CCCLXXXIX.—*Studies of Valency. Part XIV. An Optically Active Telluronium Salt: Phenyl*-p-*tolylmethyltelluronium Iodide.*

By Thomas Martin Lowry and Frank Lathe Gilbert.

The planar formula assigned by Vernon to the dimethyltelluronium di-iodides was first criticised by us on the ground that " the striking difference in colour of the α- and β-dihalides must include some factor which is not expressed completely by merely putting two halogen atoms and two alkyl radicals at adjacent or at opposite corners of a square " (J., 1928, 308). A more serious cause for criticism arose when we found that the cyclic compounds of Morgan and Burgess have the properties of the α-compounds of the dimethyl series, to which Vernon had assigned a *trans*-structure. When, therefore, Drew's discoveries shattered the foundation on which the planar formulæ had been based, our own experiments had already led us to the conclusion that quadrivalent tellurium, like quadrivalent sulphur and selenium, must be represented by a tetrahedral model and not by a square (*Chem. and Ind.*, 1928, **47**, 1246). This conclusion has now been established by positive evidence afforded by the preparation of a quadrivalent derivative of tellurium in an optically active form.

The present research was a direct continuation of work started by Lederer under the significant title "Versuch zur Darstellung optisch-aktiver Tellurverbindungen" (*Ber.*, 1916, **49**, 1615), but not pursued further, either by Lederer or by any other worker, perhaps because Vernon's discovery of the α- and β-telluronium salts was accepted almost universally as conclusive evidence of a planar configuration. When, however, we had found good reasons for doubting this configuration, two lines of experiment were started, one of which was expected to give optically active products if the planar formula were valid, whilst the other depended for a positive result upon the validity of the tetrahedral configuration. For the former experiment it was proposed to condense tellurium with the compounds $CH_3{\cdot}CH(CH_2Br)_2$ and $C_2H_5O{\cdot}CO{\cdot}CH(CH_2{\cdot}CH_2Br)_2$, but the work was stopped before the final stage was reached. For the latter experiment, it was only necessary to obtain evidence of optical activity in one or more of the compounds of which Lederer had established the composition and properties 13 years previously. With the exception of the sulphonates, therefore, all the organic tellurium compounds used in the present research had already been prepared and analysed by Lederer.

The first compound selected was phenyl-*p*-tolylmethyltelluronium iodide,* of which better yields were obtained than in the case of the *o*-tolyl salt (*Ber.*, 1920, **53**, 1680); this was converted, with the help of the corresponding silver salts, first into a *bromocamphor-π-sulphonate*, and then into a *camphor-β-sulphonate*, from which optically active iodides of opposite sign were prepared as described below. For this purpose it was not necessary to isolate the sulphonates in an analytically pure form, since they were only used as intermediaries in the resolution of the iodides. Their composition (as well as that of the iodide and silver salt) was checked, however, by collecting and weighing the precipitated silver iodide, and was afterwards established by analysis of crystallised samples of the bromocamphorsulphonate. Since a knowledge of the composition of the sulphonates was required in the first instance only in order to convert the observed rotations into molecular rotations, with a view to deducing a value for the "mole-

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* Experiments have also been made to resolve the telluroxide, $(C_7H_7)(C_6H_5)TeO$, which Lederer described in the same paper, but these have not yet (Dec. 12th, 1929) reached a stage at which a definite resolution of the oxide can be claimed.—T. M. L.

cular rotation" of the kation, a direct determination of the ratio of acid to base, by precipitation of the base with an excess of sodium hydroxide and titration of the excess with dilute hydrochloric acid (compare Harrison, Kenyon, and Phillips, J., 1926, 2088; Gaythwaite, Kenyon, and Phillips, J., 1928, 2284), was preferred to an analysis by combustion.

