C1	1.1091 (1)	−0.2060 (4)	−0.0257 (5)	0.032 (3)
C2	1.1292 (1)	−0.0909 (4)	−0.0942 (5)	0.038 (3)
C3	1.1512 (1)	−0.0235 (5)	0.0166 (6)	0.048 (3)
C4	1.1780 (1)	0.0503 (5)	−0.0582 (6)	0.060 (4)
C5	1.2013 (1)	−0.0471 (6)	−0.1264 (6)	0.060 (4)
C6	1.2198 (1)	−0.1306 (6)	−0.0142 (7)	0.063 (4)
C7	1.2363 (1)	−0.2577 (6)	−0.0795 (7)	0.067 (4)
C8	1.2151 (1)	−0.3716 (6)	−0.1360 (6)	0.064 (4)
C9	1.1966 (1)	−0.4431 (6)	−0.0134 (6)	0.061 (4)
C10	1.1675 (1)	−0.5146 (5)	−0.0670 (6)	0.054 (3)
C11	1.1425 (1)	−0.4138 (5)	−0.1157 (6)	0.044 (3)
C12	1.1272 (1)	−0.3380 (5)	0.0156 (6)	0.040 (3)
C31	1.0787 (1)	−0.2039 (5)	−0.4392 (6)	0.056 (4)
C32	1.0921 (1)	−0.2699 (5)	−0.5737 (6)	0.053 (4)

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

P—O1	1.500 (3)	C4—C5	1.510 (7)
P—O2	1.501 (3)	C5—C6	1.509 (8)
P—O3	1.598 (3)	C6—C7	1.528 (8)
P—C1	1.809 (5)	C7—C8	1.517 (8)
O3—C31	1.404 (6)	C8—C9	1.514 (8)
C1—C2	1.535 (6)	C9—C10	1.524 (7)
C1—C12	1.537 (6)	C10—C11	1.521 (7)
C2—C3	1.515 (7)	C11—C12	1.520 (7)
C3—C4	1.518 (7)	C31—C32	1.465 (8)
Na1···O21	2.718 (3)	Na2···O21	2.459 (3)
Na1···O22	2.453 (3)	Na2···O22^{i}	2.481 (3)
Na1···O23	2.395 (3)	Na2···O1	2.606 (3)
O1—P—O2	114.4 (2)	C2—C3—C4	114.4 (4)
O1—P—O3	110.2 (2)	C3—C4—C5	114.0 (4)
O1—P—C1	110.7 (2)	C4—C5—C6	115.7 (4)
O2—P—O3	107.7 (2)	C5—C6—C7	115.6 (5)
O2—P—C1	110.2 (2)	C6—C7—C8	114.0 (4)
O3—P—C1	103.0 (2)	C7—C8—C9	115.0 (5)
P—O3—C31	124.7 (3)	C8—C9—C10	115.7 (5)
P—C1—C2	112.0 (3)	C9—C10—C11	113.8 (4)
P—C1—C12	114.4 (3)	C10—C11—C12	114.0 (4)
C2—C1—C12	112.9 (4)	C1—C12—C11	116.2 (4)
C1—C2—C3	114.9 (4)	O3—C31—C32	111.3 (4)

Symmetry code: (i) $x, -y, z - \frac{1}{2}$.

Data collection: CAD-4 diffractometer software (Enraf–Nonius, 1977). Cell refinement: CAD-4 diffractometer software. Data reduction: *MolEN PROCESS* (Fair, 1990). Program(s) used to solve structure: *SIR*88 (Burla *et al.*, 1989). Program(s) used to refine structure: *MolEN LSFM*. Molecular graphics: *PLATON*92 (Spek, 1990) and *SCHAKAL*92 (Keller, 1992). Software used to prepare material for publication: *MolEN BTABLE*, *PTABLE* and *CIF IN*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry, including H-atom geometry, torsion angles and contact distances greater than 2.39Å, have been deposited with the IUCr (Reference: SE1077). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Two Anionic Indium(III)–Thiocyanate Complexes with Potassium-Centred Complex Cations

