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Crystal structure of K[Hg(SCN)$_3$] – a redetermination

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The crystal structure of the room-temperature modification of K[Hg(SCN)$_3$], potassium trithiocyanatomercurate(II), was redetermined based on modern CCD data. In comparison with the previous report [Zhdanov & Sanadze (1952). *Zh. Fiz. Khim.* **26**, 469–478], reliability factors, standard deviations of lattice parameters and atomic coordinates, as well as anisotropic displacement parameters, were revealed for all atoms. The higher precision and accuracy of the model is, for example, reflected by the Hg—S bond lengths of 2.3954 (11), 2.4481 (8) and 2.7653 (6) Å in comparison with values of 2.24, 2.43 and 2.77 Å. All atoms in the crystal structure are located on mirror planes. The Hg^{2+} cation is surrounded by four S atoms in a seesaw shape [S—Hg—S angles range from 94.65 (2) to 154.06 (3)°]. The HgS$_4$ polyhedra share a common S atom, building up chains extending parallel to [010]. All S atoms of the resulting $_\infty^1$[HgS$_{2/1}$S$_{2/2}$] chains are also part of SCN$^-$ anions that link these chains with the K$^+$ cations into a three-dimensional network. The K—N bond lengths of the distorted KN$_7$ polyhedra lie between 2.926 (2) and 3.051 (3) Å.

1. Related literature

K[Hg(SCN)$_3$] has been determined originally in the space group $P2_1/m$ with $Z = 8$, based on room-temperature data (Zhdanov & Sanadze, 1952). A subsequent redetermination revealed a doubled unit cell in $P2_1/n$, $Z = 4$, based on intensity data measured at 150 K (Bowmaker *et al.*, 1998).

However, there is no report on an apparent phase transition of K[Hg(SCN)$_3$] between these two temperatures. For symmetry relationships between crystal structures, see: Müller (2013).

2. Experimental

2.1. Crystal data

K[Hg(NCS)$_3$]	$V = 457.44$ (8) Å^3
$M_r = 413.93$	$Z = 2$
Monoclinic, $P2_1/m$	Mo $K\alpha$ radiation
$a = 11.2727$ (11) Å	$\mu = 17.90$ mm^{-1}
$b = 4.0775$ (4) Å	$T = 293$ K
$c = 10.9764$ (10) Å	$0.30 \times 0.06 \times 0.04$ mm
$\beta = 114.951$ (4)°	

2.2. Data collection

Bruker APEXII CCD diffractometer	11940 measured reflections
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)	3765 independent reflections
$T_{min} = 0.226$, $T_{max} = 0.504$	2358 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.032$

2.3. Refinement

$R[F^2 > 2\sigma(F^2)] = 0.028$	68 parameters
$wR(F^2) = 0.062$	$\Delta\rho_{max} = 1.27$ e Å^{-3}
$S = 1.03$	$\Delta\rho_{min} = -1.33$ e Å^{-3}
3765 reflections	

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT* (Bruker, 2008); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ATOMS for Windows* (Dowty, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Acknowledgements

References

Bowmaker, G. A., Churakov, A. V., Harris, R. K., Howard, J. A. K. & Apperley, D. C. (1998). *Inorg. Chem.* **37**, 1734–1743.
Bruker (2008). *APEX2, SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Dowty, E. (2006). *ATOMS for Windows*. Shape Software, Kingsport, Tennessee, USA.
Müller, U. (2013). In *Symmetry Relationships between Crystal Structures*. Oxford University Press.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
Zhdanov, G. S. & Sanadze, V. V. (1952). *Zh. Fiz. Khim.* **26**, 469–478.

supporting information

Crystal structure of K[Hg(SCN)₃] – a redetermination

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S1. Experimental

$Hg(SCN)_2$ (0.5 g) was dissolved under heating in a water–ethanol mixture (1:1 *v*/*v*) to which KSCN (0.1 g) was added. After one week, colourless crystals with a lath-like form were obtained from the remaining solution.

S2. Refinement

For better comparison with the previous determination by Zhdanov & Sanadze (1952), the original nonreduced cell setting as well as the atom labelling and the atomic coordinates were used as starting parameters for the refinement.

Bowmaker *et al.* (1998) reported a doubled unit cell for K[Hg(SCN)₃] with $a = 11.9119$ (3), $b = 4.0201$ (1), $c = 18.7095$ (3) Å, $\beta = 91.852$ (1)°, $P2_1/n$, $Z = 4$. However, no superstructure reflections were found in the current redetermination at 293 K, while Bowmaker *et al.* (1998) used intensity data measured at 150 K. Therefore it appears likely that K[Hg(SCN)₃] has a phase transition between these two temperatures. The two unit cells of the room-temperature phase in $P2_1/m$ and the low-temperature phase in $P2_1/n$ are related by the matix $(101,010,\overline{1}01)$, revealing a *klassengleiche* symmetry reduction of index 2 (Müller, 2013).

