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Mercury(II) Cyanide Complexes of Thioureas and the Crystal Structure of $[(\text{N-Methylthiourea})_2\text{Hg(CN)}_2]$[1]

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Abstract—Mercury(II) cyanide complexes of thioureas (Tu), N-methylthiourea (MeTu), and N,N'-dimethylthiourea (DmTu)) have been prepared and characterized by IR and NMR (^{1}H and ^{13}C) spectroscopy, and the crystal structure of one of them was determined by X-ray crystallography. An upfield shift in ^{13}C NMR and downfield shifts in ^{1}H NMR are consistent with the sulfur coordination to mercury(II). The appearance of a band around 2200 cm^{-1} in IR and a resonance around 145 ppm in ^{13}C NMR indicates the binding of cyanide to mercury(II). The NMR data show that the $[(\text{Thione})_2\text{Hg(CN)}_2]$ complexes are stable in solution and undergo no redistribution reactions. In the crystal structure of the title complex, mercury atom is coordinated to two thione sulfur atoms of MeTu and to two cyanide carbon atoms in a distorted tetrahedral mode with the bond angles in the range of 90.2(2)°–169.3(3)°.

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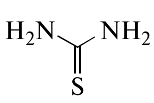
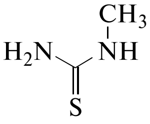
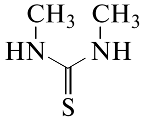
INTRODUCTION

The coordination chemistry of mercury(II) with N- and S-donor ligands is of special interest because of the importance of such complexes as structural models in biological systems [1–5]. Being a typical soft Lewis acid [6, 7] mercury(II) shows a specific affinity to sulfur donors, such as thiolates [8–13], thiones [14–24] and dithiocarbamates [25, 26]. With thiones (**L**), mercury(II) is known to form a wide variety of 1 : 1 and 1 : 2 complexes of the types LHgX_2 [16, 17] and L_2HgX_2 [18–24], respectively (where X is halide or pseudohalide), having structural arrangements entirely based on tetrahedral or pseudo-tetrahedral four-coordinate mercury(II). These studies demonstrate that the complexes may be discrete monomeric [17–21, 23], dimeric [16], or polymeric [24]. Numerous adducts of mercury halides with thiourea ligands have been structurally characterized [14–19, 24], whereas the number of complexes defined with Hg(CN)_2 is much more limited [20–23]. In our previous work on cyanidogold(I) complexes, we observed that the [Thione-AuCN] complexes underwent dissociation in solution due to the very large formation constant of $[\text{Au(CN)}_2]^-$ [27, 28], while the [Thione-AgCN] complexes remained undissociated when dissolved in solution [29, 30]. This report extends our study of thione complexes of d^{10} metals with the spectroscopic characterization of the $[\text{Hg(Thione)}_2(\text{CN})_2]$ complexes and the crystal structures of one of them, namely, $[\text{Hg(N-Methylthiourea)}_2(\text{CN})_2]$ (**I**). The purpose of the study is to see if the CN$^-$ ligand can be dissociated from the complexes to form $[\text{Hg(CN)}_4]^{2-}$ as it was seen in our previous studies on gold(I) [27, 28]. The structures of thiones used in this study are below:


Thiourea


N-Methylthiourea


N,N'-Dimethylthiourea

EXPERIMENTAL

Materials and IR and NMR measurements. Mercury(II) chloride and thiourea were obtained from Merck Chemical Company (Germany). N-Methylthiourea and N,N'-dimethylthiourea were purchased from Acros Organics (Belgium).

The solid-state IR spectra of the ligands and their mercury(II) cyanide complexes were recorded on a PerkinElmer FT-IR 180 spectrophotometer using KBr pellets over the range 4000–400 cm^{-1}. The ^{1}H NMR spectra of the complexes in DMSO-d_6 were obtained on a Jeol JNM-LA 500 NMR spectrometer operating at a frequency of 500.00 MHz at 297 K using a 0.10 M solution. The ^{13}C NMR spectra were

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Table 1. Elemental analysis and melting points of mercury(II) cyanide complexes

Complex	Contents (found/calcd), %				Yield, %	M.p., °C
	C	N	H	S		
$[Hg(Tu)_2(CN)_2]$	11.40/ 11.87	1.86/ 1.99	21.32/ 20.76	14.90/ 15.84	50	178
$[Hg(MeTu)_2(CN)_2]$	16.30/ 16.65	2.48/ 2.79	18.92/ 19.41	14.03/ 14.81	45	141–142
$[Hg(DmTu)_2(CN)_2]$	20.10/ 20.84	3.35/ 3.50	18.63/ 18.23	13.32/ 13.91	60	158–160

obtained at a frequency of 125.65 MHz with ^1H broadband decoupling at 298 K. The spectral conditions were as follows 32 K data points, 0.967 s acquisition time, 1.00 s pulse delay, and 45° pulse angle. The ^{13}C chemical shifts were measured relative to TMS.

