

Rotational Isomers of Pentathionic Compounds in Crystals

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Recent work on the crystal structure of pentathionic compounds has shown that these are, in the cases studied so far, built up of unbranched and non-planar chains. This applies to sulphur, selenium and tellurium dimethanethiosulphonate^{1,2}, $S(S_2O_2CH_3)_2$, $Se(S_2O_2CH_3)_2$ and $Te(S_2O_2CH_3)_2$, barium pentathionate and selenopentathionate dihydrate³, $BaS(S_2O_3)_2 \cdot 2H_2O$ and $BaSe(S_2O_3)_2 \cdot 2H_2O$, and ammonium telluropentathionate^{4,5}, $(NH_4)_2Te(S_2O_3)_2$.

The non-planarity of sulphur chains is principally due to the mutual repulsion of the unshared *px* electron pairs of neighbouring sulphur atoms⁶. The barrier restricting rotation about a sulphur-sulphur bond may be estimated⁶ as roughly 5 kcal/mole.

In pentathionic compounds, with five-membered, unbranched chains, *cis* and *trans* rotational isomers are possible. The terminal sulphur atoms are rotated an angle of about 90° out of the plane of the three middle atoms, either to the same side of the plane — *cis* — or to opposite sides — *trans*. There are two enantiomorphous *trans* forms.

The *cis* form arises from the eight-membered rings of orthorhombic sulphur⁷ and monoclinic selenium^{8,9} by removal of three neighbouring sulphur or selenium atoms, whereas the *trans* forms are contained in the spiral chains of fibrous sulphur⁶ and hexagonal selenium and tellurium¹⁰, and in cesium hexasulphide¹¹.

A *cis* form of a pentathionic compound possesses a mirror plane of symmetry, provided that bond distances and angles are the same in both halves of the molecule. With the same limitations, a *trans* form possesses a twofold axis of molecular symmetry. The mirror plane and the twofold axis pass through the middle atom and not through any other atoms of the chains.

In solutions, *cis* and *trans* forms probably exist in equilibrium mixtures. In crystals, with fixed atomic positions, the occurrence of isomers is determined in part by lattice energy relations. The nature of the cation,

in the case of salts, appears to play a role. The findings are as follows.

Sulphur, selenium and tellurium dimethanethiosulphonate, the crystals of which are isomorphous, occur in *trans* forms^{1,2}.

The space group of barium pentathionate dihydrate, crystallized from aqueous methanol, is $D_{2h}^{16} - Pnma$ with $Z = 4$. The pentathionate ion has a *cis* form and, by space group requirements, a mirror plane of symmetry³. The crystals of barium selenopentathionate dihydrate are orthorhombic and isomorphous with those of barium pentathionate.

The telluropentathionate ion in ammonium telluropentathionate^{4,5} has, as different from the pentathionate and selenopentathionate ions in the barium salts, a *trans* form like the methanethiosulphonates.

Now, a series of isomorphous salts of pentathionic, selenopentathionic and telluropentathionic acids exists⁴, comprising potassium pentathionate, ammonium selenopentathionate, cesium telluropentathionate, and the three rubidium salts. In the isomorphous salts, the three anions have evidently the same structure. This shows that the pentathionate and selenopentathionate ions, or the telluropentathionate ion, occur in different forms in different salts.

Unit cell and space group data are available for a series of aromatic pentathionic compounds, derived from the methanethiosulphonate series by substitution of phenyl and *p*-tolyl for methyl. These are sulphur dibenzenethiosulphonate and di-*p*-toluenethiosulphonate¹², and selenium and tellurium dibenzenethiosulphonate and di-*p*-toluenethiosulphonate¹³. A twofold axis is crystallographically required as molecular symmetry. Therefore, provided the chains are unbranched, as is strongly indicated from chemical evidence¹³ and analogy with the methanethiosulphonates, the molecules occur in *trans* forms. The crystals, except those of tellurium dibenzenethiosulphonate, are based on the enantiomorphous space group $D_2^4 - P4_12_12$ with $Z = 4$. A unit cell thus contains only one of the two enantiomorphous *trans* forms.

This is true also for triselenium di-*p*-toluenesulphinates¹³, which is isomorphous with the *p*-toluenethiosulphonates.

The above stereochemical considerations regarding pentathionic compounds are generally valid for molecules X-S-S-S-X where X may be any atom or group and

the three sulphur atoms may be partly or completely substituted by selenium or tellurium. Thus, the arguments apply to compounds of the trisulphide and trisele-nide type, as has been discussed by other authors¹⁴⁻¹⁶ on the basis of dipole moments in solutions, and with reference to Raman spectra in the case of hydrogen trisulphide¹⁷. The configurations of the following compounds are known in crystals.

Bis(2-iodoethyl) trisulphide^{18,19} has a *trans* form and a twofold axis of symmetry. The space group¹² is the enantiomorphous one, $D_2^4-P4_22$ with $Z = 4$. Selenium diselenocyanate²⁰, $\text{Se}(\text{SeCN})_2$, has the space group $D_2^{18}-Pnma$ with $Z = 4$. The molecule occurs in a *cis* form, and possesses a mirror plane of symmetry²¹.

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On the Technique of Preparative Electrophoresis of Proteins in Supporting Medium (Starch)

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In efforts to adapt the principle of electrophoresis to preparative purposes, particularly in the field of protein chemistry, several methods have been suggested¹⁻³. In their practical application, however, many unexpected factors often prevent a clear-cut and reproducible separation and/or satisfactory recovery of individual fractions. Starch as a supporting medium was recently introduced by Kunkel and Slater⁴ and it seems to have many advantages compared with other media. Nevertheless this method also is rather sensitive to various influences and, when performed as presented by them, gives reproducible and otherwise ideal results only accidentally. The following reports briefly on some modifications of the technique which seem to have improved the usefulness of preparative zone electrophoresis.

The experiments were made with human blood serum using a rectangular perspex vessel packed with buffer-moistened potato starch. A point of primary importance is completely to prevent evaporation from the surface of the medium. To this end melted paraffin was poured on the starch block and allowed to solidify, forming quite a tight cover. Serum could then be applied to the starch through a narrow window cut into this cover. The contact from the ends of the block to the buffer vessels was mediated by strips of heavy filter paper.

It appeared that the apparently poor separation of fractions was often due to gravity causing an accumulation of serum in the lower starch layers when the run was made in a horizontal position, and this led to an uneven migration velocity at different levels of the block. This effect was avoided by making the run in the