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# Synthesis, reactivity and magnetochemical studies on copper(II) complexes derived from *N*-salicylidenearoylhydrazines. X-ray structure of [mononitratoOO(-1)(N-salicylidenatobenzoylhydrazine)-ONO(-1)]copper(II) monohydrate

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#### Abstract

A series of new mononuclear and binuclear copper(II) complexes derived from *N*-salicylidenearoylhydrazines (H<sub>2</sub>L) of the types  $K_2[\{Cu(L)(OH)\}_2] \cdot nH_2O$ ,  $[Cu(HL)Cl \cdot H_2O] \cdot nH_2O$ ,  $[\{Cu(HL)Cl\}_2]$ ,  $[Cu(HL)NO_2] \cdot H_2O$ ,  $[\{Cu(HL)\}_2] \cdot 2NO_3$ ,  $[\{Cu(HL)-H_2O\}_2] \cdot 2NO_3 \cdot nH_2O$  and  $[Cu(HL)NCS] \cdot H_2O$  have been prepared and characterized. The X-ray crystal and molecular structure of  $[Cu(HSBzh)NO_3] \cdot H_2O$ , where HSBzh refers to the mononegative *N*-salicylidenebenzoylhydrazine anion, has been determined. The complex is monomeric with the copper(II) adopting a (4 + 1) distorted square pyramidal coordination, with the ONO aroylhydrazone tridentate anion and an oxygen atom of the unsymmetric bidentate nitrate ion occupying the basal plane. The fifth coordination site is occupied by the other oxygen of the nitrate ion. The magnetic susceptibilities of both mononuclear and binuclear complexes were measured within the temperature range 4.2–298 K. All binuclear copper(II) complexes show strong antiferromagnetic interactions, and the singlet–triplet separation (-2J) recorded for  $\mu$ -dihydroxy bridged complexes  $K_2[\{Cu(L)OH\}_2] \cdot nH_2O$  are within the range  $172-276 \text{ cm}^{-1}$ , while (-2J) for binuclear complexes  $[\{Cu(HL)Cl\}_2], [\{Cu(HL)\}_2] \cdot 2NO_3$  and  $[\{Cu(HL)H_2O\}_2] \cdot 2NO_3 \cdot nH_2O$  are respectively within the range 400–460, ca. 340 and ca. 390 cm<sup>-1</sup>. There are no appreciable exchange interactions between copper(II) ions in the monomeric complexes  $[Cu(HL)Cl+H_2O] \cdot nH_2O, [Cu(HL)NO_2] \cdot H_2O$  and  $[Cu(HL)NCS] \cdot H_2O$ . The IR spectra of the prepared complexes are also discussed. (©2000 Elsevier Science Ltd All rights reserved.

Keywords: N-salicylidenearoylhydrazines; Copper(II) complexes; X-ray crystal structures; Molecular structures; Magnetic properties; Infrared spectra

#### 1. Introduction

*N*-salicylideneacylhydrazines (1) ( $H_2L$ ) can act either as neutral, mononegative or dinegative ONO tridentate ligands [1–20]. A large number of monomeric and dimeric copper(II) complexes have been prepared and characterized [1– 20]. Most recent studies have been directed towards structural studies and a number of X-ray crystal and molecular structures have been reported [16–20]. Less attention, however, has been directed towards magnetochemical studies [13–18]. In this paper we report the synthesis and characterization of some new mononuclear and dinuclear copper(II) complexes with *N*-salicylidenearoylhydrazines.



The single X-ray structure of the monomeric  $[Cu(HBzh)NO_3] \cdot H_2O$  has been determined and the magnetic measurements recorded for the prepared complexes will be discussed. Hereafter, *N*-salicylidenebenzoylhydrazine

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and the corresponding *p*-methyl-, *p*-methoxy- and *p*-chlorobenzoylhydrazine are abbreviated as  $H_2SBzh$ ,  $H_2Sp-CH_3Bzh$ ,  $H_2Sp-CH_3Obzh$  and  $H_2Sp-ClBzh$ , respectively.