CLAIRE J. CARMALT, WILLIAM CLEGG,*
MARK R. J. ELSEGOOD, BORIS O. KNEISEL AND
NICHOLAS C. NORMAN

Department of Chemistry, University of Newcastle upon Tyne, Newcastle upon Tyne NE1 7RU, England

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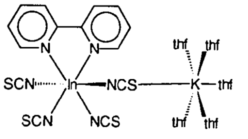
Abstract

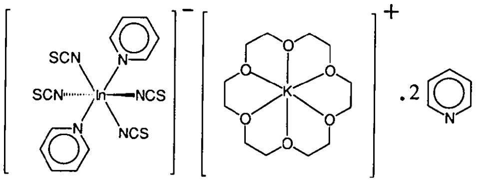
Crystallization of the product of the reaction between impure samples of $In(NCS)_3$, prepared from $InCl_3$ and KSCN, and 2,2′-bipyridyl (bipy) in tetrahydrofuran solution gave the complex pentakis(tetrahydrofuran)-potassium (2,2′-bipyridyl)tetrakis(isothiocyanato)indate-(III), $[K(C_4H_8O)_5][In(NCS)_4(C_{10}H_8N_2)]$, composed of a potassium cation coordinated by five thf ligands and one S atom of a thiocyanate group, and an octahedral indium-centred anion in which the bipy N atoms are *cis* and the four thiocyanates are bonded to indium through their N atoms. Crystallization of samples of impure $In(NCS)_3$ from pyridine in the presence of 18-crown-6 gave the compound (1,4,7,10,13,16-hexaoxacyclooctadecane)potassium bis(pyridine)tetrakis(isothiocyanato)-indate(III) pyridine solvate, $[K(C_{12}H_{24}O_6)][In(NCS)_4(C_5H_5N)_2].2C_5H_5N$, containing an octahedral indium-centred anion in which the pyridine ligands are *trans*. The potassium in both complexes arises from the contamination of $In(NCS)_3$ by the KSCN used in its preparation.

Comment

Structurally characterized thiocyanate complexes of indium(III) are not particularly common, the only reported examples being $[AsPh_4][In(NCS)_6]$ (1) (Einstein, Gilbert, Tuck & Vogel, 1976), $[K(18\text{-crown-}6)][K(18\text{-crown-}6)(H_2O)]_2[In(NCS)_6].2H_2O$ (2) (Zhan, Fan, Wang & Zhang, 1989), $[In(NCS)(OPPh_3)\{Mo(CO)_3(C_5H_5)\}_2]$ (3), $[In(NCS)(4\text{-picoline})\{Fe(CO)_2(C_5H_5)\}_2]$ (4) and $[K(18\text{-crown-}6)][In(NCS)_2\{Mo(CO)_3(C_5H_5)\}_2]$ (5) (Carmalt, Norman, Pember & Farrugia, 1995). In all cases, the thiocyanate group is bonded to indium through the harder nitrogen rather than through the softer sulfur centre, which is consistent with $\mathrm{In^{III}}$ being a hard acid. We report here the structures of $[\mathrm{K(thf)_5}][\mathrm{In(NCS)_4(bipy)}]$, (6), and $[\mathrm{K(18\text{-}crown\text{-}6)}][\mathrm{In(NCS)_4(py)_2}]\mathrm{.2py}$, (7).



(6)



(7)

The structure of (6) contains a potassium cation coordinated by five thf ligands, one of which is disordered, with K—O distances ranging from 2.695 (6) to 2.736 (6) Å, and also by an S atom from one of the thiocyanate ligands, also disordered over two positions. Disorder in the other thf ligands is possible in view of the high displacement parameters, but could not be resolved. The potassium is six-coordinate with a slightly distorted octahedral coordination geometry. The anion has the formula $[\mathrm{In(NCS)_4(bipy)}]^-$. Indium is coordinated by four thiocyanate groups bonded through their N atoms [In—N distances are in the range 2.139 (6) to 2.209 (7) Å] and by a bipy ligand [In—N 2.258 (5) and 2.265 (5) Å], producing close to regular octahedral geometry, with the bipy N atoms necessarily *cis* to one another. The only significant angular deviations from ideal octahedral values are the small value of 72.3 (2)° associated with the bite angle of the bipy ligand and the large opposite angle of 100.0 (2)° between two thiocyanate ligands. The In—N thiocyanate distances are comparable to, although somewhat shorter than, those found in (3) [2.218 (8) Å], (4) [2.214 (11) and 2.242 (12) Å] and (5) [2.199 (4) Å], but closer to the In—N distances in (1) [2.06 (2) to 2.16 (1) Å] and (2) [2.177 (4) to 2.197 (3) Å].