The trouble incurred in obtaining crystalline specimens of the bromocamphorsulphonate was fully justified when it was found to undergo a mutarotation, from which the behaviour of the optically active iodide could be foreseen in considerable detail. In particular, whilst the molecular rotation of the optically unstable solutions of the bromocamphorsulphonate varied from $[M]^{18°}_{5461}$ + 262° to + 316°, this initial rotation was always *less* than that of the bromocamphorsulphonic acid, for which $[M]^{18°}_{546}$ + 347°, but *rose* to this value, usually in the course of a few minutes after preparation of the solution. It was therefore clear (i) that the freshly prepared solutions contained a lævorotatory kation, (ii) that the molecular rotation of this kation was probably not less than about 85°, (iii) that the kation lost its optical activity very quickly in solution, presumably as a result of rapid racemisation. It was thus certain that the resolution of the iodide could only be detected by getting it into solution, and observing its rotatory power, as quickly as possible after it had been precipitated from the bromocamphorsulphonate, and that evidence of optical activity must be looked for in a rapid mutarotation of the freshly prepared solution. For this reason, any attempt to recrystallise the precipitated iodide would have been futile, except under conditions of Bakerian purity, which were obviously beyond our scope; and for the same reason, instead of analysing the imperfectly purified precipitate, we established the identity of the optically active salt by the more satisfactory process of recovering Lederer's inactive iodide from the solution, and using it again for repeated experiments on similar lines. This recovery of the iodide, which was accompanied by no very serious loss of material, also proved that the *increase* of rotatory power of the sulphonate, and the *decrease* of rotatory power which we observed in the iodide, were mainly due to racemisation. Our theoretical deductions would, however, have been precisely similar if the active iodide had in fact decomposed (as Lederer's inactive iodide did under some conditions) into phenyl tolyl telluride and methyl iodide, since this reversible decomposition provides the most probable mechanism for the racemisation of the salt.

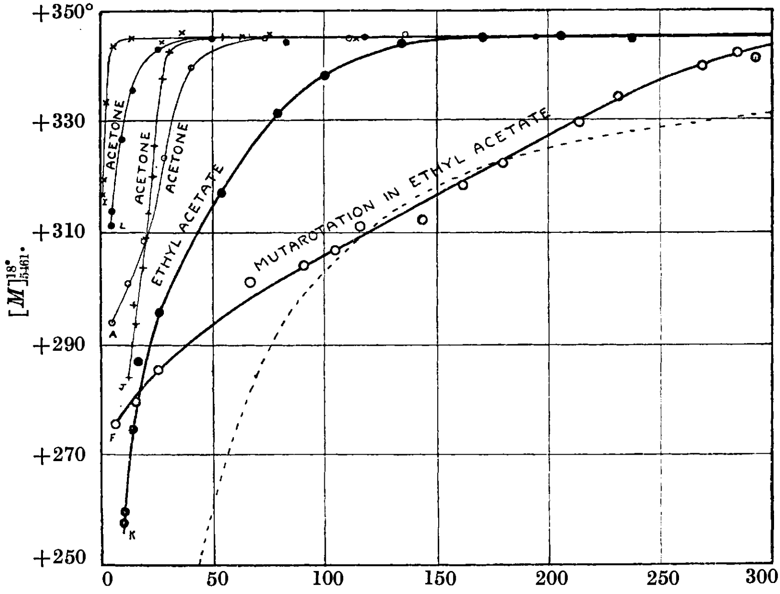
As soon as it became clear, from the first observations of mutarotation, that the optically active telluronium ion was unstable, with a half-life period of some minutes only, the later experiments were modelled on the precedents already established for this type of phenomenon by Pope and Peachey (P., 1900, **16**, 42, 116), and more recently by Mills and Gotts (J., 1926, 3121), whose methods of working we have followed closely. In particular, instead of separating *two* isomeric sulphonates, *d*A*d*B and *d*A*l*B, of widely different rotatory power, it was only necessary to attempt to prepare *one* sulphonate, *viz.*, the less soluble of these two salts, in a state of normal purity but as free as possible from the dynamically isomeric salt. Of the two bromocamphor-π-sulphonates, the *d*A*l*B compound was the less soluble, but in the case of the camphor-β-sulphonate the stable solid phase was the *d*A*d*B compound, since it gave solutions of higher molecular rotation than the parent acid. The latter salt was more stable in solution than the former, so that it was possible to measure its rotatory power for several wave-lengths (Fig. 4); but, since it was never isolated in a crystalline form, no great stress can be laid on any measurements of its physical properties.

