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Copper(II) and zinc(II) complexes with 2-benzoylpyridine-methyl hydrazone

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ABSTRACT

2-Benzoylpyridine-methyl hydrazone (HBzMe) has been obtained as well as its copper(II) [Cu(HBz-Me)Cl₂] (1) and zinc(II) [Zn(HBzMe)Cl₂] (2) complexes. Upon re-crystallization in 1 – 9 DMSO:acetone conversion of 1 into dimeric [Cu(BzMe)Cl₂] (1a) occurred. The crystal structures of HBzMe, 1, 1a, and 2 were determined. HBzMe adopts the ZE conformation in the solid. In all complexes the hydrazone adopts the *E* configuration to attach to the metal through the N_{py}–N2–O chelating system. In 1 and 2 a neutral hydrazone coordinates to the metal center while in 1a deprotonation occurs with coordination of an anionic ligand. 1a presents a dimeric structure, having two copper(II) ions per asymmetric unit. Two chlorides are also present in the copper coordination sphere, which act as bridging ligands and connect the copper centers to each other.

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1. Introduction

Hydrazones are a versatile class of compounds with innumerous chemical as well as pharmacological applications. In fact, hydrazones have shown to possess antimicrobial, anticonvulsant, analgesic, anti-inflammatory, and antitumoral properties [1–3]. Moreover, aromatic hydrazone molecules dispersed in a binder polymer are used as the main constituent of electrophotographic photoreceptors of laser printers due to their excellent hole-transporting properties and relatively simple synthesis [4]. Also, di-2-pyridyl ketone benzoyl hydrazone (dpkbh) is widely used as a sensitive analytical reagent for the determination of trace amounts of metal ions in solutions [5,6]. Recently hydrazone-based molecular glasses for solid-state dye-sensitized solar cells have been obtained [7].

Metal complexes of hydrazones proved to have potential applications as catalysts [8], luminescent probes [9], and molecular sensors [10]. In addition, it has been recently shown that hydrazones such as pyridoxal isonicotinoyl hydrazone analogues are effective iron chelators *in vivo* and *in vitro*, and may be of value for the treatment of iron overload [11]. Furthermore, some 2-formylpyridinederived hydrazones which behave as iron chelators were suggested as therapeutic agents for the treatment of neurodegenerative disorders [12].

In the present work 2-benzoylpyridine methyl hydrazone (HBzMe, Fig. 1) and its copper(II) and zinc(II) complexes were pre-

pared. Spectral and structural investigations on the studied compounds were performed.

2. Experimental

2.1. Materials and equipment

Partial elemental analyses were performed on a Perkin–Elmer CHN 2400 analyzer. Infrared spectra were recorded on a Perkin–Elmer FT-IR Spectrum GX spectrometer using CsI/nujol; an YSI model 31 conductivity bridge was employed for molar conductivity measurements. Electronic spectra were acquired with a Hewlett–Packard 8453 spectrometer in dimethyl formamide (DMF) solutions using 1 cm cells. NMR spectra were obtained at room temperature with a Brucker DPX-200 Avance (200 MHz) spectrometer using deuterated dimethyl sulfoxide (DMSO- d_6) as the solvent and tetramethylsilane (TMS) as internal reference. Crystal structures were investigated using single-crystal X-ray diffraction methods. Data were collected at room temperature on a Kappa CCD diffractometer working in the φ and ω scan mode.

2.2. X-ray cristallography

Crystal data, data collection procedure, structure determination methods and refinement results are summarized in Table 1 [13– 17]. The ligand hydrogen atoms were included in the molecular models at stereo-chemical positions and refined with the riding model. The methyl H-atoms were optimized by treating them as rigid group allowed to rotate around the corresponding C—C bond.

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E configuration

Z configuration

Fig. 1. Structural representation for 2-benzoylpyridine-methyl hydrazone (HBzMe).

The water hydrogen atoms of complex **1** were located in a difference Fourier map and refined at their found positions with Ow-H and H...H distances restrained to target values of 0.86(1) and 1.41(1) Å, respectively.

2.3. Syntheses of 2-benzoylpyridine-methyl hydrazone (HBzMe)

2-Benzoylpyridine-methyl hydrazone (HBzMe) was prepared by mixing equimolar amounts (1.0 mmol) of 2-benzoylpyridine with methyl hydrazide in methanol with addition of three drops of acetic acid as catalyst. The reaction mixture was kept under reflux for 6 h. After cooling to room temperature the resulting solid was filtered off, washed with ethanol and ether and dried *in vacuo*.

2.3.1. 2-Benzoylpyridine-methyl-hydrazone (HBzMe)

Color: white. Yield: 30% M.P.: 96.8–99.3 °C. Selected IR bands (cm⁻¹): v(C=O) 1663 s, v(C=N) 1585 m; δ (py) 620 m. UV-vis

Table 1

Crystal data and refinement results for HBzMe, [Cu(HBzMe)Cl₂]·H₂O (1), [Cu(BzMe)Cl₂ (1a) and [Zn(HBzMe)Cl₂] (2).