Both the cation and anion of (7) have crystallographic inversion symmetry. The $[\mathrm{K(18\text{-}crown\text{-}6)}]^+$ cation requires no special comment except to say that the two pyridine molecules of crystallization are both loosely associated with the potassium centre by way of η^6-type interactions, the K···N and K···C distances lying in the range 3.509 (3) to 3.919 (3) Å.

The $[\mathrm{In(NCS)_4(py)_2}]^-$ anion in (7) differs from the anion in (6) mainly in that the pyridine N atoms are mutually *trans* instead of *cis*. The two anions are, however, similar in other respects, with comparable In—N bond lengths for the thiocyanate and pyridine ligands. The coordination geometry about the indium centre in (7) is closer to regular octahedral, in the absence of any chelating ligands.

A comparison of the structures of (6) and (7) is interesting in view of the factors affecting whether a *cis* or *trans* arrangement of the two pyridine ligands is adopted for this type of complex. In (6), the *cis* geometry is a necessary consequence of the chelating nature of the bipy ligand, but no such constraint exists for (7), for which the ligands bonded to indium are very similar. Inspection of the known structures of complex ions $[EX_4L_2]^-$, where E is Ga, In or Tl, X is a halide or pseudo-halide and L is a neutral two-electron donor, and of the more numerous isoelectronic neutral Group 14 analogues $[EX_4L_2]$, where E is Si, Ge, Sn or Pb, shows that there is no discernible reason why some have a *cis* configuration while others adopt a *trans* geometry. As a specific example of the lack of obvious pattern or cause, $[\mathrm{SnCl_4(OPPh_3)_2}]$ and $[\mathrm{SnI_4(OPPh_3)_2}]$ are *cis*, but $[\mathrm{SnBr_4(OPPh_3)_2}]$ is *trans* (Tursina, Aslanov, Chernyshev, Medvedev & Yatsenko, 1986; Tursina, Yatsenko, Medvedev, Chernyshev & Aslanov, 1986). Clearly, whatever the nature of the bonding in these

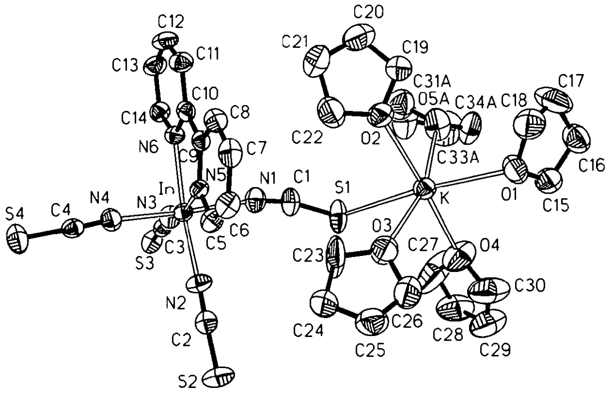


Fig. 1. The structure of complex (6) shown with 40% probability ellipsoids and without H atoms. Only the major disorder components are shown.

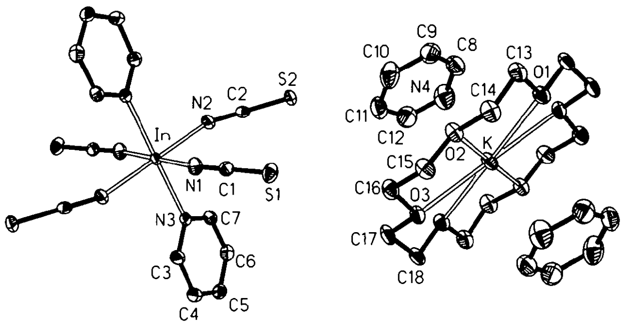


Fig. 2. The structure of compound (7) shown with 40% probability ellipsoids and without H atoms.

complexes, the energy differences between the two forms is probably small and of the same order as crystal packing forces, which will undoubtedly be significant in determining the structure actually adopted.

