# Comprehensive Comparison between the Reaction of N,N-Cyclohexane-1,2-Diylidene-Bis(4-Methoxybenzoylhydrazide) with Mercury(II) and Copper(II) Ions. Synthesis, Structure, and Kinetics of Complex Formation<sup>1</sup>

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Abstract—Comprehensive comparison between the reaction of N,N-cyclohexane-1,2-diylidene-bis(4methoxybenzoylhydrazide) (CHMBH) with HgCl<sub>2</sub> and Cu(NO<sub>3</sub>)<sub>2</sub> · 2.5H<sub>2</sub>O salts have been investigated, including the synthesis, structure and kinetic of complex formation. The reactions of CHMBH with HgCl<sub>2</sub> or Cu(NO<sub>3</sub>)<sub>2</sub> · 2.5H<sub>2</sub>O at the same synthetic conditions have been shown to produce completely different type of complexes: [Hg(CHMBH)Cl<sub>2</sub>] · CH<sub>3</sub>CN (I) and [Cu<sub>3</sub>( $\mu_3$ -OH)(CTMB)<sub>3</sub>(NO<sub>3</sub>)<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>] · 5CH<sub>3</sub>CN · H<sub>2</sub>O (II) (CTMB = cyclohexotriazole-3-(4-methoxybenzamide)). The prepared compounds were characterized using different techniques (NMR, IR, UV-Vis and mass spectroscopies, microelemental analysis, thermogravimetry as well as X-ray powder differection and X-ray single crystal crystallography for I (CIF file CCDC no. 1503398). X-ray crystallography shows that the isolated product of I is a mononuclear complex which contains the [Hg(CHMBH)]<sup>2+</sup> core. While, the isolated product of I was a trinuclear Cu(II) cluster [Cu<sub>3</sub>( $\mu_3$ -OH)(CTMB)<sub>3</sub>(NO<sub>3</sub>)<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>] · 5CH<sub>3</sub>CN · H<sub>2</sub>O which contains three differently coordinated copper sites. Kinetic studies on the formation of I have been also investigated and compared with that of II. In case of I, the reaction was so slow and exhibits a first-order dependence on the concentration of metal salt and a first-order dependence on the concentration of CHMBH. While in II, the study shows that the reaction is fast and occurs in three distinct phases.

Kyewords: bisaroylhydrazones, kinetics of complex formation, mononuclear mercury(II) complexes,  $\{Cu_3(\mu_3\text{-}OH)\}$  core

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## INTRODUCTION

In general, there has been an increased interest in hydrazide and their derivatives, particularly in the last few years, related to their coordinative and pharmacological activity as well as their use in analytical chemistry as metal-extracting agents [1, 2]. Benzohydrazide and their derivatives are polyfunctional molecules (containing multifunctional groups in their structures like -CO, -NH-, and  $-NH_2$ ) [3–5]. Due to that, a wide range of compounds have been prepared based on benzohydrazide derivatives [6-10]. Among all of these, aroylhydrozones (Schiff bases) represent one of the most known and important compounds. These compounds possessing an azomethine -NHN=CHproton constitutes an important class of compounds for different biological activities: antimicrobial, anticonvulsant, analgesic, antiinflammatory, antiplatelet, anti-tubercular, anticancer, and antitumor as well as a new drug development [11, 12].

Reaction of aroylhydrazide with dialdehyde or diketone produces bisaroylhydrazones [9, 10]. Bisarnovlhydrazones are known to be a class of versatile ligands, capable of generating different molecular architectures and coordination polyhedral [13, 14]. Furthermore, bisaroylhydrazones have the potentiality of being oxidatively cyclized to 1,2,3,4-tetrazine, 1,3,4-oxadiazine or 1,2,3-triazine derivatives [10]. Continuation of our previous studies [15-17], this work focus on the synthesis and characterization of N,N-cyclohexane-1,2-diylidene-bis(4-methoxybenzoylhydrazide) (CHMBH). This molecule coordinates to  $Hg^{2+}$  ion and mononuclear complex  $[Hg(CHMBH)Cl_2] \cdot CH_3CN$  (I) is obtained. X-ray crystallography shows that the isolated product contains the [Hg(CHMBH)]<sup>2+</sup> core in which CHMBH acts as a planar quadridentate ligand. The remainder of the coordination sphere comprises anionic ligands

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(chloride) derived from the parent metal salt. In contrast, with  $Cu^{2+}$  ion [17] and under the same conditions of preparation, the isolated product was a trinuclear Cu(II) cluster  $[Cu_3(\mu_3-OH)(CTMB)_3(NO_3)_2(CH_3CN)_2] \cdot 5CH_3CN \cdot H_2O$ (II) (CTMB = cyclohexotriazole-3-(4-methoxybenzamide)) which contains three differently coordinated copper sites.

