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One-Dimensional Mercury(II) Coordination Polymers with a Flexible Bidentate Schiff Base Ligand ($(Me_2N\text{-}Ba)_2Bn$): Synthesis, Characterization, and Crystal Structures[1]

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Abstract—Three one-dimensional mercury(II) complexes, $[Hg_2(\mu_{N,N}\text{-}((Me_2N\text{-}Ba)_2Bn)(\mu\text{-}X)_2X_2]_n$, where X = Cl (**I**), Br (**II**), and I (**III**), $(Me_2N\text{-}Ba)_2Bn$ = N,N'-bis(dimethylaminobenzylidene)butane-1,4-diamine, involving a bidentate Schiff base with a flexible spacer (=N–C–C–C–C–N=) were prepared under mild condition and characterized by elemental analyses (CHN), FT-IR, ^1H & ^{13}C-NMR spectroscopy. The crystal structure of **II** has been determined by X-ray single-crystal diffraction. Each Hg(II) center adopts a distorted $[HgNBr_3]$ tetrahedron environment arising from two crystallographically equivalent $(Me_2N\text{-}Ba)_2Bn$ Schiff base ligands. Each of ligands acts as N_2-bis-chelating ligand with the nitrogen atoms of two imine functions in anti-form leading to the dinuclear $[Hg_2(\mu_{N,N}\text{-}(Me_2N\text{-}Ba)_2Bn)Br_2]$ groups. Such dinuclear $[Hg_2(\mu_{N,N}\text{-}((Me_2Nvg\text{-}Ba)_2Bn)Br_2]$ groups are bridged two iodine anions $(\mu\text{-}Br)_2$ to form a neutral 1D-chain mercury (**II**) coordination polymer.

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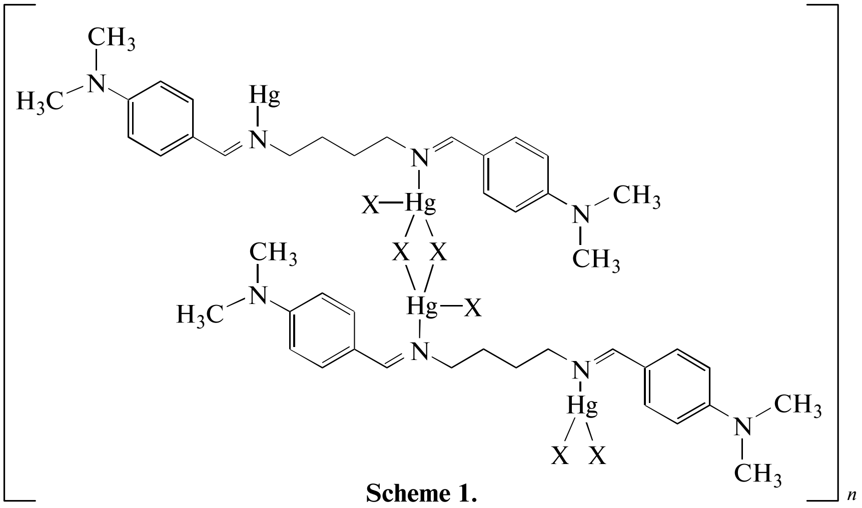
INTRODUCTION

The mercury(II) complexes have been studied widely as important part of coordination chemistry not only due to their structural novelty but also for their potential applications [1–5]. In recent years, many attempts have been made to prepare polymeric complexes using halides, pseudohalides and flexible Schiff base ligands and their structures have been determined [6–9]. In contrast to coordination polymers of transition metal complexes, the coordination polymers of mercury(II) with flexible Schiff base ligands seems to be surprisingly sparse [2, 3, 5]. Flexible Schiff base ligands, halides and pseudohalides counter ions are capable of acting as bridging ligands and thus may form polymeric structures with Hg^{2+} ion. However, isolating suitable single-crystals of polymeric mercury(II) complexes is problematic, because these complexes are very little soluble in the common organic solvents [2–5]. Continuing with our previous work on mercury(II) complexes with Schiff base ligands [10, 11], we now present the synthesis and characterization of three new one-dimensional mercury(II) complexes, $[Hg_2(\mu_{N,N}\text{-}((Me_2N\text{-}Ba)_2Bn)(\mu\text{-}X)_2X_2]_n$, where X = Cl (**I**), Br (**II**) and I (**III**); $(Me_2N\text{-}Ba)_2Bn$ = N,N'-bis(dimethylamiono)benzylidene)butane-1,4-diamine):



Scheme 1.