Synthesis of complexes. Mercury(II) cyanide was prepared by mixing solutions of $HgCl_2$ in methanol and KCN in water in a molar ratio of 1 : 2. The resulting colorless solution was concentrated by evaporation, and the white crystalline product was separated by filtration.

The complexes were prepared by adding two equivalents of thiones in 15 ml of methanol to a solution of $Hg(CN)_2$ (0.25 g, 1.0 mmol) in 10 ml of methanol, and the solutions were stirred for 0.5 h. White crystalline products were obtained from the resulting colorless solutions, which were washed with methanol. The elemental analysis of the complexes and their melting points are given in Table 1.

X-ray structure determination. Single-crystal data collection for complex **I** was performed on a Bruker-Axs Smart Apex system equipped with a graphite monochromatized MoK_α radiation ($\lambda = 0.71073$ Å). The data were collected using SMART [31]. The data integration was performed using SAINT [31]. An empirical absorption correction was carried out using SADABS [32]. The structure was solved with the direct methods and refined by full-matrix least-squares methods based on F^2, using the structure determination and the graphic packages SHELXS-97 and SHELXL-97 [33]. Hydrogen atoms were located on a difference Fourier map and refined isotropically. Crystal data and details of the data collection are summarized in Table 2. Supplementary material has been deposited with the Cambridge Crystallographic Data Centre (no. 772367; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

Selected IR spectroscopic vibration bands for the free ligands and their mercury(II) complexes are given in Table 3. The ν(C=S) vibration, which occurs around 700–600 cm^{-1} for the free ligands, is shifted to lower frequency upon complexation in accordance with the data observed for other thione complexes [22–24, 27, 29, 34, 35]. Another important vibrational band observed in the IR spectra of the thiones is ν(NH), which appears around 3200 cm^{-1}. Upon coordination to $Hg(CN)_2$ this band shifts to higher wave numbers. The presence of a band around 3200 cm^{-1} in

Table 2. Crystal data and details of the structure refinement for compound **I**

Parameter	Value
Formula	$C_6H_{12}N_6S_2Hg$
Formula weight	432.93
Crystal system	Monoclinic
Space group	$P2_1/c$
a, Å	10.805(4)
b, Å	4.2618(15)
c, Å	28.299(9)
β, deg	96.533(7)
V, Å^3	1294.7(8)
Z	4
ρ_{calcd}, g cm^{-3}	2.221
$\mu(MoK_\alpha)$, mm^{-1}	12.191
$F(000)$	808
Crystal size, mm	0.35 × 0.10 × 0.08
Temperature, K	293(2)
θ range, deg	1.45–28.40
Limiting indices	$-14 \le h \le 14$; $-5 \le k \le 5$; $-37 \le l \le 37$
Reflections	16413/3242
Collected/unique	$R_{int} = 0.0706$
Observed data ($I > 2\sigma(I)$)	2079
T_{min}, T_{max}	0.1000, 0.4422
N_{par}	138
R_1, wR_2, S ($I > 2\sigma(I)$)	0.0473, 0.1021, 1.034
Largest diff. peak and hole, e Å^{-3}	1.795 and –1.637

$w = [\sigma^2(F_o^2) + (0.0242P)^2 + 1.6454P]^{-1}$, where $P = (F_o^2 + 2F_c^2)/3$.

Table 3. Melting points and selected IR frequencies (cm^{-1}) of the free ligands and their $Hg(CN)_2$ complexes

Compound	M.p., °C	ν(C=S)	ν(C–N)	ν(NH_2, NH)	δ(NH)	ν(C≡N)
$Hg(CN)_2$						2185
Tu		730	1473	3156, 3365	1604	
$[Hg(Tu)_2(CN)_2]$	178	714	1506	3186, 3376	1620	2185
MeTu		634	1488	3163, 3245	1624	
$[Hg(MeTu)_2(CN)_2$	141–142	606	1496	3257	1625	2169
DmTu		641	1521	3203	1552	
$[Hg(DmTu)_2(CN)_2]$	158–160	639	1527	3256	1601	2172

Table 4. ^{1}H and ^{13}C NMR chemical shifts (in ppm) of various species in DMSO-d_6

