

COPPER(II) COMPLEXES OF *o*-VANILLIN ACETYLHYDRAZONE (H₂L) AND THE SINGLE-CRYSTAL X-RAY STRUCTURE OF [Cu(HL)(H₂O)(HPZ)]·NO₃

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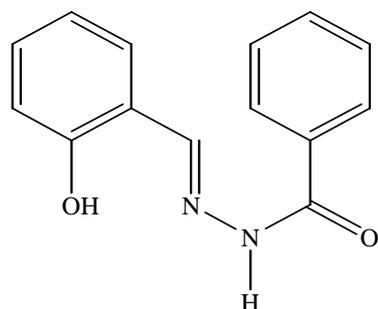
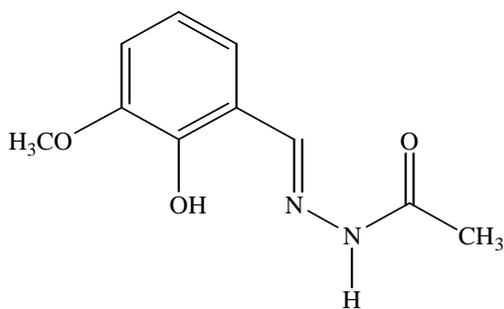
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ABSTRACT. A hydrazonic ligand, *o*-vanillin acetylhydrazone (H₂L) has been prepared and used as chelating agent towards copper(II) ion. The ligand acts like a tridentate ligand in the monodeprotonated (HL⁻) and dideprotonated (L²⁻) states. Monoanionic complexes [Cu(HL)(H₂O)]₂·2BF₄ and [Cu(HL)(Hpz)(H₂O)]·NO₃ have been isolated. After neutralization the complex [Cu(L)]₂·5/2H₂O is obtained. These complexes have been characterized by a range of physicochemical and spectroscopic studies. The X-ray crystal structure of the mononuclear complex [Cu(HL)(Hpz)(H₂O)]·NO₃ was also determined. This crystal is orthorhombic with the space group I₂₂₂, *a* = 13.417(3), *b* = 22.662(6), *c* = 22.518(5) Å, α = β = γ = 90° and *Z* = 8. The copper ion has a square-pyramidal geometry with the basal donors atoms from the tridentate ligand (ONO) and the pyrazole (N), the apical position being occupied by a coordinated water molecule weakly linked to the copper(II) center. The binuclear complexes exhibit interesting magnetic properties.

KEY WORDS: Copper(II) complexes, Tridentate ligand, *o*-Vanillin acetylhydrazone, X-Ray crystal structure

INTRODUCTION

In the last decade, a large number of copper(II) complexes have been prepared and structurally studied in attempt to mimic the potent inhibitor properties of DNA synthesis [1, 2]. H₂L (salicylaldehyde benzoylhydrazone) has been found to possess a bacterial activity [3]. The copper(II) complex of H₂L was shown to be more potent than the free ligand, suggesting that the metal center was the biologically active site. Analogous compounds have been investigated as drugs for genetic disorders such as thalassemia [4, 5]. The same behaviour has been observed for similar compounds obtained from ligands synthesized by the reaction of functionalized aldehydes and hydrazides [6, 7].



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This paper reports the synthesis and characterization of H₂L and related mono or dicationic copper(II) complexes. Mono and binuclear complexes have been synthesized and the single-crystal X-ray structure of the mononuclear adduct [$\{\text{Cu}(\text{HL})(\text{Hpz})(\text{H}_2\text{O})\}$].NO₃ has been determined. For the binuclear complexes, structures were proposed on the basis of spectroscopic and magnetic susceptibility studies.

EXPERIMENTAL

All the reagents were of commercial quality and were used without further purifications. Elemental analyses were carried out on a Carlo Erba Instrument CHNS-O EA 1108 elemental analyser. ¹H and ¹³C NMR were performed with a Bruker ARX 400 MHz instrument. IR spectra were recorded on a Nicolet 5SXC spectrophotometer as Nujol mulls or KBr pellets. The electronic transmittance spectra (acetonitrile solution of complexes) were recorded on a UV spectrophotometer model Jasco 5800 with double beam and quartz cells. Melting points were obtained with Büchi 530 melting point apparatus in open capillaries. Magnetic measurements were carried out by using a Metronique Ingegnerie SQUID M03 operating between 0 and 8 T in the range 2-300 K.