### 2. Results and discussion

### 2.1. Synthesis and stoichiometry

In methanol, the reaction of copper(II) acetate with *N*-salicylidenearoylhydrazines (H<sub>2</sub>L) (**1**,  $R = C_6H_5$ , *p*-CH<sub>3</sub>- $C_6H_4$ , *p*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub> and *p*-ClC<sub>6</sub>H<sub>4</sub>) afforded the binuclear neutral copper(II) complexes [{Cu(L)}<sub>2</sub>] (**2**,  $R = C_6H_5$ , *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>, *p*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub> and *p*-ClC<sub>6</sub>H<sub>4</sub>). These binuclear copper(II) complexes were insoluble in water, alcohols, halogenated aliphatic hydrocarbons and aromatic hydrocarbons but soluble in DMSO or DMF. The dissolution of these binuclear complexes proceeded with the rupture of Cu–O–Cu bridges giving the solvated monomeric species [Cu(L)S] or [Cu(L)S<sub>2</sub>] where S refers to the solvent molecule [12]. A similar behaviour was previously reported and recrystallization of the anhydrous dimeric copper(II) complexes with the

dinegative anion of 5-chloro-2-hydroxo acetophenone salicylhydrazide from DMF gave the corresponding DMF adduct of the formula [Cu(L)DMF] where L refers to the dinegative hydrazone anion [16,17]. Neutral monodentate nitrogen Lewis bases such as diethylamine [(Et)<sub>2</sub>NH] can also affect the rupture of the Cu–O–Cu bridges in **2** and eventually gave the corresponding monomeric ternary complex [Cu(L)HNEt<sub>2</sub>] (**3**,  $R = C_6H_5$ ).

The reaction of the neutral dimeric copper(II) complexes  $[{Cu(L)}_2]$  (2,  $R = C_6H_5$ , *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub> and *p*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>) with a large excess of KOH in dry methanol afforded the corresponding  $\mu$ -hydroxo bridged copper(II) complexes of general formula  $K_2[{Cu(L)(OH)}_2]$  (4,  $R = C_6H_5$ , *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub> and *p*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>). The isolated hydroxo complexes are soluble in methanol, ethanol and acetonitrile. In water, these complexes are readily hydrolysed giving the parent neutral dimer (2). The isolated hydroxo complexes together with elemental analysis are given in Table 1.

On the other hand, treatment of a suspension of  $[{Cu(L)}_2]$  (2,  $R = C_6H_5$ , p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>, p-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub> and p-ClC<sub>6</sub>H<sub>4</sub>) in absolute ethanol with an equivalent amount of aqueous hydrogen chloride afforded the hydrated monochloro complex  $[Cu(HL)Cl \cdot H_2O] \cdot nH_2O$  (5,  $R = C_6H_5$ , p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>, p-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub> and p-ClC<sub>6</sub>H<sub>4</sub>) (HL refers to the mononegative *N*-salicylidenearoylhydrazine anion). These

Table 1

Elemental analyses of copper(II) complexes derived from N-salicylidenearoylhydrazines

