N21	0.4868 (4)	0.0339 (3)	−0.3491 (3)	0.0755 (12)
C21	0.4738 (4)	0.0533 (4)	−0.2686 (4)	0.0666 (12)
S21	0.4575 (2)	0.0817 (2)	−0.15210 (12)	0.1125 (6)
N22	0.4365 (3)	0.1339 (3)	−0.5318 (3)	0.0756 (12)
C22	0.3941 (4)	0.2009 (3)	−0.5529 (3)	0.0585 (11)
S22	0.33085 (13)	0.29737 (10)	−0.58343 (11)	0.0873 (5)
N23	0.3470 (3)	−0.0733 (3)	−0.5104 (3)	0.0714 (11)
C23	0.2636 (5)	−0.1139 (4)	−0.5049 (3)	0.0645 (12)
S23	0.14525 (14)	−0.17358 (13)	−0.49527 (14)	0.1045 (6)
N4	0.2190 (3)	0.1352 (3)	0.2411 (3)	0.0699 (11)
C41	0.3094 (5)	0.0995 (5)	0.1882 (5)	0.103 (2)
C42	0.2757 (6)	0.0388 (6)	0.0917 (5)	0.125 (3)
C43	0.1624 (7)	0.0484 (5)	0.2900 (5)	0.130 (3)
C44	0.0965 (8)	0.0747 (8)	0.3666 (6)	0.167 (4)
C45	0.1494 (5)	0.1946 (5)	0.1826 (4)	0.097 (2)
C46	0.2076 (7)	0.2822 (5)	0.1440 (5)	0.137 (3)
N5	0.1754 (3)	0.2651 (3)	0.7387 (3)	0.0720 (11)
C51	0.2416 (6)	0.3575 (5)	0.7907 (6)	0.119 (2)
C52	0.3160 (7)	0.3338 (7)	0.8665 (6)	0.147 (3)
C53	0.2412 (5)	0.1999 (5)	0.6805 (5)	0.098 (2)
C54	0.1800 (7)	0.1021 (6)	0.6473 (5)	0.134 (3)
C55	0.0776 (5)	0.2995 (5)	0.6832 (4)	0.091 (2)
C56	0.1003 (6)	0.3532 (6)	0.5940 (5)	0.118 (2)
N6	0.3012 (4)	−0.3704 (4)	−0.7129 (4)	0.0953 (15)
C61	0.2202 (8)	−0.2974 (7)	−0.7448 (6)	0.148 (3)
C62	0.2523 (7)	−0.2242 (6)	−0.8029 (6)	0.142 (3)
C63	0.2412 (6)	−0.4611 (5)	−0.6813 (5)	0.110 (2)
C64	0.1993 (7)	−0.4583 (6)	−0.5842 (6)	0.137 (3)
C65	0.3875 (7)	−0.3266 (6)	−0.6434 (7)	0.142 (3)
C66	0.4719 (6)	−0.3983 (7)	−0.6353 (6)	0.147 (3)
N7	0.7190 (4)	0.2454 (4)	0.2120 (4)	0.0874 (13)
C71	0.6859 (7)	0.2927 (6)	0.1239 (5)	0.135 (3)
C72	0.5800 (9)	0.2408 (9)	0.0721 (7)	0.210 (5)
C73	0.6387 (6)	0.2496 (8)	0.2937 (6)	0.137 (3)
C74	0.6191 (9)	0.3591 (10)	0.3182 (8)	0.201 (5)
C75	0.7507 (9)	0.1403 (7)	0.2028 (8)	0.167 (4)
C76	0.8374 (7)	0.1280 (8)	0.1333 (7)	0.172 (4)

Table 2. *Selected geometric parameters (Å, °)*

Ni1—N11	2.078 (4)	Ni2—N23	2.072 (4)
Ni1—N12	2.080 (4)	Ni2—N21	2.083 (5)
Ni1—N13	2.097 (4)	Ni2—N22	2.091 (4)
N11—Ni1—N12	90.1 (2)	N23—Ni2—N21	90.0 (2)
N11—Ni1—N13	90.0 (2)	N23—Ni2—N22	89.9 (2)
N12—Ni1—N13	90.25 (15)	N21—Ni2—N22	90.0 (2)

