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

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

	x	y	z	U_{eq}
U1	1/2	1/2	1/2	0.01766 (15)
O1	0.6727 (7)	0.4721 (6)	0.2923 (4)	0.0283 (8)
O2	0.2963 (7)	0.2728 (6)	0.2324 (4)	0.0277 (8)
O3	0.1236 (7)	0.2428 (6)	0.4552 (4)	0.0290 (8)
O4	0.3158 (7)	0.6625 (5)	0.4503 (4)	0.0246 (7)
N1	0.2515 (8)	0.0447 (6)	−0.2179 (5)	0.0251 (8)
C1	0.4825 (9)	0.3378 (7)	0.1959 (5)	0.0216 (9)
C2	0.4797 (9)	0.2553 (7)	0.0377 (5)	0.0199 (9)
C3	0.6932 (9)	0.3145 (7)	−0.0002 (6)	0.0238 (9)
C4	0.6804 (10)	0.2377 (8)	−0.1477 (6)	0.0257 (10)
C5	0.4557 (11)	0.1041 (8)	−0.2530 (6)	0.0262 (10)
C6	0.2649 (9)	0.1217 (7)	−0.0739 (6)	0.0224 (9)

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

U1—O4	1.782 (4)	U1—O2	2.486 (4)
U1—O3	2.431 (4)	O1—C1	1.253 (7)
U1—O1	2.459 (4)	O2—C1	1.262 (7)
O3—U1—O1^i	62.76 (14)	O1—U1—O2	52.39 (13)
O3—U1—O2	65.73 (14)		

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

The temperature of the crystal was controlled using an Oxford Cryosystems Cryostream Cooler (Cosier & Glazer, 1986). The H atoms attached to the coordinated water molecule were located from difference Fourier syntheses and their coordinates were refined. Others were added at calculated positions and refined using a riding model. Anisotropic displacement parameters were used for all non-H atoms; each H atom was given an isotropic displacement parameter equal to 1.2 times the equivalent isotropic displacement parameter of the atom to which it is attached. The only significant difference density peaks were located close to the U atom and are considered to be diffraction ripples.

Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1314). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Alcock, N. W., Flanders, D. J., Kemp, T. J. & Shand, M. A. (1985). *J. Chem. Soc. Dalton Trans.* pp. 517–521.

Alcock, N. W., Kemp, T. J. & Leciejewicz, J. (1996). *Inorg. Chim. Acta*. In the press.

Bismondo, A., Casellato, U., Sitran. S. & Graziani. R. (1985). *Inorg. Chim. Acta*, **110**, 205–210.

Cosier, J. & Glazer, A. M. (1986). *J. Appl. Cryst.* **19**, 105–107.

Cousson, A., Nectoux, F., Pages, M. & Rizkalla, E. N. (1993). *Radiochim. Acta*, **61**, 177–180.

Cousson, A., Proust, P. & Rizkalla, E. N. (1991). *Acta Cryst.* **C47**, 2065–2069

Dalley, N. K., Mueller, M. H. & Simonsen, S. H. (1971). *Inorg. Chem.* **10**, 323–328.

Immirzi, A., Bombieri, G., Degetto, S. & Marangoni, G. (1975). *Acta Cryst.* **B31**, 1023–1028.

Leciejewicz, J., Alcock, N. W. & Kemp, T. J. (1995). *Struct. Bonding*, **82**, 44–83.

Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.

