Mössbauer and Other Data on the Oxides and Oxyanions of Tellurium

By N. E. Erickson and A. G. Maddock,*† Brookhaven National Laboratory, Upton, Long Island, New York, U.S.A.

Mössbauer parameters and i.r. data are reported for α - and β -TeO₃, TeO₂, cubic and monoclinic Te(OH)₆, Na₂TeO₄, Na₂TeO₃, and Na₂H₄TeO₆. Both the X-ray powder patterns diagrams and the i.r. absorption spectrum exclude a tetrahedral TeO₄ in Na₂TeO₄.

BEFORE studying the effects of radiative thermal neutron capture in tellurates by Mössbauer spectroscopy it was necessary to obtain data on the Mössbauer spectra of the oxides and oxyanions of tellurium. These compounds are much less well characterised than might be expected.¹ Detailed X-ray structures or even i.r. spectra are only available for a few of the compounds and both their identity and chemical structure are in many cases doubtful.

EXPERIMENTAL

 TeO_2 .—Tellurium dioxide (AnalaR) was resublimed to give the tetragonal form. The X-ray powder diagram and m.p. agreed with the published values.²

 $Na_2TeO_3, 5H_2O$ and Na_2TeO_3 .—Hydrated sodium tellurite was recrystallised after the addition of the calculated quantity of sodium hydroxide to a weighed amount of tellurium dioxide. The hydrate was dehydrated at 180° in a stream of dry nitrogen for 8 hr. (Weight loss 29.12%; calc. for $Na_2TeO_3, 5H_2O \rightarrow Na_2TeO_3, 28.92\%$).

 $Te(OH)_{6}$.—(a) Monoclinic form. Telluric acid (AnalaR) telluric acid was recrystallised from 1*m*-nitric acid. Although well formed crystals were obtained, they always proved to be twins when examined by X-ray diffraction. The absence of the cubic form was proved by examination of the crystals in polarised light with a microscope.

(b) *Cubic form.* The material from (a) was recrystallised from 10M-nitric acid. Occasionally small octahedra were obtained. Neither temperature of crystallisation, degree of supersaturation, nor nitric acid concentration could be changed to give conditions for reproducible formation of the cubic modification. Examination of the best crystals under polarised light showed that they contained a few percent of the monoclinic form.

Na₂H₄TeO₆.—The dihydrate was prepared by the addi-

† Present address: The Chemical Laboratories, Lensfield Road, Cambridge CB2 1EW.

¹ W. A. Dutton and W. C. Cooper, *Chem. Rev.*, 1966, 66, 657. ² (a) ASTM X-ray Powder File card 11-693; (b) J. R. Soulen, P. Sthapitamonda, and J. L. Margrave, *J. Phys. Chem.*, 1955, 59, 132. tion of an excess of sodium hydroxide to a solution of telluric acid. The product was washed with hot water and dried in the air. The anhydrous salt was prepared by dehydration *in vacuo* at 50°. (Weight loss 11.6%; calc. for Na₂H₄TeO₆, 2H₂O \rightarrow Na₂H₄TeO₆, 11.7%).

Na₂TeO₄.—Hydrated sodium orthotellurate was heated for 24 hr. at 300° in a stream of dry nitrogen (Weight loss 13.25%; calc. for Na₂H₄TeO₆,2H₂O \rightarrow Na₂TeO₄ 13.15%).

TeO₃.—(a) Orange form. Orthotelluric acid was heated for 24 hr. at 300° in a stream of dry oxygen (Weight loss 23.7; calc. for Te(OH)₆ \rightarrow TeO₃, 23.55%) (Found: Te 72.6; calc. for TeO₃ 72.65%).

(b) Grey-black β -form. This oxide was prepared according to the method of Montignie.³ The grey-black material from treatment with sodium hydroxide was difficult to free from sodium orthotellurate. Even after repeated washing of the product with hot water, examination under a microscope showed that it contained a few per cent of the sodium salt. 2 g. of Te(OH)₆ yielded only *ca*. 100 mg. of β -TeO₃ (Found: Te 72.5%).