Experimental

The preparation of '$In(NCS)_3$' was carried out according to the method of Goggin, McColm & Shore (1966), but with KSCN in place of NaSCN. Complex (6) was prepared by treatment of this starting material with bipyridyl in CH_2Cl_2 solution, followed by vacuum removal of solvent, dissolution in tetrahydrofuran and solvent diffusion with an overlayer of hexane at room temperature. Complex (7) was prepared from '$In(NCS)_3$' and 18-crown-6 in CH_2Cl_2 solution, followed by vacuum removal of solvent, dissolution in pyridine and solvent diffusion with an overlayer of diethyl ether at room temperature. Satisfactory analytical data could not be obtained for either product because of extremely facile loss of solvent from the crystal structures. Samples were handled under inert atmosphere conditions and crystals were selected under inert oil.

Compound (6)

Crystal data

$[K(C_4H_8O)_5][In(NCS)_4(C_{10}H_8N_2)]$
$M_r = 902.94$
Monoclinic
$P2_1/c$
$a = 14.985\ (6)$ Å
$b = 17.375\ (6)$ Å
$c = 16.437\ (6)$ Å
$\beta = 92.23\ (4)°$
$V = 4276.4\ (27)$ Å^3
$Z = 4$
$D_x = 1.402$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 31 reflections
$\theta = 11.12–12.37°$
$\mu = 0.889$ mm^{-1}
$T = 180\ (2)$ K
Block
0.48 × 0.36 × 0.16 mm
Pale pink

Data collection

Stoe Siemens diffractometer
ω/θ scans with on-line profile fitting (Clegg, 1981)
Absorption correction: ψ scans (Sheldrick, 1990)
$T_{min} = 0.660$, $T_{max} = 0.766$
6628 measured reflections
5582 independent reflections

4328 observed reflections $[I > 2\sigma(I)]$
$R_{int} = 0.0213$
$\theta_{max} = 22.54°$
$h = -16 \rightarrow 16$
$k = -2 \rightarrow 18$
$l = -17 \rightarrow 17$
5 standard reflections
frequency: 60 min
intensity decay: 4%

Refinement

Refinement on F^2
$R(F) = 0.0472$
$wR(F^2) = 0.1313$
$S = 1.067$
5573 reflections
516 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0054P)^2 + 25.0832P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = -0.018$
$\Delta\rho_{max} = 0.572$ e Å^{-3}
$\Delta\rho_{min} = -0.542$ e Å^{-3}
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) *for* (6)