Complex		Found (calculated) (%)					
R	п	С	Н	Ν	Cu		
$\overline{K_{2}[\{Cu(L)OH\}_{2}]\cdot nH_{2}O(4)}$							
C <sub>6</sub> H <sub>5</sub>	2	44.55 (44.73)	3.07 (3.49)	7.20 (7.45)	16.73 (16.90)		
p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	2	46.17 (46.20)	3.84 (3.88)	7.00 (7.18)	16.52 (16.30)		
p-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	1	45.06 (45.39)	3.60 (3.55)	6.86 (7.06)	16.25 (16.01)		
$[Cu(HL)Cl \cdot H_2O] \cdot nH_2O(5)$							
C <sub>6</sub> H <sub>5</sub>		47.16 (47.20)	3.59 (3.68)	7.83 (7.86)	17.57 (17.84)		
p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>		48.08 (48.65)	3.50 (4.08)	7.48 (7.57)	17.00 (17.16)		
p-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	1	44.01 (44.56)	3.69 (4.24)	6.81 (6.93)	15.87 (15.72)		
p-ClC <sub>6</sub> H <sub>4</sub>	1	40.46 (41.14)	2.75 (3.45)	7.07 (6.85)	15.41 (15.55)		
$[{Cu(HL)Cl}_2]$ (5)							
C <sub>6</sub> H <sub>5</sub>		49.57 (49.71)	3.18 (3.28)	8.43 (8.28)	18.53 (18.79)		
p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>		51.08 (51.14)	3.71 (3.72)	8.25 (7.95)	17.87 (18.04)		
$[Cu(HL)(NO_3)] \cdot nH_2O$							
C <sub>6</sub> H <sub>5</sub>	1	43.15 (43.93)	3.24 (3.42)	10.91 (10.98)	16.72 (16.60)		
$[{Cu(HL)}_{2}] \cdot 2NO_{2}(7)$							
$C_{e}H_{e}$		46.14 (46.09)	2.94 (3.04)	11.50 (11.52)	17.50 (17.42)		
p-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>		45.61 (45.63)	3.24 (3.32)	10.75 (10.64)	16.24 (16.09)		
$[{Cu(HI)(H_0)}_1] \cdot 2NO \cdot nH_0$ ( <b>7</b> a)							
<i>p</i> -CH <sub>2</sub> C <sub>2</sub> H <sub>4</sub>	1	44 88 (44 39)	3 43 (3.97)	10.72 (10.35)	15 40 (15 66)		
CH <sub>2</sub>		33.62 (33.70)	3.55 (3.46)	12.73 (13.10)	20.02 (19.81)		
$[C_{2}(\mathbf{H})(\mathbf{NC})] = \mathbf{H} \mathbf{O}(0)$							
$C H_{-}$	1	47 23 (47 55)	3 33 (3 46)	11.09 (11.09)	16 41 (16 77)		
n-CH <sub>2</sub> C <sub>4</sub> H <sub>4</sub>	1	50.95 (51.95)	3.44 (3.50)	11.19 (11.21)	17.01 (16.95)		
p-CH <sub>2</sub> OC <sub>4</sub> H <sub>4</sub>		48.92 (49.16)	3.32 (3.35)	10.94 (10.75)	16.41 (16.26)		
p-ClC <sub>6</sub> H <sub>4</sub>	2	41.52 (41.77)	3.04 (3.27)	9.35 (9.74)	14.42 (14.73)		

complexes were also prepared in situ from the reaction of salicylaldehyde with the corresponding aroylhydrazine (1:1 molar ratio) in the presence of copper(II) chloride in ethanol or methanol. However, direct reaction of *N*-salicylidenearoylhydrazine (1,  $R = C_6H_5$  and p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>) with 1 equiv. of copper(II) chloride in absolute ethanol afforded the anhydrous brown chloro complexes  $[Cu(HL)Cl]_2$  (6,  $R = C_6H_5$  and p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>). This reaction usually gave salicylaldehyde azine (HOC<sub>6</sub>H<sub>4</sub>CH=N–N=CHC<sub>6</sub>H<sub>4</sub>OH) as a side reaction product. Meanwhile, the direct reaction of p-methoxy- and p-chlorobenzoylhydrazones (1, R = p-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub> and p-ClC<sub>6</sub>H<sub>4</sub>) with copper(II) chloride in ethanol or methanol gave the hydrated copper(II) complexes [Cu(HL)Cl·H<sub>2</sub>O] (5, R = p-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub> and p-ClC<sub>6</sub>H<sub>4</sub>) and attempts to prepare the corresponding anhydrous binuclear complexes were unsuccessful. Similar to the reaction of N-salicylidenearoylhydrazines with copper(II) chloride, the reaction of copper(II) nitrate gave either monomeric and/or dimeric nitrate complexes. The reaction of 1 ( $R = p-CH_3C_6H_4$ ) with copper(II) nitrate trihydrate in boiling absolute ethanol afforded the hydrated binuclear complex  $[{Cu(HSp CH_3Bzh)H_2O_{2}(NO_3)_2 \cdot H_2O$  (7,  $R = p - CH_3C_6H_4$ ), while the reaction with 1 ( $R = C_6H_5$ , p-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>) gave the corresponding anhydrous complexes  $[{Cu(HSBzh)}_2] \cdot 2NO_3$ and  $[{Cu(HSp-CH_3OBzh)_2} \cdot 2NO_3 (7a, R = C_6H_5 \text{ and } p$ - $CH_3OC_6H_4$ ), respectively. However, the in situ preparation, using benzoylhydrazine, gave the monomeric complex  $[Cu(HSBzh)(NO_3)] \cdot H_2O$ . The prepared mononuclear and binuclear copper(II) chloride and nitrate complexes together with elemental analysis are included in Table 1.