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Table 1. Crystallographic data and structure refinement for complex **II**

Parameter	Value
Formula weight	535.7
Crystal system, space group	Triclinic, $P\bar{1}$
Z	2
a, Å	7.8927(2)
b, Å	8.6244(2)
c, Å	10.7147(3)
α, deg	75.314(2)
β, deg	81.781(2)
γ, deg	76.841(2)
V, Å^3	684.18(3)
Crystal size, mm	0.27 × 0.15 × 0.12
$T_{\min}$	0.077
$T_{\max}$	0.26
μ, mm^{-1}	17.06
Measured reflections	25396
Independent reflections, R_{int}	3511 (0.030)
Reflection with $I > 3\sigma(I)$	3203
S	1.07
Parameters	145
R ($F^2 > 3\sigma(F^2)$)	0.015
wR (F^2)	0.036
$\Delta\rho_{\max}/\Delta\rho_{\min}$, eÅ^{-3}	0.43/–0.40

EXPERIMENTAL

Materials and methods. All reagents and solvents for synthesis and analysis were commercially available and used as received without further purifications. Infrared spectra were recorded using KBr disks on a FT-IR PerkinElmer spectrophotometer. Elemental analyses were carried out using a Heraeus CHN-O-Rapid analyzer. ^{13}C & ^{1}H NMR spectra were measured on a Bruker DRX-500 Avance spectrometer at 500 MHz. All chemical shifts are reported in δ units downfleld from TMS.

Synthesis of $(Me_2N\text{-}Ba)_2Bn$ was carried out by condensation of N,N-dimethylaminobenzaldehyde with butane-1,4-diamine [7]. The yield was 88%.

For $C_{22}H_{30}N_4$

anal. calcd., %:	C, 75.39;	H, 8.63;	N, 15.98.
Found, %:	C, 75.52;	H, 8.75;	N, 15.94.

IR (KBr, ν, cm^{-1}): 2831–2923 (CH aliphatic and aromatic), 1637 s ν(C=N). ^{1}H NMR ($CDCl_3$; δ, ppm): 1.62 (s., 2H), 2.92 (s., 6H), 3.50 (s., 2H), 6.69 (d., 2H), 7.52 (d., 2H), 8.12 (s., 1H). ^{13}C NMR ($CDCl_3$; δ, ppm): 28.61, 39.64, 60.26, 111.43, 124.25, 128.91, 151.69, 159.75.

Synthesis of complex I. To a stirring solution of the Schiff base ligand $(Me_2N\text{-}Ba)_2Bn$ (0.071 g, 0.2 mmol) in 15 mL of chloroform was added $HgCl_2$ (0.028 g, 0.1 mmol) in 15 mL of hot methanol. The mixture was stirred for 0.5 h in air at 50°C and then left at room temperature for several days without disturbance, yielding micro crystals of **I**. The yield was 73%.

For $C_{22}H_{30}N_4Cl_4Hg_2$

anal. calcd., %:	C, 29.57;	H, 3.38;	N, 6.27.
Found, %:	C, 29.63;	H, 3.45;	N, 6.36.

IR (KBr; ν, cm^{-1}): 2857–2985 (CH aliphatic and aromatic), 1581 s ν(C=N). ^{1}H NMR ($CDCl_3$; δ, ppm): 1.63 (s., 2H), 2.95 (s., 6H), 3.54 (s., 2H), 6.70 (d., 2H), 7.57 (d,, 2H), 8.22 (s., 1H). ^{13}C NMR ($CDCl_3$, δ, ppm): 28.24, 39.70, 59.56, 111.45, 122.50, 129.55, 152.19, 161.44.