*Synthesis of *o*-vanillin acetylhydrazone H₂L (C₁₀H₁₂N₂O₃)*

To a solution of acetic hydrazide (3 g, 40.50 mmol) in 25 mL of absolute ethanol with few drops of glacial acetic acid, was added dropwise a solution of *o*-vanillin (6.16 g, 40.50 mmol) in 30 mL of absolute ethanol. Gentle refluxing was maintained for 2 h. 25 mL of ethanol were distilled and 20 mL of water added. After cooling the white product, which precipitate, obtained was filtered and washed with 50% ethanol/water (2 x 15 mL) and ether (2 x 15 mL) before drying in vacuo (yield 89%). ¹H NMR spectrum (CD₃CN) δ_H: 11.01 (1H, s, H–O), 8.25 (1H, s, H–C=N), 8.10 (1H, s, N–H), 6.80-7.11 (3H, m, H_{Ar}), 3.90 (3H, s, H₃C–O), 2 (3H, s, H₃C–C=O). ¹³C NMR spectrum (CD₃CN) δ_C: 166.83, 149.3, 149.2, 149, 123.50, 122.50, 120.53, 114.70, 56.81, 21.62.

Synthesis of [$\{\text{Cu}(\text{HL})(\text{H}_2\text{O})\}_2$].2BF₄ (A)

To a boiling degassed solution of H₂L (417 mg, 2.00 mmol) in 30 mL of ethanol, was added a solution of Cu(BF₄)₂·2H₂O (577 mg, 2.04 mmol) in 15 mL of degassed ethanol. This mixture was refluxed under N₂ during 45 min. After cooling the green mixture was filtered and the solution was left to slow evaporation. Emerald green crystals were recovered after 5 days (yield 69%).

Synthesis of [$\{\text{Cu}(\text{L})\}_2$].5/2H₂O (B)

To a hot solution of H₂L (417 mg, 2.00 mmol) in 30 mL of 20% ethanol, was added a LiOH·H₂O (168 mg, 4 mmol). The reflux was maintained for 15 min, a solution of Cu(NO₃)₂·3H₂O (494 mg, 2.04 mmol) in 5 mL of distilled water was added. The green precipitate formed was filtered and washed successively with distilled water, ethanol and diethyl ether. The product was dried over P₄O₁₀ (yield 25%).

Synthesis of $[\{Cu(HL)(Hpz)(H_2O)\}].NO_3$ (C)

To a hot solution of H_2L (417 mg; 2.00 mmol) in 20 mL of ethanol, was added a solution of $Cu(NO_3)_2 \cdot 3H_2O$. This mixture was refluxed during 2 h. A solution of pyrazole (Hpz) (55 mg, 0.8 mmol) in 5 mL of ethanol was added. The deep green solution was refluxed for 30 min. After cooling, the green precipitate was filtered, washed with ethanol and diethyl ether before being dried in vacuo. Crystals suitable for X-ray diffraction analyses were obtained by recrystallization from acetonitrile solution (yield 65%).

Data collection and reduction

Suitable crystals for X-rays study of complex C were obtained by slow evaporation of an acetonitrile solution of the complex. The crystal data, details of data collection and refinement parameters are summarized in Table 1. Crystal with approximate dimension 0.20 x 0.30 x 0.35 mm was mounted in a capillary used for the X-rays diffraction study. Intensities and lattice parameters were determined on a Siemens R3m/V diffractometer using $MoK\alpha$ radiation at 20 ± 1 °C. The structure was solved by direct methods and refined by full-matrix least-square techniques. All the calculations were carried out by the Siemens PC versions of the SHELX L93 [8]. CIF was deposited in the Cambridge Data Center CCDC number 223600.

Table 1. Crystal and structure refinement data for complex $[\{Cu(HL)(Hpz)(H_2O)\}].NO_3$ (C).