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

	x	y	z	U_{eq}
In	−0.56062 (3)	0.69385 (3)	0.15953 (3)	0.0389 (2)
N1	−0.4318 (4)	0.7463 (4)	0.1990 (4)	0.057 (2)
C1	−0.3754 (5)	0.7856 (5)	0.2186 (4)	0.056 (2)
S1†	−0.3070 (13)	0.8565 (9)	0.237 (2)	0.078 (6)
S1*A*†	−0.284 (2)	0.826 (3)	0.2599 (11)	0.115 (10)
N2	−0.5878 (5)	0.7911 (3)	0.0826 (4)	0.060 (2)
C2	−0.6051 (5)	0.8436 (4)	0.0427 (4)	0.049 (2)
S2	−0.6279 (2)	0.91884 (13)	−0.01201 (13)	0.0744 (7)
N3	−0.6177 (4)	0.7332 (3)	0.2693 (4)	0.053 (2)
C3	−0.6571 (5)	0.7645 (4)	0.3186 (4)	0.044 (2)
S3	−0.71260 (13)	0.80737 (11)	0.38753 (11)	0.0573 (5)
N4	−0.6806 (4)	0.6343 (3)	0.1182 (4)	0.0524 (15)
C4	−0.7442 (5)	0.6070 (4)	0.0870 (4)	0.045 (2)
S4	−0.83075 (14)	0.56690 (14)	0.04449 (14)	0.0715 (6)
N5	−0.4858 (3)	0.6323 (3)	0.0616 (3)	0.0376 (12)
C5	−0.4780 (5)	0.6603 (4)	−0.0134 (4)	0.048 (2)
C6	−0.4257 (5)	0.6260 (4)	−0.0706 (4)	0.052 (2)
C7	−0.3794 (5)	0.5601 (5)	−0.0479 (5)	0.056 (2)
C8	−0.3877 (4)	0.5295 (4)	0.0287 (4)	0.047 (2)
C9	−0.4412 (4)	0.5673 (4)	0.0836 (4)	0.0376 (15)
C10	−0.4554 (4)	0.5388 (4)	0.1666 (4)	0.043 (2)
C11	−0.4215 (5)	0.4692 (4)	0.1958 (4)	0.053 (2)
C12	−0.4426 (5)	0.4455 (4)	0.2721 (5)	0.059 (2)
C13	−0.4954 (5)	0.4896 (4)	0.3198 (5)	0.056 (2)
C14	−0.5278 (5)	0.5574 (4)	0.2884 (4)	0.047 (2)
N6	−0.5086 (3)	0.5819 (3)	0.2127 (3)	0.0397 (13)
K	−0.11826 (11)	0.83478 (10)	0.13883 (10)	0.0563 (4)
O1	0.0534 (4)	0.8509 (4)	0.0905 (4)	0.083 (2)
C15	0.1010 (6)	0.9127 (5)	0.1263 (6)	0.084 (3)
C16	0.1840 (6)	0.8817 (6)	0.1648 (7)	0.094 (3)
C17	0.1751 (8)	0.7972 (7)	0.1558 (9)	0.130 (5)
C18	0.1127 (8)	0.7871 (6)	0.0873 (8)	0.105 (4)
O2	−0.1281 (4)	0.6800 (3)	0.1337 (4)	0.082 (2)
C19	−0.0591 (6)	0.6316 (6)	0.1621 (7)	0.088 (3)
C20	−0.1019 (9)	0.5661 (8)	0.1997 (11)	0.169 (7)
C21	−0.1906 (7)	0.5600 (6)	0.1655 (7)	0.100 (3)
C22	−0.2074 (7)	0.6351 (6)	0.1240 (8)	0.105 (4)
O3	−0.2288 (4)	0.8429 (4)	0.0049 (4)	0.087 (2)
C23	−0.3151 (7)	0.8151 (10)	0.0020 (8)	0.177 (8)
C24	−0.3650 (7)	0.8484 (7)	−0.0675 (6)	0.099 (3)
C25	−0.2963 (7)	0.8882 (6)	−0.1160 (6)	0.097 (3)
C26	−0.2202 (7)	0.8966 (7)	−0.0594 (7)	0.115 (4)
O4	−0.1210 (6)	0.9891 (4)	0.1599 (5)	0.116 (3)
C27	−0.1841 (12)	1.0242 (7)	0.2122 (11)	0.190 (9)
C28	−0.1804 (9)	1.1025 (7)	0.2032 (8)	0.119 (4)
C29	−0.1311 (11)	1.1180 (7)	0.1324 (9)	0.139 (5)
C30	−0.0975 (10)	1.0453 (8)	0.1074 (8)	0.149 (6)
O5*A*†	−0.0461 (15)	0.8036 (12)	0.2935 (13)	0.092 (5)
C31*A*†	−0.0961 (14)	0.7623 (11)	0.3516 (12)	0.104 (5)
C32*A*†	−0.1066 (15)	0.8158 (17)	0.4175 (10)	0.125 (7)
C33*A*†	−0.039 (3)	0.8660 (18)	0.4126 (15)	0.118 (6)
C34*A*†	0.0089 (16)	0.8549 (14)	0.3371 (12)	0.101 (6)
O5*B*†	−0.049 (3)	0.852 (2)	0.289 (3)	0.111 (9)
C31*B*†	−0.013 (4)	0.788 (3)	0.332 (3)	0.133 (15)
C32*B*†	−0.011 (3)	0.799 (4)	0.419 (2)	0.149 (17)
C33*B*†	−0.033 (4)	0.890 (2)	0.432 (3)	0.106 (9)
C34*B*†	−0.075 (3)	0.906 (2)	0.3502 (19)	0.127 (11)

† Atoms S1 and S1*A* have occupancies of 0.47 (7) and 0.53 (7), respectively. The disordered tetrahydrofuran molecule has an occupancy of 0.63 (2) for the *A* form and 0.37 (2) for the *B* form.