Synthesis of complex II. This complex was prepared in similar manner to **I** using $HgBr_2$ (0.036 g, 0.1 mmol). The yield was 77%.

For $C_{22}H_{30}N_4Br_4Hg_2$

anal. calcd., %:	C, 24.67;	H, 2.82;	N, 5.23.
Found, %:	C, 24.66;	H, 2.86;	N, 5.28.

Table 2. Selected bond distances (Å) and angles (deg) of **II***

Bond	d, Å	Bond	d, Å
Hg(1)–Br(2)	2.8932(3)	N(2)–C(7)	1.366(3)
Hg(1)–Br(3)	2.4914(3)	N(2)–C(10)	1.453(3)
Hg(1)–N(1)	2.195(2)	N(2)–C(11)	1.444(3)
Hg(1)–Br(2)^{ii}	2.7209(3)	C(1)–C(1)^{i}	1.520(3)
N(1)–C(2)	1.474(3)	C(1)–C(2)	1.517(3)
N(1)–C(3)	1.283(3)	C(3)–C(4)	1.447(3)
Angle	**ω, deg**	**Angle**	**ω, deg**
Br(2)Hg(1)Br(3)	101.379(9)	Br(2)Hg(1)N(1)	86.40 (6)
Br(2)Hg(1)Br(2)^{ii}	92.256(8)	Br(3)Hg(1)N(1)	147.46(5)
Br(3)Hg(1)Br(2)^{ii}	104.703(9)	Br(2)^{ii}Hg(1)N(1)	106.16(5)
Hg(1)N(1)C(2)	113.10(16)	Hg(1)N(1)C(3)	127.27(15)
N(1)C(3)C(4)	127.9(2)	N(1)C(2)C(1)	111.51(19)
C(2)N(1)C(3)	119.0(2)	C(1)C(1)C(2)	111.1(2)
C(7)N(2)C(10)	120.7(2)	C(10)N(2)C(11)	118.1(2)
C(7)N(2)C(11)	121.2(2)		

* Code of equivalent position: ^{i} $-x + 1, -y, -z + 1$; ^{ii} $-x + 1, -y + 1, -z + 1$.

IR (KBr; ν, cm^{-1}): 2854–2983 (CH aliphatic and aromatic), 1582 s ν(C=N). ^{1}H NMR (CDCl$_3$; δ, ppm): 1.62 (s., 2H), 2.95 (s., 6H), 3.52 (s., 2H), 6.70 (d., 2H), 7.55 (d., 2H), 8.19 (s., 1H). ^{13}C NMR (CDCl$_3$; δ, ppm): 28.40, 39.70, 59.94, 111.44, 123.22, 129.34, 151.96, 160.84.

Synthesis of complex III. This complex was prepared in similar manner to **I** using HgI$_2$ (0.045 g, 0.1 mmol). The yield was 77%.

For $C_{22}H_{30}N_4I_4Hg_2$

anal. calcd., %:	C, 20.98;	H, 2.40;	N, 4.45.
Found, %:	C, 20.96;	H, 2.37;	N, 4.48.

IR (KBr; ν, cm^{-1}): 2854–2983 (CH aliphatic and aromatic), 1594 s ν(C=N). ^{1}H NMR (CDCl$_3$; δ, ppm): 1.62 (s., 2H), 2.94 (s., 6H), 3.51 (s., 2H), 6.69 (d., 2H), 7.53 (d., 2H), 8.16 (s., 1H). ^{13}C NMR (CDCl$_3$; δ, ppm): 28.46, 39.70, 60.10, 111.39, 123.56, 129.18, 151.78, 160.42.

