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Metal Complexes of Polycyclic Tertiary Amines.
Part VII*. Preparation and Crystal Structure Determination of Polymeric Hexamethylenetetramine–Mercury(II) Thiocyanate (1/2), $(CH_2)_6N_4\cdot 2Hg(SCN)_2$

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Abstract

A 1:2 complex of hexamethylenetetramine with mercury(II) thiocyanate, $(CH_2)_6N_4\cdot 2Hg(SCN)_2$, was prepared and shown by X-ray crystallography to be polymeric. The mixed-ligand complex crystallizes in the space group $P2_1/m$, with a = 6.059(2), b = 19.710(5), c = 7.895(2) Å, β = 105.63(2)°, and Z = 2. The structure was refined to R_F = 0.060 for 1634 observed MoKα diffractometer data. Mercury(II) atoms in a row are linked pairwise by two thiocyanato groups in an end-to-end bridging mode, to give an infinite chain running in the *a* direction. Two neighboring chains are further laterally connected, successively by bidentate organic ligands which lie on a crystallographic mirror plane. The coordination geometry about Hg(II) is distorted tetragonal pyramidal, the metal atom binding strongly to two S atoms and a tertiary amino N atom (apex), and weakly to two thiocyanato N atoms.

Introduction

According to studies reported several years ago [1, 2], hexamethylenetetramine (1,3,5,7-tetraazaadamantane, $(CH_2)_6N_4$) forms a monomeric 1:4 complex (m.p. 123 °C) with mercury(II) thiocyanate featuring a three-coordinate planar arrangement of nitrogen atoms (one from $(CH_2)_6N_4$ and two from terminal N-bonded thiocyanato groups) about each metal atom. This most unusual proposed structure, by virtue of its high symmetry, preference of Hg–NCS over Hg–SCN bonding, as well as planar three-coordination about Hg(II), attracted our interest and prompted us to embark on an X-ray crystallographic determination in order to ascertain its correct formulation and detect any novel structural features.

Despite the expenditure of considerable effort, we have had no success in repeating the preparation of the $(CH_2)_6N_4\cdot 4Hg(SCN)_2$ complex, but modified synthetic procedures yielded two new crystalline compounds of stoichiometries $(CH_2)_6N_4\cdot 2Hg(SCN)_2$ (m.p. 165–167 °C, density = 2.885 g cm^{-3}) and $(CH_2)_6N_4\cdot Hg(SCN)_2\cdot KSCN$ (m.p. 160–164.5 °C, density = 2.303 g cm^{-3}). The preparation and crystal structure analysis of $(CH_2)_6N_4\cdot 2Hg(SCN)_2$, as described in the present report, constitutes part of our continuing studies on metal complexes of polycyclic tertiary amines.

Experimental

Preparation of $(CH_2)_6N_4\cdot 2Hg(SCN)_2$

The complex was deposited as colorless flat prisms from slow evaporation of an aqueous solution of $(CH_2)_6N_4$ and $K_2Hg(SCN)_4$ in a 4:1 molar ratio. Its infrared spectrum (KBr disc, Beckman IR-10) showed absorption bands (s = strong, m = medium, w = weak, sh = shoulder, d = partially-resolved doublet, br = broad) at 2140s(br), 2080m(sh), 1655m(d,br), 1475m, 1385m, 1320w, 1290w, 1270m, 1255s, 1240s, 1070w, 1030s, 1010s, 985m, 930w, 830m, 810w(sh), and 690m(d,br) cm^{-1}.

X-Ray Crystallography

A single crystal of approximate dimensions 0.24 × 0.22 × 0.08 mm was centered on a Nicolet R3m four-circle diffractometer. Data collection using graphite-monochromatized MoKα radiation (λ = 0.71069 Å) followed established procedures in our laboratory [4], and pertinent crystal data and processing information, including the application of absorption corrections, are summarized in Table I.

Space group $P2_1/m$ was favored by intensity statistics and was later confirmed by structure solution, which was achieved by Patterson and Fourier methods. All 14 non-hydrogen atoms in the asymmetric unit were refined anisotropically, and the methylene H atoms were generated geometrically (C–H bonds fixed at 0.96 Å), assigned isotropic thermal parameters, and allowed to ride on their respective parent C atoms. Blocked-cascade [5]

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*Part V is ref. 3.

