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CRYSTAL STRUCTURES OF [Hg(*N*-ETHYLTHIOUREA)$_2$(CN)$_2$] AND [Hg(*N*-PROPYLTHIOUREA)$_2$(CN)$_2$]

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Two mercury(II) cyanide complexes of *N*-ethylthiourea (Ettu) and *N*-propylthiourea (Prtu) ligands, [Hg(Ettu)$_2$(CN)$_2$] (**1**) and [Hg(Prtu)$_2$(CN)$_2$] (**2**), were prepared and their crystal structures were determined by X-ray crystallography. In both structures, the mercury atom is coordinated to two sulfur atoms of thioureas and two cyanide carbon atoms in a pseudo-tetrahedral mode with the bond angles in the range of 90.52(11)—162.2(3)°. The structures are stabilized by N—H---S, N—H---N, and C—H---N intramolecular and intermolecular hydrogen bonds.

Keywords: mercury(II) cyanide, *N*-ethylthiourea, *N*-propylthiourea, X-ray structures.

Crystallographic reports about mercury(II) complexes containing thioamides establish that these ligands are coordinated via the sulfur atom [1—26]. The crystal structures of the 1:2 complexes usually consist of discrete monomeric molecules [1—20], while those of 1:1 often involve dimeric species [20—26]. However, in both types of complexes, mercury(II) exhibits a tetrahedral or pseudo-tetrahedral coordination environment. We have recently reported the crystal structures of Hg(CN)$_2$ complexes of methylthiourea (Metu) [7], N,N′-dimethylthiourea (Dmtu), [8], N,N′-dibutylthiourea (Dbtu) [9], and tetramethylthiourea (Tmtu) [27]. Although the structures of other thiourea complexes are usually of the type L$_2$HgX$_2$ [7—9], the Tmtu complex, [{(tetramethylthiourea)$_2$Hg(CN)$_2$}$_2$·Hg(CN)$_2$] is trinuclear consisting of two independent [(Tmtu)$_2$Hg(CN)$_2$] moieties bridged by a Hg(CN)$_2$ unit [27]. In order to investigate further about the structures of mercury cyanide complexes, we report here the crystal structures of two monomeric Hg(CN)$_2$ complexes: bis(cyanido)bis(*N*-ethylthiourea-κS)mercury(II), [Hg(Ettu)$_2$(CN)$_2$] (**1**) and bis(cyanido)bis(*N*-propylthiourea-κS)mercury(II), [Hg(Prtu)$_2$(CN)$_2$] (**2**), which are characterized by extensive hydrogen bonding.

EXPERIMENTAL

Materials. Mercury(II) chloride (HgCl$_2$) was obtained from Merck Chemical Company, Germany. *N*-ethylthiourea (Ettu) and *N*-propylthiourea (Prtu) were purchased from Acros Organics, Belgium.

Preparation of Complexes. For the preparation of the title complexes, Hg(CN)$_2$ was prepared first by the reaction of 1 mmol HgCl$_2$ in methanol with 2 mmolar KCN in water. Then 0.253 g (1 mmol) Hg(CN)$_2$ dissolved in 15 ml of methanol was mixed with 2 equivalents of thiourea ligands in

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Table 1

Crystal data and details of the structure refinement for compounds **1** *and* **2**

Compound	**1**	**2**
Formula	$C_8H_{14}HgN_6S_2$	$C_{10}H_{20}HgN_6S_2$
Formula weight	460.98	489.03
Crystal system	Monoclinic	Triclinic
Space group	$C2/c$	P-1
a, b, c, Å	14.8691(6), 12.4632(5), 8.3829(4)	8.2351(7), 8.9514(7), 12.8924(11)
α, β, γ, deg.	90.00, 94.0660(10), 90.00	89.471(4), 81.451(4), 75.023(4)
V, Å^3	1549.58(12)	907.46(13)
Z	4	2
ρ_{calc}, g·cm^{-3}	1.976	1.790
μ(MoK_α), mm^{-1}	8.708	8.708
F(000)	872	468
Crystal size, mm	0.25×0.10×0.07	0.10×0.1×0.1
Temperature, K	293	293
λMoK_α, Å	0.71073	0.71073
θ range, deg.	3.17—27.49	2.4—28.3
h, k, l limits	–19: 14, –16: 16, –9: 10	–10:10, –11:11, –17:17
Reflns: Total, Uniq. Data, R_{int}	6253, 1736, 0.0298	22732, 4397, 0.0497
Observed data [$I > 2\sigma(I)$]	1499	3388
T_{min}, T_{max}	0.08, 0.334	0.4763, 0.4763
N_{ref}, N_{par}	1736, 83	4397, 173
R_1, wR_2, S [$I > 2\sigma(I)$]	0.0290, 0.0711, 1.011	0.0773, 0.2162, 1.098
Largest diff. peak, hole (e·Å^{-3})	1.313, –1.162	5.24, –1.18