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

Acta Cryst. (1996). **C52**, 617–619

Tetrakis(triethylammonium) Hexakis(isothiocyanato-*N*)nickel(II)

Paul E. Kruger and Vickie McKee*

School of Chemistry, Queen's University, Belfast BT9 5AG, Northern Ireland. E-mail: v.mckee@qub.ac.uk

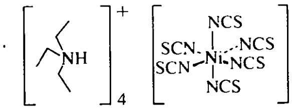
(*Received 31 July 1995; accepted 9 October 1995*)

Abstract

The unit cell of the title compound, $(C_6H_{16}N)_4[Ni(NCS)_6]$, contains two independent centrosymmetric $[Ni(NCS)_6]^{4-}$ anions and eight Et_3NH^+ cations. The Ni—N distances are in the range 2.072 (4)–2.097 (4) Å. In one anion, all six S atoms are hydrogen bonded to cations, but the second anion is involved in only two hydrogen bonds. There are no significant geometrical differences between the two anions.

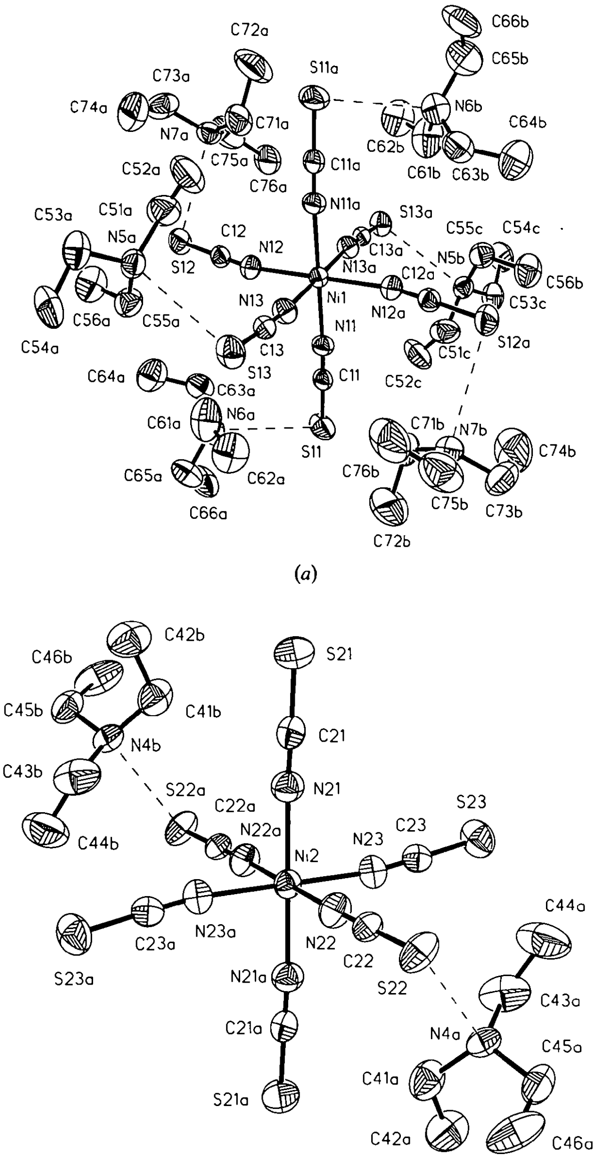
Comment

Tetrakis(triethylammonium) hexakis(isothiocyanato-*N*)nickel(II) is a potentially useful source of anhydrous nickel thiocyanate. Air-stable crystals of $(Et_3NH)_4[Ni(NCS)_6]$, (I), were readily obtained from water.



(I)

The unit cell of (I) contains two independent centrosymmetric $[Ni(NCS)_6]^{4-}$ anions and eight Et_3NH^+ cations. Fig. 1 shows the environments of the two complex anions about the Ni1 and Ni2 atoms. The anion containing Ni1 displays hydrogen bonding from all six S atoms to triethylammonium cations, whereas the second anion shows only two hydrogen bonds (details are given in Table 3). The geometry at each Ni atom is regular octahedral and all the thiocyanate groups are essentially linear [S—C—N 178.0 (4)–179.2 (5)°]. There is some variation, however, in the Ni—N—C angles, which range from 166.2 (4) at N12 to 176.1 (4)° at N21. There are no significant differences in the bond lengths or angles of the two anions which might be ascribed to the hydrogen bonding.



