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# Structures and vibrational spectra of the *N*-benzoyl *N'*-dialkylthiourea derivative and their complexes with Hg(II)

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#### Abstract

The complex Hg (MTCB)<sub>2</sub> (MTCB=*N*-(morpholinothiocarbonyl) benzamide) and Hg (PTCB)<sub>2</sub> (PTCB=*N*-(piperidylthiocarbonyl) benzamide) have been synthesized and characterized by elemental analysis, FT-IR, FT-Raman spectra and NMR methods. The complex, Hg (MTCB)<sub>2</sub>, crystallizes in the triclinic space group  $P\bar{1}$ , with Z=2. Unit cell parameters, a=10.3621(11) Å, b=11.5738(11) Å, c=12.7722(7) Å,  $\alpha=64.493(8)^{\circ}$ ,  $\beta=66.132(8)^{\circ}$ ,  $\gamma=85.811(11)^{\circ}$ , V=1254.7(2) Å<sup>3</sup>. The FT-Infrared and FT-Raman spectra were used in study of the structures of MTCB, PTCB and their complexes with mercury cation, which were agreement with the result of X-ray diffraction.

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#### 1. Introduction

The study of compounds *N*-benzoyl-*N'*-alkylthioureas and *N*-benzoyl-*N'*, *N'*-dialkylthioureas has recently attracted great interest in view of the potential use of these compounds as highly selective reagents for the concentration and separation of metal cations [1–10]. One specific use for these substances is the coordination with harmful compounds, which can be achieved in the organism by one of several ligands of adequate structure. This is an important aspect and in future more attention should be devoted to the design and synthesis of new agents able to coordinate these toxic metal ions with a view to obtain complexes that can be readily eliminated.

Mercury (II) complexes with heterocyclic molecules which may contain nitrogen, oxygen or sulphur as endocyclic or a combination of these and an exocyclic thione (thioketo) group can be used to imitate mercury cysteine thionato interactions in biosystems [11–13] as well as to establish the toxicological behavior of mercury [14,15]. As the continuation of our interest in mercury complexes, in the present study we have investigated

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complexes with N-benzoyl-N', N'-dialkylthioureas. The N-benzoyl-N', N'-dialkylthioureas ligands exhibit various donor ability in coordination compounds. The most common type of ligand bonding to the metal centre is through the S atoms and carbonyl oxygen atoms [8,9]. On the basis of spectroscopic studies of complexes in the solution and crystalline state, it was found that the complexes with Ni(II), Pt(II), Cu(II), Zn(II) and Co(II) are coordinated. Such five-membered chelate ring containing S, O donor atoms were established by X-ray analysis for the Ni(II) and Pt(II) complexes [9,16]. Mercury (II) complexes containing sulfur were described and the tetrahedral geometry postulated on the basis of IR and NMR data [17,18], and the experiments of X-ray diffraction technology have also made sure [19–22]. There is no structural studies on the mercury (II) complexes with N-benzoyl-N', N'-dialkylthioureas systems. In the present work, we have synthesized and studied ligands MTCB and PTCB and their complexes with mercury by FT-IR, NMR and FT-Raman methods. The crystal structure of complex Hg (MTCB)<sub>2</sub> has been determined by X-ray diffraction technology.

#### 2. Experiment

X-ray diffraction structure determination was carried out with Rigaku Mercury CCD. Melting points were determined on a Kofler melting point apparatus and uncorrected.

IR spectra were obtained in KBr discs using a Nicolet Magna550 spectrometer. NMR spectroscopy was recorded in CDCl<sub>3</sub> at room temperature at 400 MHz on an INOVA 400 instrument. The FT-Raman spectrum was measured with a SPEX-1377 laser Raman spectrometer at room temperature. An Ar-ion laser with a wavelength of 514.5 nm in a backscattering configuration was used to excite the crystals. The spectral resolution was  $4.0 \text{ cm}^{-1}$ .