TABLE I. Data Collection and Processing Parameters.

Molecular formula	$(CH_2)_6N_4 \cdot 2Hg(SCN)_2$
Molecular weight	773.70
Cell constants	$a = 6.059(2), b = 19.710(5), c = 7.895(2)$ Å, $\beta = 105.63(2)°$, $V = 908.0(5)$ Å^3, $Z = 2$
Density (exptl)	2.88 g cm^{-3}
Density (calcd)	2.830 g cm^{-3}
Space Group	$P2_1/m$
Absorption coefficient	173.49 cm^{-1}
Mean μr	1.0
Transmission factors	0.062–0.292
Scan type and speed	ω–2θ; 2.02–8.37 deg min^{-1}
Scan range	1° below Kα_1 to 1° above Kα_2
Background counting	stationary counts for one-half of scan time at each end of scan
Collection range	$h, k, \pm l = 2\theta_{max} = 55°$
Unique data measured	1904
Observed data with $\lvert F_o \rvert > 3\sigma(\lvert F_o \rvert)$, n	1634
Number of variables, p	116
$R_F = \Sigma\lVert F_o \rvert - \lvert F_c \rVert / \Sigma \lvert F_o \rvert$	0.060
Weighting scheme	$w = [\sigma^2(F_o) + 0.0012\lvert F_o \rvert^2]^{-1}$
$R_G = [\Sigma w(\lvert F_o \rvert - \lvert F_c \rvert)^2 / \Sigma w \lvert F_o \rvert^2]^{1/2}$	0.073
$S = [\Sigma w(\lvert F_o \rvert - \lvert F_c \rvert)^2 (n - p)]^{1/2}$	1.593
Residual extrema in final difference map	+1.72 to −2.96 eÅ^{-3}, all in the vacinity of the Hg atom

TABLE II. Atomic Coordinates (×10^5 for Hg; ×10^4 for Other Atoms) and Thermal Parameters[a] (Å^2 × 10^4 for Hg; ×10^3 for Other Atoms).

Atom	x	y	z	U_{11}/U	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Hg	15479(8)	8776(3)	36687(7)	330(3)	519(3)	572(4)	−32(3)	111(2)	−80(2)
S(1)	4327(6)	1374(2)	6171(5)	40(2)	93(3)	41(2)	−10(2)	15(1)	−13(2)
S(2)	−860(7)	−21(2)	2115(7)	37(2)	64(2)	89(3)	−32(2)	23(2)	−4(2)
C(1)	6598(21)	1434(7)	5344(16)	31(6)	56(8)	34(6)	−8(6)	4(5)	−7(6)
N(1)	8150(21)	1503(7)	4817(18)	41(7)	77(8)	66(8)	−18(7)	22(6)	−15(6)
C(2)	−3468(25)	248(7)	2158(18)	46(8)	46(7)	50(8)	−14(6)	14(6)	−8(6)
N(2)	−5270(21)	398(7)	2161(20)	38(7)	74(9)	81(9)	−24(7)	27(7)	−8(6)
N(3)	1101(16)	1872(5)	1644(14)	23(5)	58(6)	39(5)	−6(5)	15(4)	−4(5)
N(4)	−1047(26)	2500	−956(21)	22(7)	78(11)	44(9)	0	2(6)	0
N(5)	3118(22)	2500	−183(17)	20(6)	61(9)	25(6)	0	6(5)	0
C(3)	−990(20)	1895(7)	140(18)	24(6)	62(8)	49(7)	−7(6)	7(5)	−5(6)
C(4)	3148(20)	1895(8)	905(18)	27(6)	63(8)	47(7)	−5(6)	16(5)	3(6)
C(5)	1168(29)	2500	2707(24)	27(8)	53(10)	43(10)	0	24(7)	0
C(6)	979(32)	2500	−1623(23)	38(10)	68(13)	30(9)	0	10(7)	0
H(3A)	−2314	1897	588	60					
H(3B)	−1023	1498	−573	60					
H(4A)	3139	1498	198	60					
H(4B)	4519	1900	1861	60					
H(5A)	−130	2500	3186	60					
H(5B)	2554	2500	3648	60					
H(6)	949	2102	−2331	60					

