O4$^{\rm v}$—Fe4—O24$^{\rm iv}$	88.5 (2)	O20$^{\rm i}$—Fe7—O18$^{\rm iv}$	172.3 (2)
O3$^{\rm iv}$—Fe4—O16$^{\rm v}$	88.7 (2)	F5—Fe7—O18$^{\rm iv}$	87.1 (2)
O4$^{\rm v}$—Fe4—O16$^{\rm v}$	87.2 (2)	F6—Fe7—O18$^{\rm iv}$	86.7 (2)
O24$^{\rm iv}$—Fe4—O16$^{\rm v}$	162.1 (2)	O5—Fe7—O18$^{\rm iv}$	91.6 (2)
O3$^{\rm iv}$—Fe4—F2$^{\rm v}$	103.1 (2)	O1—Fe7—O18$^{\rm iv}$	83.9 (2)
O4$^{\rm v}$—Fe4—F2$^{\rm v}$	104.0 (2)	O23$^{\rm viii}$—Fe8—O11	95.5 (2)
O24$^{\rm iv}$—Fe4—F2$^{\rm v}$	100.8 (2)	O23$^{\rm viii}$—Fe8—F6$^{\rm iv}$	92.9 (2)
O16$^{\rm v}$—Fe4—F2$^{\rm v}$	97.2 (2)	O11—Fe8—F6$^{\rm iv}$	89.8 (2)
O21$^{\rm vi}$—Fe5—O10	97.3 (2)	O23$^{\rm viii}$—Fe8—F4	91.2 (2)
O21$^{\rm vi}$—Fe5—O17$^{\rm i}$	92.6 (2)	O11—Fe8—F4	91.4 (2)
O10—Fe5—O17$^{\rm i}$	90.5 (2)	F6$^{\rm iv}$—Fe8—F4	175.5 (2)
O21$^{\rm vi}$—Fe5—O15$^{\rm vi}$	91.8 (2)	O23$^{\rm viii}$—Fe8—O9$^{\rm viii}$	89.5 (2)
O10—Fe5—O15$^{\rm vi}$	91.4 (2)	O11—Fe8—O9$^{\rm viii}$	174.9 (2)
O17$^{\rm i}$—Fe5—O15$^{\rm vi}$	174.9 (2)	F6$^{\rm iv}$—Fe8—O9$^{\rm viii}$	91.3 (2)
O21$^{\rm vi}$—Fe5—F3$^{\rm i}$	93.1 (2)	F4—Fe8—O9$^{\rm viii}$	87.0 (2)
O10—Fe5—F3$^{\rm i}$	169.6 (2)	O23$^{\rm viii}$—Fe8—O14$^{\rm iv}$	173.6 (2)
O17$^{\rm i}$—Fe5—F3$^{\rm i}$	88.1 (2)	O11—Fe8—O14$^{\rm iv}$	90.5 (2)
O15$^{\rm vi}$—Fe5—F3$^{\rm i}$	89.2 (2)	F6$^{\rm iv}$—Fe8—O14$^{\rm iv}$	84.7 (2)
O21$^{\rm vi}$—Fe5—F5	174.6 (2)	F4—Fe8—O14$^{\rm iv}$	91.0 (2)
O10—Fe5—F5	87.4 (2)	O9$^{\rm viii}$—Fe8—O14$^{\rm iv}$	84.7 (2)
O17$^{\rm i}$—Fe5—F5	84.5 (2)	O24—Fe9—O13$^{\rm ix}$	118.5 (2)
O15$^{\rm vi}$—Fe5—F5	90.9 (2)	O24—Fe9—O14$^{\rm x}$	98.9 (2)
F3$^{\rm i}$—Fe5—F5	82.2 (2)	O13$^{\rm ix}$—Fe9—O14$^{\rm x}$	108.0 (2)
O22$^{\rm vii}$—Fe6—O2	95.7 (2)	O24—Fe9—O18	103.3 (2)
O22$^{\rm vii}$—Fe6—F1$^{\rm vii}$	95.4 (2)	O13$^{\rm ix}$—Fe9—O18	99.8 (2)
O2—Fe6—F1$^{\rm vii}$	89.6 (2)	O14$^{\rm x}$—Fe9—O18	129.9 (2)

Symmetry codes: (i) $\frac{1}{2}-x, \frac{3}{2}-y, -z$; (ii) $x, y-1, z$; (iii) $x-\frac{1}{2}, y-\frac{1}{2}, z$; (iv) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (v) $x-\frac{1}{2}, \frac{1}{2}+y, z$; (vi) $-x, 1-y, -z$; (vii) $\frac{1}{2}+x, \frac{1}{2}+y, z$; (viii) $x, 1+y, z$; (ix) $1-x, y, \frac{1}{2}-z$; (x) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$; (xi) $-x, y, \frac{1}{2}-z$.

