The Crystal Structures of Potassium Pentathionate, Ammonium Selenopentathionate, and Rubidium Telluropentathionate Hemitrihydrates

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The non-planarity of sulphur chains leads to two rotational-isomeric forms of the pentathionate, selenopentathionate, and telluropentathionate ions: a *trans* form with the terminal sulphur atoms located on opposite sides of the plane through the three middle atoms, and a *cis* form with the terminal atoms on the same side of the plane. The *cis* form occurs in barium salts, whereas the *trans* form so far has been found in ammonium telluropentathionate.[1]

A series of isomorphous alkali (and ammonium) pentathionate, selenopentathionate, and telluropentathionate hemitrihydrates crystallize in the space group *Pbcn* (No. 60) with eight molecules per unit cell.[1,2] The crystal structures of three of these salts, *viz.*, potassium pentathionate hemitrihydrate, $K_2S(S_2O_3)_2 \cdot 1\frac{1}{2}H_2O$ (I), ammonium selenopentathionate hemitrihydrate, $(NH_4)_2Se(S_2O_3)_2 \cdot 1\frac{1}{2}H_2O$ (II), and rubidium telluropentathionate hemitrihydrate, $Rb_2Te(S_2O_3)_2 \cdot 1\frac{1}{2}H_2O$ (III), have been determined. The unit cell dimensions (redetermined) are:

$a = 20.316$ Å, $b = 9.229$ Å, $c = 12.248$ Å for I;
$a = 20.718$ Å, $b = 9.326$ Å, $c = 12.590$ Å for II;
$a = 21.320$ Å, $b = 9.446$ Å, $c = 12.437$ Å for III.

The crystal structures were solved by three-dimensional Patterson syntheses, and refined by three-dimensional Fourier syntheses and least squares analyses. The least squares refinements were based on 1005 (I), 1414 (II), and 1186 (III) independent, observed reflections, estimated visually from Weissenberg photographs taken with Cu$K\alpha$ radiation. The reliability index, R, is 0.09 for each of the three compounds.

The pentathionate, selenopentathionate, and telluropentationate ions occur in the *trans* form in these salts, the sulphonate

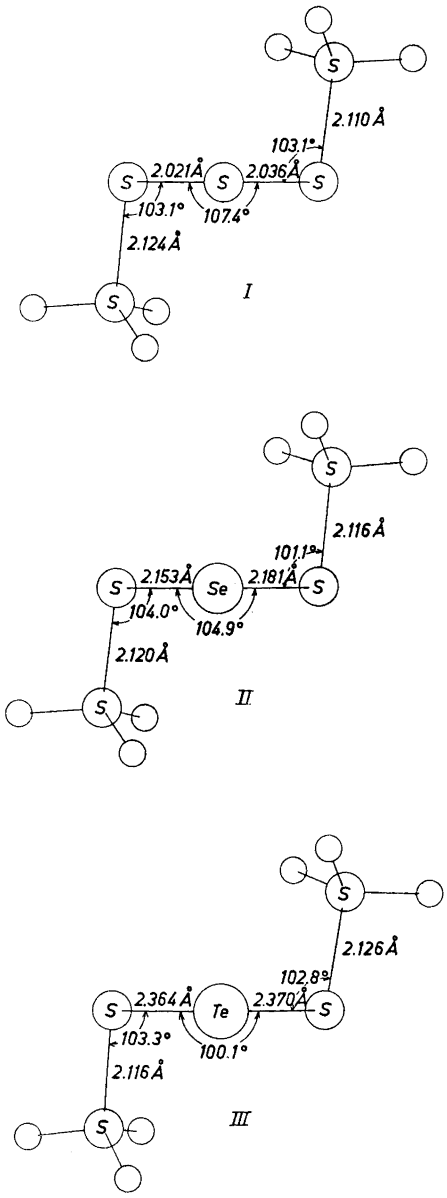

Fig. 1. The *trans* form of the pentathionate ion (I) in $K_2S(S_2O_3)_2 \cdot 1\frac{1}{2}H_2O$, of the selenopentathionate ion (II) in $(NH_4)_2Se(S_2O_3)_2 \cdot 1\frac{1}{2}H_2O$, and of the telluropentathionate ion (III) in $Rb_2Te(S_2O_3)_2 \cdot 1\frac{1}{2}H_2O$, as seen along an approximate twofold axis.