Mössbauer Spectra.---The spectra were measured on a constant-acceleration spectrometer. The drive system was similar to that described by Kistner,⁴ but was used in the constant-acceleration mode. All measurements were made with both source and absorber at liquid nitrogen temperature. The detector was a xenon-filled proportional counter, and the single-channel analyser, selecting the output from the counter, was set to accept the 6.0 Kev escape peak produced by the 35.5 Kev Mössbauer γ -ray from the ^{125m}Te. The source was a ^{125m}Te/Pt source prepared by electrodeposition of the carrier-free ^{125m}Te on a platinum foil. After deposition the foil was heated in vacuo to ca. 250° for 30 min. A rough estimate of the recoil-free fraction for such a source gave a value of 0.30 ± 0.03 , assuming the published value of f for ZnTe. The primary data were evaluated with a modified version of the program developed by Stone.⁵ The new program allows for any curvature of the base line.

³ E. Montignie, Z. anorg. Chem., 1943, 252, 111.

⁴ O. C. Kistner in 'Mössbauer Effect Methodology,' vol. 3, ed. I. J. Gruverman, Plenum Press, New York, 1967, p. 217.

⁵ G. M. Bancroft, A. G. Maddock, K. Ong, R. H. Prince, and A. J. Stone, *J. Chem. Soc.* (*A*), 1967, 1966.

J. Chem. Soc. (A), 1970

I.r. Spectra.—Preliminary measurements were made on an Infracord spectrometer. Final measurements were made with potassium bromide discs and Nujol mulls with a Perkin-Elmer 457 spectrometer. No important differences between the two sets of measurement were observed. However, measurements on the orthotelluric acidpotassium bromide discs had to be made quickly since, although not reacting appreciably on compression or on storage at room temperature, the heating of the discs by the i.r. beam induced a reaction between the potassium bromide and the telluric acid.

X-Ray Diffraction.—Powder photographs were recorded with a Phillip type 42270/0 diffractometer.

RESULTS AND DISCUSSION

(a) X-Ray Diffraction Data.—Analysis of the powder data for the cubic orthotelluric acid confirms that it

with it being isostructural with Na₂SO₄. (b) I.r. Data.—The results are collected in Tables 1 and 2, together with published data.

both cubic and monoclinic materials, reflecting the

Kraus ⁸ allocation to space group C_{2b}^{5} and a best fit to our data gave cell constants $a = 5.52 \pm 0.04$, $b = 9.26 \pm$

0.10, $c = 9.77 \pm 0.04$, and $\beta = 104.0 \pm 0.5^{\circ}$. These

values are in reasonable agreement with those given in

ref. 8. Our data were not compatible with the cell

constants on the ASTM Powder File (Card I-0329).

The orange form of TeO_3 is amorphous, but the grey-

black form gave an X-ray diffraction pattern in reason-

able agreement with that reported by Breusov et al.9 The powder diagram of Na₂TeO₄ was not compatible

The monoclinic powder data confirmed Gossner and

difficulty of obtaining pure cubic orthotelluric acid.

		ī	I.r. spectra of Te ^I	v compounds		
	TeO_2		Na	12TeO3	Na2TeO3,5H2O This work 354	Na ₂ TeO ₃ (solution Raman data) Ref. 13 364
This work 334	Ref. 10	Ref. 11	This work 354	Ref. 12 (Raman data)		
6338h 652br,st 700sh 772	648 714 760	660br,st 780	$\left. \begin{array}{c} 660 \\ 705 \end{array} ight\} \mathrm{st,br,p}$	658 700	$\left. egin{smallmatrix} 635 \ 705 \end{smallmatrix} ight\} { m st,br,p} \ 1120 \end{array}$	703 758

TABLE 1

In Tables 1 and 2, sh = shoulder, br = broad, st = strong, p = poorly resolved, and v = very.

			I.r. spect	ra of Te ^{vi} co	mpounds			
TeO3		Te(OH)6			$\rm Na_2H_4TeO_6$		KTAO (OH)	No ToO
α	β	Cubic	Mono	clinic	~~		111002(011)3	11021004
This work	This work	This work	This work	Ref. 14	This work	Ref. 14	Ref. 15	This work
			373		355st			364
	480		409	411	429sh	429		507
			603 sh	$605 \mathrm{sh}$	536	536		543
$620 \mathrm{sh}$	640		645 v. br	650 sh, st	582st	587st		582st
680v.br,st		660br,st	660st,p	658st	0.501			$622 { m sh}$
			-04	675sh,st	672br,st	675st	= 2 0 1	
	700		704	708 720-1	772 br of	700h4	720br	760br,st
1000 11005	798	1000	1190	13050	113V.DF,St	1800F,St	790SD	885
flat	Γ ,	1008	1120	1125	114201	1141	1035	
nac		1168	1180sh	1190sh	1210sh	1200sh	1095	
		1100	1218	1222		1650	1165	1440br
			2180	$2200 \mathrm{sh}$				
2280			2280sh	2280	2270	2270	2270	
		2320	2280	2370		2475		
		3200v.br,st	3150v.br,st	3100br,st	3100v.br,st	3110br,st		

