

# The Dihydrogentrisulfanediphosphonate Ion. Preparation and Crystal Structures of $\text{BaH}_2\text{S}_3\text{P}_2\text{O}_6 \cdot \text{C}_2\text{H}_5\text{OH}$ and $[\text{Co}(\text{en})_2\text{Cl}(\text{H}_2\text{O})]\text{H}_2\text{S}_3\text{P}_2\text{O}_6 \cdot \text{H}_2\text{O}$

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Janickis, V. and Marøy, K., 1994. The Dihydrogentrisulfanediphosphonate Ion. Preparation and Crystal Structures of  $\text{BaH}_2\text{S}_3\text{P}_2\text{O}_6 \cdot \text{C}_2\text{H}_5\text{OH}$  and  $[\text{Co}(\text{en})_2\text{Cl}(\text{H}_2\text{O})]\text{H}_2\text{S}_3\text{P}_2\text{O}_6 \cdot \text{H}_2\text{O}$ . – Acta Chem. Scand. 48: 465–470 © Acta Chemica Scandinavica 1994.

Barium dihydrogentrisulfanediphosphonate ethanol solvate,  $\text{BaH}_2\text{S}_3\text{P}_2\text{O}_6 \cdot \text{C}_2\text{H}_5\text{OH}$  (**1**), and *trans*-aquachlorobis(ethylenediamine)cobalt(III) dihydrogentrisulfanediphosphonate monohydrate,  $[\text{Co}(\text{en})_2\text{Cl}(\text{H}_2\text{O})]\text{H}_2\text{S}_3\text{P}_2\text{O}_6 \cdot \text{H}_2\text{O}$  (**2**), form triclinic crystals, space group *P1* with *Z* = 2. Cell dimensions are for **1**, *a* = 5.809(1), *b* = 9.085(1), *c* = 12.168(1) Å,  $\alpha$  = 97.17(1),  $\beta$  = 102.42(1),  $\gamma$  = 104.40(1)°, and for **2**, *a* = 7.328(1), *b* = 9.892(1), *c* = 13.613(1) Å,  $\alpha$  = 87.68(1),  $\beta$  = 84.04(1),  $\gamma$  = 69.33(1)°. The structures have been determined by X-ray methods and refined to *R* = 0.036 (**1**) and 0.047 (**2**) for 2292 and 3791 observed reflections, respectively. The anions of both salts have *cis* rotameric forms with PSSS torsion angles in the range 90.5–99.8°. The dimensions of the anions are: S–S = 2.0344(16)–2.0609(14) Å, S–P = 2.1047(13)–2.1223(14) Å, P–O = 1.461(3)–1.573(3) Å, S–S–S = 108.13(8)–108.42(7)°, S–S–P = 101.09(6)–104.45(6)°, S–P–O = 100.96(12)–110.61(12)°, O–P–O = 106.03(17)–120.05(17)°, O–H = 0.78(5)–0.89 Å, P–O–H = 112(5)–121°.

Two salts of trisulfanediphosphonic acid have been prepared and characterized,<sup>1,2</sup> but so far no structure determination has been reported.

As part of our investigation on sulfanediphosphonates<sup>3</sup> we report here the preparation and crystal structure determinations of two trisulfanediphosphonates,  $\text{BaH}_2\text{S}_3\text{P}_2\text{O}_6 \cdot \text{C}_2\text{H}_5\text{OH}$  (**1**) and  $[\text{Co}(\text{en})_2\text{Cl}(\text{H}_2\text{O})]\text{H}_2\text{S}_3\text{P}_2\text{O}_6 \cdot \text{H}_2\text{O}$  (**2**).

## Experimental

**Preparations.** Both compounds were obtained by metathesis from the less stable salt  $\text{KH}_3\text{S}_3\text{P}_2\text{O}_6 \cdot \text{CH}_3\text{OH}$  prepared as described by Fehér and Vial.<sup>1</sup> The products were analysed iodometrically.<sup>1</sup>

**$\text{BaH}_2\text{S}_3\text{P}_2\text{O}_6 \cdot \text{C}_2\text{H}_5\text{OH}$ .** A solution of  $\text{Ba}(\text{ClO}_4)_2$  (0.70 g, 2.1 mmol) in  $\text{H}_2\text{O}$  (2 cm<sup>3</sup>) was added with stirring to a solution of  $\text{KH}_3\text{S}_3\text{P}_2\text{O}_6 \cdot \text{CH}_3\text{OH}$  (1.0 g, 3 mmol) in 0.4 M HCl (8 cm<sup>3</sup>). The reaction mixture was heated to ca. 40°C, and then 21 cm<sup>3</sup> of ethanol was added drop by drop with stirring. The solution was filtered and stored at –2°C for a few days. The crystals were filtered off and

washed with ethanol and diethyl ether. Yield 0.42 g, 46% based on the amount of  $\text{Ba}(\text{ClO}_4)_2$  used.