Compound	HBzMe	1	1a	2
Empirical formula Formula weight Crystal system Space group	C ₁₄ H ₁₃ N ₃ O 239.27 Orthorhombic Pna2 ₁ (#33)	$C_{14}H_{15}Cl_2CuN_3O_2$ 391.73 Monoclinic $P2_1/a (#14)$	C ₂₈ H ₂₄ Cl ₂ Cu ₂ N ₆ O ₂ 674.51 Monoclinic <i>P</i> 2/ <i>n</i> (#13)	$C_{14}H_{13}Cl_2N_3OZn$ 375.54 Monoclinic $P2_1/n$ (#14)
Unit cell dimensions ^a a (Å) b (Å) c (Å) α (°) β (°) γ (°) Volume (Å ³) Z, density calc. (Mg/m ³) Absorption coefficient (mm ⁻¹) F(000) Crystal size (mm) Crystal color, shape	7.7909(4) 15.285(1) 10.6247(4) 90.00 90.00 90.00 1265.2(1) 4, 1.256 0.082 504 0.20 \times 0.16 \times 0.12 Colorless, prism	$\begin{array}{l} 8.4631(2)\\ 21.6179(8)\\ 9.3480(3)\\ 90.00\\ 104.132(2)\\ 90.00\\ 1658.50(9)\\ 4, 1.569\\ 1.647\\ 796\\ 0.31 \times 0.27 \times 0.11\\ Green, prism \end{array}$	7.3876(5) 13.323(1) 13.7890(1) 90.00 92.556(5) 90.00 1355.8(2) 2, 1.652 1.805 684 $0.28 \times 0.06 \times 0.05$ Red, prism	11.669(1) 11.483(1) 11.750(1) 90.00 98.13(1) 90.00 1558.6(2) 4, 1.600 1.919 760 0.22 \times 0.13 \times 0.03 Colorless, plate
Diffractometer, scan Rad., graph. Monoch.	KappaCCD/ ϕ and ω Mo K α , λ = 0.71073 Å	KappaCCD/ ϕ and ω Mo K α , λ = 0.71073 Å	KappaCCD/ ϕ and ω Mo K α , λ = 0.71073 Å	KappaCCD/ $φ$ and $ω$ Mo Kα, $λ$ = 0.71073 Å
ϑ range for data coll. (°) Index range (ϑ) Completeness (to $\vartheta = 26^{\circ}$) Reflections collected/unique (R_{int}) Absorption correction Max. and min. transm. Obs. Refls.[$I > 2\sigma(I)$]	$\begin{array}{l} 3.51-26.00\\ -9\leqslant h\leqslant 9,-18\leqslant k\leqslant 18,\\ -13\leqslant l\leqslant 13\\ 99.4\%\\ 2335/1303\; [R(int)=0.0151]\\ None\\ 0.990-0.984\\ 1157 \end{array}$	3.12-26.00 $-10 \le h \le 9, -24 \le k \le 26,$ $-11 \le l \le 8$ 99.1% 10367/3239 [R(int) = 0.0375] Numerical [13] 0.840-0.629 2818	3.06-25.99 $-9 \le h \le 8, -14 \le k \le 16,$ $-16 \le l \le 16$ 99.7% 6797/2665 [R(int) = 0.0703] Numerical [13] 0.915-0.632 1819	2.91–25.99 $-14 \le h \le 10, -14 \le k \le 10,$ $-14 \le l \le 14$ 99.1% 7946/3043 [<i>R</i> (int) = 0.0791] Numerical [13] 0.933–0.729 2220
Data collection Data reduction ^b Structure solution ^c Structure refinement ^d Refinement method	COLLECT [14] DENZO and SCALEPACK [15] SHELXS-97 [16] SHELXL-97 [17] Full-matrix least- squares on F ²	COLLECT [14] DENZO and SCALEPACK [15] SHELXS-97 [16] SHELXL-97 [17] Full-matrix least- squares on F ²	COLLECT [14] DENZO and SCALEPACK [15] SHELXS-97 [16] SHELXL-97 [17] Full-matrix least- squares on F ²	COLLECT [14] DENZO and SCALEPACK [15] SHELXS-97 [16] SHELXL-97 [17] Full-matrix least- squares on F ²
Weights, w Goodness-of-fit on F^2 Data/restraints/parameters $R_1(obs)$, $R(all)^e$ $wR_2(obs)$, $wR_2(all)^e$ Extinction coefficient Largest peak and hole (e Å ⁻³)	$\begin{split} \sigma^2(F_0^2) &+ (0.076P)^2 + 0.04P]^{-1}, \\ P &= [\text{Max}(F_0^2, 0) + 2F_c^2]/3 \\ 1.045 \\ 1303/1/165 \\ 0.0369, 0.1009 \\ 0.0424, 0.1067 \\ 0.07(1) \\ 0.137 \text{ and } -0.121 \end{split}$	$\sigma^{2}(F_{0}^{2}) + (0.044P)^{2} + 0.79P]^{-1},$ $P = [Max(F_{0}^{2}, 0) + 2F_{c}^{2}]/3$ 1.034 3239/3/208 0.0311, 0.0381 0.0820, 0.0867 - 0.268 and -0.381	$\sigma^{2}(F_{0}^{2}) + (0.039P)^{2}]^{-1},$ $P = [Max(F_{0}^{2}, 0) + 2F_{c}^{2}]/3$ 0.986 2665/0/182 0.0391, 0.0715 0.0843, 0.0959 - 0.351 and -0.585	$\sigma^{2}(F_{0}^{2}) + (0.048P)^{2} + 0.50P]^{-1},$ $P = [Max(F_{0}^{2}, 0) + 2F_{c}^{2}]/3$ 1.020 3043/0/191 0.0398, 0.0618 0.0942, 0.1056 - 0.294 and -0.504