TABLE 2

belongs to the space group Fd 3c, as originally proposed by Kirkpatrick and Pauling.⁶ A least-squares fit to our data gave a cell constant of 15.66 ± 0.01 Å in close agreement with Passerini and Rolliers 7 value, 15.68 \pm 0.01 Å. It should be noted, however, that the data on the ASTM Powder File (Card I-0329) contain lines from

⁶ L. M. Kirkpatrick and L. Pauling, Z. Krist., 1926, 63, 502. ⁷ L. Passerini and M. A. Rollier, Atti Accad. naz. Lincei, Rend. Classe Sci. fis. mat. nat., 1935, 21, 364.

⁸ B. Gossner and O. Kraus, Z. Krist., 1934, 88, 298.
⁹ (a) O. N. Breusov, O. I. Vorob'eva, N. A. Druz', T. V. Revzina, and B. P. Sobolev, *Izvest. Akad. Nauk. S.S.S.R. Inorganic Materials* (translation), 1966, 2, 264; (b) J. Rosicky, J. Loub and J. Boylo, Z. gauge Cham. 1065, 2924. Loub and J. Pavel, Z. anorg. Chem., 1965, 334, 312.

(c) Mössbauer Data.-The Mössbauer parameters obtained from the spectra are collected in Table 3.

The X-ray diffraction data clearly distinguish the metastable cubic from the stable monoclinic variety of Te(OH)₆. The latter form is presumably more strongly

¹⁰ V. P. Cheremisinov and V. P. Zlomanov, Optika i Spektro-skopiya, 1963, 12, 208.
 ¹¹ J. Lamb, Z. Chem., 1966, 6, 425.
 ¹² Ya. S. Bobovic and A. K. Yakhkino, Zhur strukt. Khim.,

1963, **4**, 924.

13 H. Siebert, Z. anorg. Chem., 1955, 275, 225.

 ¹⁴ H. Siebert, Z. anorg. Chem., 1959, **301**, 161.
 ¹⁵ (a) P. Lammers and J. Zemann, Z. anorg. Chem., 1965, **334**, 225; (b) P. Lammers, Naturwiss., 1964, 51, 552.

hydrogen bonded than the cubic form, and this is supported by the i.r. data. In the spectrum of the cubic form the Te-OH stretch at 660 cm.⁻¹ shows none of the poorly resolved component bands seen in the same region of the spectrum of the monoclinic form. In addition the Te-O-H distortion modes appear at a higher frequency for the monoclinic form (1120, 1180, and 1218 $cm.^{-1}$) than for the cubic form (1068 and 1168 $cm.^{-1}$) because of the stronger Te-O-H \cdots O-Te hydrogen bonding. The i.r. spectrum suggests essentially O_h symmetry about the Te in the cubic form. The close parallel between the i.r. spectra of the mono-

clinic form of the acid $Te(OH)_6$ and the salt $Na_2H_4TeO_6$

Na₂TeO₃ seem to contain the simple nonplanar TeO₃²⁻ anion. All samples of orange TeO3 showed evidence of Te-OH bonding in the i.r. spectrum. Decomposition of $Te(OH)_6$ in dry oxygen at various temperatures, and other attempts to prepare orange TeO₃ free from both Te^{IV} and combined water were unsuccessful. This result is in substantial agreement with those of Breusov et al.⁹ No evidence was found for any oxide derived from Te^{v.9b}

The spectrum of the grey-black form was simpler and the lines sharper. The Te-O stretching frequency appeared at a rather high frequency, 798 cm.⁻¹. The data would be compatible with an ReO₃-like structure.