[a] Exponents of anisotropic and isotropic (assigned values for H atoms) temperature factors take the forms: $-2\pi^2\Sigma_i\Sigma_j U_{ij} h_i h_j a_i^* \times a_j^*$ and $-8\pi^2 U \sin^2\theta/\lambda^2$, respectively.

least-squares refinement converged to the R indices listed in Table I.

All computations were performed on a Data General Corporation Nova 3/12 minicomputer with the SHELXTL program package [6]. Analytic expressions of neutral atom scattering factors were employed, and anomalous dispersion corrections were incorporated [7].

The final positional and thermal parameters of the non-hydrogen atoms are displayed in Table II.

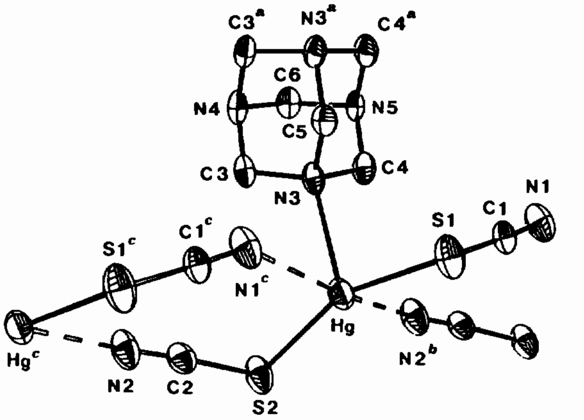

Fig. 1. Atom labelling and coordination geometry about the Hg(II) atom in polymeric $(CH_2)_6N_4 \cdot 2Hg(SCN)_2$. The strong and weak metal–ligand bonds are indicated by solid and broken lines, respectively. Symmetry transformations denoted by superscripts: $^a x, \frac{1}{2} - y, z$; $^b 1 + x, y, z$; $^c -1 + x, y, z$.

The atoms in the asymmetric unit are labelled in Fig. 1, and bond distances and angles shown in Table III. A listing of the observed and calculated structure factors has been deposited with the Editor-in-Chief.

Discussion

The coordination geometry about Hg(II) in the present complex is illustrated in Fig. 1. The $(CH_2)_6N_4$ molecule lies on Wyckoff position 2(e), with a crystallographic mirror plane passing through N(4), N(5), C(5) and C(6). The occurrence of $(CH_2)_6N_4 \cdot 2Hg(SCN)_2$ aggregates is clearly discernible, the metal atom being surrounded by N(3), S(1) and S(2) in a planar configuration with vastly different bond angles (Table III). The characteristic coordination number [8] of three for Hg(II) is modified through weaker bonding to the N-terminals of two neighboring thiocyanato groups, giving rise to a distorted tetragonal

TABLE III. Bond Distances (Å) and Bond Angles (deg.).