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4—H4···S22^{i}	0.91	2.37	3.280 (4)	176
N5—H5···S13^{ii}	0.91	2.44	3.321 (4)	164
N6—H6···S11^{iii}	0.91	2.39	3.279 (5)	167
N7—H7···S12^{iv}	0.91	2.38	3.281 (5)	173

Symmetry codes: (i) $x, 1+y, 1+z$; (ii) $-x, 1-y, 1-z$; (iii) $x, y-1, z-1$; (iv) $1+x, y, z$.

Data collection: *XSCANS* (Siemens, 1992). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990*b*). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1990*a*). Software used to prepare material for publication: *SHELXL93*.

The authors thank the EPSRC for support.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1110). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Allen, F. H., Kennard, O. & Taylor, R. (1983). *Acc. Chem. Res.* **16**, 146–152.

Hoffman, D. W. & Wood, J. S. (1982). *Cryst. Struct. Commun.* **11**, 691–694.

Sheldrick, G. M. (1990*a*). *SHELXTL/PC*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (1990*b*). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Siemens (1992). *XSCANS. X-ray Single Crystal Analysis System*. Version 2.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Acta Cryst. (1996). C**52**, 619–622

Tris(triphenylsilanolato)arsenite(III)

George Ferguson,[a] Jason W. Pollock,[a] Brian O'Leary[b] and Trevor R. Spalding[b]

[a]*Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1, and* [b]*Chemistry Department, University College, Cork, Ireland. E-mail: george@x-ray.chembio.uoguelph.ca*

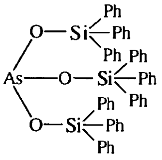
(*Received 25 October 1995; accepted 17 November 1995*)

Abstract

The title compound, [As($C_{18}H_{15}OSi$)$_3$], contains a trigonal pyramidal AsO_3 unit bonded to three tetrahedral $SiPh_3$ groups. Principal dimensions include mean As—O 1.746 (14), mean Si—O 1.646 (6) Å, O—As—O 96.70 (8)–99.42 (9), As—O—Si 133.15 (10)–146.94 (11), O—Si—C 104.44 (10)–111.67 (9)°.

Comment

Tris(triphenylsilyl)arsenite, As($OSiPh_3$)$_3$, (I), is only the second arsenosilicate containing As^{III} to be studied using single-crystal X-ray techniques; previously, the structure of the cage compound As($OSiPh_2O$)$_3$As, was reported (Ferguson, O'Leary & Spalding, 1995). In addition, a small number of As^{V} compounds containing terminal As—O—$SiMe_3$ units have been reported (Baier, Bissinger & Schmidbaur, 1992, 1993; Baier, Paul & Schmidbaur, 1993). In these compounds the arsenic is



(I)

ISSN 0108-2701

tetra-, penta- or hexacoordinated whereas in the title compound the arsenic is tricoordinated.

The compound consists of a trigonal pyramidal AsO_3 unit bonded to three tetrahedral $SiPh_3$ units arranged as shown in Fig. 1. The O—As—O angles vary between 96.70 (8) and 99.42 (9)°. The O—Si—C angles exhibit greater variation: 104.44 (10)–111.67 (9)°. The comparable data for $As(OSiPh_2O)_3As$ (Ferguson *et al.*, 1995) are: O—As—O angles varying between 97.72 (17) and 100.64 (18)° and O—Si—C angles varying from 105.0 (2) to 112.6 (2)°.

