group *Pcam* (No. 57), which contains 2 × Tl, 2 × Ti, 3 × P and 12 × O in the asymmetric unit, led to much higher residuals of $R[F > 2\sigma(F)] = 0.067$ and $wR(F^2) = 0.180$. Very elongated ellipsoids resulted from two O atoms which form Ti—O—P(pyrophosphate) [principal axis $U_{\rm min}/U_{\rm max}$ ratio for this atom = 5.3] and P—O—P [$U_{\rm min}/U_{\rm max} = 9.7$] bonds. These *Pcam* species correspond to the O atoms involved in the Ti1—O5—P5, Ti1—O6—P4 and P4—O18—P5 bonds in the $Pca2_1$ model.

The geometries of the TiO_6 octahedra are relatively unaffected by the symmetry reduction from *Pcam* to $Pca2_1$. In particular, the conformation of the Ti—O—Ti bridge is barely altered when the twofold symmetry constraint on a bridging O atom is removed. In $Pca2_1$, the unusual situation where both the Ti atoms are displaced towards the central O atom remains essentially unchanged compared with that occurring in *Pcam.* This situation is totally different to that found in phases such as $KTiOPO_4$, containing infinite chains of vertex-sharing TiO_6 octahedra, where a very distinctive alternation of Ti—O bond lengths along the chain occurs (Stucky *et al.*, 1989; Thomas *et al.*, 1992).

The application of a symmetry check (Farrugia, 1998) revealed that the atom least compatible (by ∼0.39 Å) with higher symmetry was O18, which forms the pyrophosphate P—O—P bridge. The P—O—P angle is reduced from 145 (2)° in *Pcam* to 134.9 (4)° in $Pca2_1$. In *Pcam*, the bridging O atom lies on a twofold axis, which restricts the value of the P—O—P angle, given that four of the terminal P—O bonds have their position constrained by Ti atoms. The P—O—P angles in pyrophosphate groups cover a wide range, ∼120–180° (Durif, 1995), thus in itself, the driving force for a symmetry-breaking effect involving removal of the twofold axis of the P_2O_7 group is probably a relatively weak one (Brown, 1999). Another effect may be involved, namely, optimizing the Tl^+ cation coordinations. In *Pcam*, the Tl11 species (corresponding to Tl1 in $Pca2_1$) is relatively underbonded, with only six O-atom neighbours within 3.4 Å, and a bond valence sum (BVS) of 0.66 (Brown, 1996). Tl12 (corresponding to Tl2 and Tl3) has nine O-atom neighbours within the same limits (BVS = 0.79). In $Pca2_1$, Tl1 increases its coordination number to nine and its BVS to 0.80, Tl2 (nine-coordinate) increases its BVS to 0.86, whilst that for Tl3 (eight-coordinate) is essentially unchanged from that of Tl12 at 0.79. In *Pcam*, the P—O—P bridge O atom bonds to two equivalent Tl12 cations, with d(Tl—O) = 3.23 (2) Å. In $Pca2_1$, the two distinct Tl—O bond lengths are 3.021 (7) Å for Tl2 and 3.493 (7) Å for Tl3. In *Pcam*, Tl11 makes a very long bond of 3.47 (2) Å to the Ti—O—P(pyrophosphate) O atom noted above. In $Pca2_1$, Tl1—O6 is much shorter at 3.229 (7) Å, whereas Tl1—O5 is longer at 3.693 (6) Å. To a first approximation, these improved low-symmetry thallium coordinations are achieved by distorting the P_2O_7 group and breaking the mirror symmetry of *Pcam.* Diffraction measurements as a function of temperature would be required to further substantiate this explanation.

Data collection: *SMART* (Bruker, 1997). Cell refinement: *SMART*. Data reduction: *SMART*. Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *ORTEP*-3 (Farrugia, 1997). Software used to prepare material for publication: *SHELXL*97.

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Zinc mercury thiocyanate (ZMTC)

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Abstract

The title complex, zinc mercury tetrathiocyanate, $[ZnHg(SCN)_4]_n$, consists of slightly flattened ZnN_4 and

HgS_4 tetrahedra linked by –S=C=N– bridges to form infinite three-dimensional –Hg—S=C=N—Zn– networks. This structural feature contributes to the physical and chemical stability and the non-linear optical properties of the crystals.