$w = [\sigma^2(F_0^2) + (aP)^2 + b]^{-1}$, where $P = (F_0^2 + 2F_c^2)/3$.

15 ml of methanol. After stirring for 15 minutes, the resulting mixture was filtered and the filtrate was kept at room temperature. After 24 hours white crystals were obtained. The complexes are light and moisture sensitive and should be stored in the dark.

X-ray Structure Determination. Single crystal data collection for the complexes was performed at 296 K on a Kappa APEXII Bruker diffractometer [28]. Diffraction data for **1** were collected using ω rotation scans of 0—180° at ϕ 0° and of 0—180° at ϕ 90° with the step Δω = 1.0°; exposures of 1 minute per image; 2θ range = 2.29—59.53°; $d_{min} - d_{max}$ = 17.779—0.716 Å. SAINT was used for the cell refinement and data reduction [29], while the refinement and all further calculations were carried out using SHELXL-97 [30]. ORTEP-3 for Windows [31] and PLATON [32] were used for molecular graphics. For **1** and **2**, the H-atoms were included in the calculated positions and treated as riding atoms using SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F^2. The crystal data and refinement details are presented in Table 1.

RESULTS AND DISCUSSION

The molecular structures of **1** and **2**, along with the crystallographic numbering schemes are shown in Figs. 1 and 2 respectively. Selected bond distances and bond angles are given in Table 2. Both complexes are mononuclear consisting of mercury atoms bound to two S atoms of thioureas and

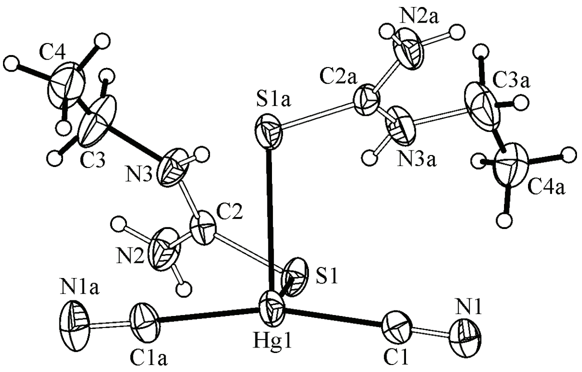

Fig. 1. Molecular structure of [Hg(Ettu)$_2$(CN)$_2$] (**1**) with the atom numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 30 % probability level

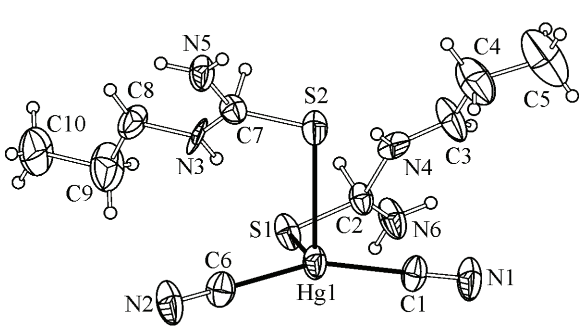

Fig. 2. Molecular structure of [Hg(Prtu)$_2$(CN)$_2$] (**2**) with the atom numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 30 % probability level