## 2.1. Synthesis and characterization of the ligands of N-benzoyl-N<sup>1</sup>-dialkylthiourea derivatives

*N*-benzoyl-*N'*-dialkylthiourea derivatives MTCB and PTCB were synthesized following the procedure given in the literature [23]. A freshly prepared acetone solution of benzoyl isothiocyanic synthesized by condensation of benzoyl chloride with NH<sub>4</sub>SCN was added dropwise to chemical calculated solutions of morpholine or piperine with stirring. After addition, the mixture was heated under reflux for 1–2 h and poured onto crushed ice with vigorous stirring. The isolated solids were filtrated, washed with water, and dried to yield.

*N*-(morpholinothiocarbonyl) benzamide: colorless, Mp: 131–132 °C. Elemental analysis: found (% C, H, N, S): 57.68, 5.30, 11.14, 12.9. Stoichiometric amounts (%C, H, N, S): 57.81, 5.26, 11.24, 12.86. FTIR (cm<sup>-1</sup>): 3236.2, 2963.3, 2924.6, 2847.0, 2448.3, 1670.5, 1530.8, 1453.3, 1418.4, 1353.7, 1276.1, 1193.4, 1141.7, 1111.9, 1060.2, 1034.4, 955.5, 938.8, 843.0, 791.3, 709.8, 658.3, 618.4, 498.7, 462.1, 408.9. <sup>1</sup>H NMR (CDCl<sub>3</sub>) (ppm): 8.439, 7.856 (doublet, d), 7.634, 7.489 (d), 4.253 (d), 3.884 (quadruplet, q), 3.675 (d). <sup>13</sup>C NMR (CDCl<sub>3</sub>) (ppm): 176.4, 164.5, 134.2, 132.2, 126.1 (d), 125.8 (d), 67.8 (d), 50.5 (d).

*N*-(piperidylthiocarbonyl) benzamide: colorless, Mp: 123–124 °C. Elemental analysis: found (%C, H, N, S): 63.01, 6.22, 11.20, 12.9. Stoichiometric amounts (% C, H, N, S): 63.13, 6.11, 11.33, 12.96. FTIR (cm<sup>-1</sup>): 3161.7, 3061.3, 2927.6, 2858.0, 2424.2, 1651.4, 1581.1, 1538.1, 1470.8, 1370.3, 1284.8, 1280.0, 1249.47, 1180.7, 1137.3, 1076.0, 1018.9, 947.4, 908.3, 971.7, 839.0, 794.4, 713.6, 655.9, 616.6, 570.1, 491.1, 448.9, 428.6, 404.0. <sup>1</sup>H NMR (CDCl<sub>3</sub>) (ppm): 8.524, 7.776 (d), 7.623, 7.489 (d), 3.243 (d), 3.024 (d) 2.043 (q), 1.724 (d). <sup>13</sup>C NMR (CDCl<sub>3</sub>) (ppm): 179.3, 138.5, 132.5, 132.1, 126.1(d), 127.8(d), 43.0(d), 34.3(d), 23.6.

### 2.2. Synthesis and characterization of the complexes *Hg* (*MTCB*)<sub>2</sub> and *Hg* (*PTCB*)<sub>2</sub>

The synthesis of complexes Hg (MTCB)<sub>2</sub> and Hg (PTCB)<sub>2</sub> are according to the reference [23]. The pure 1 mmol *N*-(morpholinothiocarbonyl) benzamide or *N*-(piperidylthiocarbonyl) benzamide was added respectively in 100 ml water. 10% NaOH was added dropwise until the suspension was dissolved. Added respectively 0.05 mmol HgCl<sub>2</sub> water solution, maintained stirring 1 h, the deposition was washed by water separately, and dried.

Hg (MTCB)<sub>2</sub>: colorless. Elemental analysis: Obs. (%C, H, N, S): 41.38, 7.82, 4.12, 9.3. Stoichiometric amounts (%C, H, N, S): 41.23, 8.00, 3.96, 9.2.

Hg (PTCB)<sub>2</sub>: colorless. Elemental analysis: Obs. (%C, H, N, S): 45.02, 4.28, 8.22, 9.04. Stoichiometric amounts (%C, H, N, S): 44.92, 4.35, 8.06, 9.2.

#### 2.3. Structure determination of the complex Hg (MTCB)<sub>2</sub>

The growth of the single crystal of the complex Hg (MTCB)<sub>2</sub> is carried out by slow evaporating solvent toluene.