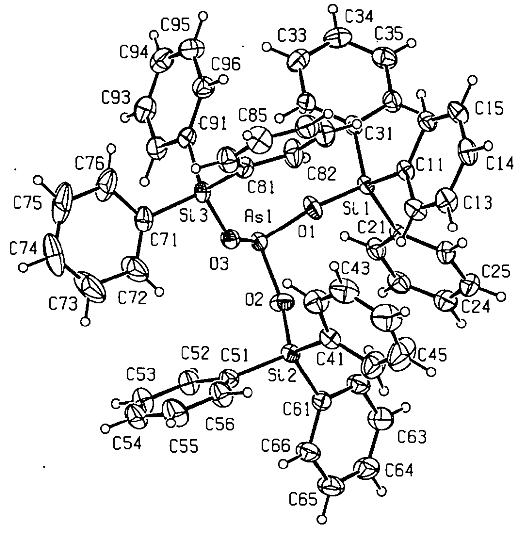


Fig. 1. A view of the title compound with our numbering scheme. Phenyl ring C atoms are labelled as C*i*1–C*i*6 ($i = 1$–9); because of overlap, some C atoms are not labelled. Displacement ellipsoids are drawn at the 30% probability level.

The As—O—Si angles show considerable flexibility. The two angles As1—O1—Si1 and As1—O2—Si2 are 144.12 (11) and 146.94 (11)°, respectively, while the third, As1—O3—Si3, is notably smaller at 133.15 (10)°. The As—O—Si angles in $As(OSiPh_2O)_3As$, which also contains three-coordinate As^{III} but in a constrained cage environment, were found to be between 136.4 (2) and 140.4 (2)° (Ferguson *et al.*, 1995). The range of As—O—Si angles in the As^V compounds $(Me_3SiO)_3AsO.(Me_3SiO)_3AsNMe$ and $(Me_3SiO)_2(PhNH)AsO$ (Baier *et al.*, 1993) and $[(Me_3SiO)_2AsN]_3$ (Baier *et al.*, 1993) is 128.5 (4)–136.0 (3)°.

The range of As—O_{Si} bond lengths in the previously reported (As—O—$SiMe_3$)-containing compounds is notably large: from 1.680 (3) Å for four-coordinate arsenic in $[(Me_3Si)_4As_2O_7]_2$ (Baier *et al.*, 1992) to 1.780 (2) Å for five-coordinate As in $(Me_3SiO)_3AsO.(Me_3SiO)_3AsNMe$ (Baier *et al.*, 1993). The range for the bonds to three-coordinate arsenic in $As(OSiPh_2O)_3As$ was found to be 1.740 (4) to 1.781 (3) Å (Ferguson *et al.*, 1995). The As—O_{Si} distances in tris(triphenylsilyl)arsenite are 1.728 (2), 1.748 (2) and 1.761 (2) Å.

The Si—O bond lengths are in the range 1.640 (2)–1.655 (2) Å with a mean value of 1.646 (6) Å. These values are similar to those in $As(OSiPh_2O)_3As$, which ranged from 1.628 (4) to 1.643 (4) Å (Ferguson *et al.*, 1995). A much broader range has been reported for the As^V compounds, with distances from 1.646 (5) to 1.732 (6) Å in, for example, $[(Me_3SiO)_2AsN]_3$ (Baier *et al.*, 1993). The mean dimensions in the $SiPh_3$ units are Si—C 1.865 (3), C—C 1.378 (15) Å. There are no unusual intermolecular contacts.

Experimental

The title compound was synthesized using a method described previously (Chamberland & MacDiarmid, 1960). Suitable crystals were obtained by recrystallization from a dichloromethane/heptane solution (1:1 by volume).