The metrically possible higher symmetry [rhombohedral cell, hexagonal setting: $a' = 12.296$, $b' = 12.304$, $c' = 58.323$ Å, $\alpha' = 89.91$, $\beta' = 90.00$, $\gamma' = 119.98°$, transformation matrix (−0.5 0.5 0 / 0 −1 0 / 1 0 3)] was rejected because of the missing symmetry of the reflections (the *R* value for averaging reflections in the space group *R*3 was 0.33). The residual electronic density of 1.22 e Å^{-3} is due to the disorder of the Cs4 atom, which was split over three sites and refined with one common isotropic displacement factor. The disordered Fe3 and Fe4 atoms were refined with a common anisotropic displacement factor.

Data collection: *CAD*-4 *EXPRESS* (Enraf-Nonius, 1994). Cell refinement: *CAD*-4 *EXPRESS*. Data reduction: *XCAD*4 (Harms, 1992). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *TROMPLEU* (Gravereau, Larroche & leLirzin, 1991) and *ZORTEP* (Zsolnai, 1994). Software used to prepare material for publication: *SHELXL*93.

The authors wish to thank N. Zinovieva for the X-ray spectral analysis and W. Massa for helpful discussions.

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: JZ1087). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Andrewes-Allen, E. M. & Robinson, W. R. (1988). *J. Solid State Chem.* **74**, 88–97.

Anisimova, N. Yu., Serafine, M. & Hoppe, R. (1995). Abstracts of the VII Conference on Crystallochemistry of Inorganic and Organic Compounds, St. Petersburg, Russia, p. 37.

Enraf-Nonius (1994). *CAD*-4 *EXPRESS*. Version 5.1/1.2. Enraf-Nonius, Delft, The Netherlands.

Gravereau, R., Larroche, A. & leLirzin, A. (1991). *TROMPLEU* (a modification of R. X. Fischer's *STRUPLO*84). University of Bordeaux I, France.

Harms, K. (1992). *XCAD*4. University of Marburg, Germany.

Klinkert, B. & Jansen, M. (1988). *Z. Anorg. Allg. Chem.* **567**, 87–94.

Matvienko, E. N., Yakubovich, O. V., Simonov, M. A. & Belov, N. V. (1981). *J. Struct. Chem.* **22**, 121–125.

Moore, P. B. (1973). *Mineral. Rec.* **4**, 103–130.

Pauling, L. (1968). *Die Natur der chemischen Bindung*. Weinheim: Verlag Chemie.

Sandomirskij, P. A. & Belov, N. V. (1984). *Crystal Chemistry of Mixed Anionic Radicals*. Moscow: Nauka.

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

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

Yakubovich, O. V., Egorov-Tismenko, Yu. K., Simonov, M. A. & Belov, N. V. (1977). *Dokl. Akad. Nauk SSSR*, **236**, 1123–1126.

Yakubovich, O. V., Matvienko, E. N., Simonov, M. A. & Mel'nikov, O. K. (1986). *Vestn. Mosk. Univ. Geol.* **4**, 36–47.

Yakubovich, O. V. & Mel'nikov, O. K. (1990). *Kristallografiya*, **35**, 1122–1125.

Zsolnai, L. (1994). *ZORTEP*. University of Heidelberg, Germany.