	TABLE 3			
Mössbauer pa	rameters. Centre shif	fts relative to P	$t/^{125m}{ m Te}$	
Centre shift δ (mm./sec.)	Quadrupole splitting Δ	ψ^2 /degrees of freedom	$\Gamma/\Gamma_{\rm nat.}$	Absorption at peak [uncorrected (%)]
${}^{+0.48\pm0.02}_{-0.08\pm0.07}$	${}^{6\cdot63}_{5\cdot94} {}^{\pm}_{\pm} {}^{0\cdot06}_{0\cdot07}$	392/367 374/360	1·10, 1·19 1·14, 1·03	9·1, 9·3 5·2, 5·6
$-1.26 \pm 0.02 \\ -1.37 \pm 0.02$	0	462/369 465/369	$1.34 \\ 1.27$	5·3 6·4
-1.44 ± 0.05 -1.44 ± 0.02	0 0	435/369 407/374 409/262	$1 \cdot 12 \\ 1 \cdot 40 \\ 1 \cdot 40$	4·7 13·1
-1.33 ± 0.02 as x% TeO ₂ + 0.02	(100 - x) % TeO ₃	498/303	1.49	8.3
$-1.42 \pm 0.05 + 0.48$	0 6-63	375/364		
	Mössbauer pa Centre shift δ (mm./sec.) $+0.48 \pm 0.02$ -0.08 ± 0.07 -1.26 ± 0.02 -1.37 ± 0.02 -1.44 ± 0.05 -1.44 ± 0.02 -1.33 ± 0.02 as $x\%$ TeO ₂ + -1.42 ± 0.05 +0.48	TABLE 3 Mössbauer parameters. Centre shift Quadrupole splitting δ (mm./sec.) Δ $+0.48 \pm 0.02$ 6.63 ± 0.06 -0.08 ± 0.07 5.94 ± 0.07 -1.26 ± 0.02 0 -1.44 ± 0.02 0 -1.44 ± 0.02 0 -1.33 ± 0.02 0 -1.33 ± 0.02 0 -1.42 ± 0.05 0 -1.42 ± 0.05 0 $+0.48$ 6.63	TABLE 3Mössbauer parameters. Centre shifts relative to PCentre shiftQuadrupole splitting $\psi^2/degrees$ δ (mm./sec.) Δ of freedom $+0.48 \pm 0.02$ 6.63 ± 0.06 $392/367$ -0.08 ± 0.07 5.94 ± 0.07 $374/360$ -1.26 ± 0.02 0 $462/369$ -1.37 ± 0.02 0 $465/369$ -1.44 ± 0.05 0 $435/369$ -1.44 ± 0.02 0 $407/374$ -1.33 ± 0.02 0 $498/363$ as $x\%$ TeO ₂ + (100 - x) % TeO ₃ -1.42 ± 0.05 -1.42 ± 0.05 0 $375/364$ $+0.48$ 6.63	TABLE 3Mössbauer parameters. Centre shifts relative to $Pt/^{125m}Te$ Centre shift Quadrupole splitting $\psi^2/degrees$ δ (mm./sec.) Δ of freedom $\Gamma/\Gamma_{nat.}$ $+0.48 \pm 0.02$ 6.63 ± 0.06 $392/367$ $1.10, 1.19$ -0.08 ± 0.07 5.94 ± 0.07 $374/360$ $1.14, 1.03$ -1.26 ± 0.02 0 $462/369$ 1.34 -1.37 ± 0.02 0 $465/369$ 1.27 -1.44 ± 0.05 0 $435/369$ 1.12 -1.44 ± 0.02 0 $407/374$ 1.40 -1.33 ± 0.02 0 $498/363$ 1.48 as $x\%$ TeO ₂ + ($100 - x$) % TeO ₃ -1.42 ± 0.05 0 $375/364$ $+0.48$ 6.63 -1.42 ± 0.05 0 $375/364$

confirm Siebert's ¹⁴ conclusion that the tellurium atom in the salt is six-co-ordinate. Ignoring the discredited earlier report that K₂TeO₄ is isostructural with K₂SO₄,¹⁶ the only evidence for a four-co-ordinate tellurate is the X-ray diffraction data of Patry,¹⁷ which also indicated similar structures for these two salts. Recently, however, detailed X-ray structures have shown that KTeO-(OH)₅,¹⁸ KTeO₂(OH)₃,^{15a} and KTeO₃OH ^{15b} all contain TeO₆ octahedra, the first salt containing a long-chain anion in which each octahedron shares two opposite corners, whereas in the last salt two edges are shared and the remaining edge forms hydrogen bonds to the adjacent anion chain. The Te₂O₆(OH)₄⁴⁻ anion has also been shown to have two six-co-ordinate tellurium atoms with a shared octahedral edge.¹⁹ The tellurium is also in octahedral co-ordination in Hg3TeO6²⁰ and in a series of perovskite-like compounds of formulae A2XTeO6.21