The highest and lowest electron densities are found 0.66 and 0.28 Å, respectively, from atom S3.
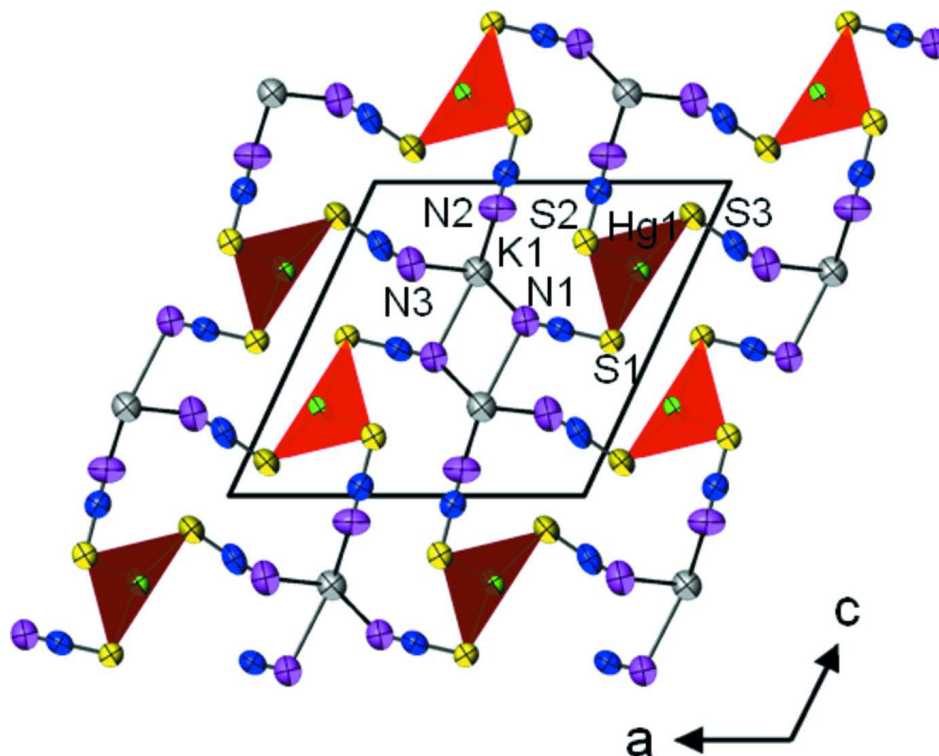
Figure 1

The crystal structure of K[Hg(SCN)$_3$] in a projection along [010]. Displacement ellipsoids are drawn at the 90% probability level. Colour code: Hg green, S yellow, C blue, N magenta, K grey. The HgS$_4$ polyhedron is shown in red.

Potassium [trithiocyanatomercurate(II)]

Crystal data

K[Hg(NCS)$_3$]
$M_r = 413.93$
Monoclinic, $P2_1/m$
Hall symbol: -P 2yb
$a = 11.2727$ (11) Å
$b = 4.0775$ (4) Å
$c = 10.9764$ (10) Å
$\beta = 114.951$ (4)°
$V = 457.44$ (8) Å^3
$Z = 2$

$F(000) = 372$
$D_x = 3.005$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 4570 reflections
$\theta = 3.4$–33.7°
$\mu = 17.90$ mm^{-1}
$T = 293$ K
Lath, colourless
$0.30 \times 0.06 \times 0.04$ mm

Data collection

Bruker APEXII CCD
  diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω and φ scans
Absorption correction: multi-scan
  (*SADABS*; Bruker, 2008)
$T_{min} = 0.226$, $T_{max} = 0.504$

11940 measured reflections
3765 independent reflections
2358 reflections with $I > 2\sigma(I)$
$R_{int} = 0.032$
$\theta_{max} = 44.4°$, $\theta_{min} = 3.4°$
$h = -19 \rightarrow 22$
$k = -7 \rightarrow 7$
$l = -21 \rightarrow 18$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.062$
$S = 1.03$
3765 reflections
68 parameters
0 restraints

