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The Dihydrogenmonothiophosphate and Trihydrogendisulfanediphosphonate Anions. Crystal Structures of KH_2SPO_3 and $[Co(en)_2Cl_2]H_3S_2P_2O_6$

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Crystal structures of potassium dihydrogenmonothiophosphate, KH_2SPO_3 (**1**), and *trans*-dichlorobis(ethylenediamine)cobalt(III) trihydrogendisulfanediphosphonate, $[Co(en)_2Cl_2]H_3S_2P_2O_6$ (**2**), have been determined from X-ray data and refined to $R = 0.015$ and 0.043 for 476 and 1871 observed reflections, respectively. Compound **1** forms monoclinic crystals, space group Cm with $Z = 2$, and $a = 6.549(1)$, $b = 6.317(1)$, $c = 5.894(1)$ Å and $\beta = 109.13(1)°$. Compound **2** forms orthorhombic crystals, space group $P2_12_12_1$ with $Z = 4$ and $a = 8.238(1)$, $b = 10.295(1)$, $c = 19.383(2)$ Å. In compound **1** the slightly distorted tetrahedral arrangement around phosphorus has the dimensions: S–P = 1.9681(7), P–O = 1.5244(16)–1.5754(11) Å, S–P–O = 112.76(5)–114.45(7)°, O–P–O = 102.00(9)–106.96(6)°. The two H atoms are bonded to the two O atoms having longest distances from P, with O–H = 0.78(3) Å and P–O–H = 113(2)°. In compound **2** the anion has an unbranched, non-planar phosphorus-sulfur chain in which the P atoms are each bonded to one S atom and 3 O atoms. It has the dimensions: S–S = 2.0561(24) Å, S–P = 2.0954(24) and 2.1120(22) Å, P–O = 1.484(4)–1.540(5) Å, S–S–P = 100.04(9) and 102.21(9)°, S–P–O = 98.63(23)–110.02(21)°, O–P–O = 107.51(30)–118.83(30)°, O–H = 0.67(6)–0.94(7) Å, P–O–H = 118(6)–123(4)°, and the PSSP torsion angle is −85.46(11)°.

Sulfanediphosphonic acids, $H_2O_3P–S_n–PO_3H_2$, and their salts, sulfanediphosphonates, $S_nP_2O_6^{4-}$, are analogous to sulfanedisulfonic acids, $HO_3S–S_n–SO_3H$, and polythionates, $S_{n+2}O_6^{2-}$. Polythionates up to hexathionate, $S_6O_6^{2-}$, form relatively stable salts, and their structures are well characterized.[1,2] Of sulfanediphosphonates, three rather unstable salts of disulfanediphosphonic acid and two salts of trisulfanediphosphonic acid have been reported.[3–5] No structure determination of these compounds or of the monothiophosphate has been reported.

We describe here the preparation and structures of potassium dihydrogenmonothiophosphate, KH_2SPO_3 (**1**), and *trans*-dichlorobis(ethylenediamine)cobalt(III) trihydrogendisulfanediphosphonate, $[Co(en)_2Cl_2]H_3S_2P_2O_6$ (**2**).

Experimental

Preparations. KH_2SPO_3 was prepared as described by Fehér and Vial,[4] as well developed, needle-shaped, colourless crystals. $[Co(en)_2Cl_2]H_3S_2P_2O_6$ was obtained by metathesis from $Ba_2S_2P_2O_6 \cdot 2H_2O$, prepared as described by Ladwig and Thilo.[3] A solution of $[Co(en)_2Cl_2]Cl \cdot H_2O$ (1.5 g, 5 mmol) in H_2O (5 cm^3) was added with stirring to a solution of $Ba_2S_2P_2O_6 \cdot 2H_2O$ (0.54 g, 1.0 mmol) in 0.5 M HCl (10 cm^3). Then 12 cm^3 of ethanol were slowly added, and the solution was kept at −2 °C for 20 h. The crystals were filtered off and washed with ethanol and then with diethyl ether. Yield 0.2 g (40% based on the Ba-salt) of dark green tetragonal bipyramidal or pseudo-hexagonal plate-like crystals. The compound was unchanged after months when kept in an argon atmosphere at −2 °C, and was even stable for weeks at room temperature. The products were analysed iodometrically.[3,4]

X-Ray structure analyses. The determination of unit cell parameters and the data collection were carried out on an ENRAF-NONIUS CAD4 diffractometer, using monochromated Mo$K\alpha$ radiation ($\lambda = 0.710\,69$ Å). Crystal data and 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

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Table 1. Crystallographic data.