**$[\text{Co}(\text{en})_2\text{Cl}(\text{H}_2\text{O})]\text{H}_2\text{S}_3\text{P}_2\text{O}_6 \cdot \text{H}_2\text{O}$ .** Suitable crystals of this compound were obtained during attempts to grow larger crystals of  $[\text{Co}(\text{en})_2\text{Cl}_2]\text{H}_3\text{S}_3\text{P}_2\text{O}_6$ . To a solution of 0.65 g (2.0 mmol) of  $\text{KH}_3\text{S}_3\text{P}_2\text{O}_6 \cdot \text{CH}_3\text{OH}$  in 5 cm<sup>3</sup> of  $\text{H}_2\text{O}$  was added a solution of 2.5 g (8 mmol) of  $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl} \cdot \text{H}_2\text{O}$  in a mixture of 7.5 cm<sup>3</sup>  $\text{H}_2\text{O}$  and 9 cm<sup>3</sup> methanol and kept at –2°C for 20 h. The majority of crystals formed were green extended, rather thin plates of  $[\text{Co}(\text{en})_2\text{Cl}_2]\text{H}_3\text{S}_3\text{P}_2\text{O}_6$ , but with a few brown crystals of  $[\text{Co}(\text{en})_2\text{Cl}(\text{H}_2\text{O})]\text{H}_2\text{S}_3\text{P}_2\text{O}_6 \cdot \text{H}_2\text{O}$ . The yield was very low, 0.035 g or 3.5% based on the amount of  $\text{KH}_3\text{S}_3\text{P}_2\text{O}_6 \cdot \text{CH}_3\text{OH}$  used. The filtrate was diluted with 5 cm<sup>3</sup> of methanol and again kept for 20 h at –2°C. The majority of the precipitate was now well developed brown crystals of  $[\text{Co}(\text{en})_2\text{Cl}(\text{H}_2\text{O})]\text{H}_2\text{S}_3\text{P}_2\text{O}_6 \cdot \text{H}_2\text{O}$  with some thin elongated green plates of  $[\text{Co}(\text{en})_2\text{Cl}_2]\text{H}_3\text{S}_3\text{P}_2\text{O}_6$ . The crystals were washed with methanol and diethyl ether.

**X-Ray structure analyses.** The determination of unit-cell parameters and the data collections were carried out on an Enraf-Nonius CAD4 diffractometer, using monochromated  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71069$  Å). Crystal data and

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conditions for data collections are given in Table 1. The cell parameters were based on a least-squares fit of accurate setting angles for 25 reflections. Intensities were corrected for Lorentz and polarization effects, decay and absorption. Secondary extinction effects were found to be negligible. Reflections with  $I > 2\sigma(I)$  were regarded as observed. As seen from Table 1, the loss of intensities was extremely high, especially for compound **1**, but according to the standard reflections used, it was isotropic and continuous. The structures were solved by direct (MUL-TAN) and Fourier difference methods. The structures were refined by least-squares calculations, using anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms bonded to carbon of the solvate in **1** and to the ethylenediamine groups in **2** were placed geometrically with C–H bond lengths 0.95 Å and N–H bond lengths 0.87 Å, and were held fixed with isotropic thermal parameters equal to  $1.3 B_{\text{eq}}$  for the atom to which they are attached.

For compound **1** the intensity statistics indicated acentric unit cell, and the structure was solved in space group  $P1$ , but was eventually refined in space group  $P\bar{1}$ . The hydrogen atoms bonded to oxygen of the anion and the solvate were located from a Fourier difference map and were refined with isotropic thermal parameters.

For compound **2** the hydrogen atoms bonded to oxygen were located from a Fourier difference map. That bonded to O(1) did not refine to an acceptable position and was held fixed with fixed isotropic thermal parameter, whereas the others were refined with isotropic thermal parameters.

The programs used were the Enraf–Nonius' Structure Determination Package 1987. All refined atomic coordinates are given in Table 2.