Compound	δ (^{1}H)		δ (^{13}C)		
	N–H	CH_3	>C=S	N–CH_3	CN
Tu	6.98, 7.25		183.81		
$[Hg(Tu)_2 (CN)_2]$	7.29, 7.52		182.10		145.66
MeTu	6.95, 7.45, 7.65	2.65, 2.86	181.10, 184.10	29.90, 31.10	
$[Hg(MeTu)_2(CN)_2$	7.09, 7.67, 8.08	2.74, 2.88	177.85, 183.13	30.11, 31.20	144.76
DmTu	7.38	2.79	182.70	30.75	
$[Hg(DmTu)_2(CN)_2]$	8.11, 8.43	2.80, 3.03	179.70	30.86	144.41
$Hg(CN)_2$					145.25

free ligands, as well as in the complexes, indicates the existence of the thione form of the ligands in the solid state. A sharp band around 2200 cm^{-1} for the CN stretch was observed for all the complexes indicating the presence of cyanide.

The ^{1}H and ^{13}C chemical shifts of the complexes in DMSO-d_6 are summarized in Table 4. In the ^{1}H NMR spectra of the complexes, the N–H signal of thioureas became less intense upon coordination and shifted downfield from their positions in free ligands. The deshielding is related to an increase in π-electron density in the C–N bond upon coordination [27, 29, 30, 34]. The appearance of the N–H signal shows that the ligands are coordinated to mercury(II) via the thione group. Table 4 shows that the N–H protons of MeTu are nonequivalent (NH_2 appears as a doublet). The N–H and CH_3 protons of DmTu are equivalent but after coordination they become nonequivalent as observed in the DmTu-AgCN [29] and DmTu-AuCN [27] complexes.

In ^{13}C NMR the C=S resonance of thioureas shifted upfield upon complexation compared to their positions in the free state. The upfield shift is attributed to a lowering of the C=S bond order upon coordination and a shift of the N → C electron density producing a partial double bond character in the C–N bond as observed in other metal complexes of thiourea [22–24, 27, 29, 30, 34]. The shift difference for the C(2) resonance of thiones upon complexation is related to the strength of the metal–sulfur bond [23, 34]. The smallest C(2) shift of 1.7 ppm was detected in the Tu complex, while the highest one was found in the MeTu complex showing that the Hg–S bond should be the strongest for $[Hg(MeTu)_2(CN)_2]$ among these complexes. It should be noted that MeTu in ^{13}C NMR gives two signals for both >C=S and N–CH_3 carbons showing that the compound exists in two isomeric forms [35]. For $[Hg(DmTu)_2(CN)_2]$, two signals were expected for N–CH_3carbon as observed in our previous studies [27, 29, 34]. Only a single broad resonance was detected, showing that methyl groups are equilibrating at different positions. A typical ^{13}C spectrum for a representative complex $[Hg(MeTu)_2(CN)_2]$ is shown in Fig. 1.

In the CN region of the ^{13}C NMR spectrum, a sharp singlet was observed around 145 ppm for all four complexes. For the analogous AuCN complexes, two resonances were observed in the CN region; one for the CN carbon of LAuCN and another due to