Fig. 1. ORTEP plot of Hg(MTCB)<sub>2</sub>, thermal ellipsoids and depicted at 50%.

A colorless block crystal with approximate dimensions of  $0.18 \times 0.60 \times 0.35$  mm<sup>3</sup> was mounted on a glass fiber. All measurements were made on a Rigaku Mercury CCD area detector with graphite monochromatic Mo-Ka  $(\lambda = 0.71070 \text{ Å})$  radiation. Data were collected by  $\omega$  scan technique. The data were collected at a temperature of  $-80\pm1$  °C to a maximum  $2\theta$  value of 55.0°. A total of 720 oscillation images were collected. A sweep of data was done using  $\theta$  scans from -80.0 to  $100.0^{\circ}$  in  $0.5^{\circ}$  step, at  $\chi = 45.0^{\circ}$ and  $\phi = 0.0^{\circ}$ . The exposure rate was 6.0 [s/deg.]. The detector swing angle was 9.97°. A second sweep was performed using scans from -80.0 to  $100.0^{\circ}$  in  $0.5^{\circ}$  step, at  $\chi = 45.0^{\circ}$  and  $\phi = 90.0^{\circ}$ . The exposure rate was 6.0 [s/deg.]. The detector swing angle was 9.97°. The crystal-to-detector distance was 34.53 mm. Readout was performed in the 0.273 mm pixel mode. The structure was solved by direct methods and expanded using Fourier techniques 'SIR97' [24]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The data were corrected for Lorentz and polarization

Table 1 Atomic coordinates and  $B_{iso}/B_{eq}$  and occupancy

Atom	x	у	z	B <sub>eq</sub>
Hg(1)	-0.00856(2)	0.41542(2)	0.32251(2)	1.785(5)
S(1)	-0.07769(13)	0.19251(12)	0.44095(13)	2.03(2)
S(2)	0.0318(1)	0.64049(12)	0.20678(13)	2.19(2)
O(1)	0.1551(5)	0.3451(4)	0.1457(4)	2.95(9)
O(2)	0.2464(4)	0.0541(4)	0.6956(4)	2.43(8)
O(3)	0.2034(4)	0.4319(4)	0.3679(4)	2.48(8)
O(4)	0.3916(5)	0.6608(5)	-0.2191(4)	3.55(10)
N(1)	0.1918(5)	0.1650(4)	0.2986(4)	2.26(9)
N(2)	0.1447(4)	0.1278(4)	0.5025(4)	1.70(7)
N(3)	0.3029(4)	0.6238(4)	0.1893(4)	2.06(8)
N(4)	0.2796(4)	0.7025(4)	0.0015(4)	1.98(8)
C(1)	0.1847(5)	0.2325(5)	0.1850(5)	1.90(9)
C(2)	0.2273(5)	0.1667(5)	0.0995(4)	1.69(9)
C(3)	0.2759(5)	0.0459(5)	0.1343(5)	1.96(9)
C(4)	0.3079(6)	-0.0138(5)	0.0553(5)	2.55(11)
C(5)	0.2886(6)	0.0432(6)	-0.0557(5)	2.71(11)
C(6)	0.2429(6)	0.1646(5)	-0.0935(5)	2.41(11)
C(7)	0.2137(6)	0.2256(5)	-0.0157(5)	2.23(10)
C(8)	0.1039(5)	0.1630(4)	0.4069(5)	1.77(9)
C(9)	0.2972(5)	0.1242(6)	0.4721(5)	2.32(10)
C(10)	0.3194(6)	0.0288(6)	0.5884(5)	2.37(10)
C(11)	0.0634(6)	0.1412(5)	0.6206(5)	2.09(9)
C(12)	0.0976(6)	0.0424(6)	0.7271(5)	2.50(10)
C(13)	0.2701(5)	0.5413(5)	0.3132(5)	1.83(9)
C(14)	0.3256(5)	0.5850(5)	0.3818(4)	1.71(9)
C(15)	0.3993(6)	0.7080(6)	0.3240(5)	2.59(11)
C(16)	0.4433(7)	0.7500(6)	0.3924(6)	3.04(13)
C(17)	0.4151(6)	0.6691(6)	0.5185(5)	2.74(12)
C(18)	0.3453(5)	0.5472(6)	0.5758(5)	2.41(10)
C(19)	0.3018(5)	0.5048(5)	0.5077(5)	2.11(10)
C(20)	0.2213(5)	0.6501(4)	0.1296(4)	1.72(9)
C(21)	0.4339(5)	0.7107(6)	-0.0692(5)	2.25(10)
C(22)	0.4627(6)	0.6275(6)	-0.1376(5)	2.92(12)
C(23)	0.2027(6)	0.7334(5)	-0.0802(5)	2.41(10)
C(24)	0.2421(7)	0.6475(7)	-0.1477(6)	3.3(1)