Chemical formula	$CuC_{13}H_{17}N_5O_7$
Formula weight	418.8
Crystal system	Orthorhombic
Space group	$I222$
a (Å)	13.417(3)
b (Å)	22.662(6)
c (Å)	22.518(5)
V (Å ³)	6846.7(3)
Z	8
Temperature (K)	293
ρ_{cal} (g cm ⁻³)	1.544
λ (Mo $K\alpha$) (Å)	0.71073
μ (mm ⁻¹)	1.32
Scan type	ω -2 θ
θ min-max (°)	2.52-21.96
Total no. data	4630
Observed data	($I > 2\sigma(I)$)
R (Rw) ^a	0.0934 (0.2522)
Goof	0.831
Residual density min., max. (eÅ ⁻³)	-1.50, 1.03
CCDC N°	223600

RESULTS AND DISCUSSIONS

It is known from the literature that the majority of the metal complexes derived from hydrazones show a pentagonal bipyramidal coordination geometry, the structures being binuclear [9] or tetranuclear [10]. Cu(II) complexes of the tridentate ligand have been synthesized in monodeprotonated (HL⁻) and dideprotonated (L²⁻) forms (Table 2). When the salt $Cu(BF_4)_2 \cdot 2H_2O$ was used complex $[\{Cu(HL)(H_2O)\}_2] \cdot 2BF_4$ (A) was formed. In the presence of

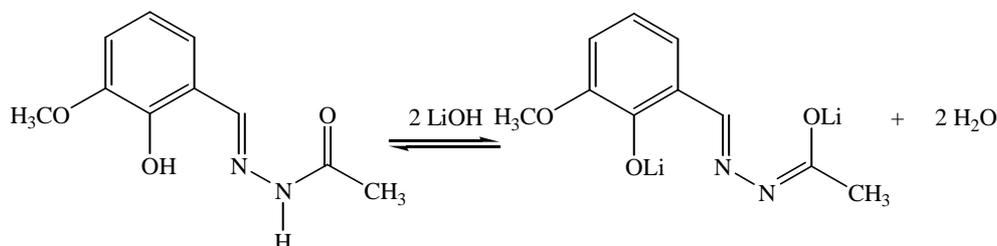
base such as LiOH the amide and phenol protons are both removed to give the complex $[\{CuL\}_2]$ (**B**). When the complex formed with $Cu(NO_3)_2 \cdot 3H_2O$ and H_2L is treated in situ with pyrazole(Hpz), ligand monodeprotonation is observed and the monomeric adduct $[\{Cu(HL)(Hpz)(H_2O)\}].NO_3$ is obtained in good yield.

Table 2. Colours, elemental analyses, yield and melting points.

Compounds	Found (calculated)			Yield (%)	m.p. (°C)	Color
	% C	% H	% N			
H_2L ($C_{10}H_{12}N_2O_3$)	57.55 (57.68)	5.79 (5.81)	13.46 (13.45)	89	199	White
A $[\{Cu(HL)(H_2O)\}_2].2BF_4$	31.92 (31.98)	3.42 (3.49)	7.42 (7.46)	69	-	Green
B $[\{Cu(L)\}_2].5/2H_2O$	44.54 (44.53)	3.75 (3.74)	10.36 (10.38)	25	>250	Green
C $[\{Cu(HL)(Hpz)(H_2O)\}].NO_3$	37.32 (37.28)	4.09 (4.10)	16.73 (16.72)	65	192	Green

Infrared and electronic spectra of the complexes

The ligand shows IR bands assigned to $\nu(O-H)$ at 3480 cm^{-1} , $\nu(C=O)$ (1680 cm^{-1}), $\nu(C=N)$ (1635 cm^{-1}) and $\nu(C-O)$ (1253 cm^{-1}) [11]. On complexation, the $\nu(C=O)$, $\nu(C=N)$ and $\nu(C-O)$ phenolic bands for the ligand shift showing the involvement of the carbonyl oxygen, phenolic oxygen and the imine nitrogen in the copper(II) coordination sphere. This is confirmed by $\nu(Cu-N)$ ($380-340\text{ cm}^{-1}$) and $\nu(Cu-O)$ ($340-280\text{ cm}^{-1}$) in their far infrared spectra. The complex **A** presents additive bands at 1080 and 500 cm^{-1} . These frequencies assigned to ν_3 and ν_4 indicate a T_d symmetry for the BF_4^- anion which plays a counter ion role. The bands of moderate intensity occurring at 3200 cm^{-1} and 830 cm^{-1} are characteristic of coordinated water [12]. The infrared spectra of complex **B** presents bands at 1620 , 1605 , 1538 and 1507 cm^{-1} . These absorptions are probably due to the conjugated diimine $\nu(C=N-N=C)$ resulting from the iminization of the ligand and dideprotonation of the hydrazone (Scheme 1). The $\nu(N-H)$ band expected at 3347 cm^{-1} disappears. This one is observed at 3348 cm^{-1} in the infrared spectra of complex **C**.