Compound	KH_2SPO_3 (**1**)	$[Co(en)_2Cl_2]H_3S_2P_2O_6$ (**2**)
Formula	H_2KO_3PS	$C_4H_{19}Cl_2CoN_4O_6P_2S_2$
M	152.2	475.1
System	Monoclinic	Orthorhombic
Space group	Cm	$P2_12_12_1$
a/Å	6.549(1)	8.238(1)
b/Å	6.317(1)	10.295(1)
c/Å	5.894(1)	19.383(2)
β/°	109.13(1)	
V/Å^3	230.3(3)	1643.8(4)
Z	2	4
T/K	293	293
D_x/g cm^{-3}	2.194	1.920
D_o/g cm^{-3}	2.198	1.931
$F(000)$	152	968
Θ_{max}	33	30
Scan mode	ω	ω
Scan speed/° min^{-1}	1.0–2.8	1.0–4.1
Min scan width/°	1.25	1.30
Loss of intensity(%)	1.0	13
$\mu=(MoK\alpha)$/cm^{-1}	17.9	18.4
Crystal volume/mm^3	0.0013	0.0016
Correction for absorption	Numerical	Numerical
Transmission factors	0.83–0.89	0.69–0.95
No. of independent measurements	486	2715
No. with $I<2\sigma(I)$	476	1871
No. of parameters refined	37	202
$R=\Sigma\|\|F_o\|-\|F_c\|\|/\Sigma\|F_o\|$	0.015	0.043
$R_w=[\Sigma w(F_o-F_c)^2/\Sigma wF_o^2]^{1/2}$	0.019	0.038
$S=[\Sigma W(F_o-F_c)^2/(n-m)]^{1/2}$	1.22	1.26
Max. $\Delta(\rho)$/e Å^{-3}	0.13	0.79

effects, decay and absorption. Reflections with $I>2\sigma(I)$ were regarded as observed.

The structure of compound **1** was solved by direct (MULTAN) and Fourier difference methods and refined by least-squares calculations, using anisotropic thermal parameters for all non-hydrogen atoms. An extinction coefficient g in $F_{corr}=F_c(1+gI_c)$ was included as a variable and refined to 4.20×10^{-5}.

An attempt was made to solve the structure of compound **2** by direct methods (MULTAN), but without success. The Patterson map, however, revealed the positions of cobalt and the two chlorine atoms, and all other atoms, except the hydrogen atoms of the ethylenediamine groups, were located from Fourier difference maps. The hydrogen atoms of the ethylenediamine groups were placed geometrically with bond lengths N–H = 0.87 and C–H = 0.95 Å, and were held fixed, with isotropic thermal parameters equal to 1.3 B_{eq} for the atoms to which they are attached. Secondary extinction effects were found to be negligible.

Both structures have acentric space groups, and were also refined with inverted coordinates, whereby the R- and S-values increased slightly. The programs used were the ENRAF-NONIUS Structure Determination Package 1987. All refined atomic coordinates are given in Table 2.