$$\begin{split} B_{\rm eq} = & 8/3\pi^2 (U_{11}({\rm aa}^*)^2 + U_{22}({\rm bb}^*)^2 + U_{33}({\rm cc}^*)^2 + 2U_{12}({\rm aa}^*{\rm bb}^*)\cos\gamma + \\ & 2U_{13}({\rm aa}^*{\rm cc}^*)\cos\beta + 2U_{23}({\rm bb}^*{\rm cc}^*)\cos\alpha. \end{split}$$

effects. The crystal structure is of the triclinic, space group:  $P\overline{1}$  (#2), a=10.3621(11) Å, b=11.5738(11) Å, c=12.7722(7) Å,  $\alpha=64.493(8)^{\circ}$ ,  $\beta=66.132(8)^{\circ}$ ,  $\gamma=85.811(11)^{\circ}$ , V=1254.7(2) Å<sup>3</sup>, Z=2.  $F_{000}=684$ ,  $R1(I>3.00\sigma(I))=0.035$ ,  $wR2(I>3.00\sigma(I))=0.097$ . The molecular structure by X-ray determination is showed in Fig. 1. The crystallographic information file is deposited with the Cambridge Crystallographic Data Center as CCDC 262322, and non-hydrogen atom coordination and thermal parameters were listed in Table 1, selected bond parameters are listed in Table 2.

### 3. Results and discussion

#### 3.1. Structure discussion

The crystal structure of Hg(MTCB)<sub>2</sub> is built up of discrete complex molecules shown in Fig. 1. The characteristic mercury coordination in Hg (MTCB)2 is diagonal since S1-Hg1-S2 valence angle is almost  $180^{\circ}(S2-Hg-S1=172.992^{\circ})$ , which is in a very good agreement with Hg-S bond distance of 2.34 Å, characteristic for the sum of covalent radius of Hg (1.30 Å for diagonal coordination and covalent radius of S, 1.04 Å according to Pauling [30] and Grdenić [31]). The Hg atom is additionally coordinated by atoms O1 and O3, at distances of 2.631 and 2.527 Å, which is less than the van der Waals radii of the corresponding atoms, so the effective coordinated can be described as 2+2. These contacts are responsible for the elongation of the Hg-S bond and for the slight deviation from linearity. In fact, the N1-C8 (1.304 Å), is similar to C=N bond length 1.298 Å [4],