Table 2. *Selected geometric parameters* (Å, °) *for* (6)

In—N3	2.139 (6)	C3—S3	1.613 (7)
In—N2	2.140 (6)	N4—C4	1.165 (8)
In—N4	2.161 (6)	C4—S4	1.608 (8)
In—N1	2.209 (7)	K—O5*B*	2.66 (5)
In—N6	2.258 (5)	K—O2	2.695 (6)
In—N5	2.265 (5)	K—O4	2.704 (7)
N1—C1	1.124 (9)	K—O3	2.706 (6)
C1—S1	1.622 (15)	K—O1	2.736 (6)

C1—S1*A*	1.663 (14)	K—O5*A*	2.78 (2)
N2—C2	1.148 (9)	K—S1	3.327 (14)
C2—S2	1.616 (8)	K—S1*A*	3.24 (2)
N3—C3	1.156 (8)		
N3—In—N2	100.0 (2)	N1—In—N5	87.3 (2)
N3—In—N4	93.6 (2)	N6—In—N5	72.3 (2)
N2—In—N4	93.1 (2)	C1—N1—In	166.9 (7)
N3—In—N1	89.6 (2)	N1—C1—S1	167.4 (14)
N2—In—N1	89.5 (2)	N1—C1—S1*A*	167 (2)
N4—In—N1	175.4 (2)	C1—S1—K	111.7 (7)
N3—In—N6	95.3 (2)	C1—S1*A*—K	114.1 (6)
N2—In—N6	164.5 (2)	C2—N2—In	177.6 (6)
N4—In—N6	88.8 (2)	N2—C2—S2	178.7 (6)
N1—In—N6	87.6 (2)	C3—N3—In	166.7 (6)
N3—In—N5	167.3 (2)	N3—C3—S3	179.3 (7)
N2—In—N5	92.4 (2)	C4—N4—In	171.6 (6)
N4—In—N5	88.8 (2)	N4—C4—S4	178.3 (6)

Compound (7)

Crystal data

$[K(C_{12}H_{24}O_6)][In(NCS)_4(C_5H_5N)_2].2C_5H_5N$
$M_r = 966.95$
Triclinic
$P\bar{1}$
$a = 8.941$ (2) Å
$b = 9.682$ (2) Å
$c = 13.113$ (3) Å
$\alpha = 87.25$ (3)°
$\beta = 72.33$ (2)°
$\gamma = 89.05$ (2)°
$V = 1080.3$ (4) Å^3
$Z = 1$
$D_x = 1.486$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 30 reflections
$\theta = 11.00$–12.48°
$\mu = 0.889$ mm^{-1}
$T = 160$ (2) K
Block
0.36 × 0.36 × 0.31 mm
Colourless

Data collection

Stoe Siemens diffractometer
ω/θ scans
Absorption correction: ψ scans (Sheldrick, 1990) $T_{\min} = 0.650$, $T_{\max} = 0.699$
5356 measured reflections
3797 independent reflections
3391 observed reflections $[I > 2\sigma(I)]$

$R_{\rm int} = 0.0215$
$\theta_{\max} = 24.99°$
$h = -10 \rightarrow 10$
$k = -11 \rightarrow 11$
$l = -14 \rightarrow 15$
5 standard reflections frequency: 60 min intensity decay: 2%

Refinement

Refinement on F^2
$R(F) = 0.0207$
$wR(F^2) = 0.0674$
$S = 1.060$
3789 reflections
256 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0267P)^2 + 0.3311P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = -0.001$
$\Delta\rho_{\max} = 0.254$ e Å^{-3}
$\Delta\rho_{\min} = -0.597$ e Å^{-3}
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (7)