two cyanide carbon atoms. In both **1** and **2**, the Hg atom lies on a twofold rotation axis possessing crystallographic C_2 symmetry. The Hg atom exhibits a distorted tetrahedral geometry completed by the two S atoms of thiourea ligands and two C atoms of the cyanide groups. The thiourea ligands behave as S-donors and bind in a terminal mode although the bridging mode has also been observed in some other metal-thioureas systems [33]. The Hg—S and Hg—C bond distances and most of the bond angle values are in agreement with those observed in the other reported complexes [1—20, 34]. The Hg—C distance in **1** (2.065(6) Å) is found to be somewhat longer than that in **2** (2.055(14) and 2.062(15) Å). A shorter Hg—C bond in **2** is consistent with a greater shift of electron density from Hg to π* orbitals of CN compared to that in **1**. This shift of electron density from Hg to CN produces a partial double bond character in the Hg—C bond [35]. However, in both the Hg—C distance is slightly longer than that in the structure of Hg(CN)$_2$ (2.015(3) Å) [34]. The C—Hg—C angles in **1** and **2** are 162.2(3)° and 156.1(7)° respectively, which are much larger than the normal tetrahedral value of 109.5°. These large angles are counter balanced by the S1—Hg1—S2 bond angles of 91.26(6)° and 90.52(11)°. This tetrahedral distortion indicates a weak binding of the thiourea ligand to Hg, which is also evident from the longer Hg—S distances. The SCN_2 moiety of thioureas is essentially planar with the C—N and C—S bond lengths corresponding to the values intermediate between single and double bonds (Table 2). This is attributed to the delocalization of electrons in the SCN_2 fragment and the

Table 2

Selected bond distances (Å) *and bond angles* (deg.) *for compounds* **1** *and* **2**

Bond Distances		Bond Angles		Bond Distances		Bond Angles	
		(**1**)				(**2**)	
Hg1—C1	2.065(6)	C1—Hg1—C1	162.2(3)	Hg1—C1	2.055(14)	C1—Hg1—C6	156.1(7)
Hg1—S1	2.8690(13)	C1—Hg1—S1	95.05(17)	Hg1—C6	2.062(15)	C1—Hg1—S2	97.3(3)
Hg1—N1	3.342(6)	C1—Hg1—S1	97.36(15)	Hg1—S1	2.782(4)	C6—Hg1—S2	102.0(5)
C1—N1	1.116(8)	S1—Hg1—S1	91.26(6)	Hg1—S2	2.868(4)	C1—Hg1—S1	97.8(4)
C2—S1	1.724(5)	N1—C1—Hg1	176.6(6)	S1—C2	1.709(12)	C6—Hg1—S1	96.0(4)
C2—N2	1.310(6)	C2—S1—Hg1	102.73(15)	S2—C7	1.734(13)	S2—Hg1—S1	90.52(11)
C2—N3	1.314(6)	N2—C2—S1	119.7(4)	C1—N1	1.127(19)	C2—S1—Hg1	98.8(4)
C3—C3	1.451(8)	N3—C2—S1	120.1(4)	C6—N2	1.11(2)	C7—S2—Hg1	100.5(4)
		N2—C2—N3	126.9(5)	C2—N4	1.57(2)	N1—C1—Hg1	177.6(16)
				C2—N6	1.321(17)	N2—C6—Hg1	178.6(17)
				C3—N4	1.367(17)	N4—C2—S1	119.7(8)

Table 3

Hydrogen bonds in complexes **1** *and* **2** (Å, deg.)

D—H···A	D—H	H···A	D···A	∠D—H···A	D—H···A	D—H	H···A	D···A	∠D—H···A
		(**1**)					(**2**)		
N3—H3···S1	0.86	2.60	3.450(5)	170	N3—H3···S1	0.8600	2.4100	3.252(15)	164.00
N2—H21···N1	0.86	2.25	3.079(8)	161	N4—H4···S2	0.8600	2.4800	3.313(15)	166.00
N2—H22···S1	0.86	2.72	3.542(5)	161	N5—H5A···N2^{i}	0.8600	2.2300	3.07(2)	165.00
C4′—H4′2···N2	0.96	2.59	3.197(16)	121	N5—H5B···S1^{ii}	0.8600	2.6300	3.492(13)	174.00
C3—H3B···N1	0.97	2.57	3.387(11)	142	N6—H6A···N1^{iii}	0.8600	2.1800	3.00(2)	159.00
C3—H3D···N2	0.97	2.48	3.846(9)	102	N6—H6B···S2^{iv}	0.8600	2.6700	3.525(14)	176.00
C3—H3D···N1	0.97	2.59	3.3587(11)	140	C3—H3A···N1^{iii}	0.9300	2.5700	3.42(3)	151.00
					C8—H8···N2^{i}	0.9300	2.4700	3.35(2)	158.00

