The second P_8O_{24} ring anion

$P(5)O_4$ tetrahedron

P(5)	O(*L*56)	O(*L*58)	O(*E*51)	O(*E*52)
O(*L*56)	1.598 (4)	2.424 (4)	2.501 (5)	2.508 (5)
O(*L*58)	98.6 (2)	1.600 (3)	2.441 (3)	2.517 (4)
O(*E*51)	108.9 (2)	104.9 (2)	1.476 (2)	2.582 (4)
O(*E*52)	109.5 (2)	110.0 (1)	122.3 (2)	1.472 (3)

$P(6)O_4$ tetrahedron

P(6)	O(*L*56)	O(*L*67)	O(*E*61)	O(*E*62)
O(*L*56)	1.589 (3)	2.454 (4)	2.551 (4)	2.436 (5)
O(*L*67)	100.4 (1)	1.606 (2)	2.469 (4)	2.537 (3)
O(*E*61)	112.9 (2)	106.6 (1)	1.471 (3)	2.573 (5)
O(*E*62)	104.5 (2)	110.0 (2)	120.6 (2)	1.490 (3)

$P(7)O_4$ tetrahedron

P(7)	O(*L*67)	O(*L*78)	O(*E*71)	O(*E*72)
O(*L*67)	1.590 (3)	2.454 (4)	2.455 (4)	2.536 (4)
O(*L*78)	99.7 (2)	1.619 (3)	2.522 (4)	2.519 (4)
O(*E*71)	106.3 (1)	109.0 (1)	1.477 (2)	2.564 (3)
O(*E*72)	111.2 (1)	108.6 (1)	120.1 (2)	1.482 (3)

$P(8)O_4$ tetrahedron

P(8)	O(*L*58)	O(*L*78)	O(*E*81)	O(*E*82)
O(*L*58)	1.595 (2)	2.434 (3)	2.524 (3)	2.521 (3)
O(*L*78)	99.5 (1)	1.595 (3)	2.524 (4)	2.492 (4)
O(*E*81)	110.2 (2)	110.2 (2)	1.482 (3)	2.541 (5)
O(*E*82)	109.8 (1)	107.9 (2)	117.7 (1)	1.486 (3)

P(5)—O(*L*56)—P(6)	136.5 (2)	P(8)—P(5)—P(6)	106.75 (4)
P(6)—O(*L*67)—P(7)	134.9 (1)	P(5)—P(6)—P(7)	103.72 (4)
P(7)—O(*L*78)—P(8)	126.3 (2)	P(6)—P(7)—P(8)	114.55 (4)
P(5)—O(*L*58)—P(8)	131.0 (1)	P(5)—P(8)—P(7)	119.87 (3)

P(5)—P(6)	2.960 (1)	P(7)—P(8)	2.868 (1)
P(6)—P(7)	2.952 (1)	P(8)—P(5)	2.908 (1)

The title compound was prepared in several stages. Firstly, the phosphoric acid $H_8P_8O_{24}$ was prepared from an aqueous solution of sodium *cyclo*-octaphosphate (Schülke, 1968*a*,*b*) using an ion-exchange resin (Amberlite IRN 77). The resulting acid was then neutralized by ammonium carbonate and the aqueous solution of $(NH_4)_8P_8O_{24}$ so obtained was added to an aqueous solution of telluric acid in stoichiometric ratio. Crystals of the title compound were obtained by slow evaporation of the resulting solution at room temperature.

During the data collection, a pseudo-body-centred distribution of the diffracted intensities was observed. This phenomenon is clearly explained by the results of the structure determination; in this atomic arrangement, the main components [$Te(OH)_6$ groups and two independent P_8O_{24} rings] are centred on $\pm(\frac{1}{4},\frac{1}{4},\frac{1}{4})$, $(0,0,\frac{1}{2})$ and $(\frac{1}{2},\frac{1}{2},0)$.

It was noticed that a pseudo-monoclinic unit cell (dimensions $a = 21.72$, $b = 11.06$, $c = 15.16$ Å, $\beta = 112.46°$) can be derived from the triclinic one used for the structure determination. However, the angles α and γ could not be refined to values acceptably close to 90° with such a setting and careful examination of the intensity repartition did not reveal a possible monoclinic symmetry.