The reaction of either mononuclear or binuclear copper(II) chloride and nitrate complexes with an equivalent amount of NH<sub>4</sub>SCN in methanol afforded the corresponding thiocyanato complexes [Cu(HL)SCN]  $\cdot nH_2O(\mathbf{8}, \mathbf{R} = C_6H_5, p$ - $CH_3C_6H_4$ , p-OCH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>) and p-ClC<sub>6</sub>H<sub>4</sub>), implying the ease of displacement of either  $Cl^-$  or  $NO_3^-$  by the thiocyanate ion. However, in the presence of large excess of NH<sub>4</sub>SCN, the reaction proceeded by the reduction of copper(II) and copper(I) thiocyanate  $[CuSCN]_2$  was precipitated. On the other hand, the reaction of thiocyanate with either µ-hydroxo bridged complexes (5) or the neutral binuclear copper(II) complexes  $[{Cu(L)}_2]$  (2) failed to give the corresponding thiocyanato complexes, suggesting that the SCN<sup>-</sup> cannot affect the rupture of Cu–O–Cu bridges in these complexes. The isolated thiocyanato complexes  $[Cu(HL)SCN] \cdot nH_2O$ together with elemental analysis are also given in Table 1.

## 2.2. X-ray crystal structure of [mononitratoOO'(-1)(N-salicylidenebenzoylhydrazinato)ONO'(-1)]copper(II) monohydrate complex [Cu(HSBzh)(NO<sub>3</sub>)] $\cdot$ H<sub>2</sub>O

The crystal data and structure refinement for  $[Cu(HSBzh)(NO_3)] \cdot H_2O$  are collected in Table 2. The molecular structure together with the numbering scheme used are shown in Fig. 1. Some selected bond distances and bond angles are listed in Table 3. In  $[Cu(HBzh)(NO_3)] \cdot H_2O$ ,

Table 2

Crystal data and structure refinement for  $[Cu(HSBzh)NO_3] \cdot H_2O$ 

Empirical formula	$C_{14}H_{13}CuN_3O_6$
Formula weight	382.84
Temperature (K)	300(2)
Wavelength (Å)	0.71093
Crystal system	orthorhombic
Space group	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
Unit cell dimensions	
a (Å)	5.331(2)
<i>b</i> (Å)	16.231(2)
<i>c</i> (Å)	17.185(3)
$\alpha$ (°)	90
$\beta$ (°)	90
$\gamma$ (°)	90
Volume (Å <sup>3</sup> )	1487.0(6)
Ζ	4
Density (calculated) (Mg m <sup>-3</sup> )	1.710
Absorption coefficient $(mm^{-1})$	1.435
F(000)	80
Crystal size (mm)	$0.88 \times 0.15 \times 0.13$
Theta range for data collection (°)	1.73-25.98
Index ranges	$-6 \le h \le 6, -1 \le k \le 19, -1 \le l \le 21$
Reflections collected	3543
Independent reflections	2908 ( $R_{\rm int} = 0.0291$ )
Refinement method	full-matrix least-squares on $F^2$
Data/restraints/parameters	2908/0/250
Goodness-of-fit on $F^2$	1.068
Final <i>R</i> indices $(I > 2\sigma(I))$	$R_1 = 0.0418, wR_2 = 0.1093$
<i>R</i> indices (all data)	$R_1 = 0.0596, wR_2 = 0.1194$
Absolute structure parameter	0.02(2)
Largest difference peak, hole	0.639, -0.942
$(e Å^{-3})$	



Fig. 1. ORTEP drawing of [Cu(HSBzh)NO<sub>3</sub>] · H<sub>2</sub>O.

Table 3

Selected bond lengths (Å) and bond angles (°) for [Cu(HSBzh)-(NO\_3)]  $\cdot \rm H_2O$ 

