Crystal Structure of Polymeric Hexamethylenetetramine–Mercury(II) Thiocyanate (1/1), $(CH_2)_6N_4 \cdot Hg(SCN)_2$*

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We recently reported the preparation and X-ray crystal structure of a polymeric 1:2 complex of hexamethylenetetramine** with mercury(II) thiocyanate, $(CH_2)_6N_4 \cdot 2Hg(SCN)_2$ [1]. The related 1:1 complex has subsequently been prepared, and its structural characterization is described in the present communication.

Experimental

Preparation of $(CH_2)_6N_4 \cdot Hg(SCN)_2$

$Hg(SCN)_2$ was freshly prepared as described in the literature [2]. The title complex was obtained from slow evaporation of a solution of $(CH_2)_6N_4$ and $Hg(SCN)_2$ (molar ratio 2:1) in MeOH/EtOH mixed solvent (1:2 *v*/*v*) at room temperature. *Anal.* Calc. for $C_8H_{12}N_6HgS_2$: C, 21.03; H, 2.65; N, 18.39; S, 14.03. Found: C, 20.88; H, 2.70; N, 17.95; S, 13.92%. IR bands (KBr disc): 2880–2980m, 2120s, 1610–1670m, 1464s, 1381m, 1237vs, 1051m, 1000s + 1020s (partially resolved), 928m, 820s, 801s, 776s, 699s, 674s, 506m, 455w cm^{-1}.

X-ray Crystallography

Formula $(CH_2)_6N_4 \cdot Hg(SCN)_2$, $M_r = 456.94$, triclinic, space group $P\bar{1}$, $a = 6.495(1)$, $b = 9.111(2)$, $c = 10.632(4)$ Å, $\alpha = 83.72(2)$, $\beta = 82.57(2)$, $\gamma = 87.74(1)°$, $V = 619.9(2)$ Å^3, $D_x = 2.459$, $D_c = 2.448$ g cm^{-3}, $Z = 2$, $F(000) = 427.83$, μ(Mo Kα) = 127.23 cm^{-1}.

A single crystal of approximate dimensions 0.24 × 0.18 × 0.10 mm was used, and data collection on a Nicolet R3m diffractometer using graphite-monochromatized Mo Kα radiation ($\lambda = 0.71069$ Å, $2\theta_{max} = 55°$, 2596 unique reflections) followed established procedures in our laboratory [3]. Absorption corrections were applied to the raw intensity data (mean $\mu r = 0.70$, transmission factors 0.130–0.300).

The structure was solved by Patterson and Fourier methods. All 17 non-hydrogen atoms were varied anisotropically, and the methylene H atoms were generated geometrically (C–H fixed at 0.96 Å), assigned isotropic temperature factors, and allowed to ride on their respective parent C atoms. Refinement of 154 variables on 2498 observed $[|F_o| > 3\sigma(|F_o|)]$ data converged to $R = 0.031$, R_w (on $|F_o|^2$) = 0.040 and $S = 1.058$, with $w = [\sigma^2(|F_o|) + 0.001|F_o|^2]^{-1}$.

Computations were performed on a Data General Nova 3/12 minicomputer using the SHELXTL package [4]. Analytic expressions of neutral atomic scattering factors were employed, and anomalous dispersion corrections were incorporated [5].

The final atomic parameters are listed in Table I. The atoms in the asymmetric unit are labelled in

TABLE I. Atomic Coordinates ($\times 10^5$ for Hg; $\times 10^4$ for Other Atoms) and Thermal Parameters[a] ($A^2 \times 10^4$ for Hg and S; $\times 10^3$ for Other Atoms)