Kinetic studies on the formation of complexes I and II suggests the factors that lead to formation of the two types of products.

#### **EXPERIMENTAL**

Materials and methods. All reagents were commercially available and used without further purification, (1,2-cyclohexanedione 97%, Aldrich Co.), (4methoxybenzhyrazide, Aldrich Co.), (acetic acid 100%, Aldrich Co.), (HgCl<sub>2</sub> 99.5%, Acros Organics Co.). Solvents used in the syntheses were distilled from the appropriate drying agent immediately prior to use. All manipulations in the synthesis of the compounds were performed under air. Infrared spectra were recorded using a Cary 630 FTIR spectrometer equipped with an ATR module. <sup>1</sup>H and <sup>13</sup>C $\{^{1}H\}$  NMR spectra were carried out in DMSO- $d_6$  using a Varian (Agilent) 400 MHz spectrometer. Mass spectrum was obtained by using a Waters Acquity UPLC with TOD detector. Elemental analyses (C, H, and N) were carried out on an EuroEA Elemental Analyzer, (Hg) was performed by the Mikroanalytisches Labor Egmont Pascher (an der Pulvermühle 3, 53424 Remagen, Germany). Electronic spectra were recorded with a Shimadzu UV-3101PC spectrophotometer. X-ray powder diffraction patterns were obtained with Shimadzu 6000 diffractometer using  $CuK_{\alpha}$  radiation  $(\lambda = 1.54178 \text{ Å})$ . Thermogravimetry (TG) and differential thermogravimetry (DTG) of the compounds (in the ranges of 20–600°C for I and 30–900°C for II) were carried out at a heating rate of 10.0 K/min by using (Linseis STA PT-1000) for I and (PerkinElmer 4000) for **II**.

Synthesis of CHMBH. This compound was prepared according to our previous study [17]. The yield was 1.7 g (93%), m.p. =  $208-210^{\circ}$ C.

For  $C_{22}H_{24}N_4O_4$ 

anal. calcd., %:	C, 64.7;	N, 13.7;	Н, 5.9.
Found, %:	C, 64.6;	N, 13.5;	H, 5.8.

<sup>1</sup>H NMR spectrum ( $\delta$ , ppm): cyclohexane protons—1.73 (CH<sub>2</sub>, m., 4H), 2.61 (CH<sub>2</sub>, t., 2H,  $J_{HH} =$ 3.1 Hz), 2.81 (CH<sub>2</sub>, t., 2H,  $J_{HH} =$  3.1Hz), aromatic protons—7.02 (CH, d., 2H,  $J_{HH} =$  8.9 Hz), 7.07 (CH, d., 2H,  $J_{HH} =$  8.9 Hz), 7.96 (CH, d., 2H,  $J_{HH} =$ 8.9 Hz), 8.19 (CH, d., 2H,  $J_{HH} =$  7.3 Hz), other protons—3.84 (OCH<sub>3</sub>, s., 6H), 10.93 (NH-keto form, s., 1H), 14.33 (OH-enol form, s., 1H). <sup>13</sup>C{<sup>1</sup>H} NMR spectrum ( $\delta$ , ppm): 21.76–34.41 (cyclohexane carbons), 56.17 (OCH<sub>3</sub>), 114.34–131.14 (aromatic carbons), 153.17 (C=N), 163.11 (C=O). IR spectrum (v, cm<sup>-1</sup>): 3365 w.m v(NH); 3059 w v(C–H<sub>ar</sub>); 2986 w v<sub>as</sub>(C–H) of CH<sub>3</sub>; 2946 w v<sub>as</sub>(C–H) of CH<sub>2</sub>); 2873 w v<sub>s</sub>(C–H) of CH<sub>3</sub>; 2833 w v<sub>s</sub>(C–H) of CH<sub>2</sub>; 1678 s v(C=O); 1602, 1575 m v(C=C<sub>ar</sub>; 1528 m v(C=N); 1486 m  $\delta$ (CH) of CH<sub>2</sub>; 1364 w  $\delta$ (CH) of CH<sub>3</sub>; 1240 v.s v(C–O).