^a Least-squares refinement of the angular settings for 2335 reflections in the $3.51 < \vartheta < 26.00^{\circ}$ range for HBzMe, 10367 reflections in the $3.12 < \vartheta < 26.00^{\circ}$ range for 1, 6797 reflections in the $3.06 < \vartheta < 25.99^{\circ}$ range for 1 and 7946 reflections in the $2.91 < \vartheta < 25.99^{\circ}$ range for 2.

^b Corrections: Lorentz, polarization, extinction (HBzMe) and absorption (1, 1a and 2).

^c Neutral scattering factors and anomalous dispersion corrections. Because this later correction was too small for HBzMe, its molecular chirality could not be determined reliably.

^d Structure solved by direct and Fourier methods. The final molecular model obtained by anisotropic full-matrix least-squares refinement of the non-hydrogen atoms. ^e *R* indices defined as: $R_1 = \Sigma ||F_0| - |F_c||/\Sigma |F_0|$, $wR_2 = [\sum w(F_0^2 - F_c^2)^2 / \sum w(F_0^2)^2]^{1/2}$.

Table 2

Selected bond distances (Å) and angles (°) in the molecular structures of HBzMe, $[Cu(HBzMe)Cl_2] \cdot H_2O$ (1), $[Cu(BzMe)Cl_2]$ (1a) and $[Zn(HBzMe)Cl_2]$ (2).