The iodide precipitated from the dextrorotatory bromocamphorsulphonate was (as expected) lævorotatory, and its molecular rotatory power was of similar magnitude to that deduced from the range of mutarotation of the sulphonate; but, since we had already found the sulphonates to be more stable than the iodides, we were not surprised to find (i) that the mutarotation of the optically active iodides was even more rapid than that of the sulphonates, (ii) that the range of observed mutarotation was therefore smaller, covering a maximum range of 70° as compared with 85° in the bromocamphorsulphonate. The observations on the iodide were also rendered more difficult by the fact that it was stained, apparently with a periodide, since the colour could not be removed by washing with chloroform; this made it necessary to work either with more dilute solutions, or with shorter columns. Although, however, the observed rotations ($-0{\cdot}25^\circ \longrightarrow 0^\circ$) were smaller than in the case of the bromocamphorsulphonate ($+2{\cdot}2^\circ \longrightarrow 2{\cdot}9^\circ$) and the factor required to convert them into molecular rotations was very large (*viz.*, 150—300), the validity of the observations can be judged from the smoothness (or otherwise) of the mutarotation curves. In particular, whilst we cannot lay any stress on the absolute values of the molecular rotations, our data afford the clearest possible evidence that *the mutarotation curves are not unimolecular*, as can be seen by comparison of the curves for the bromocamphorsulphonate with the dotted theoretical curve of Fig. 1, since the middle section is nearly straight, and in one case at least could have been drawn with a reversal of curvature, of a kind which is normal for certain types of consecutive reactions, and has been observed experimentally in camphorcarboxyamide and in camphorcarboxypiperidide (Lowry and Glover, J., 1913, **103**, 913). This characteristic feature is also seen in the mutarotation curves of the iodide (Fig. 2), which do not conform even approximately to a unimolecular law.

Whilst the form of the mutarotation curves proves that the racemisation of the kation is not a simple isomeric change, $l\text{B} \rightleftharpoons d\text{B}$, we cannot claim any knowledge either of the mechanism of racemisation or of the conditions under which it operates. We cannot explain, therefore, why the mutarotation was always more rapid in acetone than in ethyl acetate, and even less why, although the mutarotation of the camphor-β-sulphonate was slower than that of the bromocamphor-π-sulphonate, the dextrorotatory iodide precipitated from it was generally inactive and only on two occasions exhibited a rapid mutarotation (from + 34° to + 4° in 8 mins. and from + 27° to + 1° in 10 mins.; see Fig. 3), which was even more fleeting than that of the enantiomorphous lævo-salt when precipitated from the bromocamphor-π-sulphonate. Similar phenomena are, however, of frequent occurrence in other cases of dynamic

FIG. 1.

Mutarotation of l-*phenyl*-p-*tolylmethyltelluronium* d-*bromocamphor-π-sulphonate.*



isomerism, and the conditions for investigating them in the tellurium series are far too unfavourable to lead us to undertake the task.

Although the facile mutarotation of the iodide prevented us from effecting a quantitative resolution, it had a definite advantage in enabling us to distinguish sharply between the optical rotation of the telluronium kation, which was only transient in character, and that of the sulphonate anion, which is completely stable under the conditions of our experiments. Thus, the data shown in Fig. 2, where the final rotations were always positive, enable us to state at once that the observed (negative) molecular rotations of the iodide must be *increased* by 2° in order to allow for the opposite rotation of traces of the bromocamphorsulphonate which were not removed by washing, and can be shown to have amounted to about 1% of the weight of the precipitate. In the same way, we can state that in the case of the dextrorotatory iodide the observed

FIG. 2.

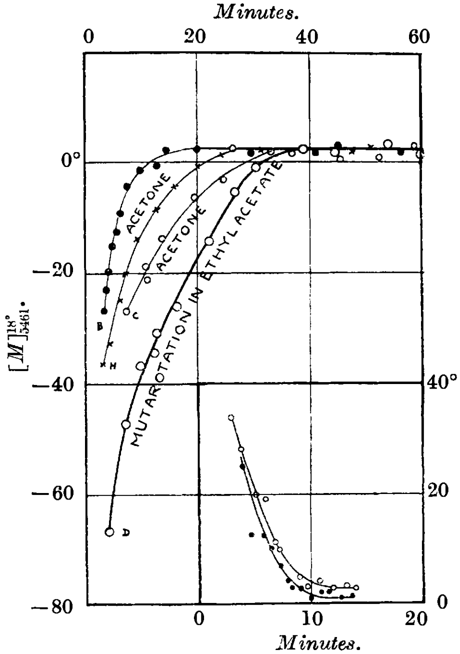


FIG. 3.