X-ray crystallography. A single crystal of **II** with the dimensions 0.27 × 0.15 × 0.12 mm was chosen for X-ray diffraction study. Crystallographic measurements were done at 120 K with four circle CCD diffractometer Gemini of Oxford diffraction, Ltd., with graphite-monochromated MoK_α radiation (λ = 0.07107 Å). The crystal structures were solved by direct methods with program SIR2002 [12] and

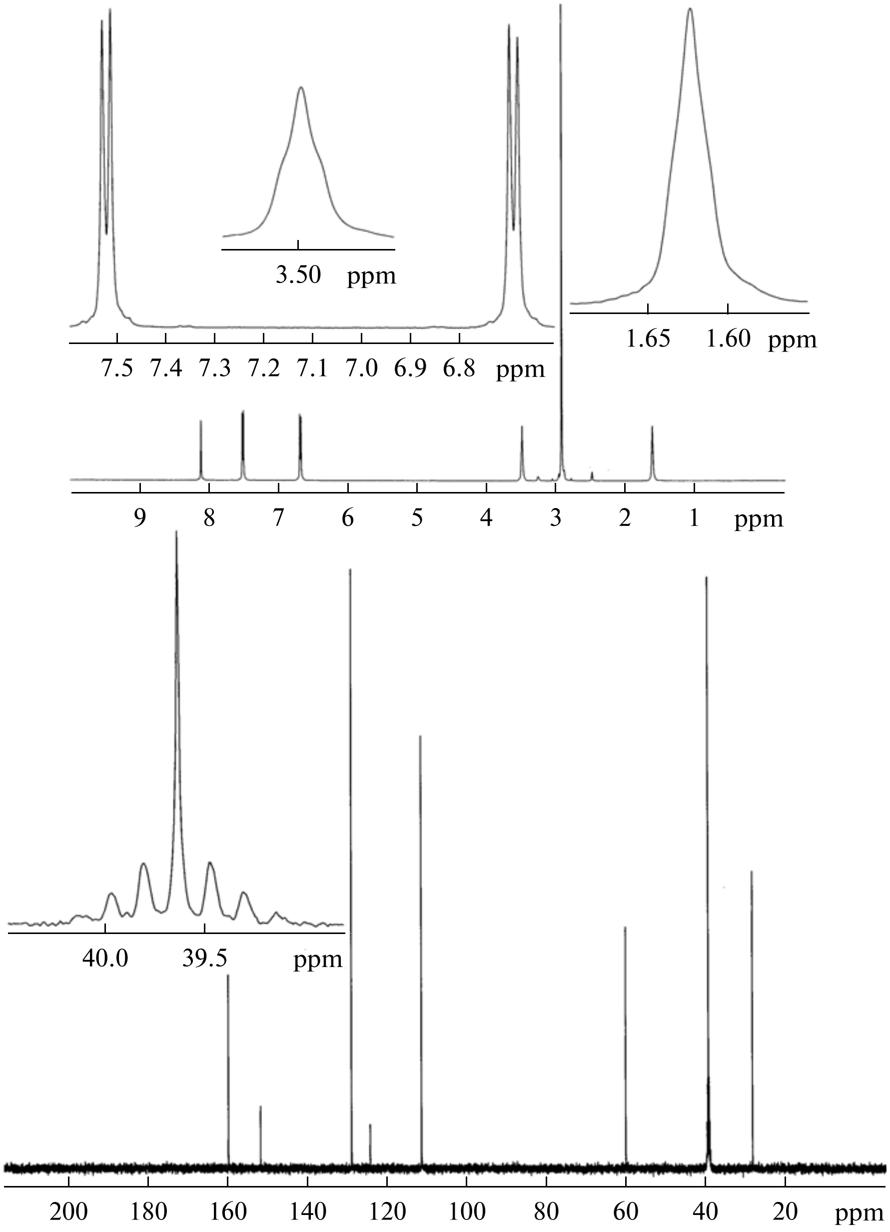

Fig. 1. ^{1}H & ^{13}C-NMR spectra of Schiff base ligand.

refined with the Jana2006 program package [13] by full-matrix least-squares technique on F^2. The molecular structure plots were prepared by ORTEP III [14]. Hydrogen atoms were mostly discernible in difference Fourier maps and could be refined to reasonable geometry. According to common practice they were nevertheless kept in ideal positions during the refinement. The isotropic atomic displacement parameters of hydrogen atoms were evaluated as 1.2–1.5 U_{eq} of the parent atom. Crystallographic data and details of the data collection and structure solution and refinements are listed in Table 1. Selected bond distances and angles are listed in Table 2.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre (no. 946793 (**II**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The reaction between ligand and mercury(II) halides in a methanol–chloroform (1 : 1 v/v) solvent