## Results and discussion

Bond lengths and angles are given in Table 3, and views of the anions are shown in Fig. 1. The unbranched, non-planar P–S–S–S–P chains of the anions give rise to possible geometrical isomerism, a *cis*-form with both P atoms on the same side of the S–S–S plane, and a *trans*-form with the P atoms on different sides. The two P atoms are each bonded to one S atom and three O atoms in a near-tetrahedral arrangement. Excluding the H atoms, the ions may be written  $S(\text{SPO}_3)_2^{4-}$ , and the shape of these ions clearly resembles their polythionate analogues, the pentathionates,  $X(\text{S}_2\text{O}_3)_2^{2-}$  ( $X = \text{S}, \text{Se}$  or  $\text{Te}$ ).<sup>4–8</sup> The penta-, selenopenta- and telluropentathionate ions are each

Table 1. Crystallographic data

| Compound  | BaH <sub>2</sub> S <sub>3</sub> P <sub>2</sub> O <sub>6</sub> ·C <sub>2</sub> H <sub>5</sub> OH( <b>1</b> ) | [Co(en) <sub>2</sub> Cl(H <sub>2</sub> O)]H <sub>2</sub> S <sub>3</sub> PO <sub>6</sub> ·H <sub>2</sub> O( <b>2</b> ) |
|---|---|---|
| Formula   | C <sub>2</sub> H <sub>8</sub> BaO <sub>7</sub> S <sub>3</sub>   | C <sub>4</sub> H <sub>22</sub> CoN <sub>4</sub> O <sub>8</sub> P <sub>2</sub> S <sub>3</sub>                          |
| <i>M</i>  | 439.6   | 506.8   |
| System  | Triclinic   | Triclinic   |
| Space group                                       | <i>P</i> 1  | <i>P</i> 1  |
| <i>a</i> /Å                                       | 5.809(1)  | 7.328(1)  |
| <i>b</i> /Å                                       | 9.085(1)  | 9.892(1)  |
| <i>c</i> /Å                                       | 12.168(1)   | 13.613(1)   |
| $\alpha$ /°                                       | 97.17(1)  | 87.68(1)  |
| $\beta$ /°  | 102.42(1)   | 84.04(1)  |
| $\gamma$ /°                                       | 104.40(1)   | 69.33(1)  |
| <i>V</i> /Å <sup>3</sup>                          | 596.6(3)  | 918.3(2)  |
| <i>Z</i>  | 2   | 2   |
| <i>T</i> /K                                       | 293   | 293   |
| <i>D<sub>x</sub></i> /g cm <sup>-3</sup>          | 2.447   | 1.833   |
| <i>D<sub>o</sub></i> /g cm <sup>-3</sup>          | 2.415   | 1.824   |
| <i>F</i> (000)                                    | 420   | 520   |
| $\Theta_{\text{max}}$ /°                          | 30  | 30  |
| Scan mode   | $\omega$  | $\omega$  |
| Scan speed/° min <sup>-1</sup>                    | 0.7–4.1   | 1.0–2.8   |
| Min scan width/°                                  | 1.00  | 1.25  |
| Loss of intensity(%)                              | 75  | 41  |
| $\mu$ (MoK $\alpha$ )/cm <sup>-1</sup>            | 41.1  | 16.2  |
| Crystal volume/mm <sup>3</sup>                    | 0.0026  | 0.0018  |
| Correction for absorption                         | Empirical <sup>a</sup>  | Numerical   |
| Transmission factors                              |   | 0.72–0.95   |
| Correction factors                                | 0.78–1.40   |   |
| No. of independent measurements                   | 3464  | 5318  |
| No. with $I > 2\sigma(I)$                         | 2992  | 3791  |
| No. of parameters refined                         | 148   | 228   |
| $R = \sum  F_o  -  F_c  / \sum  F_o $             | 0.036   | 0.047   |
| $R_w = [\sum w(F_o - F_c)^2 / \sum wF_o^2]^{1/2}$ | 0.041   | 0.046   |
| $S = [\sum w(F_o - F_c)^2 / (n - m)]^{1/2}$       | 1.530   | 1.201   |
| Max. $\Delta(\rho)/e \text{ \AA}^{-3}$            | 1.45  | 0.85  |

<sup>a</sup> Ref. 26.