Crystal data

[As($C_{18}H_{15}OSi$)$_3$]
M_r = 901.09
Triclinic
$P\bar{1}$
a = 9.843 (2) Å
b = 13.153 (5) Å
c = 18.517 (6) Å
α = 87.33 (4)°
β = 78.26 (2)°
γ = 84.45 (2)°
V = 2335.3 (13) Å^3
Z = 2
D_x = 1.281 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.7107 Å
Cell parameters from 25 reflections
θ = 9.80–17.05°
μ = 0.848 mm^{-1}
T = 294 (1) K
Block, cut from larger piece
0.40 × 0.39 × 0.36 mm
Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: seven ψ scans at 4° steps (North, Phillips & Mathews, 1968)
T_{min} = 0.6246, T_{max} = 0.7864
10 167 measured reflections
10 167 independent reflections

7781 observed reflections [$I > 2\sigma(I)$]
θ_{max} = 26.9°
$h = -12 \rightarrow 12$
$k = 0 \rightarrow 16$
$l = -23 \rightarrow 23$
3 standard reflections
frequency: 120 min
intensity decay: no decay, variation 1.0%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0386$
$wR(F^2) = 0.1133$
$S = 1.087$
10 167 reflections

$w = 1/[\sigma^2(F_o^2) + (0.0715P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max}$ = 0.601 e Å^{-3}
$\Delta\rho_{min}$ = −0.525 e Å^{-3}

550 parameters
H atoms riding [*SHELXL*93 (Sheldrick, 1993) defaults, C—H 0.93 Å]
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