Synthesis of I. To a solution of CHMBH (0.15 g, 0.367 mmol) in CH<sub>3</sub>CN (40 cm<sup>3</sup>) was added a solution of HgCl<sub>2</sub> (0.1 g, 0.367 mmol) in CH<sub>3</sub>CN (5 cm<sup>3</sup>). The solution was not stirred, and after leaving undisturbed for 1 day, yellow crystals were deposited. The crystals were removed by filtration, washed with CH<sub>3</sub>CN and dried in vacuo. The yield was 0.2 g (78%), m.p. = 214–216°C.

For (C<sub>22</sub>H<sub>24</sub>N<sub>4</sub>O<sub>4</sub>Cl<sub>2</sub>Hg)<sub>2</sub>

anal. calcd., %:	C, 38.9;	N, 8.2;	Н, 3.6;	Hg, 29.5.
Found, %:	C, 38.7;	N, 8.1;	H, 3.8;	Hg, 29.1.

<sup>1</sup>H NMR spectrum (δ, ppm): cyclohexane protons— 1.80 (CH<sub>2</sub>, m., 4H), 2.91 (CH<sub>2</sub>, t., 4H,  $J_{HH} = 3.1$  Hz), aromatic protons—7.09 (CH, d., 4H,  $J_{HH} = 8.5$  Hz), 7.925 (CH, d., 4H,  $J_{HH} = 8.5$  Hz), other protons— 3.86 (OCH<sub>3</sub>, s., 6H), 11.54 (NH, s., 2H). <sup>13</sup>C{<sup>1</sup>H} NMR spectrum (δ, ppm): 21.21–32.56 (cyclohexane carbons), 54.41 (OCH<sub>3</sub>), 112.66–129.31 (aromatic carbons), 151.18 (C=N), 161.28 (C=O). IR spectrum (v, cm<sup>1</sup>): 3263 w.m v(NH); 3071 w v(C–H<sub>ar</sub>); 2972 w  $v_{as}$ (C–H) of CH<sub>3</sub>; 2946 w  $v_{as}$ (C–H) of CH<sub>2</sub>; 2879 w  $v_{s}$ (C–H) of CH<sub>3</sub>; 2840 w  $v_{s}$ (C–H) of CH<sub>2</sub>); 1657 s v(C=O); 1598, 1575 m v(C=C<sub>ar</sub>; 1528 m v(C=N); 1458 m δ(CH) of CH<sub>2</sub>); 1353 w δ(CH) of CH<sub>3</sub>; 1248 v.s v(C–O).

Synthesis of II [17]. To a solution of CHMBH (0.15 g, 0.367 mmol) in CH<sub>3</sub>CN (40 cm<sup>3</sup>) was added a solution of Cu(NO<sub>3</sub>)<sub>2</sub> · 2.5H<sub>2</sub>O (0.085 g, 0.367 mmol) in CH<sub>3</sub>CN (5 cm<sup>3</sup>). The solution was not stirred and the colour which was initially dark brown, slowly changed with time through dark brown, dark green, light green and finally bright green. Leaving the solution undisturbed produced blue prism crystals after 24 h. The crystals were removed by filtration, washed with CH<sub>3</sub>CN and dried in vacuo. The yield was 0.1 g (57%).

For C<sub>102</sub>H<sub>127</sub>N<sub>37</sub>O<sub>27</sub>Cu<sub>6</sub>

anal. calcd., %: C, 45.6; N, 19.3; H, 4.8; Cu, 14.2. Found, %: C, 45.4, N, 19.0; H, 4.6; Cu, 13.8.