Acta Cryst. (1996). C**52**, 753–757

Triaquahexathiocyanatobismuthlanthanum Dihydrate, $[Bi(SCN)_6La(H_2O)_3].2H_2O$, and Triaquahexathiocyanatobismuthneodymium Dihydrate, $[Bi(SCN)_6Nd(H_2O)_3].2H_2O$

Waldemar Maniukiewicz, Lesław Sieroń, Maria Bukowska-Strzyżewska and Anna Turek

Institute of General & Ecological Chemistry, Technical University, 90-924 Łódź, Poland. E-mail: mbukowska@lodz1.p.lodz.pl

Abstract

In the crystal state, the title compounds form dihydrated three-dimensional polymeric complexes of general formula $[Bi(SCN)_6Ln(H_2O)_3].2H_2O$, isomorphic with and with a similar structure to the $LaFe(CN)_6.5H_2O$ structure type. The distorted octahedral BiS_6 polyhedra and LnN_6O_3 polyhedra are connected by the bridging thiocyanate groups in the three-dimensional network. Six N atoms form trigonal prisms around the Ln^{III} ions with the three rectangular faces capped by three H_2O molecules. This gives La and Nd coordination polyhedra in the form of tricapped trigonal prisms. The different structural roles of the water molecules explains the literature data regarding a two-stage dehydration of the crystals. A comparison of the bond lengths in the two structures is given.

Acta Crystallographica Section C
ISSN 0108-2701 ©1996

Comment

The synthesis of the differently hydrated complexes $Ln[Bi(SCN)_6].5H_2O$ (Ln = La, Ce, Pr, Nd, Sm and Gd), $Dy[Bi(SCN)_6].4H_2O$ and $Er(Y)[Bi(SCN)_6].3H_2O$ have been described by Cygański (1967). Thermochemical studies of the title compounds $[Bi(SCN)_6La(H_2O)_3].2H_2O$, (I), and $[Bi(SCN)_6Nd(H_2O)_3].2H_2O$, (II), showed that they dehydrate *via* a two-stage process (Turek & Cygański, 1994). This structural investigation was undertaken to determine the geometry of the Bi^{III}, La^{III} and Nd^{III} polyhedra, and to examine the role of the water molecules in the complexation and stabilization of the crystal structures. The structures of lanthanide hexathiocyanatobismuthates have not been investigated previously.

Like the structures of the $LaFe(CN)_6.5H_2O$ type (Bailey, Williams & Milligan, 1973; Dommann, Vetsch & Hulliger, 1990), the structures of (I) and (II) contain $Bi^{III}S_6$ and LnN_6O_3 coordination polyhedra formed by the bridging SCN^- ions and three $H_2O(1)$ molecules. Fig. 1 shows the structure viewed along the *c* axis. Two slightly distorted BiS_6 octahedra are located on the inversion threefold axes in the unit cell (with Bi at 0,0,0 and 0,0,1/2). Two LnN_6O_3 coordination polyhedra in the form of tricapped trigonal prisms of $\bar{6}$ symmetry are located at the 2(*c*) positions in the unit cell (with Ln at 1/3,2/3,1/4 and 2/3,1/3,3/4). Unlike $LaFe(CN)_6.5H_2O$, the four uncoordinated H_2O molecules in the unit cell do not occupy a single fourfold position 4(*f*), but are statistically placed in two fourfold positions 4(*e*) and 4(*f*) on threefold axes (this imposes disorder on the H atoms and reduces the site-occupancy factors to 0.5). Selected bond lengths and angles are given in Table 2.

The Bi—S distances in (I) and (II) [2.809 (1) and 2.807 (2) Å, respectively] are identical within the 1σ range and similar to those in $Cs_2Na[Bi(SCN)_6]$ [2.817 (2) Å; Bukowska-Strzyżewska, Cygański, Maniukiewicz, Turek & Zagajewska, 1994]. The observed Bi—S distances correspond exactly to the Bi oxidation number ν_{Bi} = 3.0, calculated using the parameters of Brese & O'Keeffe (1991). This indicates that the Bi—S bond lengths in (I) and (II) are typical for coordination number 6. The same angular deformation of the BiS_6 octahedra is observed in (I) and (II), with average equatorial S—Bi—S angles of 80.77 (5) and 99.23 (5)°.

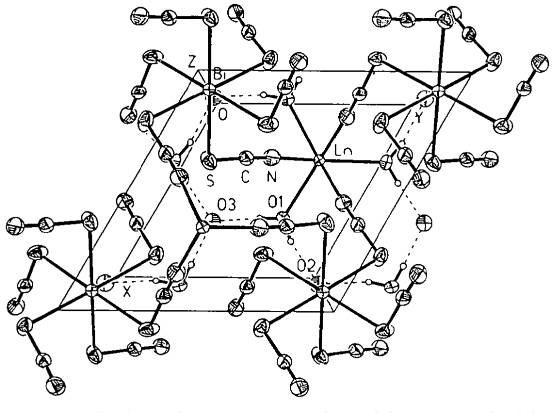

Fig. 1. A projection of the structure of $[Bi(SCN)_6Ln(H_2O)_3].2H_2O$ (Ln = La, Nd). Atomic displacement parameters are shown at the 50% probability level.

