value is widely different if the value for CH_3 obtained from CH_3I is employed. The experimental value of Bhatnagar and Lahiri is almost the same as that obtained by the author and their calculated value agrees with that given in column 1 of the above table. This is higher than the experimental value. This shows that for good agreement between the calculated and observed values the choice of the other radicals must be made from substances of similar nature.

Conclusion

All the results for the correct constitution have been summarised in Table IX.

TABLE IX

Compound	Constitution	$-\chi \times 10^6$ observed by the author	$-\chi \times 10^6$ observed by other authors	$-\chi \times 10^6$ calculated by Slater's method	$-\chi \times 10^6$ calculated by the modification of Slater's method	$-\chi \times 10^6$ calculated by Angus's method	$-\chi \times 10^6$ calculated by the modification of Angus's method
H_2TeO_3	$\text{O} \begin{array}{c} \text{Te} \\ \diagup \quad \diagdown \\ \text{O} \quad \text{OH} \\ \diagdown \quad \diagup \\ \text{O} \end{array} \text{H}$	$(\chi_a) 0.1966$ $(\chi_m) 34.89$	$(\chi_a) 0.24$ $(\chi_m) 42.60$ (Int. Crit. Tab.)	$(\chi_a) 0.19$ $(\chi_m) 33.72$	$(\chi_a) 0.1978$ $(\chi_m) 35.12$	$(\chi_a) 0.1852$ $(\chi_m) 32.88$	$(\chi_a) 0.1972$ $(\chi_m) 35.00$
TeCl_2	$\text{Te} \begin{array}{c} \text{Cl} \\ \diagup \quad \diagdown \\ \text{Cl} \end{array}$	$(\chi_a) 0.4760$ $(\chi_m) 94.45$					
TeBr_2	$\text{Te} \begin{array}{c} \text{Br} \\ \diagup \quad \diagdown \\ \text{Br} \end{array}$	$(\chi_a) 0.3701$ $(\chi_m) 106.2$					
H_2TeO_4 , $2\text{H}_2\text{O}$	$\text{O} \begin{array}{c} \text{Te} \quad \text{OH} \\ \diagup \quad \diagdown \\ \text{O} \quad \text{OH} \\ \diagdown \quad \diagup \\ \text{O} \quad \text{O} \end{array} \text{O}_2$	$(\chi_a) 0.2508$ $(\chi_m) 57.55$	$(\chi_a) 0.43$ $(\chi_m) 98.69$ (Int. Crit. Tab.)	$(\chi_a) 0.4121$ $(\chi_m) 118.43$	$(\chi_a) 0.3515$ $(\chi_m) 101.08$	$(\chi_a) 0.4117$ $(\chi_m) 118.30$	$(\chi_a) 0.3804$ $(\chi_m) 109.30$
$(\text{CH}_3)_2\text{TeI}_2$	$\text{CH}_3 \begin{array}{c} \text{Te} \quad \text{I} \\ \diagup \quad \diagdown \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$	$(\chi_a) 0.2508$ $(\chi_m) 57.55$		$(\chi_a) 0.2855$ $(\chi_m) 65.53$	$(\chi_a) 0.2757$ $(\chi_m) 63.29$	$(\chi_a) 0.2850$ $(\chi_m) 65.41$	$(\chi_a) 0.2751$ $(\chi_m) 63.15$
$(\text{CH}_3)_2\text{TeCl}_2$	$\text{CH}_3 \begin{array}{c} \text{Te} \quad \text{Cl} \\ \diagup \quad \diagdown \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$			$(\chi_a) 0.2747$ $(\chi_m) 63.05$	$(\chi_a) 0.2561$ $(\chi_m) 60.81$	$(\chi_a) 0.2743$ $(\chi_m) 62.93$	$(\chi_a) 0.2643$ $(\chi_m) 60.67$

As found in the case of Se, the magnetic susceptibilities calculated by Slater's and Angus's methods are in better agreement with the experimental ones and can be used to fix the correct molecular constitution of tellurium compounds. It may be remarked here that in the case of organometallic compounds there is a better agreement between the calculated and experimental values than in the case of inorganic compounds. This finding is in agreement with the view put forward by Pascal and other workers.

The author takes this opportunity of thanking Dr. Mata Parasad, D.Sc., F.I.C., for his suggestion of the work and guidance throughout. He is thankful also to Professor S. S. Bhatnagar, O.B.E., D.Sc., for helpful criticisms.