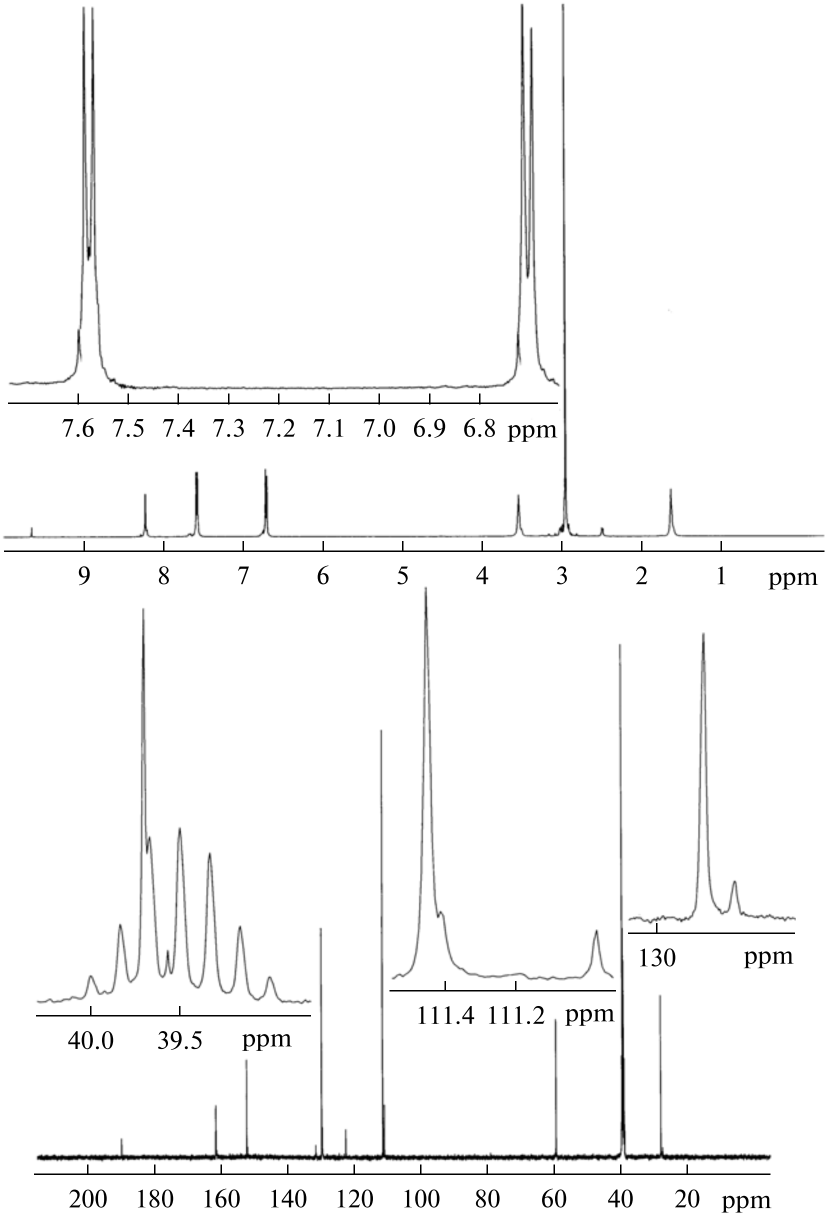

Fig. 2. ^{1}H & ^{13}C-NMR spectra of **I**.

mixture at 50°C provided polymeric mercury(II) complexes, as shown in the Scheme 1. The solubility of complexes were determined by adding the solvent to a known of complex until complete dissolution. It was found that all complexes are moderately soluble in common organic solvents, such as methanol, ethanol, chloroform, dichloromethane, acetone and completely soluble in coordinating solvents, such as DMF and DMSO. In order to confirm the chemical composition of all complexes, elemental analysis (CHN) was carried out on the re-crystallized compounds. The results of the analysis are presented in the experimental section.