Table 2. Fractional atomic coordinates with e.s.d.'s in parentheses.

| Atom  | x            | y            | z            | B <sub>eq</sub> /Å <sup>2</sup> |
|---|--------------|--------------|--------------|---------------------------------|
| (a) BaH <sub>2</sub> S <sub>3</sub> P <sub>2</sub> O <sub>6</sub> ·C <sub>2</sub> H <sub>5</sub> OH (1)           |              |              |              |                                 |
| S(1)  | 0.26469(28)  | 0.42191(13)  | -0.17585(9)  | 2.63(3)                         |
| S(2)  | 0.53059(27)  | 0.30825(13)  | -0.17584(12) | 2.84(3)                         |
| S(3)  | 0.38803(28)  | 0.08674(129) | -0.15588(9)  | 2.57(3)                         |
| P(1)  | 0.12803(21)  | 0.40963(10)  | -0.35273(9)  | 1.42(2)                         |
| P(2)  | 0.23267(21)  | -0.03295(10) | -0.32601(8)  | 1.43(2)                         |
| O(1)  | 0.3389(6)    | 0.4658(3)    | -0.4047(3)   | 1.83(6)                         |
| O(2)  | -0.0407(6)   | 0.6187(3)    | -0.3517(3)   | 2.20(7)                         |
| O(3)  | -0.0391(7)   | 0.2516(3)    | -0.4080(3)   | 2.56(8)                         |
| O(4)  | 0.3915(6)    | 0.0341(3)    | -0.3994(2)   | 1.81(6)                         |
| O(5)  | 0.2112(7)    | -0.1983(3)   | -0.3195(3)   | 2.22(7)                         |
| O(6)  | -0.0330(6)   | -0.0128(3)   | -0.3613(3)   | 1.92(6)                         |
| H(7)  | 0.038(13)    | 0.611(7)     | -0.338(5)    | 4.7(1.6)                        |
| H(8)  | -0.029(14)   | 0.074(7)     | -0.374(6)    | 5.7(1.8)                        |
| Ba  | 0.48290(5)   | 0.24623(2)   | 0.47020(2)   | 1.479(4)                        |
| C(1)  | 0.2130(12)   | 0.1936(7)    | 0.1349(5)    | 3.4(1)                          |
| C(2)  | 0.0239(14)   | 0.2489(7)    | 0.0618(5)    | 4.2(1)                          |
| O(7)  | 0.2906(8)    | 0.2744(4)    | 0.2496(3)    | 2.92(7)                         |
| H(6)  | 0.361(15)    | 0.362(8)     | 0.259(6)     | 7.7(2.2)                        |
| (b) [Co(en) <sub>2</sub> Cl(H <sub>2</sub> O)]H <sub>2</sub> S <sub>3</sub> PO <sub>6</sub> ·H <sub>2</sub> O (2) |              |              |              |                                 |
| S(1)  | 0.32871(17)  | 0.19679(11)  | 0.94881(8)   | 4.09(2)                         |
| S(2)  | 0.61153(17)  | 0.18710(12)  | 0.94363(8)   | 4.02(2)                         |
| S(3)  | 0.62589(17)  | 0.38111(11)  | 0.88962(9)   | 3.97(2)                         |
| P(1)  | 0.31418(14)  | 0.10150(10)  | 0.81456(8)   | 2.98(2)                         |
| P(2)  | 0.70003(13)  | 0.34703(9)   | 0.73546(7)   | 2.74(2)                         |
| O(1)  | 0.2870(4)    | 0.2240(3)    | 0.7346(2)    | 4.99(7)                         |
| O(2)  | 0.1219(4)    | 0.0798(3)    | 0.8320(3)    | 3.87(6)                         |
| O(3)  | 0.4945(4)    | -0.0224(3)   | 0.7940(3)    | 5.15(8)                         |
| O(4)  | 0.8531(4)    | 0.1920(3)    | 0.7237(2)    | 3.65(6)                         |
| O(5)  | 0.5240(4)    | 0.3491(3)    | 0.6871(2)    | 4.04(6)                         |
| O(6)  | 0.7781(4)    | 0.4626(3)    | 0.7046(2)    | 4.02(6)                         |
| Co  | 0.03364(6)   | 0.24838(4)   | 0.30371(4)   | 2.30(1)                         |
| Cl  | -0.24982(48) | 0.22084(10)  | 0.35366(8)   | 3.91(2)                         |
| O(7)  | 0.2764(4)    | 0.2736(2)    | 0.2567(3)    | 4.41(7)                         |
| N(1)  | 0.0283(5)    | 0.3367(3)    | 0.4301(3)    | 3.77(7)                         |
| N(2)  | 0.1818(5)    | 0.0656(3)    | 0.3636(3)    | 3.58(7)                         |
| N(3)  | 0.0382(5)    | 0.1587(3)    | 0.1777(2)    | 3.06(6)                         |
| N(4)  | -0.1001(5)   | 0.4323(3)    | 0.2401(3)    | 3.52(7)                         |
| C(1)  | 0.0805(8)    | 0.2222(6)    | 0.5056(3)    | 5.4(1)                          |
| C(2)  | 0.2423(8)    | 0.0959(5)    | 0.4589(4)    | 5.2(1)                          |
| C(3)  | -0.0935(6)   | 0.2672(5)    | 0.1143(3)    | 4.1(1)                          |
| C(4)  | -0.0742(7)   | 0.4095(4)    | 0.1311(3)    | 4.2(1)                          |
| O(8)  | 0.3480(5)    | 0.4194(4)    | 0.5080(2)    | 4.86(8)                         |
| H(17)   | 0.2887(6)    | 0.345(4)     | 0.268(3)     | 3.8(9)                          |
| H(18)   | 0.354(5)     | 0.216(3)     | 0.239(3)     | 2.3(9)                          |
| H(20)   | 0.949(7)     | 0.171(5)     | 0.750(4)     | 6(1)                            |
| H(21)   | 0.419(10)    | 0.419(7)     | 0.456(5)     | 12(2)                           |
| H(22)   | 0.425(8)     | 0.396(6)     | 0.554(4)     | 8(2)                            |