Table 1. Crystallographic data and structure refinements for complex I

	*		
Chemical moiety	$(C_{22}H_{24}N_4O_4Cl_2Hg)_2(C_2H_3N)$		
Formula weight	1400.9		
Wavelength, Å	0.71073		
Crystal size, mm	$0.32 \times 0.26 \times 0.12$		
Crystal system	Triclinic		
Space group	$P\overline{1}$		
Unit cell dimensions:			
a, Å	11.2103(15)		
b, Å	11.8606(16)		
<i>c</i> , Å	19.223(3)		
$\alpha$ , deg	86.901(5)		
$\beta$ , deg	76.165(4)		
γ, deg	75.252(4)		
Volume, Å <sup>3</sup>	2399.9(6)		
Temperature, K	120(2)		
Reflections collected	51449		
Independent reflections $(R_{int})$	16148 (0.0268)		
Observed reflections with $I \ge 2\sigma(I)$	13435		
Absorption correction	Semi-empirical from equivalents		
Trans max/min	0.5013/0.2238		
Flack parameter	0.111(11)		
Refinement method	Full-matrix least-squares on $F^2$		
Final <i>R</i> indices $I > 2\sigma(I)$	$R_1 = 0.0245; wR_2 = 0.0481$		
<i>R</i> indices (all data)	$R_1 = 0.0360; wR_2 = 0.0515$		
Largest diff. peak and hole, $e \text{ Å}^{-3}$	1.801 and -1.164		

IR spectrum (v, cm<sup>-1</sup>): 3600–3300 br, v(OH); 3059 w v(C–H<sub>ar</sub>); 2989 w v<sub>as</sub>(C–H) of CH<sub>3</sub>; 2939 w  $v_{as}$ (C–H) of CH<sub>2</sub>; 2860 w  $v_{s}$ (C–H) of CH<sub>3</sub>; 2833 w  $v_{s}$ (C–H) of CH<sub>2</sub>; 1603, 1585 m v(C=C<sub>ar</sub>); 1510 s v(C=N); 1456 w  $\delta$ (CH) of CH<sub>2</sub>; 1360 m  $\delta$ (CH) of CH<sub>3</sub>; 1246 v.s v(C–O).

**X-ray crystallography.** A crystal of I was analyzed with a Bruker APEX II system using  $MoK_{\alpha}$  radiation. Data collection was carried out using APEX2 software [18]. Initial cell constants were found by small widely separated "matrix" runs. The data collection strategy was determined using COSMO [19]. Scan speed and scan widths were chosen based on scattering power and peak rocking curves. Data were collected at – 153°C using an Oxford Cryostream low-temperature

device. Unit cell constants and orientation matrix were improved by least-squares refinement of reflections thresholded from the entire dataset. Integration was performed with SAINT [20], using this improved unit cell as a starting point. Precise unit cell constants were calculated in SAINT from the final merged dataset. Lorenz and polarization corrections were applied. Multi-scan absorption corrections were performed with SADABS [21]. Data were reduced with SHELXTL [22]. The structure was solved by direct methods without incident. Hydrogen atoms were located in idealized positions and were treated with a riding model. All non-hydrogen atoms were assigned anisotropic thermal parameters. Refinements continued to convergence, using the recommended weight-

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Bond	$d, \mathrm{\AA}$	Bond	d, Å
Comp	olex A	Comp	plex B
Hg(1)–O(27)	2.674(2)	Hg(2)–O(27)	2.683(2)
Hg(1)-O(37)	2.652(2)	Hg(2)-O(37)	2.649(2)
Hg(1)–N(11)	2.452(2)	Hg(2)-N(11)	2.449(2)
Hg(1)-N(12)	2.446(2)	Hg(2)-N(12)	2.419(2)
Hg(1)–Cl(1)	2.4137(6)	Hg(2)-Cl(3)	2.3830(6)
Hg(1)–Cl(2)	2.3779(6)	Hg(2)-Cl(4)	2.4187(6)
C(11)–N(11)	1.291(3)	C(11)–N(11)	1.280(3)
C(12)-N(12)	1.281(3)	C(12)–N(12)	1.286(3)
C(27)–N(27)	1.381(3)	C(27)–N(27)	1.374(3)
C(37)-N(37)	1.376(3)	C(37)–N(37)	1.375(3)
C(27)–O(27)	1.211(3)	C(27)–O(27)	1.220(3)
C(37)–O(37)	1.218(3)	C(37)–O(37)	1.216(3)
C(11)–C(12)	1.480(4)	C(11)–C(12)	1.493(4)
C(21)–C(27)	1.487(4)	C(21)–C(27)	1.480(4)
C(31)-C(37)	1.478(4)	C(31)–C(37)	1.484(4)
N(11)–N(27)	1.362(3)	N(11)-N(27)	1.371(3)
N(12)-N(37)	1.365(3)	N(12)-N(37)	1.370(3)

Table 2. Selected bond lengths in I

ing schemes. The crystallographic data for I are summarized in Table 1. Selected bond lengths are listed in Table 2.