The FT-IR spectra of the free ligand and complexes exhibit the characteristic band of the azomethine group which appears at 1637 cm^{-1} (ligand), and shifted to lower frequencies of the complexes, 1581 (**I**), 1582 (**II**), and 1591 cm^{-1} (**III**), due to the coordination of the azomethine group.

The ^{1}H & ^{13}C NMR spectra of the ligand and its mercury(II) complexes were recorded using DMSO (Figs. 1–4), and results suggest that the ligands and

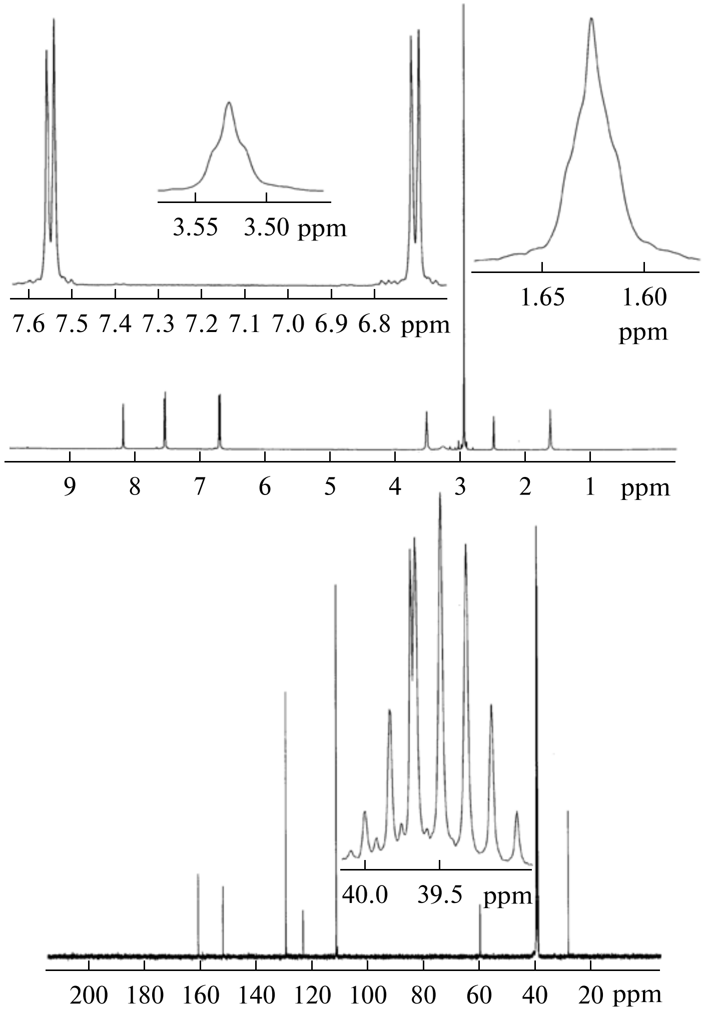

Fig. 3. ^{1}H & ^{13}C-NMR spectra of **II**.

complexes have symmetric structures [15]. In ^{1}H NMR spectra, methylene and methyl protons appear as singlets in the region ~1.62 (–C–CH_2–CH_2–C), ~2.92 (2-N–$(CH_3)_2$), and 3.49 ppm (2-N–CH_2–). The signals appearing at 6.70 and 7.53 ppm have been assigned to the hydrogen atoms of the aromatic rings. The hydrogen of azomethine group (–CH=N–) in the Schiff base shows up at 8.12 ppm as a single signal, while the signal related to this group in the complexes is shifted to the lower region (8.22 (**I**), 8.19 (**II**), and 8.16 ppm (**III**)). This shift shows that the ligand is coordinated to Hg^{2+} ion. The sharp NMR peaks are indicative of diamagnetic Hg(II) complexes. The appearance of a unique signal for each type of proton in DMSO solution indicates that the symmetry of the complexes is retained in solution, and only one isomer or exchange processes within the NMR time scale are present. ^{13}C NMR spectra of ligand and complexes show 8 carbons in the different regions.