Bond lengths N1-C2 1.351(3) 1.356(3) 1.356(4) 1.346(4) C2-C7 1.288(3) 1.481(3) 1.488(4) 1.479(4) N2-C7 1.286(3) 1.279(3) 1.287(4) 1.294(4) N2-C8 1.361(3) 1.347(3) 1.322(4) 1.357(4) O-C8 1.217(3) 1.243(3) 1.271(4) 1.225(4) M-N1 - 2.028(2) 2.006(3) 2.159(3) M-N2 - 1.962(2) 1.951(3) 2.123(3) M-O1 - 2.028(2) 2.006(1) - M-C11 - 2.4628(7) - 2.2258(9) M-C12 - 2.723(1) - M#1-C1 - - 2.723(1) - M#1-C1 - - 2.723(1) - Bond angles - 1.14.8(2) 114.7(3) 115.9(3) C2-C7-N2 126.7(2) 124.9(2) 124.3(3) 126.3(3) C2-N1-M - 127.7(Attribution	HBzMe	1	1a	2
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Bond lengths				
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	N1-C2	1.351(3)	1.356(3)	1.356(4)	1.346(4)
N2-C7 1.286(3) 1.279(3) 1.287(4) 1.294(4) N2-N3 1.369(3) 1.361(2) 1.377(3) 1.367(4) N3-C8 1.361(3) 1.347(3) 1.322(4) 1.357(4) O-C8 1.217(3) 1.243(3) 1.271(4) 1.225(4) M-N1 - 2.028(2) 2.006(3) 2.159(3) M-N2 - 1.962(2) 1.951(3) 2.123(3) M-O1 - 2.062(2) 1.958(2) 2.313(2) Cu-C1 - - 2.260(1) - M-C11 - 2.4628(7) - 2.2258(9) M-C12 - 2.2098(6) - 2.234(1) Cu-C1#1 - - 2.723(1) - Bond angles - 2.723(1) - N1-C2-C7 117.8(2) 114.8(2) 114.7(3) 115.9(3) C2-C7-N2 126.7(2) 112.0(2) 112.0(3) 113.3(3) C2-N1-M - 127.7(2) 127.8(2) 128.8(2) N2-M2-OS 119.0(2) 120.4(2) 120.7(2	C2—C7	1.488(3)	1.481(3)	1.488(4)	1.479(4)
N2-N3 1.369(3) 1.361(2) 1.377(3) 1.367(4) N3-C8 1.361(3) 1.347(3) 1.322(4) 1.357(4) O-C8 1.217(3) 1.243(3) 1.271(4) 1.225(4) M-N1 - 2.028(2) 2.006(3) 2.159(3) M-N2 - 1.962(2) 1.951(3) 2.123(3) M-O1 - 2.062(2) 1.958(2) 2.313(2) Cu-Cl - - 2.260(1) - M-C12 - 2.2098(6) - 2.234(1) Cu-Cl#1 - - 2.723(1) - M#1-Cl - - 2.723(1) - Bond angles N1-C2-C7 117.8(2) 114.8(2) 114.7(3) 115.9(3) C2-C7-N2 126.7(2) 112.0(2) 112.0(3) 113.3(3) C7-N2-N3 120.2(2) 124.9(2) 124.2(3) 121.8(3) N3-C8-O 119.0(2) 120.4(2) 125.3(3) 120.3(3) C6-N1-M - 127.7(2) 127.8(2) 125.8(2) C7-N2-M - <td< td=""><td>N2-C7</td><td>1.286(3)</td><td>1.279(3)</td><td>1.287(4)</td><td>1.294(4)</td></td<>	N2-C7	1.286(3)	1.279(3)	1.287(4)	1.294(4)
N3-C8 $1.361(3)$ $1.347(3)$ $1.322(4)$ $1.357(4)$ O-C8 $1.217(3)$ $1.243(3)$ $1.271(4)$ $1.225(4)$ M-N1 - $2.028(2)$ $2.006(3)$ $2.159(3)$ M-N2 - $1.962(2)$ $1.951(3)$ $2.123(3)$ M-O1 - $2.062(2)$ $1.958(2)$ $2.313(2)$ Cu-Cl - - $2.209(6)$ - $2.2258(9)$ M-Cl2 - $2.2098(6)$ - $2.234(1)$ Cu-Cl#1 - - $2.723(1)$ - <i>M</i> =C2-C7 $117.8(2)$ $114.8(2)$ $114.7(3)$ $115.9(3)$ C2-C7-N2 $126.7(2)$ $112.0(2)$ $112.0(3)$ $113.3(3)$ C7-N2-N3 $120.2(2)$ $124.9(2)$ $124.2(3)$ $114.3(3)$ N2-N3-C8 $120.4(2)$ $123.3(3)$ $120.3(3)$ C6-N1-M - $127.7(2)$ $127.8(2)$ $125.8(2)$ C7-N2-M - $120.4(2)$ $113.3(2)$ $115.9(2)$ C7-N2-M - $120.6(2)$ $119.4(2)$ 117.4	N2-N3	1.369(3)	1.361(2)	1.377(3)	1.367(4)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	N3-C8	1.361(3)	1.347(3)	1.322(4)	1.357(4)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0–C8	1.217(3)	1.243(3)	1.271(4)	1.225(4)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	M—N1	-	2.028(2)	2.006(3)	2.159(3)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	M—N2	-	1.962(2)	1.951(3)	2.123(3)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	M-01	-	2.062(2)	1.958(2)	2.313(2)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Cu—Cl	-		2.260(1)	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	M—Cl1	-	2.4628(7)	-	2.2258(9
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	M—C12	-	2.2098(6)	-	2.234(1)
M#1-Cl - - 2.723(1) - Bond angles N1-C2-C7 117.8(2) 114.8(2) 114.7(3) 115.9(3) C2-C7-N2 126.7(2) 112.0(2) 112.0(3) 113.3(3) C7-N2-N3 120.2(2) 124.9(2) 124.2(3) 121.8(3) N2-N3-C8 120.4(2) 113.9(2) 107.8(3) 116.1(3) N3-C8-O 119.0(2) 120.4(2) 125.3(3) 120.3(3) C6-N1-M - 127.7(2) 127.8(2) 125.8(2) C2-N1-M - 113.4(2) 113.3(2) 115.9(2) C7-N2-M - 120.6(2) 119.4(2) 120.7(2) N3-N2-M - 114.5(1) 116.4(2) 114.1(2) N1-M-N2 - 78.02(7) 79.8(1) 74.1(1) N1-M-N1 - 153.45(7) 158.0(1) 144.04(9) N1-M-C11 - 97.46(6) - 100.77(8) N1-M-C12 -	Cu—Cl#1	-	-	2.723(1)	- ``
Bond angles N1-C2-C7 117.8(2) 114.8(2) 114.7(3) 115.9(3) C2-C7-N2 126.7(2) 112.0(2) 112.0(3) 113.3(3) C7-N2-N3 120.2(2) 124.9(2) 124.2(3) 121.8(3) N2-N3-C8 120.4(2) 113.9(2) 107.8(3) 116.1(3) N3-C8-O 119.0(2) 120.4(2) 125.3(3) 120.3(3) C6-N1-M - 127.7(2) 127.8(2) 125.8(2) C2-N1-M - 113.4(2) 113.3(2) 115.9(2) C7-N2-M - 120.6(2) 119.4(2) 120.7(2) N3-N2-M - 112.4(1) 111.2(2) 114.1(2) N1-M-N2 - 78.65(7) 79.8(1) 74.1(1) N2-M-O1 - 153.45(7) 158.0(1) 144.04(9) N1-M-C11 - 97.46(6) - 100.77(8) N1-M-C12 - 99.92(6) - 101.90(8) N2-M-C11 - 96.36(6) - 95.57(7) <td>M#1—Cl</td> <td>_</td> <td>-</td> <td>2.723(1)</td> <td>-</td>	M#1—Cl	_	-	2.723(1)	-
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Dand analas				
$\begin{split} & N1- = C2- C7 & 111, N(2) & 114, N(3) & 113, 13, 31 \\ & C2- C7- N2 & 126, C(2) & 112, 0(2) & 112, 0(3) & 113, 33 \\ & C2- N3- C8 & 120, 4(2) & 124, 4(2) & 124, 4(3) & 121, 8(3) \\ & N3- C8- O & 119, 0(2) & 120, 4(2) & 125, 3(3) & 120, 3(3) \\ & C6- N1- M & - & 127, 7(2) & 127, 8(2) & 125, 8(2) \\ & C2- N1- M & - & 113, 4(2) & 113, 3(2) & 115, 9(2) \\ & C7- N2- M & - & 113, 4(2) & 119, 4(2) & 120, 7(2) \\ & C7- N2- M & - & 114, 5(1) & 116, 4(2) & 117, 4(2) \\ & C8- O1- M & - & 114, 5(1) & 116, 4(2) & 117, 4(2) \\ & C8- O1- M & - & 112, 4(1) & 111, 12(2) & 114, 1(2) \\ & N3- N2- M & - & 114, 5(1) & 116, 4(2) & 117, 4(2) \\ & C8- O1- M & - & 112, 4(1) & 111, 12(2) & 114, 1(2) \\ & N3- N2- M & - & 114, 5(1) & 116, 4(2) & 117, 4(2) \\ & C8- O1- M & - & 112, 4(1) & 111, 12(2) & 114, 1(2) \\ & N3- N2- M & - & 114, 5(1) & 116, 4(2) & 117, 4(2) \\ & C8- O1- M & - & 112, 4(1) & 111, 12(2) & 114, 1(2) \\ & N1- M- N1- N- N1- N$	Bona angles	117 0(2)	1140(2)	1147(2)	115 0(2)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	NI = C2 = C7	117.8(2)	114.8(2)	114.7(3)	112.9(3)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C2-C7-N2	126.7(2)	112.0(2)	112.0(3)	113.3(3)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C/N2N3	120.2(2)	124.9(2)	124.2(3)	121.8(3)
$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	N2-N3-C8	120.4(2)	113.9(2)	107.8(3)	116.1(3)
$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	N3-C8-0	119.0(2)	120.4(2)	125.3(3)	120.3(3)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C6—N1—M	-	127.7(2)	127.8(2)	125.8(2)
$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	C2—N1—M	-	113.4(2)	113.3(2)	115.9(2)
$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	C7—N2—M	-	120.6(2)	119.4(2)	120.7(2)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	N3—N2—M	-	114.5(1)	116.4(2)	117.4(2)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C8-01-M	-	112.4(1)	111.2(2)	114.1(2)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	N1-M-N2	-	78.65(7)	79.8(1)	74.1(1)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	N2-M-01	-	78.02(7)	79.23(9)	71.05(9)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	N1-M-01	-	153.45(7)	158.0(1)	144.04(9
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	N1-M-Cl1	-	97.46(6)	-	100.77(8
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	N1-M-Cl2	-	99.92(6)	-	101.90(8
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	N2-M-Cl1	-	93.33(6)	-	131.18(8
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	N2-M-Cl2	-	161.39(6)	-	110.62(8
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	01-M-Cl1	-	96.36(6)	-	95.57(7)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	01-M-Cl2	-	98.15(5)	-	98.30(7)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Cl1-M-Cl2	-	105.23(3)	-	117.81(4
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	N2—Cu—Cl	-	-	169.39(8)	-
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	01–Cu–Cl	-	-	99.28(7)	-
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	N1—Cu—Cl	-	-	100.06(8)	-
01-Cu-Cl#1 - - 94.74(8) - N1-Cu-Cl#1 - - 95.48(8) - Cl-Cu-Cl#1 - - 90.34(3) - Cu-Cl-Cu#1 - - 89.66(3) -	N2-Cu-Cl#1	-	-	100.24(8)	-
N1CuCl#1 95.48(8) - ClCuCl#1 90.34(3) - CuClCu#1 89.66(3) -	01-Cu-Cl#1	-	-	94.74(8)	-
Cl—Cu—Cl#1 – – 90.34(3) – Cu—Cl—Cu#1 – – 89.66(3) –	N1-Cu-Cl#1	-	-	95.48(8)	-
Cu-Cl-Cu#1 89.66(3) -	Cl—Cu—Cl#1	-	-	90.34(3)	-
	Cu—Cl—Cu#1	-	-	89.66(3)	-