The crystal structure was solved using direct methods (Main, Lessinger, Woolfson, Germain & Declercq, 1977). Table 1 gives the final atomic coordinates and B_{eq} values for the non-H atoms of this arrangement. The corresponding data for the H atoms have been deposited. The figure was drawn using *STRUPLO* (Fischer, 1985).

Lists of structure factors, anisotropic thermal parameters, coordinates of the unique molecule, H-atom coordinates and main interatomic bond distances and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55533 (57 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: PA1019]

References

Fischer, R. X. (1985). *J. Appl. Cryst.* **18**, 258–262.

Laügt, M. & Guitel, J. C. (1975). *Z. Kristallogr.* **141**, 203–216.

Main, P., Lessinger, L., Woolfson, M. M., Germain, G. & Declercq, J.-P. (1977). *MULTAN77. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Palkina, K. K., Maksimova, S. I., Kusznetsov, V. G. & Chudinova, N. N. (1979). *Dokl. Akad. Nauk SSSR*, **245**, 1386–1389.

Schülke, U. (1968*a*). *Angew. Chem. Int. Ed. Engl.* **7**, 71.

Schülke, U. (1968*b*). *Z. Anorg. Allg. Chem.* **360**, 231–246.

Schülke, U., Averbuch-Pouchot, M. T. & Durif, A. (1992*a*). *J. Solid State Chem.* In the press.

Schülke, U., Averbuch-Pouchot, M. T. & Durif, A. (1992*b*). *Z. Kristallogr.* In the press.

Stout, G. H. & Jensen, L. H. (1968). *X-ray Structure Determination.* London: Macmillan.

Acta Cryst. (1993). C**49**, 363–365

Structure of a New Sodium Thiosulfate Hydrate

Werner Hesse and Bernd Leutner

Ammoniaklaboratorium, BASF Aktiengesellschaft,
Carl Bosch Strasse 38, *D*-6700 *Ludwigshafen/Rhein,*
Germany

Karl-Heinz Böhn and Nigel P. C. Walker

Hauptlaboratorium, BASF Aktiengesellschaft,
Carl Bosch Strasse 38, *D*-6700 *Ludwigshafen/Rhein,*
Germany

(*Received* 13 *February* 1992; *accepted* 4 *September* 1992)

Abstract

A new crystal form of sodium thiosulfate hydrate with the stoichiometry $Na_2S_2O_3.\frac{2}{3}H_2O$ is reported.

Comment

During the synthesis of sodium dithionite ($Na_2S_2O_4$) following the 'formate process' (Ostertag *et al.*, 1979), a small amount of sodium thiosulfate was produced as a side product. The latter was removed from the sodium dithionite solid by washing with methanol at *ca* 323 K. On cooling the resulting methanol solution to room temperature, a white precipitate consisting of various crystalline forms of sodium thiosulfate was formed. In addition to the previously reported pentahydrate and anhydrous α-$Na_2S_2O_3$ forms, powder diffractometry showed an

0108-2701/93/020363-03$06.00

unknown form to be present. These crystals were also observable owing to their clearly different habit. By slowly cooling the solution to 293 K, thin needles longer than 1 cm were obtained. As removal of the mother liquor caused loss of crystallinity, the crystals were transferred to 100% methanol and a selected crystal was enveloped in perfluoropolyether oil RS 3000 (Riedel-de Haën). The crystal was drawn onto the tip of a glass fibre and immediately placed in a 143 K nitrogen cold stream whereupon the oil solidified, rendering the crystal immobile.

The asymmetric unit contains three molecules of the thiosulfate anion and seven unique atomic positions for Na cations. Five of the Na atoms lie on 'general positions', one lies on a centre of symmetry and hence has a site multiplicity factor of $\frac{1}{2}$, and the seventh lies 0.569 (6) Å from a crystallographic two-fold axis. The latter was successfully refined as a disordered Na atom with a site occupation factor of $\frac{1}{2}$. In addition, there are two molecules of water in the asymmetric unit. This crystal form thus has the stoichiometry $Na_2S_2O_3.\frac{2}{3}H_2O$. The large elongated ellipsoid for the anisotropic displacement parameters of the water O(11) suggested that it could be better modelled by two half-positions. These refined well, without the need for any restraints, to give an inter-atomic distance of 0.669 (7) Å. H atoms were included for both water molecules and were refined with O—H distance restraints and a common isotropic displacement parameter for each pair. Splitting of the hydrogen positions between O(11) and O(11′) was not observable but was reflected by the considerably larger displacement parameter compared with that of the other water molecule. A hydrogen-bonding system is formed along the *b* axis by the bridging of successive S(6) atoms by the water molecule O(10) [H(10*A*)···S(6) 2.50 (2), H(10*B*)···S(6) 2.42 (2) Å]. Water O(11)/O(11′) also makes a hydrogen bond to S(6) [H(11B)···S(6) 2.37 (6) Å] and a longer bond to S(2) [H(11*A*)···S(2) 2.90 (6) Å].