Supplementary material for structure I has been deposited with the Cambridge Crystallographic Data Centre (CCDC no. 1503398; deposit@ccdc. cam.ac.uk or http://www.ccdc.cam.ac.uk).

**Kinetic studies.** Kinetic studies for the reaction of CHMBH with HgCl<sub>2</sub> were performed using a Shimadzu UV-3101PC spectrophotometer. The experiments were conducted in air at 25.0°C. The wavelength used was  $\lambda = 410$  nm. Stock solutions of HgCl<sub>2</sub> and CHMBH were prepared in MeCN (freshly distilled from CaH<sub>2</sub> under an atmosphere of dinitrogen), and more dilute solutions were prepared from these stocks. The absorbance-time traces were fitted to exponential curves using the Applied Photophysics software. The observed rate constants ( $k_{obs}$ ) are the average of at least three experiments. The error bars presented in the figures show a 10% reproducibility. All experiments were performed under pseudo firstorder conditions with the concentration of CHMBH in an excess over the concentration of the metal ion [23]. The dependence on the concentration of CHMBH was determined from plots of  $k_{obs}$  versus [CHMBH].

## **RESULTS AND DISCUSSION**

CHMBH was prepared by the condensation reaction between 1,2-cyclohexanedione and 4-methoxybenzhydrazide in methanol. The reaction of CHMBH with HgCl<sub>2</sub> or Cu(NO<sub>3</sub>)<sub>2</sub> · 2.5H<sub>2</sub>O in the same conditions have been shown to produce different type of complexes. The reaction of equimolar amount of CHMBH and HgCl<sub>2</sub> in acetonitrile and ambient conditions produced a mononuclear complex I. While, the reaction of equimolar amount of CHMBH and Cu(NO<sub>3</sub>)<sub>2</sub> · 2.5H<sub>2</sub>O in acetonitrile and ambient conditions proceeds through a variety of colour changes and the ultimate isolated product is the trinuclear Cu(II) cluster II [17]. Synthetic routes for I and II are shown in Scheme 1:



A = MeCN,  $B = NO_3$  (bridge),  $C = NO_3$  (monodentate)

#### Scheme 1.

Mass spectrum of CHMBH showed the parent ion peak at m/z = 409, which corresponds to M<sup>+</sup> (Fig. 1).

The <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra of CHMBH and I displayed signals corresponding to the various proton and carbon nuclei (see Experimental and Fig. 2). Moreover, in the <sup>1</sup>H NMR spectrum of CHMBH (Fig. 2a), two singlet signals are observed at 10.93 and 14.33 ppm. These signals are assigned to the protons of NH and OH groups, respectively, consistent with the keto-enol tautomerism of CHMBH [17]. In the <sup>1</sup>H NMR spectrum of I (Fig. 2b), the signal belong to the proton of OH group (enol form) was disappeared. This observation indicate that no delocalization will further occur between C=O and C–N groups, because of the

coordination of C=O to  $Hg^{2+}$  through oxygen atom. This was further confirmed by X-ray crystallography.

In order to study the binding mode of the ligand CHMBH to the mercury or copper atom, the IR spectrum of the free ligand was compared with the spectra of compounds I and II. The IR spectrum of CHMBH shows three characteristic bands at (3365, 1678, and 1528 cm<sup>-1</sup>). These can be assigned to the stretching vibrations of NH, C=O, and C=N groups, respectively [24]. In the spectra of I and II, the following aspects have been observed: (i) the v(C=O) mode at 1678 cm<sup>-1</sup> which was observed in the spectrum of CHMBH is found to shift to lower wave number in the spectrum of I (1657 cm<sup>-1</sup>), which may indicats the coordination of (C=O) to Hg<sup>2+</sup> ion; while in the spec-



Fig. 1. Mass spectrum of CHMBH.

trum of **II**, this mode is completely disappeared, indicating the enolization of (C=O) followed by deprotonation and complexation with copper ions; (ii) the v(C=N) mode of free ligand at 1528 cm<sup>-1</sup> is found to shift to lower wave number in the spectrum of **II** (1510 cm<sup>-1</sup>), while no change in the position was observed for this mode in the spectrum of **I**. The details of the bands and their assignments can be found in Experimental part.