As shown in Fig. 5, the Hg^{2+} ion is coordinated with a nitrogen atom from the Schiff base ligand, one terminal and two bridging Br atoms in a form of strongly deformed tetrahedron. The organic Schiff base ligand acts as a bis-monodentate bridging ligand through its two iminic nitrogen atoms, forming the $[Hg_2(\mu_{N,N}\text{-}(Me_2N\text{-}Ba)_2Bn)Br_2]$ dinuclear fragment (Fig. 5). Two Br atoms act as doubly $(\mu\text{-}Br)_2$ bridging ligands and link the dinuclear fragments together into 1D mercury(II) coordination polymer $[Hg_2(\mu_{N,N}\text{-}(Me_2N\text{-}Ba)_2Bn)(\mu\text{-}Br)_2Br_2]_n$ (Fig. 6).

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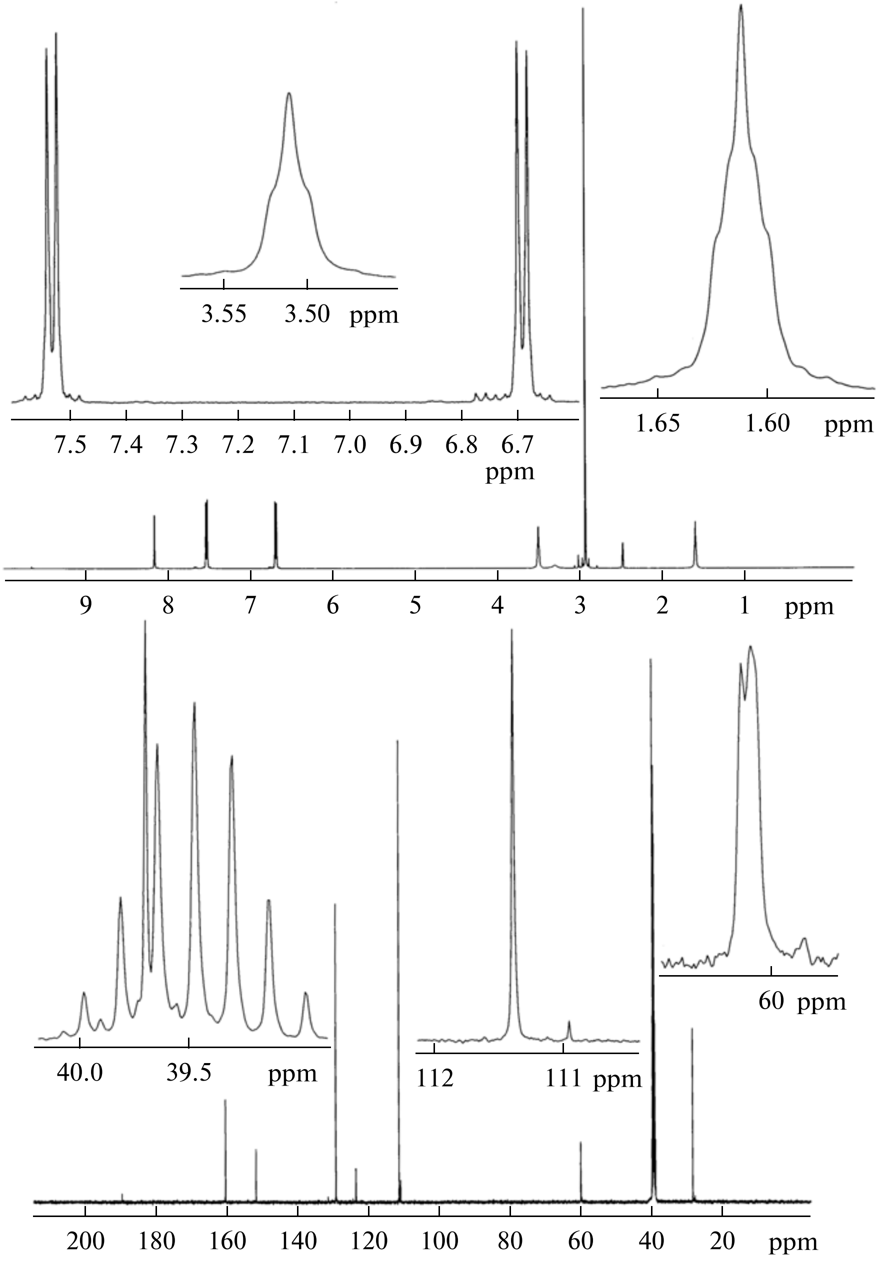

Fig. 4. ^{1}H & ^{13}C-NMR spectra of **III**.