Scheme 1

The electronic spectra were recorded in solid state or acetonitrile solution. All the spectra present band at 400 nm due to MLCT. The d-d absorptions are pointed in the range $450-750\text{ nm}$ (Table 2).

Table 3. Electronic spectra data for the complexes.

Complexes	Absorption maxima (nm)			
	Solid		Solution in CH ₃ CN	
	MLCT	d-d	MLCT	d-d
A [{Cu(HL)(H ₂ O)} ₂].2BF ₄	400	700, 730	400	500, 700, 730
B [{Cu(L)} ₂].5/2H ₂ O	400	700	400	460
C [{Cu(HL)(Hpz)(H ₂ O)}].NO ₃	400	700	400	700

Magnetism

Magnetic measurements were carried out in the range 250-2 K. The magnetic curves $\chi(T)$ (Figure 1 and 2) show a maximum at about 108 K and 101 K, respectively. The presence of this maximum indicates clearly antiferromagnetic interactions. Their χT versus T curves decrease with the temperature (Figures 3 and 4). This behaviour is characteristic of antiferromagnetic interactions between the magnetic centers. These properties are due to the depopulation of excited state triplet ($S = 1$) in aid of the ground state singlet ($S = 0$). The fitting curves (Figures 1-4 (solid line)) obtained by using the appropriate susceptibility expression derived from the corrected Bleaney Bowers equation assuming that the g factors for both copper(II) are identical [13]. The Hamiltonian $H = -J \cdot S_1 \cdot S_2$ for the isotropic exchange interaction [14] is considered.

$$\chi_M(T) = \chi_{TIP} + \chi_{dia} + \frac{\rho N g^2 \beta^2}{2KT} + (1-\rho) \frac{2N g^2 \beta^2}{KT \left(3 + e^{-\frac{J}{KT}} \right)}$$

where χ_{TIP} = contribution of temperature independant paramagnetic, χ_{dia} = diamagnetic correction, and ρ = percentage of impurities.

The best fitting curves are obtained (Figures 1-4 solid line) with the values $g = 2.14$, $J = -115 \text{ cm}^{-1}$, $\chi_{TIP} = 66 \times 10^{-6}$, $\chi_{dia} = 300 \times 10^{-6}$, $\rho = 4 \%$ for compound **B**. Whereas for **A**, $g = 1.86$, $J = -120 \text{ cm}^{-1}$, $\chi_{TIP} = 60 \times 10^{-6}$, $\chi_{dia} = 341.7 \times 10^{-6}$, $\rho = 1.5 \%$. At lower temperature, $\chi(T)$ increases on cooling owing to the contribution of the paramagnetic impurities which obeys to the Curie-Weiss law.

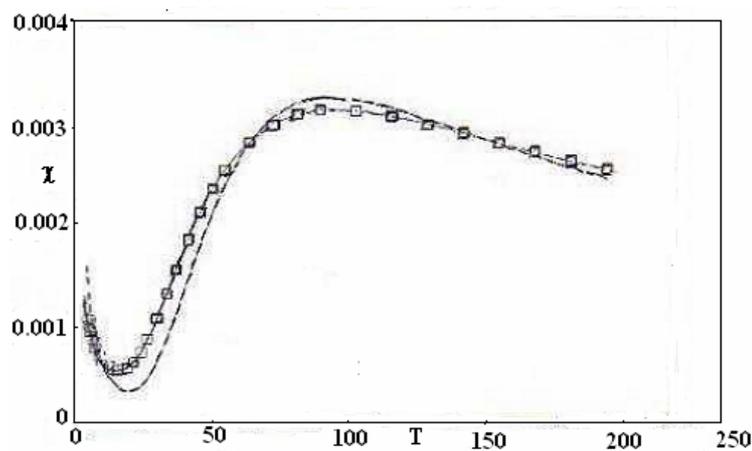


Figure 1. $\chi(T)$ of [{Cu(HL)(H₂O)}₂].2BF₄. (◇-◇-◇ experimental curve, --- fitting curve).