The La and Nd coordination polyhedra are tricapped trigonal prisms. Comparision of the individual valences of the Ln—O and Ln—N bonds (ν_{Ln-O} and ν_{Ln-N}) calculated according to Brese & O'Keeffe (1991) and expected from the valence-sum rule (Pauling, 1929; Brown, 1977) allows discussion of the bond lengths. For homoligand (H_2O and NCS^-) polyhedra LnO_9 and LnN_9, the valence-sum rule gives $\nu_{Ln-O} = \nu_{Ln-N} = 3/9 = 0.33$, and for LnN_6 $\nu_{Ln-N} = 3/6 = 0.5$. In LnN_6O_3 (if the six Ln—N and the three Ln—O bonds are identical), the valence-sum rule gives $\nu_{Ln-N} + 0.5\nu_{Ln-O} = 0.5$ (as $6\nu_{Ln-N} + 3\nu_{Ln-O} = 3$). For the title complexes, the bond valences ν_{Ln-N} and ν_{Ln-O}, calculated from the Brese & O'Keeffe parameters and the observed bond lengths, are 0.49 and 0.28 for La and 0.53 and 0.27 for Nd, respectively, which clearly exceeds the expected sum $\nu_{Ln-N} + 0.5\nu_{Ln-O} = 0.5$. The observed system of hydrogen bonds between the coordinated water molecule $H_2O(1)$ and the uncoordinated water molecules $H_2O(2)$ and $H_2O(3)$ should weaken the Ln—O bonds compared with those expected for a homoligand $[Ln(H_2O)_9]^{3+}$ complex. This is indeed observed, as the valences of the Ln—O bonds in the title complexes are less than the value of 0.33 expected for LnO_9. The calculated bond valences ν_{Ln-N} indicate that the Ln—N bonds in (I) and (II) are much shorter than one would expect from the valence-sum rule. A similar situation is observed in the known structures of the $LaFe(CN)_6.5H_2O$ type (Bailey *et al.*, 1973; Dommann *et al.*, 1990). The average La—N bonds of 2.616 (4) Å and the average La—O bonds of 2.588 (6) Å give ν_{La-N} = 0.47 and ν_{La-O} = 0.32. The La—O bonds are shorter than observed in the title complexes. In the $LaFe(CN)_6.5H_2O$ complexes, the coordinated H_2O molecules are not involved in hydrogen bonding and ν_{Ln-O} almost exactly corresponds to the ν_{Ln-O} values expected for $[Ln(H_2O)_9]^{3+}$ complexes. The La—N bonds are also much shorter than those predicted from the valence-sum rule.

Intermolecular hydrogen-bond distances (O···O) in (I) and (II) range from 2.821 (9) to 2.872 (5) Å. The structures are stabilized by these hydrogen bonds, which form condensed ten-membered rings in the planes close to z = 1/4 and 3/4. As shown in Fig. 1, each O(2) and O(3) atom is an acceptor of three hydrogen bonds and each O(1) atom is a donor of two hydrogen bonds. Examination of the short interatomic contacts involving atoms O(2) and O(3) indicates which atoms could be the acceptors of O(2)—H and O(3)—H statistically located hydrogen bonds. There are three short O(3)···S contacts of 3.553 (7) and 3.52 (2) Å, and less short

O(3)· · ·N contacts of 3.497 (6) and 3.50 (1) Å in (I) and (II), respectively. The O(2) atoms show only identical short O(2)· · ·N contacts in (I) and (II) of 3.54 (2) and 3.54 (4) Å, respectively.

A stereoscopic view of the unit cell is shown in Fig. 2. The different structural roles of the H_2O molecules explain the observed two-stage dehydration of the crystals (Turek & Cygański, 1994). The thiocyanate groups in both structures are bent in the same way, with an average N—C—S angle of 177.0 (5)°. The N—C and C—S bond lengths are similar in both structures with average values of 1.141 (6) for the N—C and 1.655 (5) Å for the C—S bonds. This shows the dominance of the mesomeric form S—C≡N, as also observed in the complexes $Cs_2Na[Bi(SCN)_6]$ and $Rb[Bi(SCN)_4]$ (Bukowska-Strzyżewska *et al.*, 1994; Gałdecki, Główka & Goliński, 1976).