Copper(II) polyh	edron		
O(1)– $Cu(1)$	1.881(3)	O(1)-Cu(1)-N(1)	92.99(14)
O(2)-Cu(1)	1.947(3)	O(1)-Cu(1)-O(2)	174.31(13)
N(1)-Cu(1)	1.913(3)	O(1)-Cu(1)-O(3)	91.71(14)
O(3) - Cu(1)	1.993(3)	O(2)-Cu(1)-O(3)	93.64(13)
O(4) - Cu(1)	2.480(3)	O(4)-Cu(1)-O(3)	55.50(13)
		N(1)-Cu(1)-O(2)	81.49(13)
		N(1)-Cu(1)-O(3)	172.33(14)
Tridentate ligand			
C(1)-O(2)	1.252(5)	C(1)-N(2)-N(1)	113.9(3)
C(1)–N(2)	1.336(5)	C(1)-O(2)-Cu(1)	113.1(3)
C(1)–C(9)	1.488(6)	C(1)-N(2)-H(2N)	133.3(3)
C(2)–N(1)	1.283(5)	C(2)-N(1)-N(2)	119.1(3)
C(3)–C(8)	1.427(6)	C(2)-N(1)-Cu(1)	128.9(3)
C(8)–O(1)	1.305(6)	C(8)–O(1)–Cu(1)	127.8(3)
N(1)-N(2)	1.383(5)	N(1)-C(2)-C(3)	122.9(4)
N(2)-H(2N)	1.20(4)	N(1)-N(2)-H(2N)	113(2)
		N(2)-N(1)-Cu(1)	112.0(2)
		N(2)-C(1)-C(9)	119.5(4)
		O(1)-C(8)-C(3)	124.3(4)
		O(2)-C(1)-N(2)	119.5(4)
		O(2)-C(1)-C(9)	120.9(4)
Nitrate ligand			
N(3) - O(3)	1.288(5)	O(4) - N(3) - O(3)	115.3(4)
N(3)–O(4)	1.231(5)	O(5)-N(3)-O(3)	119.9(4)
N(3)-O(5)	1.208(5)	O(5)-N(3)-O(4)	124.8(4)
		N(3)-O(3)-Cu(1)	105.4(3)

the *N*-salicylidenebenzoylhydrazinato anion behaves as a mononegative tridentate ligand and is coordinated to the Cu(II) via the deprotonated phenolic oxygen O(1), azomethine nitrogen N(1) and the ketoamide oxygen O(2). The Cu–O(1) (1.881 Å), Cu–N(1) (1.913 Å) and Cu–O(2) (1.97 Å) bond distances are within the range reported for other copper(II) complexes derived from *N*-salicylideneacylhydrazines [10,11,18–21]. The fourth coordinate site of the basal plane is occupied by the oxygen atom O(3) of the

nitrate group. The Cu(II) lies in the ligand plane and shows a slight deviation of 0.037 Å from the least square plane. The nitrate ion in this complex behaves as a bidentate ligand, and the fifth coordinate site is weakly bonded with the O(4) of the nitrate group. This bidentate nitrate is characterized by one short Cu–O(3) (1.993 Å) distance and a second much longer Cu–O(4) (2.480 Å) with a difference of 0.487 Å which falls within the range reported for the unsymmetrically coordinated bidentate nitrate group [22–25]. The small O(3)–Cu–O(4) angle (55.5°) is also in agreement with the bidentate nature of the nitrate ion in this complex.

The coordination polyhedron around the copper (II) is better described as (4+1) distorted square pyramidal as evident from the tetragonality parameter of Addison et al. [26],  $\tau = (\beta - \alpha)/60 = 0.033$ , where  $\alpha$  and  $\beta$  are the N(1)–Cu–O(3) (172.33°) and O(2)–Cu–O(1) (174.31°) angles, respectively. The uncoordinated water molecule O(6) is involved in strong hydrogen bonding with the N(2) hydrogen atom (O(6)···H(2)N) (1–*x*, -0.5+*y*, 1.5–*z*) (1.55 Å).

### 2.3. Magnetic measurements

At room temperature, the binuclear copper(II) complexes  $[{Cu(L)}_2]$  (**2**,  $R = C_6H_5$ , p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>, p-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub> and p-ClC<sub>6</sub>H<sub>4</sub>) show subnormal magnetic moments (1.2–1.6  $\mu_B$ ) and their electronic spectra agree with a square planar configuration [1–3,27]. The magnetic susceptibility measurements within the temperature range 97–297 K showed strong antiferromagnetic interactions. The exchange coupling constant (-2J) of these neutral dimeric complexes were found to vary from 594 to 680 cm<sup>-1</sup> [27] in agreement with the formation of dimeric copper(II) complexes with Cu–O–Cu bridges [28]. Recent X-ray studies on binuclear copper(II) complexes with A value show that dimerization takes place via the phenolic oxygen rather than the deprotonated enolic oxygen [18–21].