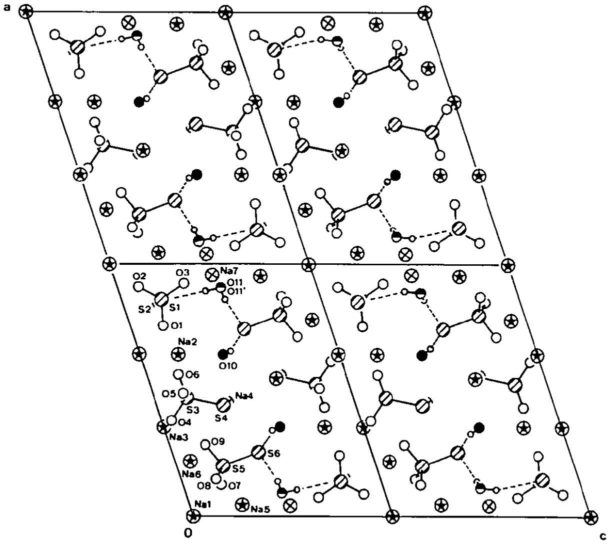

Fig. 1. Crystal packing projected along the *b* axis. Large circles represent S atoms (cross-hatched) or Na atoms [starred, except for the disordered Na(7) which is shown crossed]. O atoms are shown with smaller circles, those belonging to water molecules are filled [O(10)] or half-filled [O(11) and O(11′)]. Non-H atoms are labelled according to the atomic coordinates given in Table 1. Hydrogen bonds are drawn with dashed lines.

Four crystal forms of anhydrous sodium thiosulfate have been characterized crystallographically (von Benda, 1979) with the room-temperature-stable α-form having also been studied by neutron diffraction (Teng, Fuess & Bats, 1984). $Na_2S_2O_3$ can form hydrates with 12, 10, 6, 5, 4, 3, 2 and 0.5 molecules of H_2O (Henke, 1982), and a monohydrate has also been reported (Edwards & Woolf, 1985). However, to our knowledge, only the pentahydrate has been characterized structurally both by X-ray (Aydin Uraz & Armagan, 1977) and neutron (Lisensky & Levy, 1978) diffraction. The phase determined here, with a stoichiometry of $Na_2S_2O_3.\frac{2}{3}H_2O$, has not been reported in the literature.

Experimental

Crystal data

$Na_2S_2O_3.\frac{2}{3}H_2O$
$M_r = 170.11$
Monoclinic
$C2/c$
$a = 27.558$ (5) Å
$b = 5.550$ (2) Å
$c = 20.855$ (3) Å
$\beta = 108.790$ (10)°
$V = 3019.7$ (13) Å^3
$Z = 24$
$D_x = 2.245$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å
Cell parameters from 24 reflections
$\theta = 4.5–17.8°$
$\mu = 10.626$ mm^{-1}
$T = 143.0$ (10) K
Plate
0.50 × 0.13 × 0.05 mm
Colourless

Data collection

Syntex $P2_1$ diffractometer
$\omega–2\theta$ scans
Absorption correction: refined from ΔF (*DIFABS*; Walker & Stuart, 1983)
$T_{\min} = 0.218$, $T_{\max} = 1.000$
4006 measured reflections
2003 independent reflections

1791 observed reflections [$I > 2\sigma(I)$]
$R_{\rm int} = 0.0268$
$\theta_{\max} = 56.67°$
$h = -29 \rightarrow 29$
$k = -6 \rightarrow 5$
$l = -22 \rightarrow 22$
3 standard reflections monitored every 100 reflections intensity variation: <2%