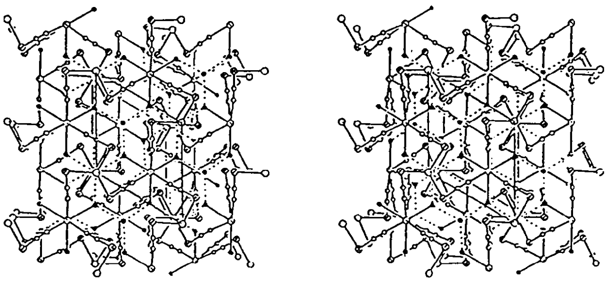

Fig. 2. A stereoscopic view of the unit-cell contents viewed down **c**. The N atoms are shown as circles and the O atoms as dots.

Experimental

The synthesis of the title compounds has been described by Cygański (1967).

Compound (I)

Crystal data

$[Bi(SCN)_6La(H_2O)_3].2H_2O$
$M_r = 786.45$
Hexagonal
$P6_3/m$
$a = 8.2508$ (6) Å
$c = 18.745$ (2) Å
$V = 1105.1$ (2) Å^3
$Z = 2$
$D_x = 2.363$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 8.0$–15.0°
$\mu = 10.450$ mm^{-1}
$T = 293$ (2) K
Sphere
0.15 mm (radius)
Orange

Data collection

Siemens *P*3 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North, Phillips & Mathews, 1968)
$T_{\min} = 0.137$, $T_{\max} = 0.183$
1785 measured reflections
1555 independent reflections

1414 observed reflections $[I > 2\sigma(I)]$
$R_{\rm int} = 0.0202$
$\theta_{\max} = 35.08°$
$h = -11 \rightarrow 0$
$k = 0 \rightarrow 13$
$l = 0 \rightarrow 25$
3 standard reflections frequency: 60 min intensity decay: 1.5%

Refinement

Refinement on F^2
$R(F) = 0.0277$
$wR(F^2) = 0.0537$
$S = 1.172$
1505 reflections
45 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0631P)^2 + 1.3722P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 1.07$ e Å^{-3}
$\Delta\rho_{\min} = -1.36$ e Å^{-3}

Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0237 (11)
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 (I)*

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

	Wyckoff position	x	y	z	$U_{\rm eq}$	Occupancy
Bi	2(*b*)	0	0	1/2	0.0227 (1)	1.0
La	2(*c*)	1/3	2/3	1/4	0.0181 (1)	1.0
S	12(*i*)	0.3454 (1)	0.1630 (1)	0.4285 (1)	0.0414 (2)	1.0
C	12(*i*)	0.3302 (4)	0.3236 (4)	0.3805 (2)	0.0306 (7)	1.0
N	12(*i*)	0.3257 (5)	0.4331 (5)	0.3452 (2)	0.0443 (7)	1.0
O(1)	6(*h*)	0.6499 (5)	0.6582 (5)	1/4	0.0480 (13)	1.0
O(2)	4(*e*)	0	0	0.233 (2)	0.074 (12)	0.5
O(3)	4(*f*)	2/3	1/3	0.2161 (5)	0.041 (2)	0.5

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

Bi—S	2.809 (1)	C—N	1.135 (4)
La—N	2.604 (3)	O(3)· · ·S$^{\rm i}$	3.553 (7)
La—O(1)	2.648 (4)	O(3)· · ·N$^{\rm i}$	3.497 (6)
S—C	1.658 (3)	O(2)· · ·N$^{\rm i}$	3.54 (2)
S$^{\rm ii}$—Bi—S	80.86 (3)	N$^{\rm iv}$—La—O(1)	136.73 (9)
S$^{\rm iii}$—Bi—S	99.14 (3)	N$^{\rm vi}$—La—O(1)	68.42 (9)
N$^{\rm iv}$—La—N	78.19 (13)	C—S—Bi	100.28 (11)
N$^{\rm v}$—La—N	137.29 (6)	N—C—S	176.7 (3)
N$^{\rm i}$—La—N	86.5 (2)	C—N—La	171.8 (3)
N—La—O(1)	68.87 (9)		

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

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

D—H· · ·*A*	*D*—H	H· · ·*A*	*D*· · ·*A*	*D*—H· · ·*A*
O(1)—H(1)· · ·O(3)	0.92	1.94	2.825 (4)	161
O(1)—H(2)· · ·O(2$^{\rm ii}$)	0.94	1.96	2.872 (5)	165

Symmetry codes: (i) $x, y, \frac{1}{2} - z$; (ii) $1 + x, 1 + y, z$.