found in both rotameric forms, but so far only the *cis*-form is found for the trisulfanediphosphonate ion. The torsion angles of the P-S-S-S-P chain are -99.78(8) and 90.53(9)° for **1** and 95.24(7) and -93.67(7)° for **2**. The corresponding angles are 103.8–108° in *cis* and 81.9–98.7° in *trans* pentathionates. In *trans* P-S-X-S-P chains (X = S, Se, Te), as found in bis(diethylthiophosphoryl) trisulfane, [(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>P(S)S]<sub>2</sub>S,<sup>9</sup> in bis(diethoxythiophosphoryl) trisulfane, [(C<sub>2</sub>H<sub>5</sub>O)<sub>2</sub>P(S)S]<sub>2</sub>S,<sup>10</sup> and the analogous selenium and tellurium compounds, [(C<sub>2</sub>H<sub>5</sub>O)<sub>2</sub>P(S)S]<sub>2</sub>X (X = Se, Te),<sup>11</sup> the corresponding

torsion angles are 82.9–91.1°, in most cases close to 90°. The S-S bonds, bonds between divalent S atoms, are 2.0344(16)–2.0609(14) Å in the present trisulfanes, 2.052(2)–2.060(2) Å in bis(diethylthiophosphoryl) trisulfane,<sup>9</sup> and 2.059(1)–2.060(1) Å in bis(diethoxythiophosphoryl) trisulfane.<sup>10</sup> These bonds are close to the value expected for normal single bonds.<sup>12,13</sup> The S-S-S angles (average 108.30°) are larger than the S-S-P angles (average 103.30°).

Dimensions and orientation of the thiophosphonate groups in thiophosphate,<sup>3</sup> disulfanediphosphonate<sup>3</sup> and

Table 3. Distances (Å) and angles (deg) with e.s.d's in parentheses.