Refinement

Refinement on F^2
Final $R = 0.0262$
$wR = 0.0699$
$S = 1.114$
2001 reflections
238 parameters

$\Delta\rho_{\min} = -0.293$ e Å^{-3}
Extinction correction: *SHELXL*92 (Sheldrick, 1992)
Extinction coefficient: 0.00028 (2)

Calculated weights
$w = 1/[\sigma^2(F_o^2)+(0.0438P)^2 +3.4506P]$ where
$P = (F_o^2+2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.000$
$\Delta\rho_{\max} = 0.481$ e Å^{-3}

Atomic scattering factors from *International Tables for Crystallography* (1992, Vol C, Tables 4.2.6.8 and 6.1.1.4)

Data collection: Siemens *P3V* v4.11 software. Cell refinement: Siemens *P3V* v4.11 software. Data reduction: *SHELXTL-Plus* (Sheldrick, 1990). Program(s) used to solve structure: *SHELXTL-Plus*. Program(s) used to refine structure: *SHELXL*92. Molecular graphics: *SHELXTL-Plus*. Software used to prepare material for publication: *SHELXL*92.

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$U_{\rm eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Na1	0.0000	0.5000	0.0000	0.0135 (9)
Na2	0.32160 (4)	0.5131 (2)	0.09582 (6)	0.0089 (6)
Na3	0.17798 (4)	0.5214 (2)	0.00112 (6)	0.0101 (6)
Na4	0.22587 (4)	0.4637 (2)	0.17752 (6)	0.0106 (6)
Na5	0.02313 (4)	−0.0277 (2)	0.13187 (6)	0.0116 (6)
Na6	0.10950 (4)	0.0306 (2)	0.03791 (6)	0.0111 (6)
Na7	0.47897 (9)	−0.0849 (5)	0.24839 (12)	0.0171 (13)
S1	0.43057 (3)	0.13967 (15)	0.10069 (3)	0.0080 (4)
S2	0.42611 (3)	−0.21709 (14)	0.09170 (4)	0.0107 (4)
S3	0.23670 (3)	0.02494 (13)	0.08171 (3)	0.0053 (4)
S4	0.22143 (3)	−0.03692 (14)	0.16767 (4)	0.0096 (4)
S5	0.10020 (3)	0.49282 (13)	0.11585 (4)	0.0058 (4)
S6	0.12770 (3)	0.51435 (14)	0.21695 (4)	0.0142 (5)
O1	0.37844 (8)	0.2337 (4)	0.08301 (14)	0.0276 (12)
O2	0.45515 (7)	0.2409 (4)	0.05329 (9)	0.0097 (11)
O3	0.46191 (9)	0.2057 (4)	0.16985 (10)	0.0214 (14)
O4	0.19106 (7)	−0.0507 (4)	0.02523 (10)	0.0103 (11)
O5	0.24484 (7)	0.2865 (4)	0.07667 (9)	0.0074 (11)
O6	0.28173 (7)	−0.1107 (4)	0.07993 (10)	0.0109 (11)
O7	0.06323 (7)	0.2927 (4)	0.09648 (9)	0.0076 (11)
O8	0.07409 (7)	0.7198 (4)	0.08794 (10)	0.0092 (10)
O9	0.14262 (7)	0.4458 (4)	0.08902 (10)	0.0096 (10)
O10	0.32138 (9)	0.5067 (4)	0.20806 (11)	0.0123 (13)
O11	0.4534 (3)	0.6422 (14)	0.2584 (4)	0.014 (3)
O11′	0.4437 (3)	0.5309 (14)	0.2565 (4)	0.014 (3)

Table 2. *Geometric parameters* (Å, °)