The i.r. data on the salt Na₂TeO₄ exclude a tetrahedral TeO_4^{2-} anion. The rather sharp absorption at 885 cm.⁻¹, the highest Te-O stretch frequency found in these spectra, suggests a linear polymeric anion,²² which may be composed of TeO₆ octahedra each sharing two edges and with the unshared oxygen atoms in cispositions on a third edge, similar to the KTeO₃OH structure.15a

On the other hand, both hydrated and anhydrous

¹⁶ A. Handl and V. von Lang, Sitzb. Akad. Wien, 1861, 43, 117; 1862, 45, 111.

- ¹⁷ M. Patry, Compt. rend., 1936, 202, 1516.
- ¹⁸ S. Raman, Inorg. Chem., 1964, 3, 634.

¹⁹ O. Lindquist and G. Lundgren, Acta Chem. Scand., 1966, 20, 2138.

The appearance of the stronger bands of $Na_2H_4TeO_6$ in the spectrum has been ignored, however, because of known contamination by this salt. This may mean that some genuine absorptions have been overlooked.

The Mössbauer spectra were very encouraging. Notwithstanding the large natural line-width $(2\Gamma_{\text{nat.}} =$ 5.32 mm./sec.), spectra of pure compounds can be analysed to yield the usual parameters with satisfactory limits to the probable errors. The magnitude of the effect is comparable with that for iron, and isotopic enrichment of the absorber would only be necessary in especially unfavourable cases. The $Pt/^{125m}Te$ source seems superior to previously reported sources.

A comparison of our data with other published data and some results kindly communicated to us by Gibbs, Greatrex, and Greenwood,²³ is most easily made by recalculating all the data to refer to tetragonal TeO₂, $\delta = 0$, as the standard. This is indeed perhaps the most readily obtainable, pure, well-characterised tellurium compound and it gives a very satisfactory absorption. The comparison is shown in Table 4. It will be observed that the TeO₂ standard leads to better agreement between results from different laboratories than the commonly chosen ZnTe and Cu/¹²⁵I. Special care may be necessary to obtain either or both these systems with a reproducible centre shift.

The spectrum of orange TeO₃ was especially interesting.

- ²⁰ M. T. Falqui, Ricerca Sci., 1963, A3, 627.

- ²¹ U.S.P. 3,309,168 and 3,309,169.
 ²² (a) W. P. Griffith and T. D. Wickins, J. Chem. Soc. (A), 1968, 400; (b) W. P. Griffith, *ibid.*, 1969, 211.
 ²³ T. C. Gibbs, R. Greatrex, N. N. Greenwood, and A. C. Sarma, J. Chem. Soc. (A), 1970, 212.



J. Chem. Soc. (A), 1970

Analysis in terms of a single-line Te^{VI} spectrum gave a very large ψ^2 . Considering our own observations and those of Breusor *et al.*⁹ that it contains Te^{IV} , the spectrum was re-computed assuming that it was due to a mixture of Te^{IV} and Te^{VI} compounds. An acceptable value for ψ^2 was then obtained and the results suggested that the material contained $17 \pm 5\%$ of Te^{IV} . It may be noted that Jung and Triftshäuser's specimen of orange TeO_3 gave an obvious quadrupole splitting and must have contained even more Te^{IV} .

The change in centre shift with oxidation state and environment of the tellurium is fortunately substantial. Even hydration or change of cation often produces a measurable change in δ .^{23,24}

The data, though consistent with a positive value for $\Delta r/r$, are not really sufficient at present for a reliable estimate of the magnitude of $\Delta r/r$.

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²⁴ P. Jung and W. Triftshäuser, Phys. Rev., 1968, 175, 512.
²⁵ (a) M. L. Unland, J. Chem. Phys., 1968, 49, 4514; (b) A. B. Buyrn and L. Grodzins, Bull. Amer. Phys. Soc., 1963, 8, 43.
²⁶ C. E. Violet and R. Booth, Phys. Rev., 1966, 144, 225.