The spectrum of CHMBH exhibited two absorption peaks at 274 ( $v_{max} = 14200$ ) and 338 nm ( $v_{max} =$ 7800 dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>) attributable to the ( $\pi$ - $\pi$ \*) and  $(n-\pi^*)$  transitions, respectively. The spectra of I and II caused bathochromic shift of ligand band related to the  $(\pi - \pi^*)$  transition. This band was appeared at 335  $(v_{max} = 18200)$  and 320 nm  $(v_{max} = 18000 \text{ dm}^3 \text{ mol}^{-1})$  $cm^{-1}$ ) for I and II, respectively. No band related to (*n*- $\pi^*$ ) transition could be clearly observed in the spectrum of **II**. The band may be hidden by  $(\pi - \pi^*)$  band. But in the spectrum of I a shoulder with low intensity is detected at 430 nm ( $v_{max} = 1180 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ), which can be attributed to this transition. The appearance of new medium intensity band at lower wave numbers 385 ( $v_{max} = 11000$  and 373 nm ( $v_{max} =$  $10800 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) for I and II, respectively, were observed slightly separated from the intraligand ( $\pi$ - $\pi^*$ ) band. These bands were attributed to charge transfer transition. A further broad band with low extinction coefficient is observed in the visible and near IR regions (580–1000 nm,  $v_{max} = 1600 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) in the spectrum of II. This broad band was assigned to ligand field d-d transitions. No ligand field transitions are observed in the spectrum of I because of filled *d*-orbital [25–27].

The X-ray structure of I is shown in Fig. 3, which consist of two independent complexes: A and B (the

two complexes have almost the same structure). The structure clearly shows that CHMBH acts as a quadridentate ligand with the two imine nitrogen atoms and two oxygen atoms coordinating to the metal. The CHMBH ligand is effectively planar, presumably because of the inflexibility in this ligand due to the extensive multiple bonding. The overall geometry is best described as octahedral (Hg is six coordinated) with the two imine nitrogen atoms and the two oxygen atoms of the CHMBH ligand occupying the basal positions and two chloro ligand occupying the apical site. Previous studies [9] on other Schiff base benzohydrazide complexes have reported the X-ray crystal structures of  $[Ni(benzohydrazone-2H^+)]$  in which the Schiff base benzohydrazone ligand (BBH) is deprotonated at the hydrazide atoms. BBH has the following structure:



Thus, in the structure of [Ni(BBH)], the average of the two C–N hydrazide bond lengths is 1.329 Å and the average C–O bond length is 1.299 Å. A comparison with the analogous bond lengths for [Hg(CHMBH)Cl<sub>2</sub>] presented in Table 2 shows that the C–O distance in the CHMBH complex is significantly shorter than in the deprotonated BBH complex. Similarly, the C–N hydrazide bond length in the CHMBH complex is appreciably longer than in the BBH complex. These observations indicate that, whilst there is delocalisation in the BBH ligand, and both the C–N and C–O bonds have partial double bond character, in the CHMBH ligand, the C–O bond has more double bond character and the C–N



Fig. 2. <sup>1</sup>H NMR spectra of CHMBH (a) and I (b).

(hydrazide) bond more single bond character. This was further confirmed by <sup>1</sup>HNMR spectroscopy.

Similarly, the asymmetric unit of II contains two independent molecules (Fig. 4)—A and B, respec-

tively [17]. But the structure of these molecules is completely different from that of **I**. The structure of each molecule comprises a triangle of Cu(II) atoms, centered around  $\mu_3$ -OH, to form {Cu<sub>3</sub>( $\mu_3$ -OH)} motif.

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Fig. 3. Ball and stick representation of the two independent complexes A (a) and B (b) in I.

The {Cu<sub>3</sub>( $\mu_3$ -OH)} core is supported by three triazole benzamide ligands [17].

The experimental powder diffraction and the calculated pattern from the crystal data of **I** show a close correspondence.

Thermal thermograms (TG and DTG) of I and II are illustrated in Figs. 5a and 5b, respectively. The curve of II shows significant weight loss at the range  $50-200^{\circ}$ C, which revealed to the presence of hydrate water and coordinated acetonitrle mole-

cules. No weight loss could be detected in the thermgram of I at this range of temperatures. These facts get in agreement with the X-ray single crystal data for the structures of I and II.