|  |            |                  |            |
|--|------------|------------------|------------|
| (a) BaH <sub>2</sub> S <sub>3</sub> P <sub>2</sub> O <sub>6</sub> ·C <sub>2</sub> H <sub>5</sub> OH(1)                         |            |                  |            |
| P(1)—S(1)  | 2.1062(13) | P(1)—S(1)—S(2)   | 101.09(6)  |
| S(1)—S(2)  | 2.0604(17) | S(1)—S(2)—S(3)   | 108.13(8)  |
| S(2)—S(3)  | 2.0431(14) | S(2)—S(3)—P(2)   | 102.76(5)  |
| S(3)—P(2)  | 2.1047(13) | P(1)S(1)S(2)S(3) | -99.79(8)  |
|  |            | S(1)S(2)S(3)P(2) | 90.53(9)   |
| P(1)—O(1)  | 1.497(3)   | S(1)—P(1)—O(1)   | 109.05(12) |
| P(1)—O(2)  | 1.558(3)   | S(1)—P(1)—O(2)   | 100.96(12) |
| P(1)—O(3)  | 1.497(3)   | S(1)—P(1)—O(3)   | 110.61(12) |
| O(2)—H(7)  | 0.83(6)    | O(1)—P(1)—O(2)   | 113.72(15) |
|  |            | O(1)—P(1)—O(3)   | 115.51(17) |
|  |            | O(2)—P(1)—O(3)   | 106.03(17) |
|  |            | P(1)—O(2)—H(7)   | 113(4)     |
| P(2)—O(4)  | 1.493(3)   | S(3)—P(2)—O(4)   | 108.80(11) |
| P(2)—O(5)  | 1.490(2)   | S(3)—P(2)—O(5)   | 104.66(12) |
| P(2)—O(6)  | 1.573(3)   | S(3)—P(2)—O(6)   | 106.21(11) |
| O(6)—H(8)  | 0.82(6)    | O(4)—P(2)—O(5)   | 115.30(16) |
|  |            | O(4)—P(2)—O(6)   | 112.41(15) |
|  |            | O(5)—P(2)—O(6)   | 108.79(16) |
|  |            | P(2)—O(6)—H(8)   | 112(5)     |
| C(1)—C(2)  | 1.489(8)   | O(7)—C(1)—C(2)   | 112.8(4)   |
| C(1)—O(7)  | 1.414(5)   | C(1)—O(7)—H(6)   | 116(5)     |
| O(7)—H(6)  | 0.78(7)    |                  |            |
| (b) [Co(en) <sub>2</sub> Cl(H <sub>2</sub> O)]H <sub>2</sub> S <sub>3</sub> P <sub>2</sub> O <sub>6</sub> ·H <sub>2</sub> O(2) |            |                  |            |
| P(1)—S(1)  | 2.1191(14) | P(1)—S(1)—S(2)   | 104.37(6)  |
| S(1)—S(2)  | 2.0344(16) | S(1)—S(2)—S(3)   | 108.42(7)  |
| S(2)—S(3)  | 2.0609(14) | S(2)—S(3)—P(2)   | 104.45(6)  |
| S(3)—P(2)  | 2.1223(14) | P(1)S(1)S(2)S(3) | 95.24(7)   |
|  |            | S(1)S(2)S(3)P(2) | -93.67(7)  |
| P(1)—O(1)  | 1.569(3)   | S(1)—P(1)—O(1)   | 105.52(13) |
| P(1)—O(2)  | 1.492(3)   | S(1)—P(1)—O(2)   | 102.19(12) |
| P(1)—O(3)  | 1.461(3)   | S(1)—P(1)—O(3)   | 108.56(14) |
| O(1)—H(19)   | 0.89       | O(1)—P(1)—O(2)   | 106.12(16) |
|  |            | O(1)—P(1)—O(3)   | 113.02(20) |
|  |            | O(2)—P(1)—O(3)   | 120.05(16) |
|  |            | P(1)—O(1)—H(19)  | 121        |
| P(2)—O(4)  | 1.550(3)   | S(3)—P(2)—O(4)   | 106.12(12) |
| P(2)—O(5)  | 1.502(3)   | S(3)—P(2)—O(5)   | 109.86(12) |
| P(2)—O(6)  | 1.478(3)   | S(3)—P(2)—O(6)   | 103.23(12) |
| O(4)—H(20)   | 0.78(5)    | O(4)—P(2)—O(5)   | 106.99(17) |
|  |            | O(4)—P(2)—O(6)   | 114.27(16) |
|  |            | O(5)—P(2)—O(6)   | 115.88(16) |
|  |            | P(2)—O(4)—H(20)  | 119(4)     |
| Co—Cl(1)   | 2.2231(10) | N(1)—C(1)        | 1.473(6)   |
| Co—O(7)  | 1.923(3)   | N(2)—C(2)        | 1.488(6)   |
| Co—N(1)  | 1.951(3)   | N(3)—C(3)        | 1.481(5)   |
| Co—N(2)  | 1.947(3)   | N(4)—C(4)        | 1.493(5)   |
| Co—N(3)  | 1.955(3)   | C(1)—C(2)        | 1.495(7)   |
| Co—N(4)  | 1.952(3)   | C(3)—C(4)        | 1.492(6)   |
| Cl(1)—Co—N(1)  | 89.89(10)  | N(1)—Co—N(2)     | 86.47(14)  |
| Cl(1)—Co—N(2)  | 91.90(10)  | N(3)—Co—N(4)     | 86.34(13)  |
| Cl(1)—Co—N(3)  | 89.74(9)   | N(1)—Co—N(4)     | 93.98(14)  |
| Cl(1)—Co—N(4)  | 91.48(10)  | N(2)—Co—N(3)     | 93.24(13)  |
| O(7)—Co—N(1)   | 91.37(14)  | Co—N(1)—C(1)     | 108.7(3)   |
| O(7)—Co—N(2)   | 89.18(14)  | Co—N(2)—C(2)     | 108.7(2)   |
| O(7)—Co—N(3)   | 89.01(14)  | Co—N(3)—C(3)     | 108.9(2)   |
| O(7)—Co—N(4)   | 87.43(13)  | Co—N(4)—C(4)     | 108.4(2)   |
| Cl(1)—Co—O(7)  | 178.39(12) | N(1)—C(1)—C(2)   | 107.2(4)   |
| N(1)—Co—N(3)   | 179.52(13) | N(2)—C(2)—C(1)   | 108.0(4)   |
| N(2)—Co—N(4)   | 176.59(13) | N(3)—C(3)—C(4)   | 107.8(3)   |
|  |            | N(4)—C(4)—C(3)   | 107.0(3)   |
| O(7)—H(17)   | 0.76(4)    | H(17)—O(7)—H(18) | 122(4)     |
| O(7)—H(18)   | 0.68(4)    |                  |            |
| O(8)—H(21)   | 0.84(8)    | H(21)—O(8)—H(22) | 106(6)     |
| O(8)—H(22)   | 0.86(7)    |                  |            |