Table 2The selected structure parameters of X-ray experimental

Bond lengths (nm)	Bond lengths (Å)	Bond angles (°)	Torsion angles
Hg(1)–S(1)	2.343(1)	S(1)-Hg(1)-S(2)	173.00(5)
Hg(1)-S(1)	2.343(1)	S(1)-Hg(1)-O(3)	99.29(9)
Hg(1)–O(3)	2.526(5)	S(1)-Hg(1)-O(1)	81.94(9)
Hg(1)–O(1)	2.631(5)	O(1)-Hg(1)-O(3)	88.7(2)
S(1)-C(8)	1.794(5)	C(8)-S(1)-Hg (1)	91.1(1)
O(1)–C(1)	1.243(7)	C(1)-O(1)-Hg (1)	115.8(3)
O(2)–C(10)	1.428(7)	C(10)-O(2)-C(12)	108.6(5)
N(1)–C(8)	1.304(7)	C(8)-N(1)-C(1)	126.1(5)
N(1)–C(1)	1.350(8)	C(8)-N(2)-C(9)	117.9(4)
N(2)–C(8)	1.341(8)	C(8)-N(2)-C(11)	124.3(4)
N(2)–C(9)	1.469(7)	C(9)-N(2)-C(11)	113.4(5)
C(1)–C(2)	1.499(9)	S(1)-C(8)-N(1)	123.0(1)
C(9)–C(10)	1.519(8)	S(1)-C(8)-N(2)	116.1(2)
C(11)–C(12)	1.508(8)	N(1)-C(8)-N(2)	119.9(4)
C(2)–C(3)	1.392(8)	C(2)-C(1)-O(1)	119.6(5)
C(2)–C(7)	1.396(7)	C(2)-C(1)-N(1)	115.4(5)
C(3)–C(4)	1.38(1)	O(1)-C(1)-N(1)	124.7(3)
C(4)–C(5)	1.391(8)	C(10)-C(9)-N(2)	110.4(4)
C(6)–C(7)	1.38(1)	O(2)-C(10)-C(9)	112.2(1)
C(5)–C(6)	1.37(1)	C(11)-C(12)-O(2)	111.5(4)

N1-C1 (1.350 Å) has values between C-N single bond and double bonds. The bonds S1-C8 (1.794 Å), is longer than double bonds (1.63 Å), so it must derive from the electron de-localization along the N2-C8-N1-C1 fragment. Whereas, the bond O1-C1 (1.244 Å), is close to C=O double bonds. These bond lengths are similar to those observed for related complexes and thiourea derivatives [25–27]. No significantly difference exists for morpholine ring in the crystal comparing with 4,4'-carbonyl-di-morpholine[28]. The intramolecular hydrogen bonding between NH and benzoyl oxygen is inexistence due to de-protonated of the N(2) nitrogen atom. That would be responsible for the conformational dispositions were seen in this compound and it must derive from the electron delocalization along the C(Ph)-N-C(S)-N fragment. The intramolecular hydrogen bonding are found, C9-H···N1, nonbonding distance, 2.703 Å, <C9HN1, 102.8° and C3H····O1, nonbonding distance, 2.802 Å, <C3HO1, 99.0°.

A interaction is found between the mercury ion and the phenyl ring of MTCB, and the distances are Hg(1)–C(20A), 3.263 Å, Hg(1)–C(21A), 3.282 Å, shown in Fig. 2. It is attributed empty out-nucleus atomic orbits of metal ion and  $\pi$  electrons of phenyl ring, which formed the interaction of donor ( $\pi$  electrons)–acceptor (Hg<sup>2+</sup>). A intermolecular hydrogen boned interaction is C(11) H(12)...O(2), the distance of C(11) H(12)...O(2) is 3.206 Å, <C(11)H(12)O(2) is 149.8°.

There is a weakly  $\pi$ - $\pi$  interaction between two phenyl rings. The distance between C15 and C17(A) is 3.419 Å, the distance C16–C16(A), 3.392 Å.

#### 3.2. FT-IR and FT-Raman analysis

The FT-IR spectra of two compounds, MTCB and PTCB together with their two complexes are shown in Fig. 3. The C=S and C=O stretch of two complexes shifted to lower value than pure their ligands due to its coordinate interaction with  $Hg^{2+}$ . In addition, this interaction is also evident by a shift in the N-C-N stretch of thiourea to higher value in the complexes compared to the ligands. C=S and C=O coordination to mercury ion enhances the resonance delocalization of nitrogen atom lone pair electrons, thus providing more double bond character for N-C-N, hence both symmetric and asymmetric N-C-N stretching is shifted to higher values. In pure ligands, C=S and C=O are bonded to NH, whereas in the complexes are bonded to Hg<sup>2+</sup> and therefore increasing C-S and C-O bonding length, bonding vibrational mode are also shifted to lower values (Fig. 3).

As all thiosemicarbazones, our ligands can exhibit thione-thiol tautomerism, since it contains a thioamide -NH-C=S functional group. There is an IR band at 2400–2500 cm<sup>-1</sup> in the spectrum of the free ligands, and these indicate the existence of S-H group in the free ligands.



Fig. 2. The interactions of the mercury cations and the phenyl rings.



