CRYSTALLOGRAPHIC COMMUNICATIONS

OPEN ACCESS

ISSN 2056-9890

Crystal structure of bis(thiocyanato-κS)-bis(thiourea-κS)mercury(II)

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Received 6 January 2015; accepted 12 January 2015

Edited by H. Stoeckli-Evans, University of Neuchâtel, Switzerland

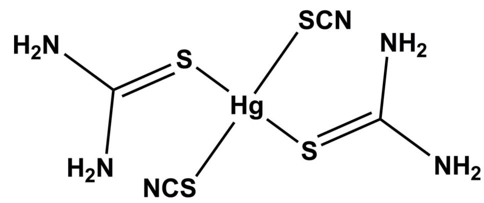
In the title complex, $[Hg(NCS)_2(CH_4N_2S)_2]$, the Hg^{II} atom is four-coordinated having an irregular four-coordinate geometry composed of four thione S atoms of two thiocyanate groups and two thiourea groups. The S—Hg—S angles are 172.02 (9)° for the *trans*-thiocyanate S atoms and 90.14 (5)° for the *cis*-thiourea S atoms. The molecular structure is stabilized by an intramolecular N—H···S hydrogen bond, which forms an *S*(6) ring motif. In the crystal, molecules are linked by a number of N—H···N and N—H···S hydrogen bonds, forming a three-dimensional framework. The first report of the crystal structure of this compound appeared in 1966 [Korczynski (1966). *Rocz. Chem.* **40**, 547–569] with an extremely high *R* factor of 17.2%, and no mention of how the data were collected.

Keywords: crystal structure; thiourea; thiocyanate; mercury(II); molecular complex; hydrogen bonding.

CCDC reference: 1043131

1. Related literature

For literature on thiourea- and thiocyanate-based metal–organic crystalline materials and their derivatives, see: Ramesh *et al.* (2012); Shihabuddeen Syed *et al.* (2013). For the concept of hard and soft acids and bases, see: Ozutsumi *et al.* (1989); Bell *et al.* (2001). For the crystal structures of similar compounds, see: Nawaz *et al.* (2010); Safari *et al.* (2009); Shihabuddeen Syed *et al.* (2013). For the first report of the crystal structure of the title compound, see: Korczynski (1966).



2. Experimental

2.1. Crystal data

$[Hg(NCS)_2(CH_4N_2S)_2]$
M_r = 468.99
Orthorhombic, $Pbc2_1$
a = 8.5359 (5) Å
b = 9.0337 (5) Å
c = 15.7575 (10) Å
V = 1215.07 (12) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 13.33 mm^{-1}
T = 293 K
0.20 × 0.20 × 0.15 mm

2.2. Data collection

Bruker Kappa APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2004)
T_{min} = 0.176, T_{max} = 0.240
19798 measured reflections
2397 independent reflections
2158 reflections with $I > 2\sigma(I)$
R_{int} = 0.058

2.3. Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.075
S = 1.15
2397 reflections
137 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.44 e Å^{-3}
$\Delta\rho_{min}$ = −1.03 e Å^{-3}
Absolute structure: Flack (1983), 1149 Freidel pairs.
Absolute structure parameter: 0.034 (12)

Table 1
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3*B*···S1	0.86	2.55	3.404 (7)	174
N3—H3*A*···N2^{i}	0.86	2.37	3.103 (10)	143
N4—H4*A*···N2^{i}	0.86	2.17	2.952 (10)	151
N4—H4*B*···N1^{ii}	0.86	2.56	3.085 (11)	121
N5—H5*A*···N1^{iii}	0.86	2.26	3.025 (10)	149
N5—H5*A*···S4^{iv}	0.86	2.80	3.384 (7)	126
N5—H5*B*···N2^{v}	0.86	2.21	3.025 (10)	158
N6—H6*A*···N1^{iii}	0.86	2.25	3.019 (10)	149
N6—H6*B*···S2^{vi}	0.86	2.56	3.419 (8)	172

Symmetry codes: (i) $-x+1, y-\frac{1}{2}, z$; (ii) $x, -y+\frac{3}{2}, z+\frac{1}{2}$; (iii) $x-1, y, z$; (iv) $-x, -y+2, z-\frac{1}{2}$; (v) $x, -y+\frac{5}{2}, z-\frac{1}{2}$; (vi) $-x, y-\frac{1}{2}, z$.

Data collection: *APEX2* (Bruker, 2004); cell refinement: *APEX2* and *SAINT* (Bruker, 2004); data reduction: *SAINT* and *XPREP* (Bruker, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2015); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *PLATON* (Spek, 2009); software used to prepare material for publication: *WinGX* (Farrugia, 2012) and *PLATON*.