The newly prepared di- $\mu$ -hydroxo-bridged binuclear copper(II) complexes K<sub>2</sub>[{Cu(L)OH)}<sub>2</sub>] (**4**, R=C<sub>6</sub>H<sub>5</sub>, *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub> and *p*-OCH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>) also show subnormal magnetic moments (1.50–1.65  $\mu_B$ ) at room temperature. The variation of  $\chi_M$  and  $\mu_{eff}$ , recorded for K<sub>2</sub>[{Cu(S*p*-CH<sub>3</sub>Bzh)OH}<sub>2</sub>] (**4**, R=*p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>), as a function of temperature (4.2–298 K) is shown in Fig. 2. The remarkable decrease in  $\mu_{eff}$  (per copper atom) from 1.5  $\mu_B$  at 290 K to about 0.4  $\mu_B$  at 4.5 K suggests strong antiferromagnetic exchange interaction. Similar behaviour was also observed for the other di- $\mu$ -hydroxo-bridged copper(II) complexes (**4**, R=C<sub>6</sub>H<sub>5</sub>, and *p*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>). The experimental data were fitted to the modified Bleaney–Bowers equation Eq. (1),

$$\chi_{\rm M} = (1 - X_{\rm p}) \frac{2 N_{\rm L} g^2 \mu_{\beta}^2}{kT} \frac{\exp(2J/kT)}{1 + 3 \exp(2J/kT)}$$
(1)  
+  $X_{\rm p} \frac{2NLg^2 \mu_{\beta}^2}{3k(T - \theta)} S(S + 1) + 2N_{\alpha}$ 

where 2J is the singlet-triplet splitting or exchange integral,



Fig. 2. Magnetic susceptibilities  $\chi$  (•) and magnetic moments (o) vs. temperature for K<sub>2</sub>[{Cu(S*p*-CH<sub>3</sub>Bzh)OH}<sub>2</sub>]·2H<sub>2</sub>O. Solid lines represent the best least squares fit to Eq. (1), with J = -138, g = 2.10 and  $X_p = 4.1\%$ .

 $X_{\rm p}$  represents the fraction of a possible magnetically dilute copper(II) impurity (S=1/2),  $N_{\alpha}$  is the temperature independent paramagnetism ( $60 \times 10^{-6}$  cm<sup>3</sup> mol<sup>-1</sup> per copper(II) ion) and the other symbols have their usual meaning and a non-linear regression analysis was carried out with *J*, *g*, and  $X_{\rm p}$  as floating parameters. The obtained best fit parameters for the di- $\mu$ -hydroxo-bridged copper(II) complexes (**4**, R=C<sub>6</sub>H<sub>5</sub>, *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub> and *p*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>) are listed in Table 4. The recorded -2J values are within the range reported for other bis- $\mu$ -hydroxy bridged dicopper complexes with nearly planar Cu<sub>2</sub>O<sub>2</sub> [28–33] and a binuclear structure (**4**) can be proposed for these complexes.

For di- $\mu$ -hydroxo dicopper(II) complexes with almost planar Cu<sub>2</sub>O<sub>2</sub>, the 2*J* values were found to decrease linearly with increasing either Cu–O–Cu angle  $\varphi$  (°) or Cu···Cu separation  $r_{\text{Cu-Cu}}$  (Å), and least square regression analyses of the available data gave [28]:

$$2J = -77.6\varphi + 7555 \text{ cm}^{-1} (R = -0.95)$$
(2)

$$2J = -46.0r_{\rm Cu\cdots Cu} + 13389 \,\rm cm^{-1} \,(R = -0.95)$$
(3)

Substitution of the 2*J* values, recorded for **4** ( $R = C_6H_5$ , *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub> and *p*-OCH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>), in Eq. (2) gave 99.6, 100.9 and 100.7° for the values of Cu–O–Cu angles, respectively. While 2.948, 2.971 and 2.967 Å are, respectively, the values calculated from Eq. (3) for the Cu—Cu separation.