Fig. 2.—*Mutarotation of* l-*phenyl*-p-*tolylmethyltelluronium iodide* (*from* d-*bromocamphor*-π-*sulphonate*).

Fig. 3.—*Mutarotation of* d-*phenyl*-p-*tolylmethyltelluronium iodide* (*from* d-*camphor*-β-*sulphonate*).

molecular rotations of the kation must be *decreased* by 4° out of 34° and 1° out of 27°, in order to allow for contamination with unchanged camphorsulphonate, so that the molecular rotation due to the kation was + 30° and + 26°, respectively, when the first readings were taken. Although, therefore, we cannot assign a numerical value to the molecular rotation of the kation $[TePhMe{\cdot}C_7H_7]^+$, which is probably >85°, the optical activity of this radical, and therewith its tetrahedral configuration, appears to be established by evidence which in the case of other elements has been accepted as conclusive proof of molecular dissymmetry.

EXPERIMENTAL.

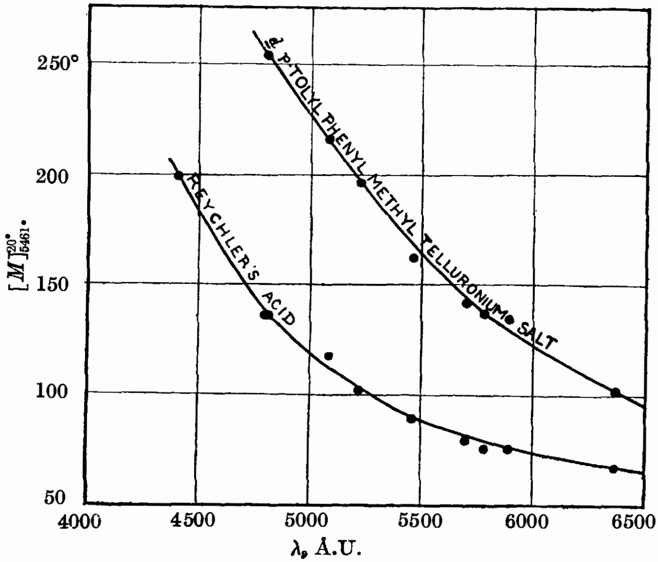
Preparation of l-*Phenyl*-p-*tolylmethyltelluronium* d-*Bromocamphor-π-sulphonate.*—Theoretical quantities of silver *d*-bromocamphor-π-sulphonate and phenyl-*p*-tolylmethyltelluronium iodide, m. p. 73—74°, were mixed in dry acetone, vigorously stirred, kept for 1 hour, and the silver iodide was removed by filtration. The colourless filtrate was evaporated to a syrup on the water-bath and placed in a vacuum desiccator; the *bromocamphorsulphonate* frothed extensively and was transformed into a solid foam. This was dissolved in the minimum quantity of a 50% mixture of acetone and ethyl acetate, and on the addition of dry ether, star-shaped clusters of colourless crystals were obtained, m. p. 180—181°. These crystals lost their shape, however, and became sticky, after evaporation of the ether and exposure to air (Found, by titration: $C_{10}H_{15}O_4BrS$, 51·1. $C_{24}H_{29}O_4BrSTe$ requires $C_{10}H_{15}O_4BrS$, 50·2%).

Mutarotation of the d-*Bromocamphor-π-sulphonate.*—The bromocamphorsulphonate was dissolved in acetone and examined in a 2-dm. polarimeter tube at 18°. Four minutes after the solvent was added, the solution showed an initial rotation $[M]_{5461}^{18^\circ}$ + 294°, rising to a steady value $[M]_{5461}^{18^\circ}$ + 344° in 75 minutes (Fig. 1, curve A). The salt was then fractionally crystallised six or seven times, and filtered when necessary through a fine-grained filter of sintered Jena glass. The fractions were analysed by titration, but no change of composition could be detected. A solution in ethyl acetate of the most soluble portion (Fig. 1, curve F) gave $[M]_{5461}^{18^\circ}$ + 275° 8 minutes after the salt was wetted; the rotation then rose to a steady value $[M]_{5461}^{18^\circ}$ + 342—344° in 5 hours. The molecular rotation of the least soluble portion (Fig. 1, curve I) changed from + 316° to + 346° in 13 minutes. Other samples behaved similarly (see Fig. 1, curves J, K, L), but in no case was any evidence obtained of the formation of a *d*-telluronium bromocamphorsulphonate of higher rotatory power than the parent acid.