Acknowledgements

The authors are grateful to the SAIF, IIT, Madras, India, for the data collection. KR thanks the University Grants Commission, Government of India, for financial support granted under a Major Research Project [F. No. 41–1008/2012 (SR)].

Supporting information for this paper is available from the IUCr electronic archives (Reference: SU5058).

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supporting information

Acta Cryst. (2015). E**71**, m28–m29 [doi:10.1107/S2056989015000584]

Crystal structure of bis(thiocyanato-*κS*)bis(thiourea-*κS*)mercury(II)

A. Baskaran, K. Rajarajan, M. NizamMohideen and P. Sagayaraj

S1. Synthesis and crystallization

A mixture of thiourea, ammonium thiocyanate and mercury (II) chloride were dissolved in aqueous solution in the molar ratio 2:2:1 and thoroughly mixed for 1 h to obtain a homogeneous mixture. The solution was allowed to evaporate slowly at ambient temperature. Colourless block-like crystals were obtained in a week.

S2. Refinement

All the H atoms were positioned geometrically with N—H = 0.86 Å and constrained to ride on their parent atoms with U_{iso}(H) = 1.2U_{eq}(N).

S3. Comment

This work is part of a research project concerning the investigation of thiourea (N_2H_4CS) and thiocyanate (SCN) based metal organic crystalline materials and their derivatives (Ramesh *et al.*, 2012; Shihabuddeen Syed *et al.*, 2013). Transition metal thiourea and thiocyanate coordination complexes are candidate materials for device applications including their nonlinear optical properties. As ligands, both thiourea and thiocyanate are interesting due to their potential formation of metal coordination complexes as they exhibit multifunctional coordination modes due to the presence of ′S′ and ′N′ donor atoms. With reference to the hard and soft acids and bases) concept (Ozutsumi *et al.*, 1989; Bell *et al.*, 2001), the soft cations show a pronounced affinity for coordination with the softer ligands, while hard cations prefer coordination with harder ligands. Several crystallographic reports about mercury(II) complexes usually consist of discrete monomeric molecules with tetrahedral (somewhat distorted) coordination environments around mercury(II) (Nawaz *et al.*, 2010). Herein, we report on the synthesis and crystal structure of the title complex.

The title monomeric complex is composed of two thiocyanate and two thiourea ligands coordinated to the Hg atom via the softer thione S atom (Fig. 1). The four-coordinate mercury atom adopts a severely distorted tetrahedral geometry. The S—Hg—S angles are S3-Hg1-S4 = 172.02 (9) ° for the *trans* thiocyanate S atoms and S1-Hg1-S2 = 90.14 (5) ° for the *trans* thiourea S atoms. The bond distances Hg1-S3 and Hg1-S4 are 2.390 (3) and 2.381 (3) Å, respectively, while bond distances Hg1—S1 and Hg1—S2 are 3.064818) and 3.0836 (18) Å, respectively. Bond distances and angles are in agreement with those reported for related compounds (Shihabuddeen Syed *et al.*, 2013; Safari *et al.*, 2009; Nawaz *et al.*, 2010). The SCN moiety is planar [to within 0.007 (1) Å with the C-N and C-S bond lengths corresponding to the values intermediate between single and double bonds. The S2-C2-N2 and S1-C1-N1 units are nearly linear with bond angles of 178.5 (7) and 179.4 (8)°, respectively. The compound is closely related with (thiocyanato-*k*S)tris(thiourea-*k*S)mercury(II) chloride (Shihabuddeen Syed *et al.*, 2013). The molecular structure is stabilized by intramolecular an N-H···S hydrogen bond, which forms an S(6) ring motif (Fig. 1 and Table 1).

In the crystal, molecules are connected via N-H···N hydrogen bonds, involving the thiourea NH_2 H atoms and the thiocyanate N atom (Fig. 2 and Table 1). This gives rise to the formation of a three-dimensional framework which is reinforced by N-H···S hydrogen bonds (Fig. 2 and Table 1).

The first report of the crystal structure of the title compound appeared in 1966 (Korczynski, 1966) with an extremely high R factor of 17.2 %, and no mention of how the data were collected.