Hg–S(1)	2.430(4)	Hg–S(2)	2.409(4)	Hg–N(3)	2.50(1)
Hg–N(1)^c	2.76(1)	Hg–N(2)^b	2.70(1)	S(1)–C(1)	1.68(2)
C(1)–N(1)	1.14(2)	S(2)–C(2)	1.68(2)	C(2)–N(2)	1.13(2)
N(3)–C(3)	1.49(1)	N(3)–C(4)	1.51(2)	N(3)–C(5)	1.49(2)
N(4)–C(3)	1.47(2)	N(4)–C(6)	1.46(3)	N(5)–C(4)	1.47(2)
N(5)–C(6)	1.48(2)				
S(1)–Hg–S(2)	154.4(2)	S(1)–Hg–N(3)	97.8(2)	S(2)–Hg–N(3)	107.7(2)
S(1)–Hg–N(1)^c	88.2(3)	S(1)–Hg–N(2)^b	94.5(3)	S(2)–Hg–N(1)^c	95.3(3)
S(2)–Hg–N(2)^b	85.7(3)	N(3)–Hg–N(1)^c	84.1(4)	N(3)–Hg–N(2)^b	87.7(4)
Hg–S(1)–C(1)	100.0(4)	S(1)–C(1)–N(1)	177(1)	Hg–N(1)^c–C(1)^c	147(1)
Hg–S(2)–C(2)	101.6(5)	S(2)–C(2)–N(2)	177(1)	Hg–N(2)^b–C(2)^b	154(1)
Hg–N(3)–C(3)	117.2(8)	Hg–N(3)–C(4)	108.2(7)	Hg–N(3)–C(5)	108.0(8)
C(3)–N(3)–C(4)	108(1)	C(3)–N(3)–C(5)	108(1)	C(4)–N(3)–C(5)	107(1)
C(3)–N(4)–C(6)	109(1)	C(3)–N(4)–C(3)^a	109(2)	C(6)–N(4)–C(3)^a	109(2)
C(4)–N(5)–C(6)	109(1)	C(4)–N(5)–C(4)^a	109(1)	C(6)–N(5)–C(4)^a	109(1)
N(3)–C(3)–N(4)	112(1)	N(3)–C(4)–N(5)	112(1)	N(3)–C(5)–N(3)^a	112(2)
N(4)–C(6)–N(5)	112(1)				

^{a,b,c}See caption of Fig. 1.

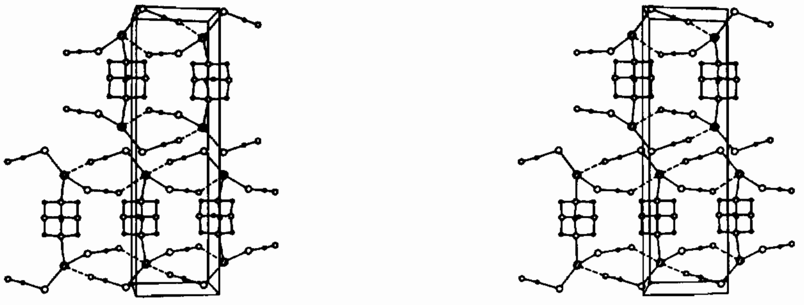

Fig. 2. Stereoview of the crystal structure of polymeric $(CH_2)_6N_4 \cdot 2Hg(SCN)_2$. The origin of the unit cell lies at the lower left corner, with *a* pointing from left to right, *b* upwards, and *c* towards the reader. The weaker Hg–NCS bonds are represented by broken lines.

TABLE IV. Salient Structural Features of Neat and Mixed-ligand Mercury(II) Thiocyanates $L_n \cdot Hg(SCN)_2$ (n = 2, 1, 0.5).

Complex	Coordination geometry about Hg(II)	Metal–ligand bond lengths (A)			Module of crystal packing	Reference
		Hg–SCN	Hg–NCS	Hg–L		
$Hg(SCN)_2$	centrosymmetric *trans*-octahedral, 2S + 4N	2.381(6)	2.81(1)		corrugated layer	[9]
$Ph_3As \cdot Hg(SCN)_2$	distorted trigonal bipyramidal, 2S + As + 2N	2.462(3) 2.514(3)	2.673(7) 2.736(9)	2.557(1)	doubly-bridged chain	[10]
α-$Ph_3P \cdot Hg(SCN)_2$	distorted trigonal bipyramidal, 2S + P + 2N	2.469(4) 2.539(4)	2.68(1) 2.80(1)	2.461(4)	doubly-bridged chain	[11]
β-$Ph_3P \cdot Hg(SCN)_2$	Hg(1), distorted trigonal bipyramidal, 2S + P + 2N	2.491(5) 2.519(5)	2.74(1) 2.89(1)	2.429(4)	doubly-bridged chain 1	[12]
	Hg(2), approximate tetrahedral, 2S + P + N	2.454(5) 2.648(5)	2.40(1)	2.432(4)	singly-bridged chain 2	
$2Ph_3P \cdot Hg(SCN)_2$	distorted tetrahedral, 2S + 2P	2.565(4) 2.577(3)		2.487(3) 2.489(3)	monomeric molecules	[13]
$(CH_2)_6N_4 \cdot 2Hg(SCN)_2$	distorted tetragonal pyramidal, 2S + N(L) + 2N	2.409(4) 2.430(4)	2.70(1) 2.76(1)	2.50(1)	composite doubly-bridge chain	This work