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

	x	y	z	$U_{\rm eq}$
In	0	0	0	0.01819 (6)
N1	0.0044 (2)	0.0034 (2)	0.16611 (13)	0.0288 (4)
C1	0.0342 (2)	0.0337 (2)	0.2422 (2)	0.0237 (4)
S1	0.07322 (6)	0.07167 (6)	0.35059 (4)	0.03416 (13)
N2	0.0723 (2)	0.2156 (2)	−0.02246 (14)	0.0279 (4)
C2	0.1297 (2)	0.3132 (2)	−0.00205 (14)	0.0212 (4)
S2	0.21006 (6)	0.45002 (5)	0.02391 (4)	0.03139 (12)
N3	0.2550 (2)	−0.0657 (2)	−0.04980 (13)	0.0224 (3)
C3	0.2946 (2)	−0.1890 (2)	−0.0145 (2)	0.0302 (4)
C4	0.4483 (2)	−0.2353 (2)	−0.0418 (2)	0.0343 (5)
C5	0.5649 (2)	−0.1520 (2)	−0.1074 (2)	0.0307 (4)
C6	0.5252 (2)	−0.0247 (2)	−0.1439 (2)	0.0290 (4)
C7	0.3695 (2)	0.0156 (2)	−0.11340 (15)	0.0246 (4)
N4	0.4409 (3)	0.6839 (3)	0.2753 (2)	0.0620 (6)
C8	0.3308 (3)	0.7371 (3)	0.3563 (2)	0.0508 (6)
C9	0.1908 (3)	0.6748 (3)	0.4071 (2)	0.0542 (7)
C10	0.1609 (3)	0.5507 (3)	0.3713 (2)	0.0612 (8)
C11	0.2716 (3)	0.4941 (3)	0.2881 (2)	0.0516 (6)
C12	0.4073 (3)	0.5632 (3)	0.2429 (2)	0.0546 (7)
K	1/2	1/2	1/2	0.02977 (14)
O1	0.3375 (2)	0.65825 (15)	0.67191 (12)	0.0312 (3)
C13	0.1789 (2)	0.6178 (2)	0.7264 (2)	0.0363 (5)
C14	0.1729 (3)	0.4643 (2)	0.7417 (2)	0.0352 (5)
O2	0.2173 (2)	0.40402 (14)	0.63920 (11)	0.0294 (3)
C15	0.2043 (3)	0.2573 (2)	0.6513 (2)	0.0357 (5)
C16	0.2556 (2)	0.1977 (2)	0.5424 (2)	0.0349 (5)
O3	0.4198 (2)	0.22124 (15)	0.49545 (12)	0.0305 (3)
C17	0.4771 (3)	0.1617 (2)	0.3937 (2)	0.0369 (5)
C18	0.6478 (2)	0.1960 (2)	0.3466 (2)	0.0348 (5)

Table 4. *Selected geometric parameters* (Å, °) *for* (7)

In—N2$^{\rm i}$	2.175 (2)	N2—C2	1.163 (2)
In—N1$^{\rm i}$	2.192 (2)	C2—S2	1.615 (2)
In—N3$^{\rm i}$	2.262 (2)	K—O2	2.775 (2)
N1—C1	1.160 (3)	K—O1	2.795 (2)
C1—S1	1.622 (2)	K—O3	2.8120 (15)
N2—In—N1	88.85 (7)	N1—C1—S1	178.2 (2)
N2—In—N3	89.73 (6)	C2—N2—In	154.0 (2)
N1—In—N3	89.09 (6)	N2—C2—S2	178.9 (2)
C1—N1—In	161.7 (2)		

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

For both (6) and (7), the data set consisted of a complete unique set of reflections together with a partial set of Friedel opposites; the index limits do not imply complete coverage of the index ranges. Isotropic H atoms were refined with a riding model, with U(H) set at $1.2U_{\rm eq}$(C) for aromatic H atoms and $1.5U_{\rm eq}$(C) for tetrahydrofuran H atoms. For (6), twofold disorder was refined for atom S1 and for the thf ligand containing O5*A*/O5*B*, for which restraints were applied to the anisotropic displacement parameters.