Atom	*x*	*y*	*z*	U_{eq}/U_{iso}
Hg	21952(3)	13707(2)	31564(2)	321(1)
S(1)	1289(2)	1610(2)	5434(1)	360(4)
C(1)	3622(9)	1284(6)	5901(5)	33(2)
N(1)	5256(10)	1056(6)	6238(6)	47(2)
S(2)	2152(4)	568(2)	1069(2)	575(7)
C(2)	1978(9)	−1264(7)	1424(6)	40(2)
N(2)	1837(10)	−2506(6)	1583(7)	57(2)
N(3)	5195(7)	3082(5)	2677(4)	28(1)
N(4)	8917(7)	3255(5)	2705(4)	28(1)
N(5)	6588(7)	5300(5)	3314(5)	30(1)
N(6)	7200(7)	4783(6)	1087(5)	35(2)
C(3)	7137(8)	2273(5)	2931(5)	26(1)
C(4)	4876(8)	4305(6)	3520(5)	31(2)
C(5)	5466(9)	3772(2)	1331(5)	33(2)
C(6)	8509(8)	4447(6)	3541(6)	32(2)
C(7)	6854(9)	5948(6)	1968(6)	39(2)
C(8)	9097(8)	3935(6)	1362(5)	32(2)
H(3A)	7384	1504	2376	34
H(3B)	6991	1843	3803	34
H(4A)	4729	3881	4393	39
H(4B)	3634	4858	3354	39
H(5A)	4216	4305	1150	43
H(5B)	5742	3001	781	43
H(6A)	9655	5105	3383	42
H(6B)	8372	4024	4414	42
H(7A)	5631	6524	1799	50
H(7B)	8034	6574	1829	50
H(8A)	9328	3167	807	43
H(8B)	10251	4584	1206	43

[a] For non-hydrogen atoms, U_{eq} is the equivalent isotropic temperature factor defined as 1/3 of the trace of the orthogonalized U matrix. For H atoms, the assigned isotropic temperature factor exponent takes the form $-8\pi^2 U_{iso} \sin^2\theta/\lambda^2$.

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*Part X of Metal Complexes of Polycyclic Tertiary Amines.

**IUPAC name is 1,4,7,10-tetraazaadamantane.

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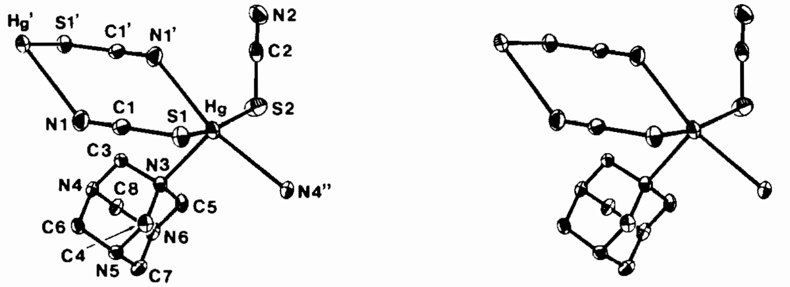

Fig. 1. Atom labelling and coordination geometry about the Hg(II) atom in polymeric $(CH_2)_6N_4 \cdot Hg(SCN)_2$. The thermal ellipsoids have been drawn at the 35% probability level. Symmetry transformations denoted by superscripts: $'$, $1-x, -y, 1-z$; $''$, $-1+x, y, z$.

Fig. 1, and bond distances and angles in Table II. See also 'Supplementary Material'.

TABLE II. Bond Distances (A) and Angles (°)