Primary atom site location: isomorphous
  structure methods
$w = 1/[\sigma^2(F_o^2) + (0.0218P)^2 + 0.0583P]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.27$ e Å^{-3}
$\Delta\rho_{min} = -1.33$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick,
  2008), Fc*=kFc[1+0.001xFc$^2\lambda^3$/sin(2θ)]$^{-1/4}$
Extinction coefficient: 0.0219 (8)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Hg1	0.145383 (12)	0.2500	0.725128 (12)	0.03813 (6)
K1	0.59433 (8)	0.7500	0.71536 (7)	0.03802 (15)
S1	0.12455 (7)	0.2500	0.49391 (8)	0.03495 (17)
S2	0.32808 (7)	0.7500	0.80993 (8)	0.03121 (14)
S3	0.06157 (10)	0.2500	0.89262 (10)	0.0704 (4)
C1	0.2848 (3)	0.2500	0.5314 (3)	0.0313 (6)
C2	0.3579 (3)	0.7500	0.9719 (3)	0.0312 (6)
C3	0.9019 (4)	0.2500	0.7977 (4)	0.0357 (6)
N1	0.3940 (3)	0.2500	0.5574 (3)	0.0477 (8)
N2	0.6210 (4)	0.2500	0.9165 (3)	0.0500 (8)
N3	0.7909 (4)	0.2500	0.7382 (4)	0.0601 (10)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Hg1	0.03374 (7)	0.05407 (10)	0.03323 (8)	0.000	0.02060 (5)	0.000
K1	0.0377 (3)	0.0421 (4)	0.0364 (3)	0.000	0.0177 (3)	0.000
S1	0.0247 (3)	0.0544 (5)	0.0247 (3)	0.000	0.0094 (3)	0.000
S2	0.0292 (3)	0.0372 (4)	0.0296 (3)	0.000	0.0147 (3)	0.000
S3	0.0341 (4)	0.1516 (14)	0.0307 (4)	0.000	0.0188 (4)	0.000
C1	0.0334 (14)	0.0392 (16)	0.0243 (12)	0.000	0.0150 (11)	0.000
C2	0.0268 (12)	0.0344 (15)	0.0309 (14)	0.000	0.0107 (11)	0.000
C3	0.0376 (15)	0.0406 (17)	0.0398 (16)	0.000	0.0269 (13)	0.000
N1	0.0329 (14)	0.075 (2)	0.0379 (15)	0.000	0.0175 (12)	0.000
N2	0.0529 (19)	0.064 (2)	0.0292 (14)	0.000	0.0134 (13)	0.000

N3	0.0394 (17)	0.096 (3)	0.050 (2)	0.000	0.0248 (15)	0.000

Geometric parameters (Å, º)

Hg1—S3	2.3954 (11)	K1—K1ⁱⁱⁱ	4.7485 (14)
Hg1—S1	2.4481 (8)	S1—C1	1.675 (3)
Hg1—S2	2.7653 (6)	S2—C2	1.664 (3)
Hg1—S2ⁱ	2.7653 (6)	S2—Hg1ⁱⁱ	2.7653 (6)
K1—N2ⁱⁱ	2.926 (2)	S3—C3ⁱᵛ	1.657 (4)
K1—N2	2.926 (2)	C1—N1	1.140 (4)
K1—N3ⁱⁱ	2.943 (3)	C1—K1ⁱⁱⁱ	3.508 (3)
K1—N3	2.943 (3)	C2—N2ᵛ	1.145 (5)
K1—N1	2.993 (2)	C3—N3	1.141 (6)
K1—N1ⁱⁱ	2.993 (2)	C3—S3ᵛⁱ	1.657 (4)
K1—N1ⁱⁱⁱ	3.051 (3)	N1—K1ⁱ	2.993 (2)
K1—C1ⁱⁱⁱ	3.508 (3)	N1—K1ⁱⁱⁱ	3.051 (3)
K1—S2	3.5657 (12)	N2—C2ᵛ	1.145 (5)
K1—K1ⁱ	4.0775 (4)	N2—K1ⁱ	2.926 (2)
K1—K1ⁱⁱ	4.0775 (4)	N3—K1ⁱ	2.943 (3)
S3—Hg1—S1	154.06 (3)	C1ⁱⁱⁱ—K1—K1ⁱ	90.0
S3—Hg1—S2	102.74 (2)	S2—K1—K1ⁱ	90.0
S1—Hg1—S2	94.65 (2)	N2ⁱⁱ—K1—K1ⁱⁱ	45.83 (5)
S3—Hg1—S2ⁱ	102.74 (2)	N2—K1—K1ⁱⁱ	134.17 (5)
S1—Hg1—S2ⁱ	94.65 (2)	N3ⁱⁱ—K1—K1ⁱⁱ	46.15 (5)
S2—Hg1—S2ⁱ	95.00 (2)	N3—K1—K1ⁱⁱ	133.85 (5)
N2ⁱⁱ—K1—N2	88.34 (9)	N1—K1—K1ⁱⁱ	132.94 (4)
N2ⁱⁱ—K1—N3ⁱⁱ	67.60 (10)	N1ⁱⁱ—K1—K1ⁱⁱ	47.06 (4)
N2—K1—N3ⁱⁱ	125.76 (10)	N1ⁱⁱⁱ—K1—K1ⁱⁱ	90.0
N2ⁱⁱ—K1—N3	125.76 (10)	C1ⁱⁱⁱ—K1—K1ⁱⁱ	90.0
N2—K1—N3	67.60 (10)	S2—K1—K1ⁱⁱ	90.0
N3ⁱⁱ—K1—N3	87.70 (10)	K1ⁱ—K1—K1ⁱⁱ	180.00 (5)
N2ⁱⁱ—K1—N1	136.39 (10)	N2ⁱⁱ—K1—K1ⁱⁱⁱ	155.60 (6)
N2—K1—N1	76.98 (8)	N2—K1—K1ⁱⁱⁱ	108.20 (5)
N3ⁱⁱ—K1—N1	151.42 (11)	N3ⁱⁱ—K1—K1ⁱⁱⁱ	112.78 (8)
N3—K1—N1	86.24 (8)	N3—K1—K1ⁱⁱⁱ	78.02 (8)
N2ⁱⁱ—K1—N1ⁱⁱ	76.98 (8)	N1—K1—K1ⁱⁱⁱ	38.66 (6)
N2—K1—N1ⁱⁱ	136.39 (10)	N1ⁱⁱ—K1—K1ⁱⁱⁱ	78.70 (6)
N3ⁱⁱ—K1—N1ⁱⁱ	86.24 (7)	N1ⁱⁱⁱ—K1—K1ⁱⁱⁱ	37.79 (4)
N3—K1—N1ⁱⁱ	151.42 (11)	C1ⁱⁱⁱ—K1—K1ⁱⁱⁱ	52.26 (4)
N1—K1—N1ⁱⁱ	85.87 (8)	S2—K1—K1ⁱⁱⁱ	102.20 (3)
N2ⁱⁱ—K1—N1ⁱⁱⁱ	135.00 (5)	K1ⁱ—K1—K1ⁱⁱⁱ	64.574 (8)
N2—K1—N1ⁱⁱⁱ	135.00 (5)	K1ⁱⁱ—K1—K1ⁱⁱⁱ	115.426 (8)
N3ⁱⁱ—K1—N1ⁱⁱⁱ	75.01 (9)	C1—S1—Hg1	97.08 (11)
N3—K1—N1ⁱⁱⁱ	75.01 (9)	C2—S2—Hg1	98.38 (7)
N1—K1—N1ⁱⁱⁱ	76.45 (8)	C2—S2—Hg1ⁱⁱ	98.38 (7)
N1ⁱⁱ—K1—N1ⁱⁱⁱ	76.45 (8)	Hg1—S2—Hg1ⁱⁱ	95.00 (2)
N2ⁱⁱ—K1—C1ⁱⁱⁱ	129.27 (7)	C2—S2—K1	119.70 (11)