Precipitation of l-*Phenyl*-p-*tolylmethyltelluronium Iodide.*—The bromocamphorsulphonate, which is almost insoluble in water, was dissolved in a minimum quantity of acetone; a cold dilute aqueous solution of potassium iodide was added quickly, and, after stirring, a yellow precipitate was formed, which was allowed to settle, filtered, and dried quickly below 60°. The iodide is pale yellow and almost insoluble in water, whereas the bromide and chloride were too soluble to be precipitated in this way. Solutions of the *l*-iodide in acetone and ethyl acetate gave the mutarotation curves B, C, D, H (Fig. 2).

FIG. 4.

Dispersion curves of d-*phenyl*-p-*tolylmethyltelluronium* d-*camphor-β-sulphonate and of the free acid in ethyl acetate at* 20°.



The precipitated iodide melted 6° below the temperature (73—74°) recorded by Lederer. This difference might at first sight be regarded as evidence that the active iodides have a lower m. p. than the racemate; but we regard this conclusion as improbable, in view of the optical instability of the salt, which would almost certainly racemise during the operation of taking the melting point unless special precautions were taken on lines that have already been indicated (Lowry, MacConkey, and Burgess, J., 1928, 1333). We therefore prefer to attribute the lowering of m. p. to the presence of impurities in the hastily washed precipitate, and in particular of about 1% of the *d*-bromocamphorsulphonate, the presence of which can be demonstrated from the mutarotation curves.

Preparation of d-*Phenyl*-p-*tolylmethyltelluronium* d-*Camphor*-β-*sulphonate.*—Equivalent quantities of phenyltolylmethyltelluronium iodide and of the silver salt of Reychler's acid were mixed in acetone solution, and freed from silver iodide by filtration. In spite of many attempts, the *camphorsulphonate* could not be obtained in a crystalline form; when dried for a few days in a vacuum desiccator it formed a gum, and only occasionally frothed up to a solid foam like the bromocamphorsulphonate (Found, by titration: $C_{10}H_{16}O_4S$, 44·0. $C_{24}H_{30}O_4STe$ requires $C_{10}H_{16}O_4S$, 42·8%).

Solutions of the camphorsulphonate in acetone gave $[M]^{18^\circ}_{5461} = + 119^\circ, 150^\circ, 123^\circ, 138^\circ$. Mutarotation was so slow that a solution, with initial rotation $[M]^{18^\circ}_{5461} = 138^\circ$, only changed to $[M]^{18^\circ}_{5461} = 126^\circ$ in 1 week. Again, a solution having $[M]^{18^\circ}_{5461} = 123^\circ$ was heated in a sealed tube on a water-bath at 100° and showed no change of rotation in 4 hours, but a fall to 81° after 16 hours; the solid which separated on evaporation to dryness, however, gave $[M]^{18^\circ}_{5461} = 120^\circ$ again. The dispersion curves set out in Fig. 4 indicate the presence of a kation having a dextrorotation $[M]^{20^\circ}_{5461} =$ *ca.* 72°, but, as the camphorsulphonate had not been crystallised, this can only be regarded as a minimum value.

Precipitation of d-*Phenyl*-p-*tolylmethyltelluronium Iodide.*—The *d*-iodide was precipitated by adding cold aqueous potassium iodide to a solution of the *d*-camphorsulphonate in acetone. The product was a pale yellow precipitate, m. p. 70—72°, but was usually inactive. The mutarotation of two active samples is shown in Fig. 3 (inset in Fig. 2).

We are indebted to the Salters' Institute for a Fellowship to one of us (F. L. G.) during the period in which this investigation was carried out, as well as for financial assistance in the preparation of materials; we are also indebted to Dr. F. Hüther for preparing the inactive compounds which formed the starting point for the investigation.

Rotation Data for Figs. 1—4.