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

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

	x	y	z	$U_{\rm eq}$
As1	0.21768 (2)	0.22226 (2)	0.30443 (1)	0.03952 (8)
Si1	0.38128 (6)	0.34830 (4)	0.39960 (3)	0.03751 (13)
Si2	0.24414 (6)	0.36081 (5)	0.15428 (3)	0.04087 (14)
Si3	0.40927 (7)	0.02149 (5)	0.25938 (4)	0.0462 (2)
O1	0.3494 (2)	0.26816 (13)	0.34117 (10)	0.0523 (4)
O2	0.1975 (2)	0.31873 (13)	0.23984 (9)	0.0546 (4)
O3	0.3261 (2)	0.13381 (12)	0.24512 (9)	0.0494 (4)
C11	0.5712 (2)	0.3649 (2)	0.37504 (12)	0.0412 (5)
C12	0.6306 (3)	0.3964 (2)	0.30351 (14)	0.0547 (6)
C13	0.7696 (3)	0.4127 (2)	0.2843 (2)	0.0608 (7)
C14	0.8534 (3)	0.3968 (2)	0.3354 (2)	0.0583 (7)
C15	0.7980 (2)	0.3647 (2)	0.4061 (2)	0.0578 (6)
C16	0.6580 (2)	0.3485 (2)	0.42601 (14)	0.0468 (5)
C21	0.2801 (2)	0.4748 (2)	0.39395 (11)	0.0386 (4)
C22	0.1361 (2)	0.4818 (2)	0.41106 (14)	0.0499 (5)
C23	0.0559 (3)	0.5741 (2)	0.4098 (2)	0.0598 (7)
C24	0.1195 (3)	0.6628 (2)	0.3923 (2)	0.0627 (7)
C25	0.2624 (3)	0.6588 (2)	0.3765 (2)	0.0643 (7)
C26	0.3423 (3)	0.5665 (2)	0.37624 (14)	0.0513 (6)
C31	0.3293 (2)	0.2950 (2)	0.49512 (12)	0.0407 (5)
C32	0.2816 (3)	0.1981 (2)	0.51033 (15)	0.0519 (6)
C33	0.2410 (3)	0.1625 (2)	0.5823 (2)	0.0646 (7)
C34	0.2494 (3)	0.2219 (2)	0.6404 (2)	0.0677 (8)
C35	0.2958 (3)	0.3169 (2)	0.62715 (15)	0.0634 (7)
C36	0.3347 (3)	0.3528 (2)	0.55528 (14)	0.0510 (6)
C41	0.4345 (2)	0.3763 (2)	0.12981 (13)	0.0503 (6)
C42	0.5316 (3)	0.2950 (2)	0.1355 (2)	0.0657 (7)
C43	0.6727 (3)	0.3036 (3)	0.1165 (2)	0.0797 (9)
C44	0.7188 (3)	0.3951 (4)	0.0899 (2)	0.0967 (12)
C45	0.6272 (4)	0.4767 (3)	0.0842 (3)	0.118 (2)
C46	0.4840 (3)	0.4679 (3)	0.1036 (2)	0.0830 (10)
C51	0.2006 (2)	0.2694 (2)	0.09001 (12)	0.0453 (5)
C52	0.0732 (3)	0.2274 (2)	0.1045 (2)	0.0593 (6)
C53	0.0409 (3)	0.1591 (2)	0.0574 (2)	0.0726 (8)
C54	0.1345 (4)	0.1314 (2)	−0.0055 (2)	0.0759 (9)
C55	0.2600 (4)	0.1717 (3)	−0.0211 (2)	0.0828 (10)
C56	0.2933 (3)	0.2402 (2)	0.02571 (14)	0.0637 (7)
C61	0.1381 (2)	0.4856 (2)	0.15052 (12)	0.0416 (5)
C62	0.1181 (3)	0.5528 (2)	0.20831 (14)	0.0589 (6)
C63	0.0362 (4)	0.6439 (2)	0.2079 (2)	0.0746 (9)
C64	−0.0277 (4)	0.6699 (2)	0.1505 (2)	0.0739 (8)
C65	−0.0095 (4)	0.6068 (2)	0.0925 (2)	0.0799 (10)
C66	0.0712 (3)	0.5148 (2)	0.0928 (2)	0.0666 (8)
C71	0.3791 (3)	−0.0668 (2)	0.1897 (2)	0.0570 (6)
C72	0.3362 (5)	−0.0350 (3)	0.1275 (2)	0.1044 (14)
C73	0.3161 (6)	−0.1049 (4)	0.0762 (3)	0.139 (2)
C74	0.3343 (5)	−0.2048 (4)	0.0896 (3)	0.125 (2)
C75	0.3829 (6)	−0.2403 (3)	0.1514 (3)	0.129 (2)
C76	0.4041 (5)	−0.1723 (2)	0.2015 (2)	0.0964 (12)
C81	0.5992 (3)	0.0348 (2)	0.25048 (14)	0.0495 (5)
C82	0.6453 (3)	0.1098 (2)	0.2881 (2)	0.0684 (8)
C83	0.7846 (3)	0.1189 (2)	0.2847 (2)	0.0738 (8)
C84	0.8823 (3)	0.0534 (2)	0.2429 (2)	0.0682 (8)
C85	0.8417 (3)	−0.0214 (3)	0.2053 (2)	0.0739 (8)
C86	0.7028 (3)	−0.0306 (2)	0.2091 (2)	0.0632 (7)
C91	0.3338 (2)	−0.0277 (2)	0.35416 (14)	0.0469 (5)
C92	0.1920 (3)	−0.0411 (2)	0.3732 (2)	0.0577 (6)
C93	0.1319 (3)	−0.0758 (2)	0.4423 (2)	0.0650 (7)
C94	0.2119 (4)	−0.0997 (2)	0.4943 (2)	0.0723 (8)
C95	0.3524 (3)	−0.0881 (2)	0.4772 (2)	0.0724 (8)
C96	0.4117 (3)	−0.0524 (2)	0.4077 (2)	0.0586 (6)

Table 2. *Selected geometric parameters* (Å, °)