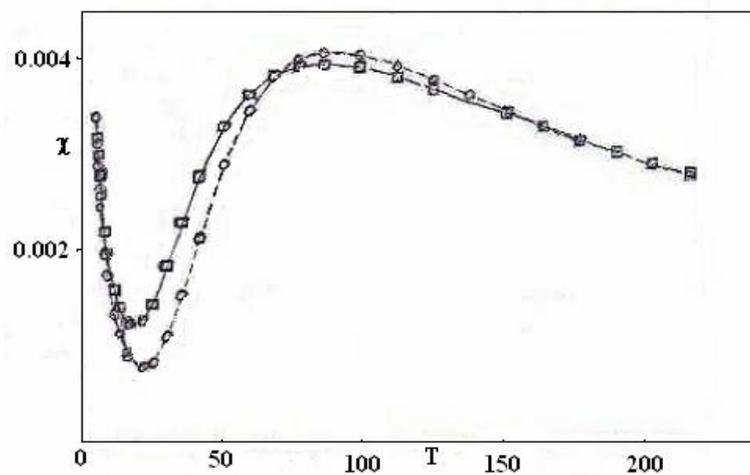


Figure 2. $\chi(T)$ of $[\text{Cu}(\text{L})]_2 \cdot 5/2\text{H}_2\text{O}$. (\diamond - \diamond - \diamond experimental curve, --- fitting curve).

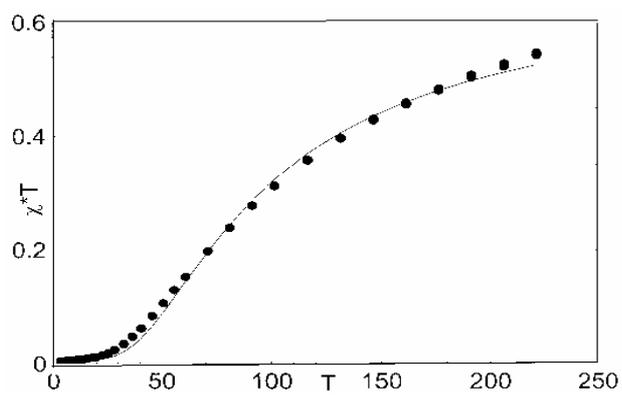


Figure 3. $\chi(T)$ of $[\text{Cu}(\text{HL})(\text{H}_2\text{O})]_2 \cdot 2\text{BF}_4$. ($\bullet\bullet\bullet$ experimental curve, solid line represents the best fit).

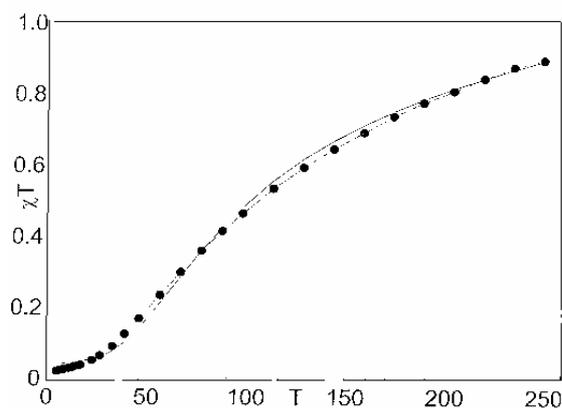


Figure 4. $\chi(T)$ of $[\text{Cu}(\text{L})]_2 \cdot 5/2\text{H}_2\text{O}$. ($\bullet\bullet\bullet$ experimental curve, solid line represents the best fit).