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

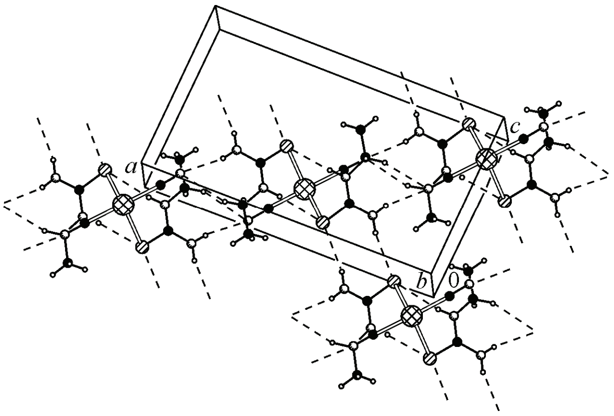

Fig. 3. Packing and hydrogen bonding of (**1**) viewed down the *b* axis

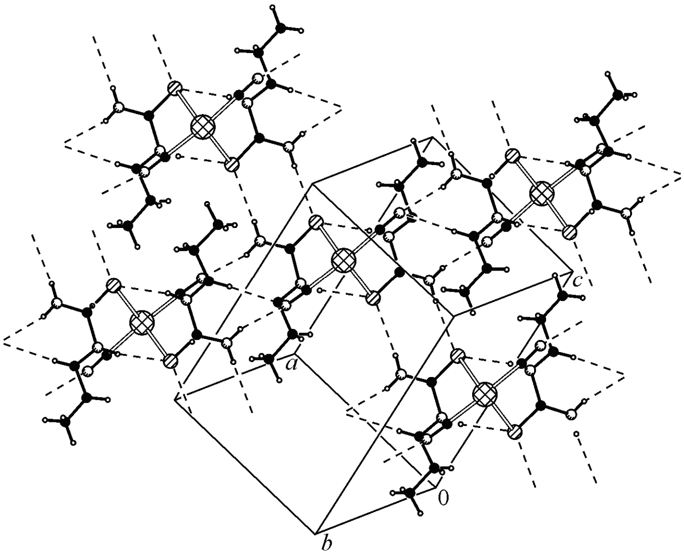

Fig. 4. View of crystal packing and hydrogen bonding of (**2**) in the unit cell

significant sp^2 character of the two nitrogen atoms. Compound **1** is isostructural to the reported mercury(II) complex bis(cyanido)bis(*N*,*N′*-dibutylthiourea-κS)mercury(II), $[Hg(Dbtu)_2(CN)_2]$ [9].

In the crystal packing, the adjacent molecules are connected by intermolecular N—H…S, N—H…N and N—H…N hydrogen bonds (Table 3). Intermolecular hydrogen bonding involving N—H hydrogen atoms with the cyanide ions of the adjacent molecules is also observed. The crystal packing and hydrogen bonding patterns of **1** and **2** are illustrated in Figs. 3 and 4 respectively. The hydrogen bonding scheme is believed to stabilize the encountered distorted tetrahedral geometry.

The present report shows that the interaction of *N*-ethylthiourea (Ettu) and *N*-propylthiourea (Prtu) with mercury cyanide results in complexes with a distorted tetrahedral geometry, in which thiourea ligands are coordinated through the sulfur atom in a monodentate terminal mode.

Supplementary material. Crystallographic data for structures (**1**) and (**2**) reported in this paper have been deposited with the Cambridge Crystallographic Center, CCDC Nos. 771411 and 769542 respectively. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, e-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk.

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