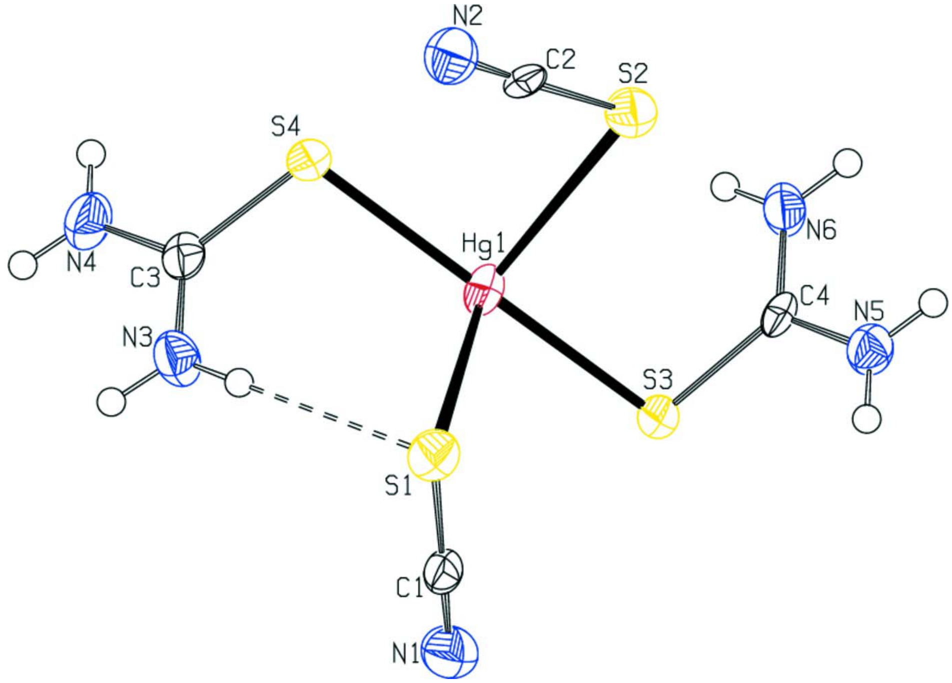

Figure 1

A view of the molecular structure of the title complex, with atom labelling. Displacement ellipsoids are drawn at the 50% probability level. The intramolecular N—H···S hydrogen bond is shown as a double dashed line (see Table 1 for details).

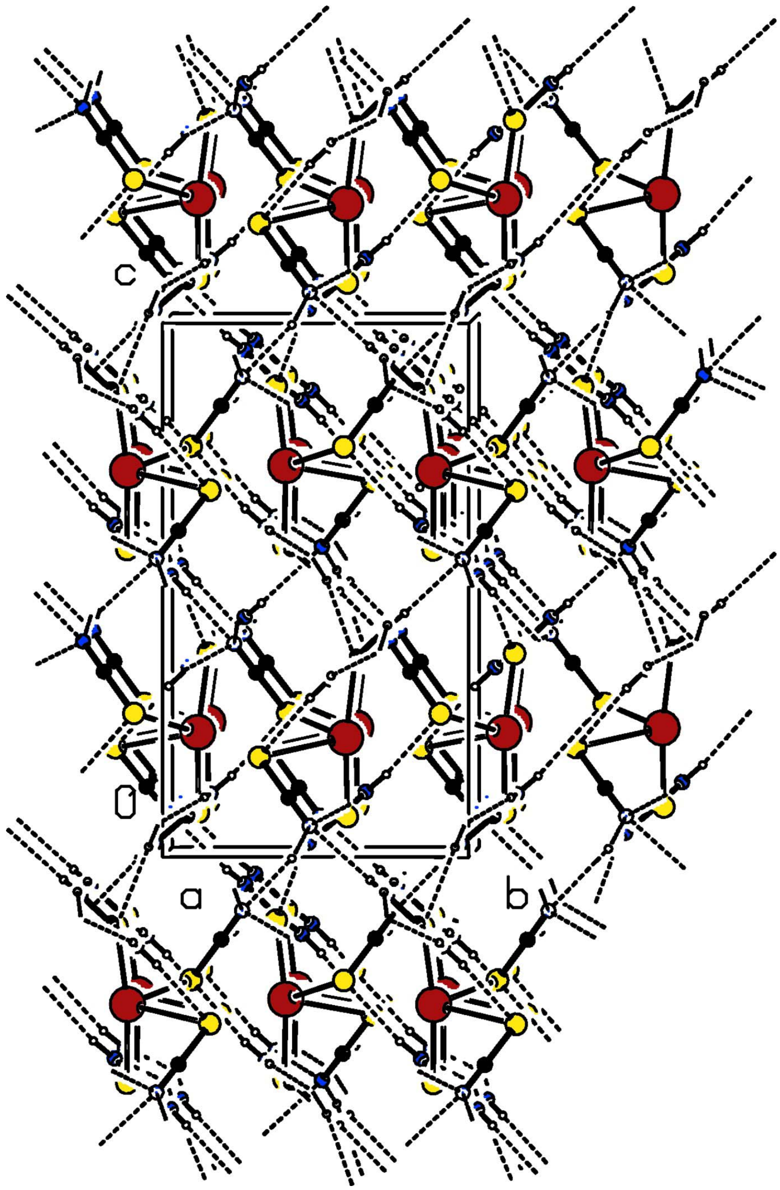

Figure 2

The crystal packing of the title complex, viewed along the *a* axis. Hydrogen bonds are shown as dashed lines (see Table 1 for details).