Compound (II)

Crystal data

$[Bi(SCN)_6Nd(H_2O)_3].2H_2O$
$M_r = 791.78$
Hexagonal
$P6_3/m$
$a = 8.200$ (2) Å
$c = 18.606$ (3) Å
$V = 1083.5$ (4) Å^3
$Z = 2$
$D_x = 2.427$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 8.0$–15.0°
$\mu = 11.084$ mm^{-1}
$T = 293$ (2) K
Sphere
0.18 mm (radius)
Orange

Data collection

Siemens *P*3 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North, Phillips & Mathews, 1968)
$T_{\min} = 0.072$, $T_{\max} = 0.144$
1695 measured reflections
1483 independent reflections
1314 observed reflections [$I > 2\sigma(I)$]
$R_{\rm int} = 0.0638$
$\theta_{\max} = 35.08°$
$h = -10 \rightarrow 0$
$k = 0 \rightarrow 13$
$l = 0 \rightarrow 25$
3 standard reflections frequency: 60 min intensity decay: 1.5%

Refinement

Refinement on F^2
$R(F) = 0.0464$
$wR(F^2) = 0.1199$
$S = 1.078$
1445 reflections
45 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0631P)^2 + 6.9674P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 3.01$ e Å^{-3}
$\Delta\rho_{\min} = -2.22$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0195 (17)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 4. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (II)*

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

	Wyckoff positions	x	y	z	$U_{\rm eq}$	Occupancy
Bi	2(*b*)	0	0	1/2	0.0258 (2)	1.0
Nd	2(*c*)	1/3	2/3	1/4	0.0211 (2)	1.0
S	12(*i*)	0.3478 (3)	0.1684 (3)	0.4284 (11)	0.0435 (5)	1.0
C	12(*i*)	0.3310 (8)	0.3272 (8)	0.3793 (4)	0.0325 (15)	1.0
N	12(*i*)	0.3259 (9)	0.4388 (9)	0.3437 (4)	0.0443 (14)	1.0
O(1)	6(*h*)	0.6467 (11)	0.6583 (11)	1/4	0.045 (2)	1.0
O(2)	4(*e*)	0	0	0.233 (6)	0.09 (4)	0.5
O(3)	4(*f*)	2/3	1/3	0.2163 (15)	0.051 (5)	0.5

Table 5. *Selected geometric parameters (Å, °) for (II)*

Bi—S	2.807 (2)	C—N	1.147 (8)
Nd—N	2.534 (6)	O(3)···S$^{\rm i}$	3.52 (2)
Nd—O(1)	2.604 (7)	O(3)···N$^{\rm i}$	3.50 (1)
S—C	1.652 (6)	O(2)···N$^{\rm i}$	3.54 (4)
S$^{\rm ii}$—Bi—S	80.69 (6)	N$^{\rm iv}$—Nd—O(1)	136.5 (2)
S$^{\rm iii}$—Bi—S	99.31 (6)	N$^{\rm vi}$—Nd—O(1)	68.5 (2)
N$^{\rm iv}$—Nd—N	77.9 (3)	C—S—Bi	100.7 (2)
N$^{\rm v}$—Nd—N	137.43 (13)	N—C—S	177.2 (6)
N$^{\rm i}$—Nd—N	86.9 (4)	C—N—Nd	171.3 (7)
N—Nd—O(1)	68.9 (2)		

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

Table 6. *Hydrogen-bonding geometry (Å, °) for (II)*

D—H···A	D—H	H···A	D···A	D—H···A
O(1)—H(1)···O(3)	0.92	1.94	2.821 (9)	161
O(1)—H(2)···O(2$^{\rm ii}$)	0.93	1.97	2.869 (14)	163

Symmetry codes: (i) $x, y, \frac{1}{2} - z$; (ii) $1 + x, 1 + y, z$.