As1—O1	1.748 (2)	Si2—C41	1.865 (2)
As1—O2	1.728 (2)	Si2—C51	1.867 (2)
As1—O3	1.761 (2)	Si2—C61	1.864 (2)
Si1—O1	1.640 (2)	Si3—O3	1.655 (2)
Si1—C11	1.864 (2)	Si3—C71	1.861 (3)
Si1—C21	1.865 (2)	Si3—C81	1.868 (3)
Si1—C31	1.862 (2)	Si3—C91	1.873 (3)
Si2—O2	1.643 (2)		
O1—As1—O2	99.42 (9)	C41—Si2—C51	109.04 (11)
O1—As1—O3	96.70 (8)	C41—Si2—C61	111.56 (11)
O2—As1—O3	98.26 (8)	C51—Si2—C61	110.48 (10)
O1—Si1—C11	107.00 (9)	O3—Si3—C71	107.50 (11)
O1—Si1—C21	111.67 (9)	O3—Si3—C81	110.08 (10)
O1—Si1—C31	108.95 (10)	O3—Si3—C91	108.63 (10)
C11—Si1—C21	109.43 (10)	C71—Si3—C81	110.96 (12)
C11—Si1—C31	111.97 (10)	C71—Si3—C91	109.39 (12)
C21—Si1—C31	107.85 (10)	C81—Si3—C91	110.21 (11)
O2—Si2—C41	111.61 (10)	As1—O1—Si1	144.12 (11)
O2—Si2—C51	109.65 (10)	As1—O2—Si2	146.94 (11)
O2—Si2—C61	104.44 (10)	As1—O3—Si3	133.15 (10)

Fig. 1 was prepared using *ORTEP*II (Johnson, 1976) as implemented in *PLATON* (Spek, 1995*a*). Examination of the structure with *PLATON* showed that there were two symmetry-related voids in the crystal lattice, each of volume 24.1 Å^3; these voids are too small to accommodate any small solvent molecule but are adjacent to phenyl C atoms C73–C75, inspection of the anisotropic displacement parameters of which, as well as the *ORTEP* plot, shows them to have the largest displacement parameters in the crystal structure.

Data collection: *CAD*-4-*PC* (Enraf–Nonius, 1992). Cell refinement: *SET*4 and *CELDIM* (Enraf–Nonius, 1992). Data reduction: *DATRD*2 in *NRCVAX*94 (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *NRCVAX*94. Program(s) used to refine structure: *NRCVAX*94 and *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *NRCVAX*94, *PLATON* (Spek, 1995*a*) and *PLUTON* (Spek 1995*b*). Software used to prepare material for publication: *NRCVAX*94 and *SHELXL*93.

GF thanks NSERC (Canada) for Grants in Aid of Research. TRS and BO'L thank EOLAS (Ireland) for financial support.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1333). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Baier, M., Bissinger, P. & Schmidbaur, H. (1992). *Chem. Ber.* **125**, 373–376.

Baier, M., Bissinger, P. & Schmidbaur, H. (1993). *Chem. Ber.* **126**, 351–354.

Baier, M., Paul, M. & Schmidbaur, H. (1993). *Organometallics*, **12**, 3527–3530.

Chamberland, B. L. & MacDairmid, A. G. (1960). *J. Am. Chem. Soc.* **82**, 4542–4546.

Enraf–Nonius (1992). *CAD*-4-*PC*. Version 1.1. Enraf–Nonius, Delft, The Netherlands.

Ferguson, G., O'Leary, B. & Spalding, T. R. (1995). *Acta Cryst.* **C51**, 2312–2315.

Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.

Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.
Spek, A. L. (1995*a*). *PLATON. Molecular Geometry Program.* July 1995 version. University of Utrecht, The Netherlands.
Spek. A. L. (1995*b*). *PLUTON. Molecular Graphics Program.* July 1995 version. University of Utrecht, The Netherlands.

Acta Cryst. (1996). C**52**, 622–624

Lithium Croconate Dihydrate

NORBERTO S. GONÇALVES,[a] PAULO S. SANTOS[b] AND IVO VENCATO[c]

[a]*Departamento Química, UFSC, 88040-900 Florianópolis, SC, Brazil,* [b]*Instituto de Química, USP, 01498-970 São Paulo, SP, Brazil, and* [c]*Departamento Física, UFSC, 88040-900 Florianópolis, SC, Brazil. E-mail: fsclivo@ibm.ufsc.br*

(*Received 27 February 1995; accepted 25 August 1995*)

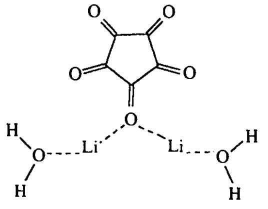
Abstract

The lithium salt of croconic acid (4,5-dihydroxy-4-cyclopentene-1,2,3-trione), or lithium croconate, consists of planes containing almost parallel croconate units interconnected by water molecules and Li^+ ions ($2Li^+.C_5O_5^{2-}.2H_2O$).