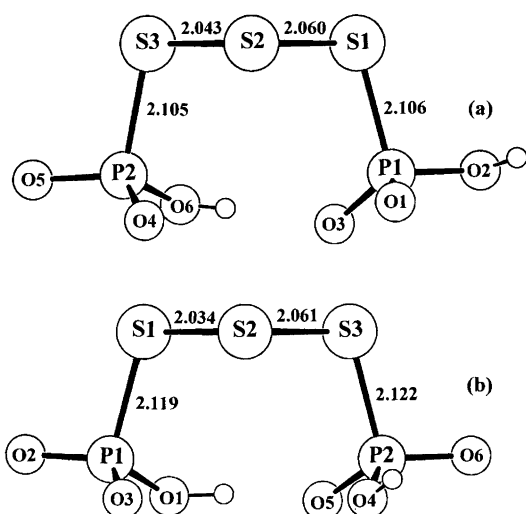


Fig. 1. Views of the dihydrogentrisulfanediphosphonate ions in BaH<sub>2</sub>S<sub>3</sub>P<sub>2</sub>O<sub>6</sub>·C<sub>2</sub>H<sub>5</sub>OH (a) and [Co(en)<sub>2</sub>Cl(H<sub>2</sub>O)]·H<sub>2</sub>S<sub>3</sub>P<sub>2</sub>O<sub>6</sub>·H<sub>2</sub>O (b).

the trisulfanediphosphonate ions are given in Table 4. As seen from O–P–O bond angles and S–S–P–O torsion angles, the PO<sub>3</sub> groups have distorted trigonal symmetry. The internal rotation about the trigonal axis is in each case such that the deviation from ideal staggered con-

formation increases the O···O distance between O atoms of the two moieties of the ion, 2.485(4)–2.544(4) Å. The S–P–O angle of the nearly planar, *transoid* S–S–P–O group is in each case significantly smaller than the two others, average 102.02 and 108.14°, respectively. This tilt of the PO<sub>3</sub> pyramid also increases the distances between O atoms of the two moieties of the ion, and it increases the distances between the S atom to which the thiophosphonate group is bonded and the two nearest O atoms. A similar orientation was found for the thiosulfate groups in polythionates.<sup>4–8,14–16</sup>

The P–S bond, 1.9681(7) Å in thiophosphate, increases to 2.0954(24)–2.1223(14) Å in the sulfanediphosphonates. The shortest bond is a little longer than P–S double bonds as found in organic thiophosphoryl di- and trisulfanes,<sup>9–11,17–21</sup> 1.906(2)–1.949(2) Å. The longer bonds are in accordance with P–S single bonds of the same sulfanes in the cases where the X–S–P–S group has planar, *transoid* geometry, 2.072(2)–2.116(3) Å.

Generally it has been shown that in tetrahedral TO<sub>4</sub><sup>n-</sup> anions, the observed T–O bond lengths correlate with the average of the three O–T–O angles common to each bond in such a way that the shorter the bond, the larger the triple angle average.<sup>22–24</sup> In the thiosulfonate groups, S–SO<sub>2</sub>R, of some disulfonyl sulfanes and related compounds, the S–S bond length was found to correlate with the average of the S–S–C and the two S–S–O

Table 4. Dimensions of the thiophosphonate group in thiophosphate, disulfanediphosphonate, and trisulfanediphosphonate salts.