The choice between the space groups $P6_3/m$ and $P6_3$ was made in the same way for both structures. Numerical values for (II) are given in parentheses after those for (I). The two space groups were initially tested using the *XPREP* program in *SHELXTL/PC* (Sheldrick, 1990*b*). The statistics were closer to those expected for the centrosymmetric space group, but were not conclusive [mean $|E^2 - 1| = 0.869$ (0.870), with expected values of 0.968 for the centrosymmetric space group and 0.736 for the non-centrosymmetric space group]. The combined figures of merit (CFOMs) for $P6_3/m$ and $P6_3$ were 3.14 (3.44) and 5.26 (5.61), respectively. The structures were solved by conventional Patterson and Fourier methods, and were refined by full-matrix least-squares calculations in both space groups in order to decide between them. In $P6_3$, an ideally centrosymmetrical arrangement of Bi, Ln, S, C, N and O(1) was found with very large correlation coefficients for positional and displacement parameters for the groups S(1), C(1), N(1) and S(2), C(2), N(2). The atom O(2) in the 2(*a*) position refined to give a very large U_{33} anisotropic displacement parameter of 0.22 (3) [0.23 (1)] Å^2. Modelling this atom as disordered gave z[O(2′)] = 0.28 (2) [0.27 (2)] and z[O(2″)] = 0.24 (2) [0.23 (1)], suggesting a statistical mirror plane at $z = 1/4$. Thus, we decided upon the centrosymmetric space group $P6_3/m$. This choice was supported by the observed wR^2 factors [0.0624 (0.1311) and 0.0537 (0.1199) in $P6_3$ and $P6_3/m$, respectively].

In the chosen space group $P6_3/m$, the atoms O(2) and O(3) belonging to water molecules were placed at the fourfold positions 4(*e*) and 4(*f*) with occupancy factors of 0.5. Placing them at $z = 1/4$ and 3/4 in the 2(*a*) and 2(*c*) positions resulted in very large U_{33}[O(2)] and U_{33}[O(3)] displacement parameters. The location of these molecules on the threefold axes results in disorder of their H atoms.

The position of the H atom H(1) of the H$_2$O(1) molecule was found from a difference map, while the position of the second H atom, H(2), was fixed from geometrical considerations. Their positional parameters were not refined and they were assigned isotropic displacement factors 1.5 times $U_{\rm eq}$ of O(1). The H atoms of H$_2$O(2) and H$_2$O(3) were not located.

For both compounds, data collection: Siemens *P*3 software; cell refinement: Siemens *P*3 software; data reduction: *SHELXTL/PC XDISK* (Sheldrick, 1990*b*); program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1990*a*); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *SHELXTL/PC XP*; software used to prepare material for publication: *SHELXL*93.

This work is being supported by the Polish Scientific Research Council (KBN) under grant 20575.91.01.

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: BR1118). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Bailey, W. E., Williams, R. J. & Milligan, W. O. (1973). *Acta Cryst.* B**29**, 1365–1368.
Brese, N. E. & O'Keeffe, M. (1991). *Acta Cryst.* B**47**, 192–197.
Brown, I. D. (1977). *Acta Cryst.* B**33**, 1305–1310.
Bukowska-Strzyżewska, M., Cygański, A., Maniukiewicz, W., Turek, A. & Zagajewska, K. (1994). *J. Chem. Cryst.* **24**, 425–429.

Cygański, A. (1967). *Rocz. Chemii*, **41**, 39–44.
Dommann, A., Vetsch, H. & Hulliger, F. (1990). *Acta Cryst.* C**46**, 1994–1996.
Gałdecki, Z., Główka, M. & Goliński, B. (1976). *Acta Cryst.* B**32**, 2319–2321.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Pauling, L. (1929). *J. Am. Chem. Soc.* **51**, 1010–1026.
Sheldrick, G. M. (1990*a*). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1990*b*). *SHELXTL/PC User's Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Turek, A. & Cygański, A. (1994). *Thermochim. Acta*, **232**, 205–214.