(DMF, cm⁻¹): 32890. ¹H NMR (200 MHz, DMSO- d_6) [δ (ppm)] main signals: 13.85 (*Z*), 12.77 (*E*) [s, 1H, N3H (*Z* and *E* isomers)]; 8.77 (*Z*), 8.57 (*E*) [d, 1H, H6 (*Z* and *E* isomers)]; 7.39 (*Z*), 8.01 (*E*) [d, 1H, H3 (*E* isomer)]; 7.78 (*Z* and *E*) [m, 2H, H4 (*Z* and *E* isomers)]; 7.36 (*Z*), 7.29 (*E*) [m, H5 (*Z* and *E* isomers)]; 2.16 (*Z*), 2.38 (*E*) [s, 3H, CH₃ (*Z* and *E* isomers)]; 1³C NMR (200 MHz, DMSO- d_6) [δ (ppm)] main signals: 174.3 (*Z*), 172.9 (*E*) [C8 (*Z* and *E* isomers)]; 152.3 (*Z*), 154.6 (*E*) [C2 (*Z* and *E* isomers)]; 148.8 (*Z*), 148.7 (*E*) [C6 (*Z* and *E* isomers)]; 144.3 (*Z*), 148.0 (*E*) [C7 (*Z* and *E* isomers)]; 137.2 (*Z*), 137.0 (*E*) [C4 (*Z* and *E* isomers)]; 125.8 (*Z*), 123.8 (*E*) [C5 (*Z* and *E* isomers)]; 124.0 (*Z*), 121.6 (*E*) [C3 (*Z* and *E* isomers)]; 20.7 (*Z*), 20.0 (*E*) [C9 (*Z* and *E* isomers)].