Fig. 3. The FT-IR spectra of MTCB and PTCB and their complexes with mercury cation(II).

However, there are bands in the regions of 843.0, 838.98 cm<sup>-1</sup> and 3241.2, 3161.7 cm<sup>-1</sup>, characteristic of  $\nu$ (C=S) and  $\nu$ (N–H), respectively, indicating that the ligand remains as the thione tautomer.

The experimental band about  $3200 \text{ cm}^{-1}$  in free ligands, corresponding to the stretching  $\nu(\text{NH})$  vibrations of the hydrogen bond NH groups is disappeared in the complex along with the disappearance of the N–H bond. The peak at  $3048.2 \text{ cm}^{-1}$  is assigned to  $\nu(\text{Ph}-\text{H})$ , and this absorb peak is covered with wide absorb bands at the  $3236.2 \text{ cm}^{-1}$  in the ligand MTCB. The bands at 2936.18,  $2847.80 \text{ cm}^{-1}$  are assigned to  $\nu(\text{CH}_2)$  and appeared almost at the same wave number in the complex. The bands at 1667.7 cm<sup>-1</sup> in the free ligands are disappeared in the corresponding complexes. The substituted bands about at 1600 cm<sup>-1</sup> are found. In the laser Raman spectra, these bands appear at the same frequency with very strong intensity. The appearance of the bands are attributed to C=N double bonded. The bands

at about 1530 cm<sup>-1</sup> in free ligand also discovered in the complex is attributed to  $\delta$ (Ph–H).

In addition, this interaction is also evident of the N-C-N stretching vibrations of thiourea occur at 1443 and  $1406 \text{ cm}^{-1}$  in ligands thioureas and shift to about  $1500 \text{ cm}^{-1}$  in the complexes, these frequencies is strongly increased because of the greater double bond character of C–N bond. As expected, a appears at  $1500 \text{ cm}^{-1}$  due to N-C-N asymmetric stretching vibrations. The weak bands at  $669 \text{ cm}^{-1}$  are attributed to C=S symmetric stretching vibration. Some of the C=S vibration bands overlap with N-C-N. The bands 1583.2,15, 1530.8, 1581.14,  $1538.06 \text{ cm}^{-1}$  found in the ligands are attributed to  $\delta$ (Ph–H) shift to 1517.7 and 1511.7 cm<sup>-1</sup> in their mercury complexes. The shown thionyl asymmetric stretching vibration band at about 1260 cm<sup>-1</sup> for ligands shifts to  $1220 \text{ cm}^{-1}$  for the complexes, as resulting of coordination to metal mercury. Both ligands and complexes, the bands



Fig. 4. FT-Raman spectra of Hg(MTCB)<sub>2</sub>.



The laser Raman spectra recorded for both complexes to compliment the FTIR results are shown in Figs. 4 and 5. The presence of all functional groups is confirmed from FTIR. The bands about  $290-300 \text{ cm}^{-1}$  of the complexes are assigned to Hg–S stretching vibrations. The peaks around  $370 \text{ cm}^{-1}$  absorb peaks are assigned to Hg–O stretching vibrations. It is supported by the work of Bertin [29] and is in a very good agreement with experimental X-ray diffraction results.

#### 4. Conclusion

According to the X-ray data of the structure of  $Hg(MTCB)_2$ , the intramolecular hydrogen bonding between NH and benzoyl oxygen is inexistence due to no hydrogen atom bonded to nitrogen atom. All of C–N bonds lengths in the complex crystal are shorter than the normal C–N. The coordination interaction between the oxygen atoms



Fig. 5. FT-Raman spectra of Hg(PTCB)<sub>2</sub>.

and the  $Hg^{2+}$  cations is weaker than between the sulfur atoms and the  $Hg^{2+}$ . A weaken interaction donor( $\pi$  electrons)–acceptor( $Hg^{2+}$ ) is found between the mercury ion and the phenyl ring of ligand MTCB. The results of FT-IR, FT-Raman and NMR experiments are agreement with the X-ray diffraction. The ligands thioureas can be examined thione–thiol tautomerism by FT-IR method, since it contains a thioamide –NH–C=S functional group.

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