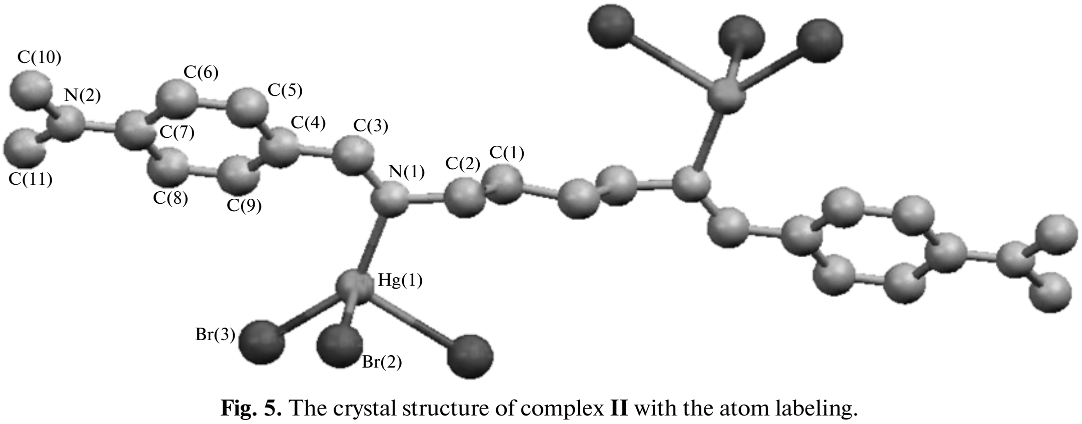

Fig. 5. The crystal structure of complex **II** with the atom labeling.

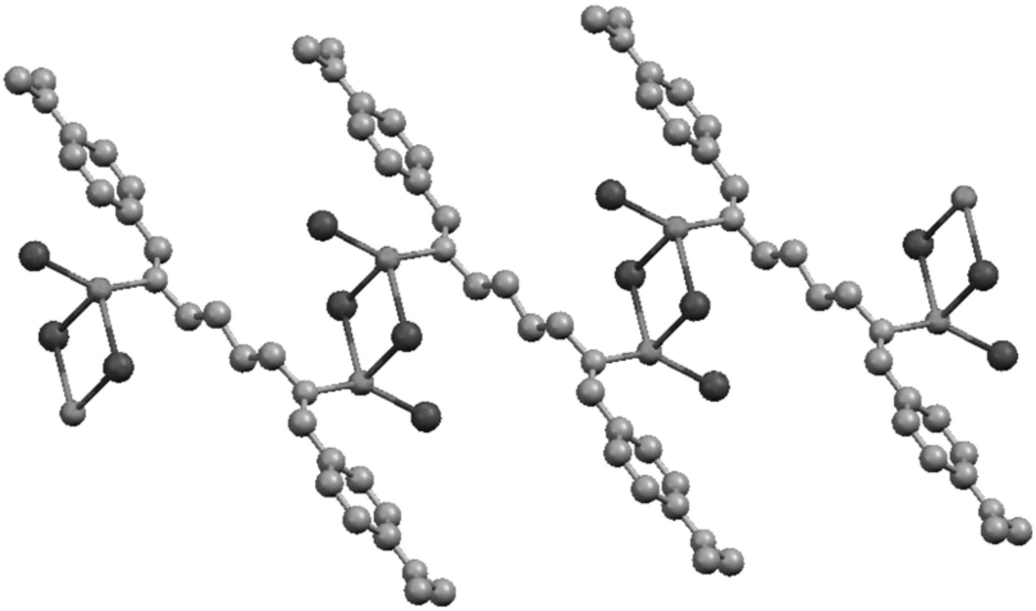

Fig. 6. The fragment of 1D-chain of complex **II**.

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