(*w* G. of substance in *v* c.c. of solution.)

d-*Bromocamphorsulphonate*, $M = 618$; $l = 2$; $t = 18^\circ$.

	w.	*v.*	Solvent.	α_{5461}.	$[M]/\alpha$.	$[M]_{5461}$.
(i) K	0·518	20	EtAc	$2{\cdot}19_4 \longrightarrow 2{\cdot}91_8^\circ$	119	$262 \longrightarrow 347^\circ$
(ii) A	0·325	20	$COMe_2$	$1{\cdot}55 \longrightarrow 1{\cdot}81$	190	$294 \longrightarrow 344$
(iii) F	0·611	20	EtAc	$2{\cdot}72_5 \longrightarrow 3{\cdot}40_2$*	101	$275 \longrightarrow 344$*
(iv) I	0·417	20	$COMe_2$	$2{\cdot}13_5 \longrightarrow 2{\cdot}34_6$	148	$316 \longrightarrow 346$
(v) L	0·522	20	$COMe_2$	$2{\cdot}63_0 \longrightarrow 2{\cdot}93_0$	118	$311 \longrightarrow 346$
(vi) J	0·482	20	$COMe_2$	$2{\cdot}22_0 \longrightarrow 2{\cdot}72_0$	128	$284 \longrightarrow 346$

* Mutarotation not quite complete; final value $[M]_{5461} = 346^\circ$ (300 mins.).

Rotation Data for Figs. 1—4 (contd.).

(w G. of substance in v c.c. of solution.)

l-*Iodide*, $M = 437$; $l = 2$; $t = 18°$.

	w.	v.	Solvent.	α_{5461}.	$[M]/\alpha$.	$[M]_{5461}$.
(i) D	0·105	15	EtAc	$-0{\cdot}21_5 \longrightarrow +0{\cdot}00_6$	312	$-67 \longrightarrow +2$
(ii) B	0·129	15	$COMe_2$	$-0{\cdot}10_6 \longrightarrow +0{\cdot}00_8$	254	$-27 \longrightarrow +2$
(iii) H	0·367	25	$COMe_2$	$-0{\cdot}24_8 \longrightarrow +0{\cdot}01_3$	149	$-37 \longrightarrow +2$
(iv) C	0·182	20	$COMe_2$	$-0{\cdot}11_2 \longrightarrow +0{\cdot}00_8$	240	$-27 \longrightarrow +2$

d-*Iodide*, $M = 437$; $l = 1$; $t = 18°$.

	w.	v.	Solvent.	α_{5461}.	$[M]/\alpha$.	$[M]_{5461}$.
(i)	0·211	10	EtAc	$+0{\cdot}16_4 \longrightarrow +0{\cdot}00_9$	207	$+34 \longrightarrow +4$
(ii)	0·146	10	EtAc	$+0{\cdot}09_1 \longrightarrow +0{\cdot}00_3$	299	$+27 \longrightarrow +1$

d-*Camphorsulphonate*, $M = 541$; $l = 2$; $t = 18°$.

	w.	v.	Solvent.	α_{5461}.	$[M]/\alpha$.	$[M]_{5461}$.
(i)	0·562	20	$COMe_2$	1·26 —	94·6	119 —
(ii)	1·138	20	$COMe_2$	3·14 —	48	150 —
(iii)	1·785	20	$COMe_2$	4·05 —	30·4	123 —
(iv)	1·514	20	$COMe_2$	3·85 —	35·9	138 —

Dispersion curves (Fig. 4). Solvent, EtAc; $l = 2$; $t = 20°$.

	d-*Camphorsulphonic acid*; $w = 0{\cdot}571$; $v = 20$; $[M]/\alpha = 40{\cdot}5$.			d-*Telluronium salt*; $w = 0{\cdot}622$; $v = 20$; $[M]/\alpha = 87$.		
	α.	$[\alpha]$.	$[M]$.	α.	$[\alpha]$.	$[M]$.
Zn 6362	1·67°	29·2°	68°	1·18°	19·0°	103°
Na 5893	1·87	32·8	76	1·54	24·8	134
Hg 5780	1·88	32·9	76	1·59	25·3	137
Cu 5700	1·97	34·5	80	1·63	26·2	143
Hg 5461	2·21	38·7	90	1·86	30·0	162
Cu 5219	2·53	44·1	102·5	2·25	36·2	196
Cd 5086	2·91	50·9	118	2·48	39·9	216
Zn 4810	3·35	58·6	136	2·91	46·8	253
Cd 4800	3·36	58·7	136	2·91	46·8	253
Hg 4358	4·90	85·7	199	—	—	—

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