Hg–S(1)	2.449(2)	Hg–S(2)	2.415(2)
Hg–N(1′)	2.779(6)	Hg–N(3)	2.509(4)
Hg–N(4″)	2.740(4)	S(1)–C(1)	1.661(7)
C(1)–N(1)	1.167(9)	S(2)–C(2)	1.676(7)
C(2)–N(2)	1.131(9)	N(3)–C(3)	1.476(7)
N(3)–C(4)	1.496(7)	N(3)–C(5)	1.490(7)
N(4)–C(3)	1.470(7)	N(4)–C(6)	1.472(8)
N(4)–C(8)	1.485(7)	N(5)–C(4)	1.442(7)
N(5)–C(6)	1.476(7)	N(5)–C(7)	1.478(7)
N(6)–C(5)	1.463(8)	N(6)–C(7)	1.483(8)
N(6)–C(8)	1.472(7)		
S(1)–Hg–S(2)	160.9(1)	S(1)–Hg–N(1′)	89.4(1)
S(1)–Hg–N(3)	99.5(1)	S(1)–Hg–N(4″)	88.1(1)
S(2)–Hg–N(1′)	89.1(1)	S(2)–Hg–N(3)	99.7(1)
S(2)–Hg–N(4″)	88.6(1)	N(1′)–Hg–N(3)	92.7(2)
N(1′)–Hg–N(4″)	165.7(2)	N(3)–Hg–N(4″)	101.6(1)
Hg–S(1)–C(1)	99.0(2)	Hg–S(2)–C(2)	101.4(3)
S(1)–C(1)–N(1)	179.6(7)	S(2)–C(2)–N(2)	175.4(7)
Hg–N(1′)–C(1′)	137.9(5)	Hg–N(3)–C(3)	109.9(3)
Hg–N(3)–C(4)	109.9(3)	Hg–N(3)–C(5)	113.0(3)
Hg–N(4″)–C(3″)	103.0(3)	Hg–N(4″)–C(6″)	116.1(3)
Hg–N(4″)–C(8″)	112.3(3)	C(3)–N(3)–C(4)	107.9(4)
C(3)–N(3)–C(5)	108.4(4)	C(4)–N(3)–C(5)	107.5(4)
C(3)–N(4)–C(6)	108.6(4)	C(3)–N(4)–C(8)	108.5(4)
C(6)–N(4)–C(8)	108.0(4)	C(4)–N(5)–C(6)	108.7(4)
C(4)–N(5)–C(7)	109.3(5)	C(6)–N(5)–C(7)	107.4(4)
C(5)–N(6)–C(7)	109.6(4)	C(5)–N(6)–C(8)	107.9(4)
C(7)–N(6)–C(8)	107.9(5)	N(3)–C(3)–N(4)	111.4(4)
N(3)–C(4)–N(5)	112.4(4)	N(3)–C(5)–N(6)	111.7(5)
N(4)–C(6)–N(5)	111.9(5)	N(5)–C(7)–N(6)	111.3(4)
N(4)–C(8)–N(6)	111.7(4)		

Discussion

The coordination geometry about the metal atom in the $(CH_2)_6N_4 \cdot Hg(SCN)_2$ complex is illustrated in Fig. 1. The Hg(II) atom forms strong coordinate bonds with the S-terminals of two thiocyanato groups and the N(3) atom of the organic ligand, yielding a trigonal planar configuration with vastly different valence angles (Table II). The characteristic coordination number [6] of three for Hg(II) is increased to five through weaker bonding to the N-terminal of a neighboring thiocyanato group and the N(4″) atom of a neighboring $(CH_2)_6N_4$ ligand, giving rise to a distorted tetragonal pyramid with N(3) at the apex. The resulting polymeric structure (Fig. 2) may be described in an alternative manner. Lattice translation *a* generates a chain of $(CH_2)_6N_4 \cdot Hg(SCN)_2$ moieties bridged by Hg–N(4″) type bonds. Further linkage of two adjacent chains, by pairs of Hg–N(1′) type bonds arranged about inversion centers at Wyckoff positions 1(*f*) ($\frac{1}{2}$, 0, $\frac{1}{2}$), then generates a composite chain which serves as the basic building 'pillars' of the entire crystal structure.

The present structure exhibits some of the principal characteristics of the related $(CH_2)_6N_4 \cdot 2Hg(SCN)_2$ complex [1]. In each complex, the metal binds strongly to three neighboring ligands in a trigonal planar fashion, with preference of Hg–SCN over Hg–NCS bonding, so that the stoichiometric formula faithfully reflects the nature of the resulting molecular aggregate. Through the formation of additional weaker Hg–N bonds, both complexes feature similar distorted tetragonal pyramidal coordination geometry about the Hg(II) atom, with one tertiary amino N atom at the apex, leading to the formation of composite chains extending along the shortest crystallographic axis. However, the 1:1 complex differs from its 1:2 analog in several important aspects: firstly, only one of the two independent thiocyanato groups, S(1)C(1)N(1), is involved in bridging the metal atoms; secondly, the resulting cyclic $Hg_2(SCN)_2$ fragment has crystallographically imposed $\bar{1}$ symmetry; thirdly, the Hg(II) atom is bound to two $(CH_2)_6N_4$ groups and one N-bonded