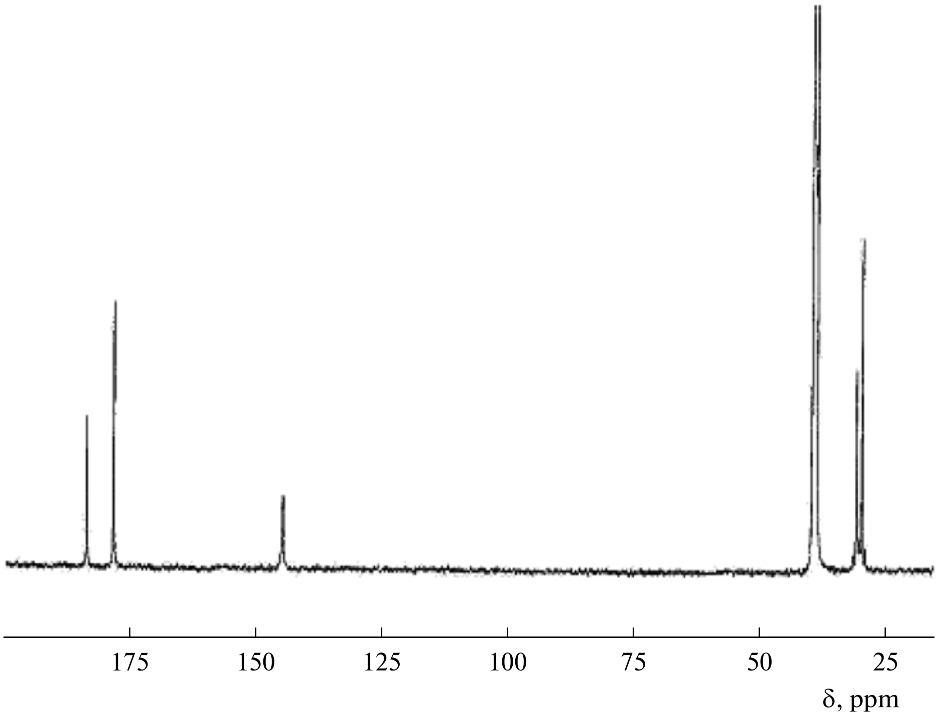

Fig. 1. ^{13}C NMR spectrum of [$Hg(MeTu)_2(CN)_2$] (showing two sets of resonances for the CH_3 and C=S carbon atoms).

$[Au(CN)_2]^-$ [27, 28]. This showed that they underwent disproportionation in solution according to the equation

$$2L{-}Au{-}CN \rightleftarrows [AuL_2]^+ + [Au(CN)_2]^-. \qquad (1)$$

The formation of ionic species was related to the very high stability constant of $[Au(CN)_2]^-$ (logβ of $[Au(CN)_2]^- \approx 36$) [27, 28, 36]. However, for the LAgCN complexes only one CN resonance was observed [29, 30]. For the complexes under study (of the type $L_2Hg(CN)_2$) only one CN resonance was detected, which suggests that they do not dissociate in solution and, hence, equilibrium of the type (1) does not exist for $L_2Hg(CN)_2$.

The molecular structure of **I** together with the atomic labeling scheme is shown in Fig. 2. Selected bond lengths and bond angles are presented in Table 5. The complex is mononuclear consisting of mercury atoms bound to two S atoms of thiourea and to two cyanide carbon atoms. The Hg atom lies on a twofold rotation axis possessing crystallographic C_2 symmetry and exhibits a severely distorted tetrahedral geometry completed by the two S atoms of thiourea ligands and two C atoms of the cyanide groups. The methylthiourea ligands behave as S-donors and bind in a terminal mode, although the bridging mode has also been observed in some other metal-thiourea systems [17]. The Hg–S distances are comparable to that in [$(H4pymthH)_2Hg(CN)_2$] (~2.9 Å) [23] (H4pymthH is 3,4,5,6-tetrahydropyrimidine-2-thione) to Hg(II). However, this distance is somewhat longer than the reported mean distance of ~2.6 Å in many other mercury(II) complexes of thiones [17–21, 23, 24]. This shows relatively weaker binding of sulfur to Hg(II). The Hg–C distance is slightly longer than that in the structure of $Hg(CN)_2$ (2.015(3) Å) [37].

In **I**, the C(1)Hg(1)C(6) angle is 169.3(3)°, which is much larger than the normal tetrahedral value of 109.5°. This large angle is counterbalanced by the S(1)Hg(1)S(2) bond angles of 98.52(6)°. This tetrahedral distortion in-

Table 5. Selected bond distances (Å) and bond angles (deg) for compound **I**

Bond	d, Å	Angle	ω, deg
Hg(1)–S(1)	2.9658(18)	S(1)Hg(1)S(2)	98.52(6)
Hg(1)–S(2)	2.992(2)	S(1)Hg(1)C(1)	95.9(2)
Hg(1)–C(1)	2.2048(8)	S(1)Hg(1)C(2)	90.2(2)
Hg(2)–C(2)	2.2055(8)	S(2)Hg(1)C(1)	93.9(2)
C(1)–N(1)	1.150(10)	S(2)Hg(1)C(2)	93.9(2)
C(2)–N(2)	1.141(10)	C(1)Hg(1)C(2)	169.3(3)
S(1)–C(3)	1.717(6)	C(1)S(1)Hg(1)	102.8(2)
S(2)–C(5)	1.729(7)	N(1)C(1)Hg(1)	175.7(7)
N(4)–C(3)	1.302(8)	N(2)C(2)Hg(1)	177.2(7)
N(4)–C(4)	1.434(8)	N(4)C(3)S(1)	120.5(5)