Our previous studies on Schiff base thiosemicarbazone complexes,  $[Cd(CHMTSC)(NO_3)]^+$  (III) [15] and  $[Cd(PHMTSC-2H^+)]$  (IV) [16] have reported the kinetics of the reactions of CHMTSC or PHMTSC with Cd<sup>2+</sup> ion:



[Cd(PHMTSC-2H<sup>+</sup>)]

The rate constant of the reactions were determined and the mechanism of the formation of the complexes



 $[Cd(CHMTSC)(NO_3)]^+$ 

have been proposed. In the current work, the kinetic of the reaction of CHMBH with  $Hg^{2+}$  has been investi-



Fig. 4. The structures of the two independent complexes A (a) and B (b) in II.

gated (Table 3). This study aimed to (i) determine the rate constant of the reaction; (ii) propose a mechanism of the formation of complex I; (iii) compare the results with that of our previous studies II-IV. The reactions were studied under pseudo-first-order con-

ditions with [CHMBH]  $\geq 10[\text{Hg}^{2+}]$ , using UV-Vis spectrophotometer technique, monitoring the reaction at  $\lambda = 410$  nm. The experimental trace can be fitted to a single exponential curve (Fig. 6), indicating that the reaction exhibits a first-order dependence on

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Fig. 5. Thermographmetric analyses of I (a) and II (b).

the concentration of Hg<sup>2+</sup>. This conclusion is confirmed in studies where the concentration of Hg<sup>2+</sup> was varied in the range 0.2–1.0 mmol dm<sup>-3</sup> with [CHMBH] = 10 mmol dm<sup>-3</sup>, but the values of the observed  $k_{obs}$  for each reaction did not change (Table 3). Consistent with our previous studies [15, 16], the dependence of  $k_{obs}$  on the concentration of CHMBH, exhibiting a first-order dependence on the concentration of CHMBH, as typified by the plot shown in Fig. 6 and the corresponding rate law in Eq. (1).

$$-d[Hg^{2+}]/dt = k_a[CHMBH][Hg^{2+}],$$
(1)

$$-d[Hg^{2+}]/dt = k_1 k_2 [CHMBH][Hg^{2+}]/k_{-1} [MeCN] + k_2 [CHMBH],$$
(2)

$$-d[Hg^{2+}]/dt = k_1 k_2 [CHMBH][Hg^{2+}]/k_{-1} [MeCN].$$
(3)

A proposed mechanism for the formation of I from the reaction of  $Hg^{2+}$  with CHMBH in MeCN at 25°C

consistent with the observed kinetics is shown in Scheme 2:



Scheme 2.

As in our previous studies [15, 16] and in line with other studies on chelate formation [28], the initial binding of CHMBH to  $[Hg(NCMe)_n]^{2+}$  by replacement of one of the coordinated MeCN molecules can be proposed to be the rate-limiting step of the chelate formation. The usual intimate mechanism for such a reaction is dissociative and involves initial dissociation of a coordinated solvent from  $[Hg(NCMe)_n]^{2+}$ , generating  $[M(NCMe)_{(n-1)}]^{2+}$  containing a vacant site at which CHMBH can bind as shown in Scheme 2. The full rate law for this mechanism is shown in Eq. (2) and indicates that, over a large concentration range of CHMBH, the kinetics would exhibit a non-linear dependence on concentration of CHMBH. However, when the concentration of CHMBH is small,  $k_{-1}$  $[MeCN] > k_2$  [CHMBH] the rate law would simplify to that shown in Eq. (3), which is of the same form as observed experimentally in Eq. (1). For the reaction studied, the value of  $k_a = k_1 k_2 / k_{-1}$  [MeCN] is  $2.0 \times 10^{-4}$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>, which is  $3.1 \times 10^{6}$  times less than that of  $[Cd(CHMTSC)(NO_3)]^+$  (III) and  $[Cd(PHMTSC-2H^+)]$  (IV) (Table 4); i.e., the reaction of CHMBH with  $Hg^{2+}$  is  $3.1 \times 10^6$  times slower than the reactions of CHMTSC or PHMTSC with Cd<sup>2+</sup>. This can be attributed to the Hard-Soft Acid-Base concept (in case of  $[Cd(CHMTSC)(NO_3)]^+$  and  $[Cd(PHMTSC-2H^+)]$ , S atom is soft base and  $Cd^{2+}$  is soft acid, while in case of [Hg(CHMBH)], O atom is hard base and  $Hg^{2+}$  is soft acid) [29–32].