For both compounds, data collection: *DIF*4 (Stoe & Cie, 1988); cell refinement: *DIF*4; data reduction: local programs; program(s) used to solve structures: *SHELXTL*/*PC* (Sheldrick, 1990); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *SHELXTL*/*PC*; software used to prepare material for publication: *SHELXL*93 and local programs.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1159). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Sodium Bis(2,3-dimethylbutane-2,3-diolato)hydroxogermanate(IV)–Methanol (1/3)

HUNG-CHEH CHIANG,* SHIN-FUNG HWANG AND CHUEN-HER UENG*

Department of Chemistry, National Taiwan Normal University, Taipei, Taiwan

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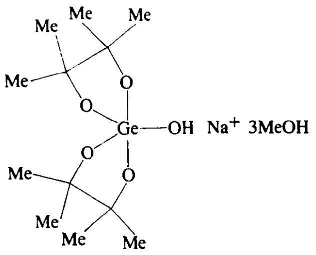
Abstract

$Na[Ge(OH)(C_6H_{12}O_2)_2].3CH_3OH$ has been prepared from germanium dioxide, pinacol (2,3-dimethyl-2,3-butanediol) and methanol and characterized by IR, ^1H NMR and ^{13}C NMR spectroscopy and by elemental analysis. Diffraction analysis reveals that the Ge atom has trigonal bipyramidal coordination geometry, with one O atom of each bidentate ligand and the hydroxo group in equatorial positions; the other two O atoms of the bidentate ligands are in axial sites. The Ge—OH bond length [1.769 (2) Å] is significantly shorter than the other two equatorial Ge—O bonds [1.796 (2) and 1.806 (2) Å] which in turn are shorter than the axial Ge—O bonds [1.866 (3) and 1.870 (3) Å].

Comment

The coordination number displayed by germanium in its complexes varies from 4 to 6 (Mehrotra & Chandra, 1963; Yoder & Zukerman, 1967; Sau & Holmes, 1981; Day, Holmes, Sau & Holmes, 1982; Gurkova *et al.*, 1984; Sau, Holmes, Day & Holmes, 1986; Eujen, Brauer & Wilke, 1986; Breliere, Carre, Corriu & Royo, 1988; Mizuta, Yoshida & Miyoshi, 1989; Lazraq *et al.*, 1990; Cereau, Chuit, Corriu & Reye, 1991). We have described previously the syntheses and crystal structures of two tetrahedral germanium complexes (Chen, Chiang & Ueng, 1993), a trigonal bipyramidal complex (Chiang, Lin & Ueng, 1992) and four octahedral complexes (Chiang, Wang & Ueng, 1993; Chiang, Yang & Ueng, 1994; Chiang, Hwang & Ueng, 1995). In a continuation of these studies, the title complex, (I), was synthesized and its crystal structure determined.



(I)

The complex contains a central Ge atom bonded to a hydroxo group and to the four O atoms of two deprotonated pinacol ligands. The coordination around the metal is distorted trigonal bipyramidal with the hydroxo group and one O atom of each pinacolate in equatorial positions; the remaining two pinacolate O atoms occupy axial positions. The deviation of the Ge atom from the equatorial plane is 0.022 (1) Å. The O(1)—Ge—O(4) angle is 173.5 (1)°, the angles in the equatorial plane are 115.6 (1), 120.6 (1) and 123.8 (1)° and the six O_a—Ge—O_e (a = axial, e = equatorial) angles are in the range 87.4 (1)–95.9 (1)°. The Ge—O(5) bond is significantly shorter than Ge—O(2) and Ge—O(3), which in turn are shorter than Ge—O(1) and Ge—O(4). This variation is expected since the coordinating ability of the hydroxo group is greater than that of the alkoxide, and equatorial Ge—O bonds are usually stronger than axial Ge—O bonds (Chiang, Lin & Ueng, 1992).

The coordination around the Na^+ cation is also distorted trigonal bipyramidal, with the hydroxo group and two methanol O atoms equatorial and a further two methanol O atoms axial. The deviation of the Na atom from the equatorial plane is −0.182 (3) Å. The O_a—Na—O_a angle is 168.5 (1)°, the angles in the equatorial plane are 98.3 (1), 116.4 (1) and 143.3 (1)° and the six O_a—Na—O_e angles are in the range 82.6 (1)–105.8 (1)°. It is obvious that the distortion of the coordination polyhedron around the Na atom from an ideal trigonal bipyramid is larger than for that around the Ge atom. In addition to the hydroxo group [O(5)] which bridges the