Crystal structure of $[\{Cu(HL)(Hpz)(H_2O)\}]\cdot NO_3$

The X-ray structure of **C** show (Figure 5) that the copper(II) has a distorted square pyramidal geometry. The structure displays five and six membered chelating ring from the ligand around the metallic ion (one CuOCNN and one CuOCCCN) in which the copper(II) is pentacoordinated. The three donors atoms (one iminolic oxygen, one phenolic oxygen and one nitrogen) of the ligand and one nitrogen of the pyrazole moiety are occupied the equatorial position. The water molecule is weakly link at the apical position. Three types of Cu-O distances have been found: $d(Cu(O)-O_{phenolic}) = 1.920(7) \text{ \AA}$; $d(Cu-O_{iminolic}) = 2.041(6) \text{ \AA}$, $d(Cu-O_{water}) = 2.362(5) \text{ \AA}$ [15]. The N-N distance $1.390(9) \text{ \AA}$ indicate single N-N bond [16]. The angles involving adjacent equatorial atoms and the oxygen at the apical do not differ notably $N(11)-Cu(1)-O(6)$, $O(3)-Cu(1)-O(6)$, $O(3)-Cu(1)-(6)$, $N(8)-Cu(1)-O(6)$ and $O(4)-Cu(1)-O(6)$ being $95.3(2)$, $93.1(2)$, $92.0(2)$ and $90.3(2)$, respectively. The nitrate ion is not coordinated to the copper(II) ion [16]. The selected bonds distances and angles are given in Table 4 and 5.

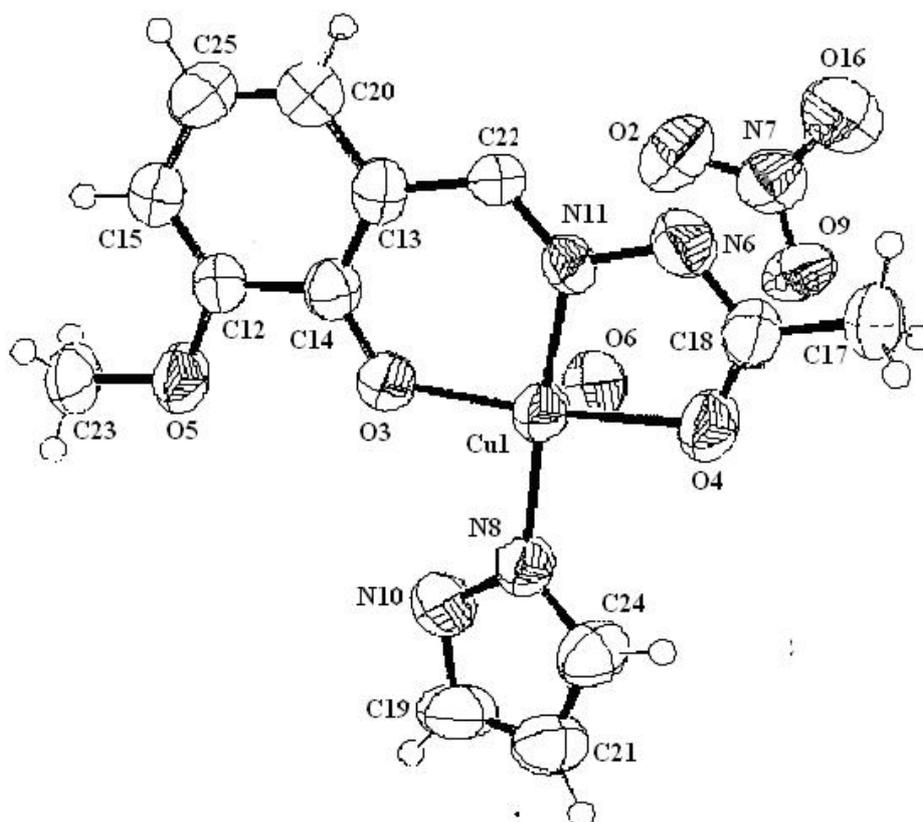


Figure 5. Crystal structure of $[\{Cu(HL)(Hpz)(H_2O)\}]\cdot NO_3$.