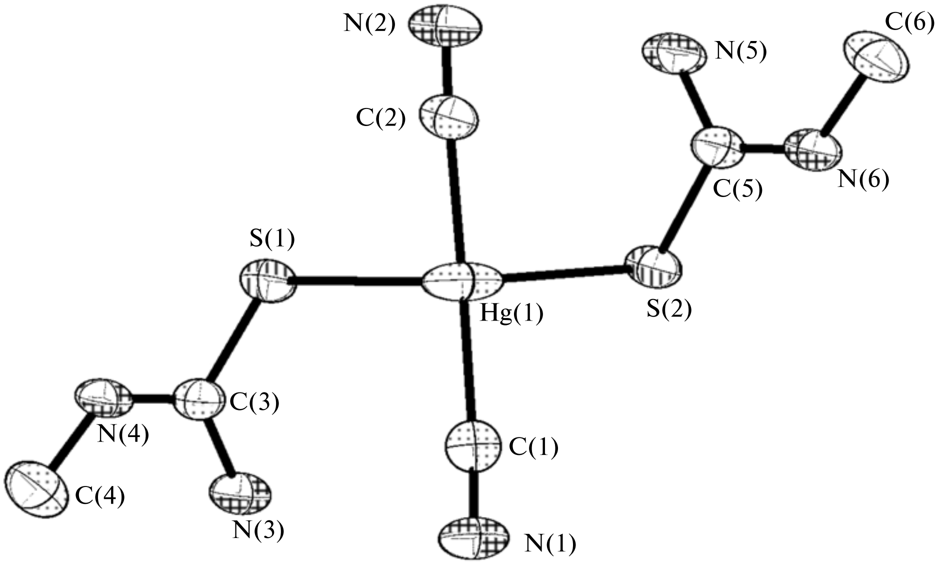

Fig. 2. Molecular structure of **I**. Displacement ellipsoids are drawn at the 50% probability level.

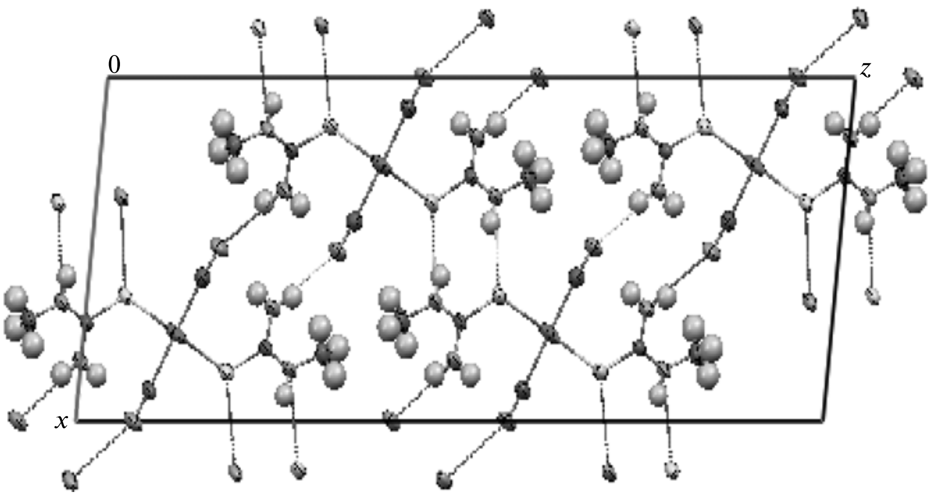

Fig. 3. View of the crystal packing in compound **I** showing the N–H···NC and N–H···S hydrogen bonds.

dicates a weak binding of 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 5). This is attributed to the delocalization of electrons in the SCN_2 fragment and the significant sp^2 character of the two nitrogen atoms. The complex **I** crystallizes in the monoclinic space group $P2_1/c$ (Table 2), while the crystals of the two closely related compounds (bis(cyanido)bis(N,N'-dibutylthiourea-κ*S*)mercury(II), $[Hg(Dbtu)_2(CN)_2]$, and bis(cyanido)bis(N,N'-dimethylthiourea-κ*S*)mercury(II), $[Hg(Dmtu)_2(CN)_2]$), were found to belong to $C2/c$ space group [20, 21].

In the crystal packing, the adjacent molecules are connected by intermolecular N–H···NC (cyanide) and N–H···S hydrogen bonds between adjacent molecules. The crystal packing and hydrogen bonding patterns of **I** is illustrated in Fig. 3. The hydrogen bonding scheme is believed to stabilize the encountered distorted tetrahedral geometry.

The present report shows that the reaction of N-methylthiourea (MeTu) with mercury cyanide results in complexes with a distorted tetrahedral geometry in which thiourea ligands are coordinating through the sulfur atom in a monodentate terminal mode. The study also shows that the $L_2Hg(CN)_2$ complexes are stable in solution, unlike the LAuCN complexes, which undergo dissociation in solution.

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