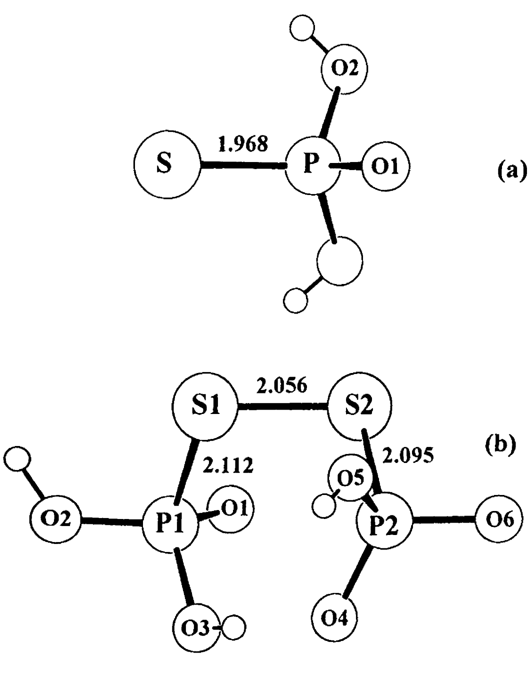

Fig. 1. Views of the dihydrogenmonothiophosphate ion in KH_2SPO_3 (a) and the trihydrogendisulfanediphosphonate ion in $[Co(en)_2Cl_2]H_3S_2P_2O_6$ (b).

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

Atom	*x*	*y*	*z*	$B_{eq}/Å^2$
(a) KH_2SPO_3 (**1**)				
K	0.1525	0	0.3917	1.964(8)
S	0.60808(11)	0	0.20729(11)	1.589(9)
P	0.65164(9)	0	0.89235(10)	0.961(7)
O(1)	0.88779(24)	0	0.90453(28)	1.29(2)
O(2)	0.53991(19)	0.19382(19)	0.73107(18)	1.64(2)
H	0.493(4)	0.275(5)	0.800(4)	3.4(6)
(b) $[Co(en)_2Cl_2]H_3S_2P_2O_6$ (**2**)				
S(1)	−0.12005(23)	0.76907(17)	0.29011(8)	2.97(3)
S(2)	0.10149(23)	0.86038(15)	0.28418(9)	3.11(3)
P(1)	−0.19080(21)	0.76001(16)	0.19548(8)	2.48(3)
P(2)	0.25182(25)	0.70009(19)	0.26530(9)	3.23(4)
O(1)	−0.1703(6)	0.8898(4)	0.1534(2)	3.5(1)
O(2)	−0.3579(6)	0.7029(5)	0.1899(2)	4.1(1)
O(3)	−0.0812(6)	0.6595(5)	0.1495(2)	3.5(1)
O(4)	0.1972(6)	0.6309(4)	0.2002(2)	3.5(1)
O(5)	0.2500(9)	0.6198(5)	0.3312(3)	6.4(2)
O(6)	0.4139(7)	0.7709(6)	0.2113(3)	6.0(1)
Co	0.13229(9)	0.00536(7)	0.00487(4)	1.65(1)
Cl(1)	0.13557(19)	0.22375(13)	0.01631(8)	2.70(3)
Cl(2)	0.12841(20)	−0.21160(13)	−0.00552(8)	2.84(3)
N(1)	−0.1051(5)	0.0037(5)	0.0085(2)	2.3(1)
N(2)	0.1055(6)	0.0261(5)	−0.0941(2)	2.3(1)
N(3)	0.3694(5)	0.0020(5)	−0.0006(3)	2.5(1)
N(4)	0.1613(6)	−0.0145(5)	0.1034(2)	2.5(1)
C(1)	−0.1697(6)	−0.0159(6)	−0.0620(3)	2.5(1)
C(2)	−0.0659(8)	0.0611(6)	−0.1096(3)	2.6(1)
C(3)	0.4372(8)	−0.0006(9)	0.0695(4)	4.2(2)
C(4)	0.3284(9)	−0.0378(14)	0.1197(4)	9.1(4)
H(17)	−0.439(8)	0.735(6)	0.220(3)	4.6(1.8)
H(18)	−0.004(7)	0.648(5)	0.163(3)	2.2(1.3)
H(19)	0.244(8)	0.554(5)	0.330(3)	3.4(1.5)

Results and discussion

Bond lengths and angles are given in Table 3. Views of the dihydrogenmonothiophosphate and trihydrogendisulfanediphosphonate ions are shown in Fig. 1.