Comment

In recent years, a series of highly efficient non-linear optical (NLO) materials have been investigated on the basis of molecular engineering and the double-ligand model (Xu *et al.*, 1987, 1994; Yuan *et al.*, 1990; Hou *et al.*, 1993). More recently, there has been considerable interest in the synthesis of novel high quality NLO crystals, especially those complex crystals which can generate high efficiency second harmonic blue–violet light using GaAlAs laser diodes. The NLO properties of cadmium mercury thiocyanate (CMTC) crystals were reported previously (Yuan *et al.*, 1997). As part of continuing work, we report here the structure and properties of zinc mercury thiocyanate (ZMTC). The new crystals are shown to have some useful characteristics which are comparable to those of CMTC. Some crystal data for ZMTC have been reported by Straumanis & Ence (1936) and Stahl & Straumanis (1944), but its crystal structure has not been clarified.

Thiocyanate (SCN^-) can bind to metal ions through either S or N, and it has been shown to bind to Hg^{II} through the S atom and to Zn^{II} through the N atom, giving, in both cases, mononuclear species up to the tetra-complex (Yamaguchi *et al.*, 1985; Ozutsumi *et al.*, 1989). In ZMTC, the Zn^{2+} ions are surrounded tetrahedrally by four N atoms, with a Zn—N bond distance of 1.947 (11) Å and angles of 107.1 (4) and 114.3 (8)°, and the Hg^{2+} ions are surrounded by four S atoms, with an Hg—S bond distance of 2.563 (2) Å and angles of 117.25 (7) and 105.73 (6)°, which can be explained successfully by the hard and soft acid–base concept (Pearson, 1966; Balarew & Duhlew, 1984).

The C1—N1 bond distance is slightly longer than the normal triple-bond length, and the S1—C1 bond is shorter than a normal single bond due to the thiocyanate ion acting as a bridging ligand. From the bonds and angles, it is obvious that the structure of ZMTC consists of slightly flattened ZnN_4 and HgS_4 tetrahedra. The central Zn and Hg atoms of the flattened tetrahedra are located on $\bar{4}$ rotation axes. The most striking features are the –S=C=N– bridges, which connect Zn and Hg, forming an infinite three-dimensional network. The macroscopic non-linear susceptibility of ZMTC may be related to microscopic hyperpolarizabilities of the dipolar thiocyanate ions and the distorted tetrahedra. The three-dimensional network donates larger polarization, which in turn, we believe, induces greater macroscopic non-linearity than the sum of the individual SCN^- dipoles in distorted tetragonal ZnN_4 and HgS_4 (Zyss, 1991). The second harmonic generation (SHG) effect of the crystals was studied by the Kurtz powder technique (Kurtz & Perry, 1968). It was found that the ZMTC crystals are superior to urea in their SHG effect.

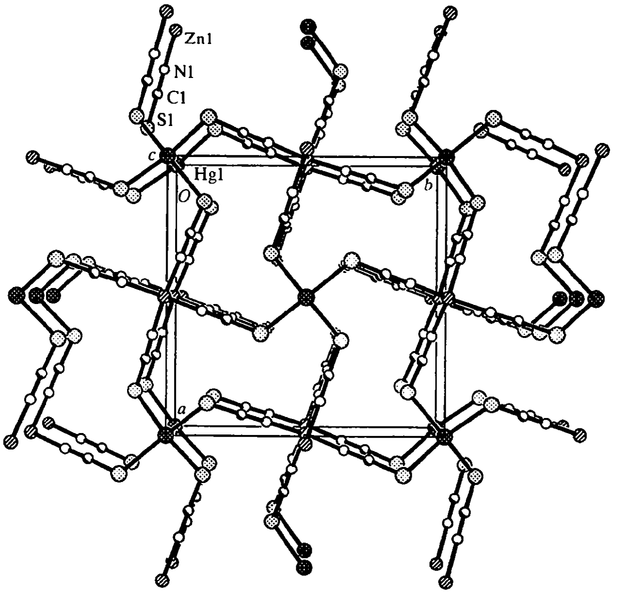

Fig. 1. Packing diagram of ZMTC viewed down the *c* axis.