groups being located on opposite sides of the plane through the three middle atoms, as shown in Fig. 1. The dihedral angles, SXS/XSS (X=S, Se, or Te), are 82° and 84° in I, 83° and 85° in II, and 78° and 89° in III. The middle sulphur-sulphur bonds, between two divalent atoms, are 2.021 ± 0.007 Å and 2.036 ± 0.007 Å in I, the selenium-sulphur bonds are 2.153 ± 0.004 Å and 2.181 ± 0.003 Å in II, and the tellurium-sulphur bonds are 2.364 ± 0.009 Å and 2.370 ± 0.007 Å in III. The weighted mean of the six terminal sulphur-sulphur bonds, between a divalent and a sulphonate sulphur atom, is 2.118 Å; the calculated standard deviations of these bond lengths are 0.006 Å in I, 0.004 Å in II, and $0.009-0.011$ Å in III.

Further details of the structures will be published later.

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2. Foss, O. and Jahr, J. *Acta Chem. Scand.* **4** (1950) 1560.

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Evidence of the Presence of 1-Phosphohistidine as the Main Phosphorylated Component at the Active Site of Bovine Liver Nucleoside Diphosphate Kinase

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Nucleoside diphosphate kinase (ATP:nucleoside diphosphate phosphotransferase, EC 2.7.4.6) obtained from various sources has been shown to be phosphorylated during incubation with adenosine triphosphate-^{32}P (Refs. 1–4). From an alkaline hydrolysate of ^{32}P-labelled NDP kinase * from Jerusalem artichoke, Norman *et al.*[2] isolated 3-^{32}P-phosphohistidine. It was recently demonstrated in this laboratory that alkaline hydrolysates of ^{32}P-labelled bovine-liver and erythrocytic NDP kinase contained not only 3-^{32}P-phosphohistidine but also 1-^{32}P-phosphohistidine and N-ε-^{32}P-phospholysine.[4,5] The main part of the covalently bound ^{32}P-phosphate of the hydrolysates was, however, recovered as two unidentified fractions denoted as X and Y.[6] The type of linkage of ^{32}P-phosphate in Fraction X has been investigated in the present work.

The reason why three different phosphoamino acids were obtained from a single phosphorylenzyme is not known. In order to rule out that one or more of them is formed during alkaline inactivation, an experiment with acid inactivation was performed. Finally the pH-dependence of the stability of the phosphoryl linkage of the non-inactivated phosphorylated enzyme was examined.

In order to investigate the phosphoryl linkage of Fraction X, 2 mg of purified bovine-liver NDP kinase were incubated with AT^{32}P as previously described.[5] From the alkaline hydrolysate of the ^{32}P-labelled enzyme, Fraction X was prepared by electrophoresis at pH 8.25 (Ref. 6), and hydrolyzed in 3 M KOH for 3 h at 100°C. When the hydrolysate was chromatographed on Dowex 1 together with synthetic 1-phosphohistidine, 3-phosphohistidine, and N-ε-phospholysine,[5] a large ^{32}P-labelled component was eluted together with 1-phosphohistidine. Fractions, corresponding to each of the three reference phosphoamino acids, were pooled, and rechromatographed on separate columns of Dowex 1 under identical conditions. The identity of the main labelled component with 1-^{32}P-phosphohistidine was finally established by paper electrophoresis and paper chromatography in altogether seven systems, as previously described.[5,7]

Of the total radioactivity of the hydrolysate of Fraction X, 9 % was obtained as 1-^{32}P-phosphohistidine, 0.3 % as 3-^{32}P-phosphohistidine, and no detectable amounts (less than 0.05 %) as N-ε-^{32}P-phospholysine. The yield of 1-^{32}P-phosphohistidine suggests that the ^{32}P-phosphate of Fraction X is bound as 1-^{32}P-phosphohistidine. The small amounts of 3-^{32}P-phosphohistidine isolated may represent transformed 1-^{32}P-phosphohistidine.[8]

On further alkaline hydrolysis Fraction X was found to give rise to Fraction Y, which is in agreement with previous work on rat-liver cell sap.[6] Thus, it may be suggested that the ^{32}P-phosphate of Fraction Y is also bound as 1-^{32}P-phosphohistidine. The two fractions

* Abbreviation: NDP kinase, nucleoside diphosphate kinase.