All atoms of the monothiophosphate ion, except O(2) and the hydrogen bonded to this atom, are situated in a mirror plane. P–S bond lengths in tetrathiophosphates are in the range 2.033(2)–2.080(2) Å,[6–9] in dithiophosphate of neodymium[10] it is somewhat shorter, 2.002(4)–2.026(5) Å, and in the present monothiophosphate considerably shorter, 1.9681(7) Å. The corresponding bonds in bis(dicyclohexylthiophosphoryl)disulfane[11] and two bis(dialkylthiophosphoryl)disulfanes[12] are 1.9312(8)–1.9456(8) Å. Two of the O atoms of the monothiophosphate ion are connected to H atoms and have P–O bond lengths of 1.5754(11) Å, and the third P–O bond length is 1.5244(16) Å. In a paper on the crystal structure determination of phosphoric acid[13] it was pointed out that three of the P–O bonds, presumably P–OH bonds, are 1.57 Å, whereas the fourth bond is 1.52 Å. An increase in P–O bond lengths when O is bonded to H has later been found in numerous structures of phosphoric acids and phosphates. The average value of the S–P–O angles is 113.32° and of the O–S–O angles 105.30°. The K cation, also situated in a mirror plane, is surrounded by 5 O atoms with distances K–O = 2.826(16)–3.0415(12) Å and angles O–K–O = 49.32(4)–142.94(3)°.

The disulfanediphosphonate ion has an unbranched non-planar P–S–S–P chain and may have left-handed and right-handed forms. The space group is enantiomorphous, and in the crystal studied the left-handed form was found, with torsion angle −85.46(11)°. No symmetry is crystallographically required for the disulfanediphosphonate anion, but, neglecting H atoms, the bond lengths, bond angles and orientation of the phosphonate groups are nearly the same in the two halves, and so the ion possesses a pseudo-twofold symmetry axis passing through the S–S bond. The disulfanediphosphonate ion is the oxidative dimerization product of the thiophosphonate ion. The bonding through the S atoms leads to elongation of the S–P bond from 1.9861(7) Å to an average of 2.1037 Å, a decrease of the average S–P–O angle from 113.32 to 105.67°, an increase of the average O–S–O angle from 105.30 to 112.86°, and to slightly shorter S–O bonds. The anion clearly resembles its polythionate analogue, the tetrathionate, $S_4O_6^{2-}$, as found in its Ba and Na salts.[14,15] The S–S bond, 2.0561(24) Å, is longer than in tetrathionate, 2.019(1) Å, but is within the range of S–S bonds in other disulfanes with –S–S– torsion angles

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

(a) KH_2SPO_3 (**1**)			
P–S	1.9681(7)	S–P–O(1)	114.45(7)
P–O(1)	1.5244(16)	S–P–O(2)	112.76(5)
P–O(2)	1.5754(11)	O(1)–P–O(2)	106.96(6)
O(2)–H	0.78(3)	O(2)–P–O(2′)	102.00(9)
		P–O(2)–H	113(2)
(b) $[Co(en)_2Cl_2]H_3S_2P_2O_6$ (**2**)			
P(1)–S(1)	2.1120(22)	P(1)–S(1)–S(2)	102.21(9)
S(1)–S(2)	2.0561(24)	S(1)–S(2)–P(2)	100.04(9)
S(2)–P(2)	2.0954(24)		
P(1)–O(1)	1.484(4)	S(1)–P(1)–O(3)	107.58(22)
P(1)–O(2)	1.499(5)	O(1)–P(1)–O(2)	118.83(30)
P(1)–O(3)	1.540(5)	O(1)–P(1)–O(3)	110.38(28)
O(2)–H(17)	0.94(7)	O(2)–P(1)–O(3)	107.51(30)
O(3)–H(18)	0.70(6)	P(1)–O(2)–H(17)	123(4)
S(1)–P(1)–O(1)	109.38(19)	P(1)–O(3)–H(18)	118(6)
S(2)–P(1)–O(2)	102.44(21)		
P(2)–O(4)	1.486(4)	S(2)–P(2)–O(6)	98.63(23)
P(2)–O(5)	1.522(6)	O(4)–P(2)–O(5)	115.35(30)
P(2)–O(6)	1.523(6)	O(4)–P(2)–O(6)	116.97(32)
O(5)–H(19)	0.67(6)	O(5)–P(2)–O(6)	108.11(42)
S(2)–P(2)–O(4)	110.02(21)	P(2)–O(5)–H(19)	121(6)
S(2)–P(2)–O(5)	105.97(30)		
Co–Cl(1)	2.2593(16)	N(1)–C(1)	1.480(7)
Co–Cl(2)	2.2429(16)	N(2)–C(2)	1.488(7)
Co–N(1)	1.957(4)	N(3)–C(3)	1.469(7)
Co–N(2)	1.942(4)	N(4)–C(4)	1.433(8)
Co–N(3)	1.957(4)	C(1)–C(2)	1.486(8)
Co–N(4)	1.936(4)	C(3)–C(4)	1.377(10)
Cl(1)–Co–N(1)	91.00(15)	N(1)–Co–N(2)	85.57(19)
Cl(1)–Co–N(2)	89.38(14)	N(3)–Co–N(4)	85.88(20)
Cl(1)–Co–N(3)	90.62(16)	N(1)–Co–N(4)	94.99(19)
Cl(1)–Co–N(4)	90.39(16)	N(2)–Co–N(3)	93.57(20)
Cl(2)–Co–N(1)	88.85(15)	Co–N(1)–C(1)	109.3(3)
Cl(2)–Co–N(2)	91.08(14)	Co–N(2)–C(2)	109.5(3)
Cl(2)–Co–N(3)	89.54(16)	Co–N(3)–C(3)	109.2(4)
Cl(2)–Co–N(4)	89.15(16)	Co–N(4)–C(4)	110.7(4)
Cl(1)–Co–Cl(2)	179.50(7)	N(1)–C(1)–C(2)	107.1(5)
N(1)–Co–N(3)	178.16(19)	N(2)–C(2)–C(1)	107.0(4)
N(2)–Co–N(4)	179.40(21)	N(3)–C(4)	114.3(6)
		N(4)–C(4)–C(3)	115.0(7)