Na1—O2$^{\rm i}$	2.331 (2)	Na5—O2$^{\rm vi}$	2.422 (2)
Na1—O7	2.480 (2)	Na5—O3$^{\rm vi}$	2.554 (3)
Na1—O8	2.571 (2)	Na6—O8$^{\rm v}$	2.381 (3)
Na1—S5	3.0275 (9)	Na6—O4	2.389 (2)
Na2—O1	2.280 (3)	Na6—O2$^{\rm iii}$	2.494 (2)
Na2—O6$^{\rm ii}$	2.332 (3)	Na6—O7	2.497 (2)
Na2—O10	2.343 (3)	Na6—O9	2.579 (3)
Na2—O5	2.381 (2)	Na7—O3	2.238 (4)
Na2—O4$^{\rm iii}$	2.444 (2)	Na7—O11$'^{\rm v}$	2.372 (8)
Na3—O6$^{\rm iii}$	2.355 (2)	Na7—O11$^{\rm vii}$	2.441 (8)
Na3—O9	2.374 (2)	Na7—O3$^{\rm viii}$	2.524 (4)
Na3—O5	2.389 (2)	S1—O1	1.460 (2)
Na3—O1$^{\rm iii}$	2.396 (3)	S1—O3	1.469 (2)
Na3—O4$^{\rm ii}$	2.430 (3)	S1—O2	1.477 (2)
Na4—O9	2.440 (2)	S1—S2	1.9890 (14)
Na4—O10	2.512 (3)	S3—O6	1.462 (2)
Na4—O5	2.525 (2)	S3—O5	1.478 (2)
Na4—S4$^{\rm ii}$	2.779 (2)	S3—O4	1.480 (2)
Na4—S4	2.786 (2)	S3—S4	1.9987 (13)
Na5—O11$'^{\rm iv}$	2.233 (8)	S5—O9	1.473 (2)
Na5—O7	2.335 (2)	S5—O7	1.473 (2)
Na5—O11$^{\rm iv}$	2.365 (8)	S5—O8	1.474 (2)
Na5—O8$^{\rm v}$	2.367 (3)	S5—S6	2.0013 (11)

Symmetry codes: (i) $x - \frac{1}{2}, \frac{1}{2} + y, z$; (ii) $x, 1 + y, z$; (iii) $\frac{1}{2} - x, \frac{1}{2} - y, -z$; (iv) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; (v) $x, y - 1, z$; (vi) $x - \frac{1}{2}, y - \frac{1}{2}, z$; (vii) $1 - x, y - 1, \frac{1}{2} - z$; (viii) $1 - x, y, \frac{1}{2} - z$.

The structure was solved by direct methods. Refinement was on F^2 for all reflections except those flagged for possible systematic errors; the observed threshold $I > 2\sigma(I)$ was used only for calculating *R*(obs.) *etc.* and is given here for comparison with refinements on *F*.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55580 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SE1007]

References

Aydin Uraz, A. & Armagan, N. (1977). *Acta Cryst.* **B33**, 1396–1399.
Benda, H. von (1979). *Z. Naturforsch. Teil B*, **34**, 957–968.
Edwards, D. A. & Woolf, A. A. (1985). *Polyhedron*, **4**, 513–516.
Henke, K.-H. (1982). *Ullmans Encyklopädie der technischen Chemie*, Vol. 21, 4th ed. Weinheim: Verlag Chemie.
Lisensky, G. C. & Levy, H. A. (1978). *Acta Cryst.* **B34**, 1975–1977.
Ostertag, W., Ertl, G., Wunsch, G., Kiener, V., Voelkl, E. & Schreiner, S. (1979). German patent No. 2 748 935.
Sheldrick, G. M. (1990). *SHELXTL-Plus*. Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1992). *SHELXL*92. Program for the refinement of crystal structures. Univ. of Göttingen, Germany.
Teng, S. T., Fuess, H. & Bats, J. W. (1984). *Acta Cryst.* **C40**, 1785–1787.
Walker, N. & Stuart, D. (1983). *Acta Cryst.* **A39**, 158–166.

Acta Cryst. (1993). **C49**, 365–368

Structure du Bis(π-allylhimachalène)-α,α-dichlorodipalladium

ANGÈLE CHIARONI ET CLAUDE RICHE

Institut de Chimie des Substances Naturelles, CNRS, 91198 Gif sur Yvette CEDEX, France

L. EL FIRDOUSSI, A. BENHARREF ET A. KARIM

Département de Chimie, Faculté des Sciences Semlalia, Université Cadi Ayyad, BP S15, Marrakech, Maroc

(*Reçu le* 17 *juillet* 1992, *accepté le* 6 *octobre* 1992)

Abstract

Reaction of β-himachalene with palladium(II) chloride gives bis(chloro)bridged cyclopalladated dimers with high regioselectivity. The allyl groups adopt a *cis* arrangement to one another resulting in a pseudo C_2 axis in the complex. The palladium is coordinated along the α face

0108-2701/93/020365-04$06.00