Comment

Despite the interest in the coordinating properties of the croconate ion (Glick, Downs & Dahl, 1964; Glick & Dahl, 1966; Deguenon, Bernardinelli, Tuchagues & Castan, 1990; Castro *et al.*, 1992; Brouca-Cabarrecq & Trombe, 1992*a*,*b*), the structure of the ion has been reported in only a few cases, for example, the ammonium (Baenziger & Hegenbarth, 1964), rubidium hydrogen and ammonium hydrogen salts (Baenziger, Hegenbarth & Williams, 1963; Baenziger & Williams, 1966). These structures contain extended networks of intermolecular hydrogen bonding, enhancing the stability of the crystals. Another motivation for a detailed X-ray investigation of lithium croconate is the possibility of interpreting the solid-state vibrational spectra on the basis of a factor group analysis, for which a knowledge of the crystal structure is mandatory.

The Li^+ ions are tetrahedrally coordinated to two croconate O atoms (O1 and O3^{i}) and two water molecules (*OW* and *OW*^{ii}) with an average O—Li—O angle of 109.4°. It should be noted that in the case of lithium squarate monohydrate, $LiHC_4O_4.H_2O$ (Semmingsen, 1976), tetrahedral coordination is also found, although much more distorted. In fact, it has been shown that tetrahedral coordination is quite usual for the Li^+ ion in a great variety of its salts (Olsher, Izatt, Bradshaw & Dalley, 1991).



(I)

The water molecules are also coordinated to two Li^+ ions and two O atoms belonging to different croconate units, with tetrahedral geometry. It is worth noting that O2 is connected to two different water molecules by hydrogen bonding: $OW\cdots O2$ = 2.747 (2), $H1\cdots O2$ = 1.81 (2) Å and $OW—H1\cdots O2$ = 157.8 (2)°; $OW\cdots O2$ ($\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$) = 2.692 (2), $H2\cdots O2$ = 1.95 (2) Å and $OW—H2\cdots O2$ = 169.0 (1)°; this is accompanied by an appreciable distortion of the H1—*OW*—H2 angle [108.7 (2)°].

The croconate ion in lithium croconate does not show a significant deviation from planarity, or from pentagonal geometry, as was reported for the ammonium salt (Baenziger & Hegenbarth, 1964). The C=O distances are also very much comparable with those observed in other croconates. However, it is worth noting that the C1—O1 distance [1.268 (3) Å] is slightly greater than the C2—O2 [1.245 (2) Å] and C3—O3 [1.235 (2) Å] distances, suggesting a displacement of charge in the C1—O1 bond towards the O atom, as a consequence of its interaction with two Li^+ ions. Consequently, although the O2 atom is interacting with two H atoms, the electrostatic effect originating from the positive charge

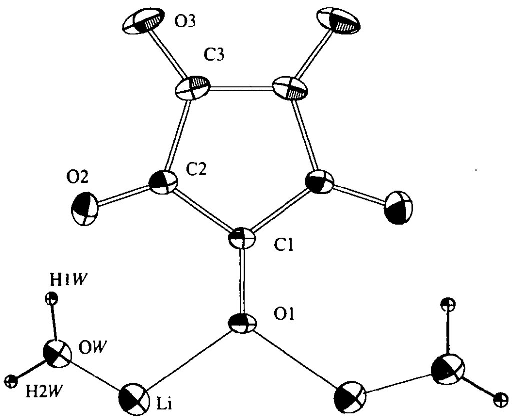


Fig. 1. Perspective view of the title compound showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.