2.4. Syntheses of the zinc(II) and copper(II) complexes with HBzMe

The zinc(II) and copper(II) complexes (**1** and **2**) were obtained by refluxing an ethanol solution of HBzMe with the metal chloride (ZnCl₂ or CuCl₂·2H₂O) in 1:1 ligand-to-metal molar ratio (1.0 mmol). After cooling to room temperature the resulting solids were filtered off and washed with ethanol followed by diethylether and then dried *in vacuo*.



Fig. 2. Molecular plot of HBzMe showing the labeling scheme of the non-H atoms and their displacement ellipsoids at the 50% probability level.



Fig. 3. Molecular plot of monomeric $[{\rm Cu}({\rm HBzMe}){\rm Cl}_2]$ (1). Metal–ligand bonds are indicated by open lines.

2.4.1. Dichloro(2-benzoylpyridine-methyl-hydrazone)copper(II) [Cu(HBzMe)Cl₂] (1)

Green solid. Yield: 71%. Anal. Calc. (C₁₄H₁₃Cl₂CuN₃O): C, 44.99%; H, 3.51%; N, 11.24%. Found: C, 44.79%; H, 3.47; N, 11.17%. FW: 373.72 g mol⁻¹. Selected IR bands (cm⁻¹): *v*(C=O) 1630 m; *v*(C=N) 1600 m; *δ*(py) 646 m; *v*(Cu–N) 415 m. UV–vis (DMF, cm⁻¹): 34010, 26100, 22200 and 11173. Molar conductivity (1 × 10⁻³ mol L⁻¹, DMF): 16.28 Ω⁻¹ cm² mol⁻¹.

2.4.2. Dichloro(2-benzoylpyridine-methyl-hydrazone)zinc(II) [Zn(HBzMe)Cl₂] (**2**)

White solid; Yield: 80%. Anal. Calc. ($C_{14}H_{13}Cl_2N_3OZn$): C, 44.77%; H, 3.49%; N 11.19%. Found: C, 44.83%; H, 3.53%; N,



Fig. 4. Diagram showing dimeric [Cu(BzMe)Cl]₂ (1a). The molecular halves are related through a crystallographic inversion center.



Fig. 5. Molecular plot of [Zn(HBzMe)Cl₂] (2).

11.25%. FW: 375.57 g mol⁻¹. Selected IR bands (cm⁻¹): v(C=0) 1655 s; v(C=N) 1594 m; $\delta(p_y)$ 640 m; v(Zn-N) 412 m. UV-vis (DMF, cm⁻¹): 34250 and 27000. Molar conductivity (1 × 10⁻³ mol L⁻¹, DMF): 13.67 Ω^{-1} cm² mol⁻¹. ¹H NMR (200 MHz, DMSO- d_6) [δ (ppm)] main signals: 12.19 (s, 1H, N3H); 8.68 (d, 1H, H6); 7.76 (d, 1H, H3); 7.98 (t, 2H, H4); 7.32 (m, 1H, H5); 2.16 (s, 3H, CH₃). ¹³C NMR (200 MHz, DMSO- d_6) [δ (ppm)] main signals: 173.1 (C8); 151.5 (C2); 149.5 (C7); 149.1 (C6); 138.2 (C4); 124.9 (C5); 125.4 (C3); 20.4 (C9).

Crystals of HBzMe, **1**, $[Cu(BzMe)Cl]_2$, *bis*[(μ -chloro)-2-benzoylpyridine-methyl-hydrazonato)copper(II)] (**1a**) and **2** were obtained from a mixture of 1:9 DMSO-acetone and were stable in the air. Crystals of **1** and **1a** co-crystallized from the same DMSO-acetone solution. We were unable to obtain enough quantity of complex **1a** to perform any experiments other than crystal structure determinations.

3. Results and discussion

Microanalyses (powder) suggest the formation of $[Cu(HBz-Me)Cl_2](1)$ and $[Zn(HBzMe)Cl_2](2)$ in which the hydrazone coordi-

nates as a neutral ligand. The molar conductivity data reveal that the complexes are non-electrolytes, indicating that in both cases two chlorides are attached to the metal center, in accordance the proposed formulations.