Experimental

The title compound was obtained by the reaction of zinc chloride, mercury chloride and potassium thiocyanate (molar ratio 1:1:4) in water. The crystals used for the X-ray structure analysis were obtained from a more dilute aqueous solution using a temperature-lowering method.

Crystal data

$ZnHg(SCN)_4$
$M_r = 498.28$
Tetragonal
$I\bar{4}$
$a = 11.0912 (4)$ Å
$c = 4.4414 (4)$ Å
$V = 546.36 (6)$ Å^3
$Z = 2$
$D_x = 3.029$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 61 reflections
$\theta = 6.16$–$16.97°$
$\mu = 16.953$ mm^{-1}
$T = 293 (2)$ K
Prism
0.12 × 0.11 × 0.10 mm
Colourless

Data collection

Bruker *P*4 diffractometer
$2\theta/\omega$ scans
Absorption correction: empirical (Sheldrick, 1997*a*)
$T_{min} = 0.225$, $T_{max} = 0.345$
1210 measured reflections
555 independent reflections (plus 449 Friedel-related reflections)

980 reflections with $I > 2\sigma(I)$
$R_{int} = 0.052$
$\theta_{max} = 32.49°$
$h = -16 \rightarrow 16$
$k = -16 \rightarrow 16$
$l = -6 \rightarrow 6$
3 standard reflections every 97 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.095$
$S = 1.115$
1004 reflections
33 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0524P)^2 + 1.7690P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 1.27$ e Å^{-3}
$\Delta\rho_{\min} = -0.94$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.026 (2)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = 0.010 (16)

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	$U_{\rm eq}$
Hg1	0	0	0	0.0329 (2)
Zn1	−1/2	0	1/4	0.0322 (3)
C1	−0.2730 (6)	−0.0789 (6)	−0.1170 (16)	0.0262 (11)
N1	−0.3609 (5)	−0.0490 (6)	0.012 (4)	0.0389 (13)
S1	−0.15323 (17)	−0.12430 (19)	−0.3005 (5)	0.0362 (4)

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

Hg1—S1	2.5631 (19)	C1—N1	1.180 (12)
Zn1—N1	1.947 (11)	C1—S1	1.637 (7)
S1—Hg1—S1$^{\rm i}$	105.73 (5)	N1—C1—S1	178.1 (7)
S1—Hg1—S1$^{\rm ii}$	117.25 (10)	C1—N1—Zn1	176.2 (11)
N1—Zn1—N1$^{\rm iii}$	107.1 (4)	C1—S1—Hg1	96.5 (3)
N1—Zn1—N1$^{\rm iv}$	114.3 (8)		

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

The largest peak in the difference map (1.27 e Å^{-3}) is at (0.0917, 0.9756, 0.0025), 1.05 Å from Hg1, and the largest hole (−0.94 e Å^{-3}) is at (0.0324, 0.8843, 0.0126), 1.33 Å from Hg1.

Data collection: *XSCANS* (Siemens, 1996). Cell refinement: *XSCANS*. Data reduction: *SHELXTL* (Bruker, 1997). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*a*). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*b*). Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

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Pentaamminenitrocobalt(III) hexafluorosilicate(IV) at 293 and 150 K

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Abstract

The crystal structure of $[\mathrm{Co(NO_2)(NH_3)_5}](\mathrm{SiF_6})$ has been determined at 293 and 150 K. The complex cations in the structure are linked by N—H···F hydrogen bonds to the $(\mathrm{SiF_6})^{2-}$ anions and by N—H···O hydrogen bonds to other cations. The role of these hydrogen bonds and of the repulsive O···F interactions in the anisotropy of the structural distortion on cooling is discussed.

Comment

Hydrogen bonds (N—H···O, N—H···Cl, N—H···Br and N—H···I) were shown to be important both for the formation of the crystal structures of a series of Co$^{\rm III}$–nitropentaammines and for the anisotropy of their structural distortion on cooling (Boertin, 1968; Boldyreva, 1996; Boldyreva & Podberezskaya, 1995; Boldyreva *et al.*, 1997*a*,*b*; Cotton & Edwards, 1968; Kubota & Ohba, 1992). The title compound, (I), was