The green hydrated chloro complexes  $[Cu(HL)Cl \cdot H_2O] \cdot nH_2O$  (5,  $R = C_6H_5$ , *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>, *p*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>, and *p*-ClC<sub>6</sub>H<sub>4</sub>) show normal magnetic moments (1.80–1.84  $\mu_B$ ), Table 4, and the temperature dependent magnetic susceptibilities measured for these hydrated complexes, assuming Curie–Weiss behaviour, suggest a very weak antiferromagnetic coupling with  $\theta$  values in the range of ca. – 1.5 K. These mononuclear chloro complexes may adopt a square pyramidal coordination, the four in-plane donor atoms are provided by the tridentate ONO hydrazone and an oxygen from a coordinated water while the axial site is occupied by the chloride ion. A similar structure has been reported for [Cu(HSAch)Cl·H<sub>2</sub>O]·H<sub>2</sub>O, where HSAc refers to the mononegative *N*-salicylideneacetylhydrazine anion (1, R=CH<sub>3</sub>) [21]. On the other hand, the brown anhydrous

Table 4
The magnetic parameters recorded for the prepared copper(II) complexes derived from N-salicylidenearoylhydrazone

Complex		$\mu_{eff}\left(\mu_{B}\right)\left(298K\right)$	$\theta\left(\mathrm{K}\right)$	$-2J ({\rm cm}^{-1})$	g	<i>X</i> <sub>p</sub> (%)
R	п					
$[{Cu(L)(OH)}_2] \cdot nH_2O(4)$						
C <sub>6</sub> H <sub>5</sub>	2	1.65		171	2.05	6.75
p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	2	1.54		276	2.12	4.20
p-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	1	1.52		261	2.10	4.10
$[Cu(HL)Cl.H_2O] \cdot nH_2O(5)$						
C <sub>6</sub> H <sub>5</sub>		1.80	-16.8			
p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>		1.83	-15.4			
p-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	1	1.83	-17.2			
p-ClC <sub>6</sub> H <sub>4</sub>	1	1.84	-16.7			
$[{Cu(HL)Cl}_2] (6)$						
C <sub>6</sub> H <sub>5</sub>		1.12		452	2.20	1.56
p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>		1.21		406	2.19	1.80
$[Cu(HL)(NO_3)] \cdot nH_2O$						
C <sub>6</sub> H <sub>5</sub>	1	1.85	-8.5			
$[{Cu(HL)(H_2O)}_2](NO_3)_2$ (7a)						
C <sub>6</sub> H <sub>5</sub>		1.30		390	2.21	1.70
$[{Cu(HL)(H_2O)}_2](NO_3)_2 \cdot nH_2O(7)$						
CH <sub>3</sub>		1.30		340	2.20	0.50
p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	1	1.45		338	2.21	1.60
$[Cu(HL)NCS] \cdot nH_2O(8)$						
C <sub>6</sub> H <sub>5</sub>	1	1.87	1.35			
<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>		1.89	1.75			
p-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>		1.89	3.15			

chloro complexes [{Cu(HL)Cl}<sub>2</sub>] show, at room temperature, low lying magnetic moments within the range 1.12–1.21  $\mu_B$ . A plot of  $\chi_M$  and  $\mu_{eff}$ , measured for [{Cu(HS*p*-CH<sub>3</sub>Bzh)Cl}<sub>2</sub>], as a function of temperature, Fig. 3, suggests strong antiferromagnetc interaction. Fitting the data to the Bleaney–Bowers equation gives  $J = -203 \text{ cm}^{-1}$ , g = 2.19, and  $X_p = 0.0179$ . These values are comparable with those previously reported for [{Cu(HSBzh)Cl}<sub>2</sub>] (**6**, R = C<sub>6</sub>H<sub>5</sub>) [18]. The obtained -2J values, Table 4, are within the range reported for bis- $\mu$ -aryloxo bridged dicopper complexes [18,28]. The copper(II) in these complexes has a distorted (4+1) tetragonal pyramidal coordination where the apical site is occupied by a chloride ion. Dimerization is achieved



Fig. 3. Magnetic susceptibilities  $\chi$  (•) and magnetic moments (o) vs. temperature for [{Cu(HSp-CH<sub>3</sub>Bzh)Cl}<sub>2</sub>]. Solid lines represent the best least squares fit to Eq. (1), with J = -203, g = 2.19 and  $X_p = 1.8\%$ .

by sharing of phenoxy oxygen from each ligand through two copper atoms [18].