N2—K1—C1^{iii}	129.27 (7)	Hg1—S2—K1	120.06 (2)
N3^{ii}—K1—C1^{iii}	62.76 (8)	Hg1^{ii}—S2—K1	120.06 (2)
N3—K1—C1^{iii}	62.76 (8)	C3^{iv}—S3—Hg1	101.12 (13)
N1—K1—C1^{iii}	89.79 (8)	N1—C1—S1	179.8 (3)
N1^{ii}—K1—C1^{iii}	89.79 (8)	N1—C1—K1^{iii}	57.5 (2)
N1^{iii}—K1—C1^{iii}	18.38 (8)	S1—C1—K1^{iii}	122.68 (14)
N2^{ii}—K1—S2	67.14 (8)	N2^{v}—C2—S2	179.7 (3)
N2—K1—S2	67.14 (8)	N3—C3—S3^{vi}	176.4 (4)
N3^{ii}—K1—S2	132.15 (6)	C1—N1—K1	128.00 (14)
N3—K1—S2	132.15 (6)	C1—N1—K1^{i}	128.00 (14)
N1—K1—S2	69.32 (6)	K1—N1—K1^{i}	85.87 (8)
N1^{ii}—K1—S2	69.32 (6)	C1—N1—K1^{iii}	104.1 (2)
N1^{iii}—K1—S2	132.49 (6)	K1—N1—K1^{iii}	103.55 (8)
C1^{iii}—K1—S2	150.86 (6)	K1^{i}—N1—K1^{iii}	103.55 (8)
N2^{ii}—K1—K1^{i}	134.17 (5)	C2^{v}—N2—K1^{i}	135.73 (5)
N2—K1—K1^{i}	45.83 (5)	C2^{v}—N2—K1	135.73 (5)
N3^{ii}—K1—K1^{i}	133.85 (5)	K1^{i}—N2—K1	88.34 (9)
N3—K1—K1^{i}	46.15 (5)	C3—N3—K1^{i}	130.79 (15)
N1—K1—K1^{i}	47.06 (4)	C3—N3—K1	130.79 (15)
N1^{ii}—K1—K1^{i}	132.94 (4)	K1^{i}—N3—K1	87.70 (10)
N1^{iii}—K1—K1^{i}	90.0		

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