near 90°, see for example Refs. 11 and 12 and references therein.

Some further details of the present structures are discussed in a paper on the crystal structures of two salts of dihydrogentrisulfanediphosphonate.[16]

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References

1. Foss, O. *Adv. Inorg. Chem. Radiochem. 2* (1960) 237.
2. Marøy, K. *Doctoral Dissertation*, University of Bergen, 1975.
3. Ladwig, G. and Thilo, E. *Z. Anorg. Allgem. Chem. 335* (1965) 126.
4. Fehér, F. and Vial, F. *Z. Anorg. Allgem. Chem. 335* (1965) 113.
5. Wagner, H. and Müller, R. *Z. Anorg. Allgem. Chem. 429* (1977) 270.
6. Toffoli, P., Khodadad, P. and Rodier, N. *Acta Crystallogr., Sect. B 33* (1977) 285.
7. Toffoli, P., Rouland, J. C., Khodadad, P. and Rodier, N. *Acta Crystallogr., Sect. C 41* (1985) 645.
8. Mercier, R., Malugani, J. P., Fahys, B. and Robert, G. *Acta Crystallogr., Sect. B 38* (1982) 1887.
9. Simon, A., Peters, K., Peters, E.-M. and Hahn, H. *Z. Naturforsch., Teil B 38* (1983) 426.
10. Palkina, K., Maksimova, S., Chibiskova, N., Tripolskaya, T., Wolf, G. and Kurzhinova, T. *Izv. Akad. Nauk. SSSR, Neorg. Mater. 27* (1991) 1028.
11. Buranda, T., Gallacher, A. C. and Pinkerton, A. A. *Acta Crystallogr., Sect. C 47* (1991) 1414.
12. Gallacher, A. C. and Pinkerton, A. A. *Acta Crystallogr., Sect. C 48* (1992) 2085.
13. Furberg, S. *Acta Chem. Scand. 9* (1955) 1557.
14. Foss, O., Furberg, S. and Zachariasen, H. *Acta Chem. Scand. 8* (1954) 459.
15. Foss, O. and Hordvik, A. *Acta Chem. Scand. 18* (1964) 662; Christidas, P. C., Renzeperis, P. J. and Bolas, C.A. *Z. Kristallogr. 177* (1986) 107.
16. Janickis, V. and Marøy, K. *Acta Chem. Scand. 48* (1994) 465.

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