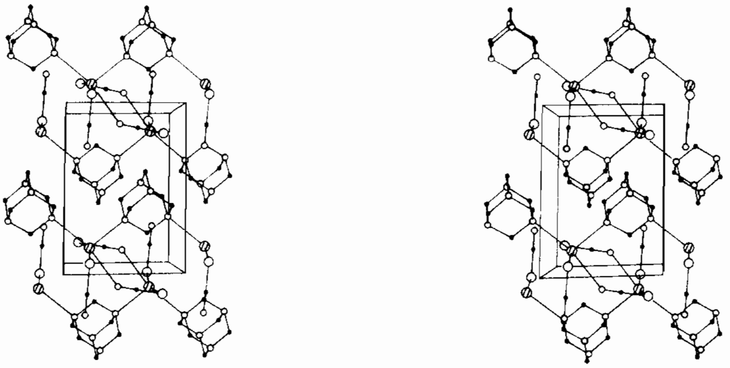

Fig. 2. Stereo view of the crystal structure of polymeric $(CH_2)_6N_4 \cdot Hg(SCN)_2$. The origin of the unit cell lies at the lower left corner, with *a* pointing from left to right, *b* upwards, and *c* towards the reader.

thiocyanato group; and finally, the bidentate $(CH_2)_6N_4$ ligand is primarily responsible for chain propagation, whereas pairs of end-to-end bridging S(1)C(1)N(1) groups serves to cross-link two parallel $\{(CH_2)_6N_4 \cdot Hg(SCN)_{terminal}\}_\infty$ chains at successive joints to generate a composite double chain. In contrast to this, the composite double chain in the 1:2 complex is generated by the lateral linkage of two parallel $\{Hg(SCN)_2\}_\infty$ chains by successive $(CH_2)_6N_4$ groups located on a mirror plane [1].

In the present $(CH_2)_6N_4 \cdot Hg(SCN)_2$ complex, the Hg–S bond lengths involving the bridging and terminal thiocyanato groups (2.449(2) and 2.415(2) Å, respectively) are significantly different, both lying between the lower limit of 2.381(6) Å for $Hg(SCN)_2$ [7] and values in the range 2.454(5)–2.648(5) Å observed in its tripenyl phosphine and arsine adducts (see Table IV of ref. 1). To our knowledge the S(1)–Hg–S(2) angle of 160.9(1)° is the largest yet reported to date, surpassing the value of 154.4(2)° in $(CH_2)_6N_4 \cdot 2Hg(SCN)_2$ and greatly exceeding corresponding angles in the range 106.4(2)–123.4(1)° for the aforementioned Ph_3P and Ph_3As adducts.

As noted previously, the bridging bonds involving the $(CH_2)_6N_4$ moiety are unequal: the axial ligand atom N(3) forms a much stronger coordinate bond (2.509(4) Å) with the Hg(II) atom as compared to the basal ligand atom N(4″) (2.740(4) Å). The measured dimensions of the organic cage ligand are in fairly good agreement with those (C–N = 1.476(2) Å, C–N–C = 107.2(1)°, N–C–N = 113.6(2)°) of crystalline $(CH_2)_6N_4$ [8], apart from some minor distortions from idealized $\bar{4}3m$ symmetry due to metal coordination. As commonly found in metal thiocyanato complexes [9], both bridging and terminal SCN groups are nearly linear with normal dimensions, the Hg–S–C angles are close to 100°, and the Hg–N–C angle lies within the range 132–138° for end-to-end thiocyanato bridging.

Supplementary Material

Anisotropic thermal parameters and structure factors are available from the first author on request.

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