Table 4. Relevant interatomic distances (Å) in $[\{\text{Cu}(\text{HL})(\text{Hpz})(\text{H}_2\text{O})\}]\cdot\text{NO}_3$ with standard deviations in parenthesis

Cu(1) – N(11)	1.890(7)	N(8) – C(24)	1.341(9)
Cu(1) – O(3)	1.920(7)	N(8) – N(10)	1.345(9)
Cu(1) – N(8)	1.925(6)	N(10) – C(19)	1.374(11)
Cu(1) – O(4)	2.041(6)	N(11) – C(22)	1.327(10)
Cu(1) – O(6)	2.362(5)	C(12) – C(15)	1.340(11)
O(2) – N(7)	1.230(10)	C(12) – C(14)	1.399(11)
O(3) – C(14)	1.309(9)	C(13) – C(14)	1.402(11)
O(4) – C(18)	1.247(11)	C(13) – C(20)	1.418(12)
O(5) – C(12)	1.380(9)	C(13) – C(22)	1.437(12)
O(5) – C(23)	1.412(9)	C(15) – C(25)	1.417(13)
N(6) – C(18)	1.319(11)	C(17) – C(18)	1.449(11)
N(6) – N(11)	1.390(9)	C(19) – C(21)	1.318(14)
N(7) – O(16)	1.198(10)	C(20) – C(25)	1.331(12)
N(7) – O(9)	1.232(10)		

Table 5. Selected bond angles (°) in $[\{\text{Cu}(\text{HL})(\text{Hpz})(\text{H}_2\text{O})\}]\cdot\text{NO}_3$ with standard deviations in parenthesis.

N(11) – Cu(1) – O(3)	93.0(2)	C(22) – N(11) – Cu(1)	129.1(5)
N(11) – Cu(1) – N(8)	170.0(3)	N(6) – N(11) – Cu(1)	114.0(5)
O(3) – Cu(1) – N(8)	93.5(2)	C(15) – C(12) – O(5)	121.5(7)
N(11) – Cu(1) – O(4)	79.7(3)	C(15) – C(12) – C(14)	124.0(7)
O(3) – Cu(1) – O(4)	172.2(3)	O(5) – C(12) – C(14)	114.5(6)
N(8) – Cu(1) – O(4)	93.5(2)	C(14) – C(13) – C(20)	119.1(8)
N(11) – Cu(1) – O(6)	95.3(2)	C(14) – C(13) – C(22)	124.8(8)
O(3) – Cu(1) – O(6)	93.1(2)	C(20) – C(13) – C(22)	116.1(8)
N(8) – Cu(1) – O(6)	92.0(2)	O(3) – C(14) – C(12)	119.2(7)
O(4) – Cu(1) – O(6)	90.3(2)	O(3) – C(14) – C(13)	124.4(7)
C(14) – O(3) – Cu(1)	127.1(5)	C(12) – C(14) – C(13)	116.4(7)
C(18) – O(4) – Cu(1)	111.8(5)	C(12) – C(15) – C(25)	119.1(8)
C(12) – O(5) – C(23)	118.4(7)	O(4) – C(18) – N(6)	119.7(8)
C(18) – N(6) – N(11)	114.5(7)	O(4) – C(18) – C(17)	121.1(8)
O(16) – N(7) – O(2)	119.7(9)	N(6) – C(18) – C(17)	119.1(8)
O(16) – N(7) – O(9)	118.0(9)	C(21) – C(19) – N(10)	107.1(8)
O(2) – N(7) – O(9)	122.3(8)	C(25) – C(20) – C(13)	122.3(9)
C(24) – N(8) – N(10)	102.7(7)	C(19) – C(21) – C(24)	105.9(7)
C(24) – N(8) – Cu(1)	133.9(5)	N(11) – C(22) – C(13)	121.6(8)
N(10) – N(8) – Cu(1)	122.9(5)	N(8) – C(24) – C(21)	112.7(7)
N(8) – N(10) – C(19)	111.6(7)	C(20) – C(25) – C(15)	119.0(9)
C(22) – N(11) – N(6)	116.9(7)		

CONCLUSION

As many tridentate ligands the *o*-vanillin acetylhydrazone can give also dimer complexes. The magnetic measurements show antiferromagnetic interactions between the copper ions. The X-ray of mononuclear compound **C** shows a pseudo square pyramidal geometry. The pyrazole and the coordinated atoms of the ligand occupy the equatorial positions whereas the water molecule is located at the apical position.

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