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 row of Hg(II) atoms, which are bridged pairwise by two thiocyanato groups in the end-to-end mode to give an infinite chain. Neighboring chains related by reflection symmetry are further linked laterally by $(CH_2)_6N_4$ groups at pairs of matching metal sites, thus yielding a composite chain as the basic module for building up the crystal structure by means of the 2_1 symmetry operation.

The crystal structures of mercury(II) thiocyanate [9] and several 1:1 and 1:2 complexes with triphenylphosphine and triphenylarsine have been reported by Beauchamp and his co-workers [10–13], and salient structural features are summarized in Table IV. The $2Ph_3P \cdot Hg(SCN)_2$ complex consists of monomeric units, as represented by its structural formula [13], which may be rationalized by the fact that the binding of two bulkly phosphines to the metal center precludes the close approach of the N-terminals of neighboring molecules. In contrast to this, $Hg(SCN)_2$ [9], $Ph_3As \cdot Hg(SCN)_2$ [10], α-$Ph_3P \cdot Hg(SCN)_2$ [11] and β-$Ph_3P \cdot Hg(SCN)_2$ [12] are all polymeric; in each instance Hg(II) binds strongly to the soft donors (2S + P or As) and weakly to neighboring N atoms of the SCN group, resulting in the formation of singly- and/or doubly-bridging infinite zigzag chains. The $(CH_2)_6N_4 \cdot 2Hg(SCN)_2$ complex possesses similar polymeric features attributable to the bridging thiocyanato groups, yet differs from the above structures in that the polycyclic tertiary amine, by virtue of its ability to serve as a bidentate bridging ligand, cross-links two parallel $\{Hg(SCN)_2\}_\infty$ chains progressively to give a double chain. It is also noteworthy that the tertiary amino lone pair functions as a much stronger hard donor compared to a N-bonded SCN group (see Hg–N bond lengths in Table IV).

The Hg–S bond lengths in $(CH_2)_6N_4 \cdot 2Hg(SCN)_2$ lie between the values observed in $Hg(SCN)_2$ and its phosphine and arsine adducts (Table IV). The S–Hg–S angle of 154.4(2)° is unusually large for a Hg(II) complex of characteristic coordination number three, since the corresponding angles are 123.4(1)° in $Ph_3As \cdot Hg(SCN)_2$ [10], 118.3(1)° in α-$Ph_3P \cdot Hg(SCN)_2$ [11], and 106.4(2)° and 110.5(2)° in β-$Ph_3P \cdot Hg(SCN)_2$ [12]. The Hg(II) atom is not symmetrically disposed with respect to the organic ligand, as the Hg–N(3)–C(3) angle of 117.2(8)° far exceeds other bond angles at N(3) (Table III).

As commonly found in metal thiocyanato complexes [14], the SCN groups are essentially linear, the Hg–S–C angles are close to 100°, and the S–C and C–N bond lengths agree with commonly observed values. On the other hand, the angles at the thiocyanato N atoms, 147(1)° and 154(1)°, are much larger than the values in the range 132–138° for weak SCN end-to-end bridging, but comparable to the 152(1)° angle involving a moderately strong Hg–NCS bond in chain 2 of the β-$Ph_3P \cdot Hg(SCN)_2$ structure [12].

Previous workers have established that the strong $\nu(CN)$ absorption bands at 1225 and 1000 cm^{-1} for uncoordinated $(CH_2)_6N_4$ [15] are split up into well-separated doublets when the organic molecule acts as a bidentate bridging ligand in a metal complex [16]. The validity of this useful diagnostic is amply substantiated by the infrared and structural data reported herein for $(CH_2)_6N_4 \cdot 2Hg(SCN)_2$ in the solid state.

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