3.1. Infrared spectra

The v(C=N) mode at 1585 cm⁻¹ in the spectrum of the free hydrazone shifts to 1600 cm⁻¹ in the spectrum of complex **1** and to 1594 cm⁻¹ in that of complex **2**, suggesting coordination of the azomethine nitrogen N2 [18].

The v(**C**=**O**) absorption at 1663 cm⁻¹ in the spectrum of the uncomplexed hydrazone shifts to 1630 and 1655 cm⁻¹ in the spectra of complexes **1** and **2**, respectively, in accordance with coordination through the carbonyl oxygen [18,19].

The pyridine in-plane deformation mode at 620 cm^{-1} in the spectrum of HBzMe shifts to 646 and 640 cm⁻¹ in those of complexes **1** and **2**, respectively, indicating coordination of the heteroaromatic nitrogen [18]. Therefore, the infrared data for the complexes indicate coordination of the hydrazones through the N_{pv}–N–O chelating system.

3.2. NMR spectra

The ¹H and ¹³CNMR assignments for HBzMe and its zinc(II) complex (**2**) in DMSO- d_6 are reported in Sections 2.2 and 2.3. The ¹H resonances were attributed based on chemical shifts, multiplicities and coupling constants. The carbon type (C, CH) was determined by using DEPT135 experiments. The assignments of the protonated carbons were made by 2D heteronuclear-correlated experiments (HMQC) using delay values which correspond to ¹J(C, H).

In the ¹H and ¹³C NMR spectra of HBzMe the signals of all hydrogens and carbons are duplicated suggesting the existence of the *E* and *Z* configurations in solution [20–24] (see Fig. 1). In fact, two signals of N3—H were observed at δ 13.85 and 12.77, which were attributed to the *Z* and *E* forms, respectively. In the first N3—H is hydrogen bonded to the pyridine nitrogen, while in the latter it is hydrogen bonded to the solvent [20–24]. Similarly, the signals of C8=O at δ 174.3 and 172.9 were attributed to the *Z* and *E* isomers, respectively.

In the ¹H and ¹³C NMR spectra of **2** only one signal was observed for all hydrogens and carbons. The signals of N3—H and C8=O were found at δ 12.15 and 173.1, respectively, indicating that the hydrazone adopts the *E* configuration in the complex as confirmed by crystal structure determinations. The signals of C7 and those of the pyridine carbons undergo shifts upon coordination. Therefore, the NMR spectra suggest coordination of HBzMe through the N_{py} —N2—O chelating system, forming a complex in which HBzMe adopts the *E* configuration.

3.3. Electronic spectra

In the electronic spectrum of HBzMe the $n-\pi^*$ transitions associated to the azomethine and carbonyl functions overlap at 32890 cm⁻¹ [18]. In the spectra of complexes **1** and **2** two absorptions attributed to these transitions were observed at 34010 and 26100 cm⁻¹ (**1**) and at 34250 and 27000 cm⁻¹ (**2**). In the spectrum of **1** a shoulder at 22200 cm⁻¹ is associated to a ligand-to-metal charge transfer transition and a broad new band at 11173 cm⁻¹ to a combination of ligand-field transitions [25,26].

3.4. Structural study of HBzMe, [Cu(HBzMe)Cl₂] (1) [Cu(BzMe)Cl₂ (1a) and [Zn(HBzMe)Cl₂] (2)

Table 2 shows selected bond distances and angles in the crystal structures of HBzMe, **1**, **1a** and **2**. Figs. 2–5 are ORTEP [27] drawings of the complexes.

HBzMe crystallizes in the ZE conformation (see Fig. 2). In the structures of 1 and 2 the copper(II) and zinc(II) ions in a fivefold environment are attached to a neutral hydrazone molecule acting as a tridentate ligand which binds the metal center through the pyridine and imine nitrogens, and the carbonyl oxygen. Two chloride ions occupy the remaining coordination positions. In complex 1 N1, N2, O and Cl2 occupy the basal plane of a distorted square pyramid, and Cl1 is located in the apical position. In 2 N2, Cl1 and Cl2 form the equatorial plane of a distorted trigonal bipyramid, and N1 and O occupy the axial positions. In dimeric [Cu(BzMe)Cl]₂ (1a) each copper(II) center in a distorted square pyramidal arrangement is attached to an anionic hydrazone and to two chloride ions which act as bridging ligands and connect the two copper(II) ions to each other [d(Cu-Cl) = 2.260(1) Å.d(Cu-Cl') = 2.723(1)Å]. Complex **1a** is centrosymmetric.

In all complexes, the hydrazone Pyr(C=N)N-(C=O) skeletal fragment defines a coordination plane [rms deviation of atoms from the least-squares plane of 0.045 Å (1), 0.086 Å (1a) and

0.052 Å (**2**)] with the metal ion laying close onto this plane [at 0.273(1) Å (**1**), 0.228(2) Å (**1a**) and 0.209(2) Å (**2**)]. The phenyl ring and the coordination plane subtend dihedral angles of 82.53 (7)° (**1**), 53.2 (10)° (**1a**) and 85.5 (1)° (**2**).