Acta Cryst. (1996). C**52**, 757–759

Octacaesium Decatungstosilicate Nonahydrate

Hans Hartl and Vera Hubert

Institut für Anorganische und Analytische Chemie der Freien Universität Berlin, Fabeckstrasse 34/36, D-14195 Berlin, Germany. E-mail: hartl@fu-berlin.chemie.de

(*Received 6 January 1995; accepted 17 October 1995*)

Abstract

The title compound {octacaesium silicodecatungstate nonahydrate, $Cs_8[SiW_{10}O_{36}].9H_2O$} is the first caesium salt of the heteropolyoxometalate anion γ-$[SiW_{10}O_{36}]^{8-}$. The stability of the well known heteropolyanion depends on the size of the alkali metal cations. The polyanions are connected into infinite columns by Cs cations.

Comment

Heteropolytungstates have been known for a long time and are interesting for many reasons (Pope & Müller, 1991; Lunk, 1990). Polyanions $[SiW_{10}O_{36}]^{8-}$ can be described as fragments of the well known Keggin structure (Keggin, 1933). The Keggin structure $[XW_{12}O_{40}]^{z-}$ (where X = P, Si, Ge, C or one of many other elements) is built up from twelve WO_6 octahedra. Three octahedra are connected by edges to four W_3O_{13} groups, which themselves form a polyanion with T_d symmetry by corner sharing. According to Baker & Figgis (1970), there are five possible isomers, α, β, γ, δ and ε, which differ by rotation of one, two, three or four W_3O_{13} groups by $\pi/3$. Until now, only the α and β isomers are known as isolated polyanions (Pope, 1983). Other isomers, such as ε, are known as polycations {$[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$; Johansson, 1963} and as parts of larger structures (Khan, Müller, Dillinger, Bögge, Chen & Zubieta, 1993). γ-$[SiW_{10}O_{36}]^{8-}$ can be described as a fragment of the γ-Keggin structure, removing those two octahedra which become edge-sharing by the rotation. The result is a lacunary structure with a central cavity above the SiO_4 tetrahedron. The symmetry of the polyanion is lowered from T_d to C_{2v} (Figs. 1 and 2).

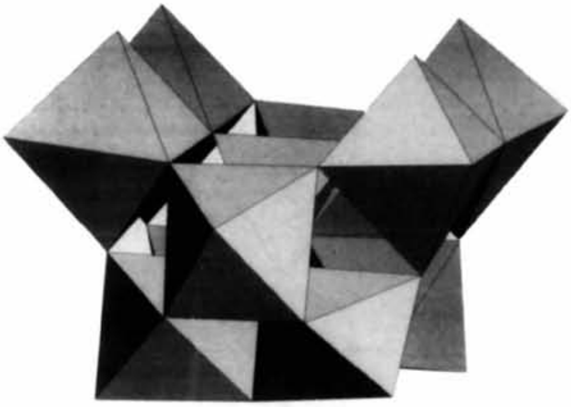

Fig. 1. Polyhedral representation of the polyanion, showing the central cavity (plane *ac*, 10° rotation of *a*).

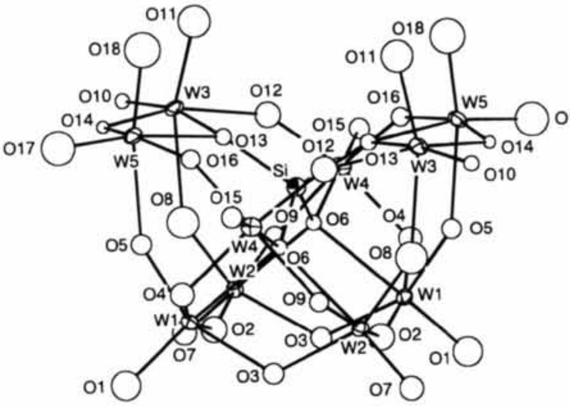

Fig. 2. Ball-and-stick representation of the polyanion (plane *ac*, 10° rotation of *a*).

The stability of the polyanion in solution depends on the size of the alkali metal cations, as reported by Canny, Tézé, Thouvenot & Hervé (1986). They investigated solutions of the lithium, sodium, potassium and rubidium salts and described the crystal structure of the rubidium salt. One Rb atom is located in the central cavity of the polyanion and seems to be responsible for its stability. Compounds of the γ-$[SiW_{10}O_{36}]^{8-}$ anion with cations smaller than potassium are not stable. The title structure completes the series of alkali metal salts of this type of lacunary polyanion.

There are five crystallographically independent Cs^+ cations with different coordination polyhedra in the