Bis(thiocyanato-*κS*)bis(thiourea-*κS*)mercury(II)

Crystal data

$[Hg(NCS)_2(CH_4N_2S)_2]$	$F(000) = 872$
$M_r = 468.99$	$D_x = 2.564$ Mg m^{-3}
Orthorhombic, $Pbc2_1$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: P 2c -2b	Cell parameters from 2397 reflections
$a = 8.5359$ (5) Å	$\theta = 2.4–31.2°$
$b = 9.0337$ (5) Å	$\mu = 13.33$ mm^{-1}
$c = 15.7575$ (10) Å	$T = 293$ K
$V = 1215.07$ (12) Å^3	Block, colourless
$Z = 4$	0.20 × 0.20 × 0.15 mm

Data collection

Bruker Kappa APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω and φ scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2004)
T_{min} = 0.176, T_{max} = 0.240
19798 measured reflections
2397 independent reflections
2158 reflections with $I > 2\sigma(I)$
R_{int} = 0.058
θ_{max} = 26.0°, θ_{min} = 2.4°
$h = -10 \rightarrow 10$
$k = -11 \rightarrow 11$
$l = -19 \rightarrow 19$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.075
S = 1.15
2397 reflections
137 parameters
1 restraint
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0237P)^2 + 4.6956P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 1.44 e Å^{-3}
$\Delta\rho_{min}$ = −1.03 e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0082 (3)
Absolute structure: Flack (1983), 1149 Friedel pairs.
Absolute structure parameter: 0.034 (12)

Special details

Geometry. Bond distances, angles etc. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell esds are taken into account in the estimation of distances, angles and torsion angles

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 (Å²)

	x	y	z	U_{iso}*/U_{eq}
Hg1	0.25569 (4)	0.89378 (3)	0.72851 (8)	0.0374 (1)
S1	0.4564 (2)	1.1691 (2)	0.69569 (13)	0.0336 (6)
S2	−0.0283 (2)	1.0924 (2)	0.76929 (13)	0.0334 (6)
S3	0.2017 (3)	0.8900 (3)	0.57967 (14)	0.0329 (7)
S4	0.3068 (3)	0.8610 (3)	0.87589 (15)	0.0353 (7)
N1	0.6053 (9)	1.0000 (9)	0.5700 (5)	0.041 (3)
N2	0.0984 (9)	1.2628 (8)	0.9017 (5)	0.037 (3)
N3	0.6051 (8)	0.9346 (7)	0.8444 (5)	0.034 (2)
N4	0.5630 (8)	0.7508 (9)	0.9391 (4)	0.039 (2)
N5	−0.0507 (8)	1.0248 (7)	0.5262 (4)	0.031 (2)
N6	−0.0982 (7)	0.8404 (8)	0.6204 (5)	0.032 (2)
C1	0.5444 (9)	1.0700 (9)	0.6213 (5)	0.026 (2)
C2	0.0478 (9)	1.1927 (9)	0.8463 (5)	0.025 (2)
C3	0.5073 (8)	0.8485 (9)	0.8853 (5)	0.026 (2)