In HBzMe the C8—O1 bond distance is 1.217(3) Å while in complexes **1** and **2** this distance is 1.243(3) and 1.225(4) Å, respectively, due to the formation of the M—O bond which makes the C—O bond weaker. In complex **1a** the C8—O1 bond distance is 1.271(4) Å due to deprotonation at N3 which leads to a higher single bond character for C8—O. In HBzMe the N2—N3 and N3—C8 bond distances are 1.369(3) and 1.361(3) Å. These distances are 1.361(2) and 1.347(3) Å in **1**, and 1.367(4) and 1.357(4) Å in **2**. In complexes **1** and **2** Cu—L bonds are stronger than Zn—L bonds (see Table 2). In fact, while complex **1** exhibits ligand field stabilization energy (LFSE), in the case of **2**, the d¹⁰ configuration of Zn²⁺ leads to no LFSE. In **1a** N2—N3 and N3—C8 bond distances are 1.377(3) and 1.322(4) Å and the Cu—L distances are 2.006(3) Å (M—N1), 1.951(3) Å (M—N2), 1.958(2) Å (M—O), 2.260(1) Å (M—Cl), 2.723(1) Å (M—Cl#1) and 2.723(1) Å (M#1—Cl).

In going from HBzMe to **1**, **1a** and **2** the C2–C7–N2 angle undergoes a great variation from $126.7(2)^{\circ}$ to $112.0(2)^{\circ}$, $112.0(3)^{\circ}$ and $113.3(3)^{\circ}$, respectively, due to the change in configuration of the hydrazone, from *Z* when uncomplexed to *E* in the complexes. The C7–N2–N3 angle goes from $120.2(2)^{\circ}$ in HBzMe to $124.9(2)^{\circ}$, $124.2(3)^{\circ}$ and $121.8(3)^{\circ}$ in **1**, **1a** and **2**, due to the formation of the N1–M–N2 chelate ring. Similarly N2–N3–C8 changes from $120.4(2)^{\circ}$ in HBzMe to $113.9(2)^{\circ}$, $107.8(3)^{\circ}$ and $116.1(3)^{\circ}$ in **1**, **1a** and **2**, respectively, due to the formation of the N2–M–O1 chelate ring.

The N2—M—Cl2 and N2—M—Cl1 angles are $161.39(6)^{\circ}$ and $93.33(6)^{\circ}$ in **1** and $110.62(8)^{\circ}$ and $131.18(8)^{\circ}$ in **2** indicating that **1** adopts a distorted square pyramidal structure whereas **2** adopts a distorted trigonal bipyramidal arrangement. In fact the M—Cl1 and M—Cl2 distances are 2.2098(6) Å and 2.4628(7) Å in **1** and 2.2258(9) and 2.234(1) Å in **2** as a consequence of the presence of two electrons in the d_z^2 orbital in the first case, which makes the M—Cl bond longer as a consequence of repulsion along the *z* axis [28].

The [Cu(HBzMe)Cl₂]·H₂O (**1**) crystal is further stabilized by a net of N–H...Ow [d(N...Ow) = 2.740 Å, \angle (N–H...Ow) = 164.2°] and



Fig. 6. Crystal packing of 1 as seen down the *c*-axis. The *b*-axis is along the horizontal. H-bonds are indicated by dashed lines. The largest open disks are Cu(II) ions, the ones of intermediate size are chloride ions.



Fig. 7. Crystal packing of **2** as seen down the *a*-axis showing the H-bonded dimeric structure. The *b*-axis is along the vertical. H-bonds are indicated by dashed lines. The largest open disks are Zn(II) ions, the ones of intermediate size are chloride ions.

Ow—H...Cl [Ow...Cl1 distances of 3.152 and 3.202 Å, Ow—H...Cl1 angles of 167.30° and 169.07°, respectively] bonds. These are shown in the PLATON [I] [13] packing diagram in Fig. 6. Further details of the H-bonding structure are provided as Supplementary material.

The [Zn(HBzMe)Cl₂] (**2**) molecules are arranged in the lattice as centrosymmetric dimers. The complexes within a dimer are linked to each other by a pair of N—H...Cl bonds [d(N3...Cl2') = 3.422 Å, \angle (N3—H...Cl2') = 138.6°]. A view of this H-bonded structure is shown in Fig. 7.

4. Conclusions

2-Benzoylpyridine-methyl hydrazone (HBzMe, HL) forms [M(HL)Cl₂] complexes [M = Cu(II), Zn(II)] in which the hydrazone acts as a tridentate ligand and binds to the metal though the N_{py}–N–O chelating system. In [Cu(HBzMe)Cl₂] (1) the coordination geometry around the metal is distorted square pyramidal, with one chloride occupying the apical position. In [Zn(HBzMe)Cl₂] (2) the arrangement around the metal is distorted trigonal, with the pyridine nitrogen and the oxygen occupying the axial positions. Re-crystallization of 1 in 1:9 DMSO-acetone gives dimeric [Cu(BzMe)Cl₂ (1a) in which a tridentate N_{py}–N–O anionic ligand is attached to the metal center, along with two chlorides acting as bridging ligands and connecting the copper centers to each other.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2008.10.025.

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