| S–P bond   | P–O bond | S–P–O angle | O–P–O angle | S–S–P–O torsion angle | O–H bond |
|--|----------|-------------|-------------|-----------------------|----------|
| (a) KH <sub>2</sub> SPO <sub>3</sub> (Ref. 3)  |          |             |             |                       |          |
| 1.9681(7)  | 1.524(2) | 114.45(7)   | 106.96(6)   |                       |          |
|  | 1.575(1) | 112.76(5)   | 106.96(6)   |                       | 0.78(3)  |
|  | 1.575(1) | 112.76(5)   | 102.00(9)   |                       | 0.78(3)  |
| (b) [Co(en) <sub>2</sub> Cl <sub>2</sub> ] <sub>2</sub> H <sub>3</sub> S <sub>2</sub> P <sub>2</sub> O <sub>6</sub> (Ref. 3) |          |             |             |                       |          |
| 2.1120(22)   | 1.484(4) | 109.38(19)  | 118.83(30)  | –48.87(24)            |          |
|  | 1.499(5) | 102.44(21)  | 110.38(28)  | –175.81(22)           | 0.94(7)  |
|  | 1.540(5) | 107.58(22)  | 107.51(30)  | 71.07(23)             | 0.70(6)  |
| 2.0954(24)   | 1.486(4) | 110.02(21)  | 115.35(30)  | 57.13(23)             |          |
|  | 1.522(6) | 105.97(30)  | 116.97(32)  | –68.19(28)            | 0.67(6)  |
|  | 1.523(6) | 98.63(23)   | 108.11(42)  | –179.91(24)           |          |
| (c) BaH <sub>2</sub> S <sub>3</sub> P <sub>2</sub> O <sub>6</sub> ·C <sub>2</sub> H <sub>5</sub> OH (This work)              |          |             |             |                       |          |
| 2.1062(13)   | 1.497(3) | 109.05(12)  | 113.72(15)  | –50.92(14)            |          |
|  | 1.558(3) | 100.96(12)  | 115.51(17)  | –170.93(14)           | 0.83(6)  |
|  | 1.497(3) | 110.61(12)  | 106.03(17)  | 77.15(19)             |          |
| 2.1047(13)   | 1.493(3) | 108.80(11)  | 115.30(16)  | 35.72(17)             |          |
|  | 1.490(2) | 104.66(12)  | 112.41(15)  | 159.49(18)            |          |
|  | 1.573(3) | 106.21(11)  | 108.79(16)  | –85.50(14)            | 0.82(6)  |
| (d) [Co(en) <sub>2</sub> Cl(H <sub>2</sub> O)]H <sub>2</sub> S <sub>3</sub> O <sub>6</sub> ·H <sub>2</sub> O (This work)     |          |             |             |                       |          |
| 2.1191(14)   | 1.569(3) | 105.52(13)  | 106.12(16)  | –81.86(15)            | 0.89     |
|  | 1.492(3) | 102.19(12)  | 113.02(20)  | 167.36(12)            |          |
|  | 1.461(3) | 108.56(14)  | 120.05(16)  | 39.56(16)             |          |
| 2.1223(14)   | 1.550(3) | 106.12(12)  | 106.99(17)  | –39.90(14)            | 0.78(5)  |
|  | 1.502(3) | 109.86(12)  | 114.27(16)  | 75.43(13)             |          |
|  | 1.478(3) | 103.24(12)  | 115.88(16)  | –160.40(13)           |          |

angles.<sup>25</sup> In the present sulfanediphosphonates, the range of S–P bond lengths is small, and no such correlation will be found when individual thiophosphonate groups are compared. When, however, the thiophosphate group (a) is compared to thiophosphonate groups (b)–(d), the increase of the S–P bond from 1.9681(7) to an average of 2.1100 Å is accompanied by a decrease of the average S–P–O angle from 113.32 to 106.10°.

As seen from Tables 4 (a), (c) and (d), the P–OH bonds are 0.051–0.108 Å longer than the P–O bonds of the same phosphonate group. For the disulfanediphosphonate ion (b) the picture is not so clear, perhaps because such bonds are also influenced by hydrogen bonds, cation coordination and electrostatic crystal forces. The difference between the average of all P–OH and all P–O bonds is 0.053 Å. The P–OH and P–O bonds in the di- and trisulfanediphosphonates are decreased by an average of 0.031 and 0.033 Å, respectively, compared with the corresponding bonds in the thiophosphate, and the corresponding triple angle average has increased by 1.5 and 1.9°, respectively.

The Ba ion of compound 1 is surrounded by eight O atoms with distances Ba–O = 2.746(3)–2.900(3) Å. All O atoms of the phosphonate groups, except O(2), and the O atom of the solvate are involved in these contacts. O(1) and O(4) are each in contact with two different Ba atoms.

*Acknowledgement.* This investigation was supported by The Research Council of Norway.

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Received October 18, 1993.