C4	0.0009 (9)	0.9200 (8)	0.5772 (4)	0.022 (2)
H3A	0.70430	0.92670	0.85300	0.0410*
H3B	0.57020	0.99910	0.80900	0.0410*
H4A	0.66240	0.74400	0.94710	0.0460*
H4B	0.50010	0.69370	0.96640	0.0460*
H5A	−0.14960	1.04050	0.52150	0.0370*
H5B	0.01460	1.07740	0.49760	0.0370*
H6A	−0.19710	0.85630	0.61570	0.0380*
H6B	−0.06470	0.77190	0.65370	0.0380*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Hg1	0.0319 (2)	0.0600 (2)	0.0205 (2)	−0.0029 (1)	−0.0073 (2)	0.0032 (3)
S1	0.0359 (11)	0.0344 (10)	0.0304 (10)	−0.0005 (9)	−0.0003 (8)	−0.0009 (9)
S2	0.0319 (11)	0.0370 (10)	0.0314 (11)	0.0017 (9)	0.0016 (9)	−0.0026 (9)
S3	0.0231 (10)	0.0548 (14)	0.0209 (11)	0.0038 (9)	−0.0006 (9)	−0.0002 (9)
S4	0.0243 (11)	0.0616 (14)	0.0200 (11)	0.0005 (10)	0.0013 (9)	−0.0005 (10)
N1	0.035 (4)	0.051 (5)	0.038 (4)	0.000 (4)	0.003 (4)	−0.005 (4)
N2	0.039 (4)	0.035 (4)	0.037 (5)	0.002 (3)	−0.002 (3)	0.002 (3)
N3	0.026 (4)	0.033 (4)	0.044 (4)	−0.001 (3)	−0.005 (3)	0.011 (3)
N4	0.041 (4)	0.044 (4)	0.031 (4)	0.010 (3)	−0.005 (3)	0.009 (3)
N5	0.031 (4)	0.031 (4)	0.030 (4)	0.000 (3)	−0.003 (3)	0.006 (3)
N6	0.026 (3)	0.036 (4)	0.033 (4)	−0.001 (3)	−0.007 (3)	0.007 (3)
C1	0.024 (4)	0.032 (4)	0.022 (4)	−0.004 (3)	−0.004 (3)	0.008 (3)
C2	0.025 (4)	0.036 (4)	0.015 (4)	0.003 (3)	0.005 (3)	0.011 (3)
C3	0.028 (4)	0.031 (4)	0.019 (4)	0.008 (3)	−0.002 (3)	−0.010 (3)
C4	0.028 (4)	0.026 (4)	0.012 (4)	0.001 (3)	−0.005 (3)	−0.001 (3)

Geometric parameters (Å, º)

Hg1—S1	3.0641 (18)	N4—C3	1.313 (11)
Hg1—S2	3.0836 (18)	N5—C4	1.318 (9)
Hg1—S3	2.390 (3)	N6—C4	1.302 (10)
Hg1—S4	2.381 (3)	N3—H3A	0.8600
S1—C1	1.655 (8)	N3—H3B	0.8600
S2—C2	1.648 (8)	N4—H4A	0.8600
S3—C4	1.736 (8)	N4—H4B	0.8600
S4—C3	1.722 (7)	N5—H5A	0.8600
N1—C1	1.151 (11)	N5—H5B	0.8600
N2—C2	1.162 (11)	N6—H6A	0.8600
N3—C3	1.310 (10)	N6—H6B	0.8600
S1—Hg1—S2	90.14 (5)	C3—N3—H3A	120.00
S1—Hg1—S3	87.35 (8)	C3—N3—H3B	120.00
S1—Hg1—S4	99.39 (8)	H3A—N3—H3B	120.00
S2—Hg1—S3	93.51 (8)	S3—C4—N5	117.1 (6)
S2—Hg1—S4	90.75 (8)	S3—C4—N6	122.9 (6)

S3—Hg1—S4	172.02 (9)	N5—C4—N6	119.9 (7)
Hg1—S1—C1	86.2 (3)	C3—N4—H4A	120.00
Hg1—S2—C2	99.4 (3)	C3—N4—H4B	120.00
Hg1—S3—C4	102.1 (2)	H4A—N4—H4B	120.00
Hg1—S4—C3	105.9 (3)	C4—N5—H5A	120.00
S1—C1—N1	179.4 (8)	C4—N5—H5B	120.00
S2—C2—N2	178.4 (8)	H5A—N5—H5B	120.00
S4—C3—N3	123.5 (6)	C4—N6—H6A	120.00
S4—C3—N4	117.4 (6)	C4—N6—H6B	120.00
N3—C3—N4	119.1 (7)	H6A—N6—H6B	120.00

S2—Hg1—S1—C1	−145.2 (3)	S2—Hg1—S3—C4	−26.2 (3)
S3—Hg1—S1—C1	−51.7 (3)	S1—Hg1—S4—C3	−55.8 (3)
S4—Hg1—S1—C1	124.0 (3)	S2—Hg1—S4—C3	−146.1 (3)
S1—Hg1—S2—C2	−56.6 (3)	Hg1—S3—C4—N6	−53.0 (7)
S3—Hg1—S2—C2	−144.0 (3)	Hg1—S3—C4—N5	129.8 (5)
S4—Hg1—S2—C2	42.8 (3)	Hg1—S4—C3—N4	−139.9 (6)
S1—Hg1—S3—C4	−116.2 (3)	Hg1—S4—C3—N3	42.8 (8)

Hydrogen-bond geometry (Å, º)

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