Table 3. Kinetic data for the reaction of  $Hg^{2+}$  and CHMBH in MeCN at 25°C

$[\mathrm{Hg}^{2+}],$ mmol dm <sup>-3</sup>	[CHMBH], mmol dm <sup>-3</sup>	$k_{\rm obs},{ m s}^{-1}$
0.2	2.0	$7.0 \times 10^{-7}$
	4.0	$10.6 \times 10^{-7}$
	6.0	$14.5 \times 10^{-7}$
	8.0	$21.0 \times 10^{-7}$
	10.0	$23.2 \times 10^{-7}$
0.5	10.0	$24.1 \times 10^{-7}$
1.0	10.0	$23.7 \times 10^{-7}$



**Fig. 6.** Typical kinetic data for the reactions of Hg<sup>2+</sup> with CHMBH in MeCN at 25°C. (a) A typical experimental absorbancetime curve when  $[Hg^{2+}] = 0.2 \text{ mmol dm}^{-3}$  and  $[CHMBH] = 2 \text{ mmol dm}^{-3}$ , ((—) is the experimental data and (……) is the fit, defined by the equation  $A_t = -0.103 \text{ e}^{(-t/4.907)+0.115}$ ); (b) the first-order dependence of  $k_{obs}$  on [CHMBH] (error bars show 10% reproducibility; straight line fit to the data is that defined by the equation  $k_{obs} = 2.0 \times 10^{-4}$  [CHMBH]).

Our previous study [17] reports the kinetisc of the reaction of CHMBH with Cu<sup>2+</sup>. It is evident from the colour changes observed during its synthesis that **II** is formed in a series of steps. Whilst the synthesis is performed using equimolar amounts of Cu(NO<sub>3</sub>)<sub>2</sub> · 2.5H<sub>2</sub>O and CHMBH, the kinetic studies have been performed under a range of conditions ([Cu<sup>2+</sup>]  $\geq$  [CHMBH] and [CHMBH] > [Cu<sup>2+</sup>]) using stopped-flow spectrophotometry, monitoring the reaction at  $\lambda = 410$  nm. Irrespective of the conditions, the reac-

tion occurs in three distinct phases and the kinetics of each phase have been determined.

The reaction is characterised by an intial absorbance increase (phase 2) followed by an absorbance decrease (phase 3). Phase 1 has occurred in the dead-time of the stopped-flow apparatus. Typical stopped-flow absorbance-time traces are shown in Fig. 7. The rate constant of the reaction was determined and the proposed mechanism for the reaction of  $Cu^{2+}$  with CHMBH in MeCN to form complex II has been given in Scheme 3:

Metal ion $(M^{2+})$	Ligand	$k_{\rm a}/{ m dm^3~mol^{-1}~s^{-1}}$	Reference
Hg	СНМВН	$2.0 \pm 0.5  imes 10^{-4}$	This work
Cd	CHMTSC	$6.2\pm0.5\times10^2$	[15]
Cd	PHMTSC	$6.2\pm0.5\times10^2$	[16]

Table 4. Rate constant details of different reactions in MeCN at 25°C

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Scheme 3.

 $[Cu_3(\mu\text{-OH})(CTMB)_3(NO_3)_2(NCMe)_2]$ 



**Fig. 7.** Absorbance-time curves for the reaction of Cu<sup>2+</sup> (0.60 mmol dm<sup>-3</sup>) with CHMBH (0.5 mmol dm<sup>-3</sup>) in MeCN at 25.0°C ( $\lambda = 410$  nm): (a) absorbance-time curve for phase 2 of the reaction; (b) absorbance-time curve for the phase 3 (final phase) of the reaction. The curve fit is that defined by the equations A<sub>t</sub> = 1.13 - 0.90 e<sup>-12.2t</sup> (a) and A<sub>t</sub> = 0.576 + 0.558 e<sup>-0.009t</sup> (b). The experimental trace is shown in black and the exponential fit is the grey line.

The study revealed that the three phases observed in the formation of **II** could reasonably correspond to: (i) the bidentate (or possibly tridentate) coordination of CHMBH to  $Cu^{2+}$  (phase 1); (ii) chelation of the bidentate coordinated CHMBH (phase 2) and (iii) the oxidation of the coordinated hydrazone (by Cu(II)) to form the triazole (D) and, ultimately, **II** (phase 3) (for more details, see reference 17). The comparison shows that the stories of the formation of **I** and **II** are completely different!

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