

of an "extra-cyclic" acid that tends to accumulate in certain succulents, and so is piscidic acid, which has lately been found to make up a major part of the acids in *Agave americana* L. (Agavaceae)¹ and *Opuntia ficus-indica* L. (Cactaceae).² Succulents from the plant family Compositae, too, seem to contain interesting acids that might serve to throw light on the biology of succulent plants.

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X-Ray Crystallographic and IR Data on Some Divalent Selenium and Tellurium Compounds

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The unit cells, space groups and IR data of the following derivatives of divalent selenium and tellurium have been determined in the course of crystal structure work on analogous compounds.¹⁻³ The X-ray data were derived from single-crystal oscillation and Weissenberg photographs using CuK radiation with $\lambda = 1.5418$ Å. The calculated cell parameters are believed to be accurate within 0.5 %.

Selenium bis(diethylthioselenophosphate), $\text{Se}[\text{Et}_2\text{P}(\text{S})\text{Se}]_2$ (I). Yellow monoclinic prisms from benzene, elongated along *c*, with $a = 12.94$ Å, $b = 12.30$ Å, $c = 13.31$ Å, $\beta = 126.0^\circ$. There are four molecules per unit cell; density calc. and found 1.85 g/cm³. The space group, from systematic extinctions, is C_{2h}^6-C2/c or C_s^4-Cc . However, three of the compounds reported here, (I), (II), and (III), show the same morphology and X-ray extinctions. Further similarities are found in unit cell data and X-ray reflection patterns. The three compounds are thus isomorphous. Structure work on II and III is in progress in this laboratory. Patterson and Fourier maps of the *b* and *c* axis projections indicate that the molecules possess twofold symmetry, with the central atoms on twofold symmetry axes parallel with *b*. The two structures seem to be similar to that of tellurium bis(dimethyldithiophosphate).³ Accordingly space groups without twofold symmetry axes are not likely in any of the three isomorphous compounds I, II, and III. Thus C_{2h}^6-C2/c is the probable space group for I, as the other possible space group does not possess such an axis.

Tellurium bis(diethylthioselenophosphate), $\text{Te}[\text{Et}_2\text{P}(\text{S})\text{Se}]_2$ (II). Orange, monoclinic prisms from a mixture of ethanol and benzene. The crystals are elongated along *c*, with $a = 13.07$ Å, $b = 12.37$ Å, $c = 13.37$ Å, $\beta = 126.5^\circ$ and four molecules in the unit cell. The density is, calc. 2.01 , found 1.99 g/cm³. The space group, from systematic extinctions and structure work in progress, is C_{2h}^6-C2/c .

Selenium bis(diethyldiselenophosphate),^{4,5} $\text{Se}[\text{Et}_2\text{P}(\text{Se})\text{Se}]_2$ (III). Yellow and orange, monoclinic prisms from a mixture of ethanol and benzene, elongated along *c*, with $a = 12.92$ Å, $b = 12.49$ Å, $c = 13.43$ Å, $\beta = 125.0^\circ$. There are four molecules in the unit cell, with density, calc. and found 2.14 g/cm³. The space group from systematic extinctions and structure work in progress, is C_{2h}^6-C2/c .

Tellurium bis(diethyldiselenophosphate), $\text{Te}[\text{Et}_2\text{P}(\text{Se})\text{Se}]_2$ (IV). Orange-red, monoclinic prisms from mixtures of ethanol and benzene. The crystals are elongated along *b*, with $a = 21.40$ Å, $b = 11.03$ Å, $c = 16.99$ Å and $\beta = 117.3^\circ$. There are eight molecules in the unit cell, with density, calc. 2.31 , found 2.33 g/cm³. The space group from systematic extinctions, is either C_{2h}^6-C2/c or C_s^4-Cc .

The isolation of selenium bis(diethylthioselenophosphate) has been reported

Table 1. IR absorptions in the range 375–860 cm^{-1} , in cm^{-1} .

$\text{Se}[\text{Et}_2\text{P}(\text{S})\text{Se}]_2$	(I)		567(m-s)	691(w-m)	740(sh)	760(s)
$\text{Te}[\text{Et}_2\text{P}(\text{S})\text{Se}]_2$	(II)	441(w)	568 »	689 »	729(m-s)	760 »
$\text{Se}[\text{Et}_2\text{P}(\text{Se})\text{Se}]_2$	(III)	[449(s)	467(sh)]*	689 »	707 »	749 »
$\text{Te}[\text{Et}_2\text{P}(\text{Se})\text{Se}]_2$	(IV)	[449 »	467(sh)]*	665(w)	690(sh)	704 »
					750 »	

*Doublet

earlier.³ The other three compounds were obtained by reaction between sodium diethylthioselenophosphinate or sodium diethyldiselenophosphinate, and tetravalent selenium or tellurium in hydrochloric acid solution. The analogous preparation of selenium and tellurium bis(diethylthio-phosphinate) is described elsewhere.¹ The diethyldiselenophosphinates are relatively unstable, but stored in a cold and dark place, some samples could be kept for months without decomposition.

The two triselenides, I and III, have been reported by Kuchen and Knop and elementary analyses have been made.^{4,5} The melting points were found by these authors to be 117–121°C and 135–137°C for I and III, respectively. The melting points found in this laboratory are for I–IV: 118–120°C, 138–142°C (decomp.), 137–139°C, and 141–143°C, respectively.

No chemical analyses have been made here, but the X-ray data together with the known composition of the analogous dithiophosphinates prepared in the same manner, appear sufficient to establish the formulas given above. In addition, the melting points reported by Kuchen and Knop for I and III correspond well to those reported here.

The infrared spectra were recorded in the range 375–1200 cm^{-1} and the absorptions in the range 375–860 cm^{-1} are listed in Table 1. The measurements were made on a Unicam spectrophotometer, Model SP 100, by the KBr disc method. The absorptions of I have been reported before by the author,³ but is included for comparison.

The strong absorption band near 570 cm^{-1} found for I and II, is undoubtedly due to P=S stretching, as shown in the earlier note.³ This absorption is absent in III and IV, as these compounds do not possess a P=S double bond. Instead, strong absorptions (doublets) occur near 450 cm^{-1} in the two diethyldiselenophosphinates; these are probably due to P=Se stretching. Kuchen and Knop^{4,5} have studied the IR spectra of selenium bis

(diethyldiselenophosphinate) (III) and related compounds with P=Se bonds, and find strong absorptions due to P=Se stretching in the range 470–480 cm^{-1} . A range of 422–577 cm^{-1} has been suggested for the P=Se double bond.⁶ The X-ray structural evidence suggests weak intermolecular association through double-bonded selenium; the P=Se frequencies for III and IV are correspondingly found in the lower part of the range given above.

The data of Table 1 do not reveal evidence for two widely separated P=S absorption bands in the reported frequency range as suggested by Chittenden and Thomas⁷ for compounds with P=S double bonds. If two such bands were present in I and II, they should not be found in III and IV. This is apparently not the case. Only one band, namely that near 570 cm^{-1} is absent, although there are some shifts in the bands near 730 cm^{-1} and 760 cm^{-1} .

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