(b)

Fig. 1. (a) The environment of the Ni1 atom and (b) the environment of the Ni2 atom. Both show 30% probability displacement ellipsoids and H atoms have been omitted for clarity.

A search of the April 1995 release of the Cambridge Structural Database (Allen, Kennard & Taylor, 1983) showed only one previous determination of the $[Ni(NCS)_6]^{4-}$ ion (Hoffman & Wood, 1982). The counterion was tetramethylammonium, which precludes any hydrogen bonding, and the refinement was relatively poor ($R = 0.11$), but the geometry of the anion is essentially the same as in the present case.

Experimental

Crystal data

$(C_6H_{16}N)_4[Ni(NCS)_6]$
$M_r = 815.98$
Triclinic
$P\bar{1}$
$a = 12.575\,(2)$ Å
$b = 13.4200\,(10)$ Å
$c = 13.530\,(2)$ Å
$\alpha = 93.64°$
$\beta = 93.23°$
$\gamma = 95.23°$
$V = 2264.7\,(5)$ Å^3
$Z = 2$
$D_x = 1.197$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 28 reflections
$\theta = 8–11°$
$\mu = 0.737$ mm^{-1}
$T = 298\,(2)$ K
Hexagonal prism
$0.65 \times 0.60 \times 0.43$ mm
Green

Data collection

Siemens *P*4 four-circle diffractometer
1.2° ω scans
Absorption correction: ψ scans (*SHELXTL/PC*; Sheldrick, 1990*a*)
$T_{min} = 0.792$, $T_{max} = 0.810$
7301 measured reflections
6905 independent reflections

4906 observed reflections $[I > 2\sigma(I)]$
$R_{int} = 0.0152$
$\theta_{max} = 25°$
$h = 0 \rightarrow 13$
$k = -15 \rightarrow 15$
$l = -16 \rightarrow 16$
3 standard reflections monitored every 97 reflections intensity decay: 5%

Refinement

Refinement on F^2
$R(F) = 0.0552$
$wR(F^2) = 0.1638$
$S = 1.024$
6893 reflections
439 parameters
H atoms riding, with N—H 0.91 and C—H 0.96–0.97 Å
$w = 1/[\sigma^2(F_o^2) + (0.0689P)^2 + 2.8778P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.132$
$\Delta\rho_{max} = 0.628$ e Å^{-3}
$\Delta\rho_{min} = -0.438$ e Å^{-3}
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)*

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

	x	y	z	U_{eq}
Ni1	0	1/2	0	0.0488 (2)
N11	0.1649 (3)	0.5140 (3)	0.0293 (3)	0.0640 (10)
C11	0.2538 (4)	0.5188 (4)	0.0502 (3)	0.0644 (12)
S11	0.38257 (12)	0.5276 (2)	0.08151 (14)	0.1144 (7)
N12	−0.0215 (3)	0.4633 (3)	0.1451 (3)	0.0646 (10)
C12	−0.0368 (4)	0.4240 (3)	0.2160 (3)	0.0599 (11)
S12	−0.06046 (15)	0.36590 (12)	0.31691 (10)	0.0954 (5)
N13	−0.0041 (3)	0.6524 (3)	0.0433 (3)	0.0655 (10)
C13	−0.0155 (4)	0.7345 (4)	0.0636 (3)	0.0571 (11)
S13	−0.03591 (13)	0.85189 (10)	0.09447 (11)	0.0826 (4)
Ni2	1/2	0	−1/2	0.0588 (2)

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: *SHELXS*86 (Sheldrick, 1990*b*). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1990*a*). Software used to prepare material for publication: *SHELXL*93.

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*

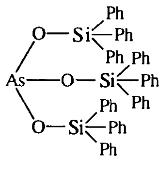
(*Received 25 October 1995; accepted 17 November 1995*)

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 $As(OSiPh_2O)_3As$, 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)