Similar to the chloro complexes [{Cu(HL)Cl}<sub>2</sub>] (6, R=C<sub>6</sub>H<sub>5</sub>, *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>), the isolated binuclear nitrate complexes [{Cu(HSBzh)}<sub>2</sub>]  $\cdot$ 2NO<sub>3</sub>, [{Cu(HS*p*-CH<sub>3</sub>Bzh)  $\cdot$ H<sub>2</sub>O}<sub>2</sub>]  $\cdot$ H<sub>2</sub>O  $\cdot$ 2NO<sub>3</sub> and [{Cu(HS*p*-CH<sub>3</sub>OBzh)}<sub>2</sub>]  $\cdot$ 2NO<sub>3</sub> show subnormal magnetic moments (1.30–1.45  $\mu$ <sub>B</sub>) at room temperature. A plot of the magnetic susceptibility data measured for [{Cu(HSBzh)<sub>2</sub>]  $\cdot$ 2NO<sub>3</sub> as a function of temperature (5–298 K), Fig. 4, indicates strong antiferromagnetic exchange coupling. Similar behaviour was also observed for both [{Cu(HS*p*-CH<sub>3</sub>Bzh)  $\cdot$ H<sub>2</sub>O}<sub>2</sub>]  $\cdot$ H<sub>2</sub>O  $\cdot$ 2NO<sub>3</sub> and



Fig. 4. Magnetic susceptibilities  $\chi$  (•) and magnetic moments (o) vs. temperature for [{Cu(Sp-Bzh)}\_2] · 2NO\_3. Solid lines represent the best least squares fit to Eq. (1), with J = -195, g = 2.21 and  $X_p = 1.7\%$ .

 $[{Cu(HSp-OCH_3Bzh)}_2] \cdot 2NO_3$ . The best fit parameters (J, J)g and  $X_{\rm p}$ ) obtained by fitting the variable temperature magnetic susceptibility data to the Bleaney-Bowers equation are listed in Table 4. The obtained -2J values  $(338-390 \text{ cm}^{-1})$ suggest strong antiferromagnetic exchange interaction via bridged phenoxy oxygens [28]. Recently, the preparation and X-ray crystal and molecular structure of the analogous dinuclear complex  $[{Cu(HSAc)H_2O}_2] \cdot 2NO_3$  have been reported [20]. This complex is a centrosymmetric (planar) dimer, the monomeric units being bridged through the phenoxy oxygen. The copper atom has a square-pyramidal geometry with the basal donor atoms coming from the ONO mononegative tridentate ligand and the symmetry related phenolate oxygen, while the fifth coordination site is occupied by water oxygen. The nitrate ions are not coordinated and act as counter ions [20]. Unfortunately, no variabletemperature magnetic data have been reported for this complex. In the present work, the room temperature magnetic moment of the dinuclear complex  $[{Cu(HSAc)H_2O}_2]$ .  $2NO_3$  was found to be 1.29  $\mu_B$  which is more or less similar to the value reported previously by Chan et al. (1.28  $\mu_B$ ) [20]. Fitting the variable temperature susceptibility data recorded for  $[{Cu(HSAc)H_2O}_2] \cdot 2NO_3$  to a modified Bleaney–Bowers equation gives  $J = -340 \text{ cm}^{-1}$ , g = 2.20 and $X_{\rm p} = 2.2\%$ . The obtained (-2J) is comparable to that reported for  $[{Cu(HSp-CH_3Bzh) \cdot H_2O}_2] \cdot H_2O \cdot 2NO_3$  and a similar dimeric structure  $(7, R = p-CH_3C_6H_4)$  can be proposed for this complex, where the copper(II) is weakly bound to the oxygen of the coordinated water molecule. The anhydrous dimeric  $[{Cu(HSBzh)_2} \cdot 2NO_3 \text{ and } [{Cu(HSp OCH_3Bzh)_{2}$  · 2NO<sub>3</sub> complexes, on the other hand, show relatively higher -2J values (ca. 392 cm<sup>-1</sup>) implying stronger antiferromagnetic exchange interaction between the two copper(II) centres. It seems that coordination of a water molecule in 7a (R = p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>) results in a slight distortion from planarity and decreases the strength of antiferromagnetic interactions relative to the more planar anhydrous dimers.

The thiocyanate complexes  $[Cu(HL)SCN] \cdot nH_2O$ , Table 1, have room temperature magnetic moments in excess of 1.8  $\mu_B$ , Table 4, suggesting that the paramagnetic centres are quite shielded by the diamagnetic matrix, and if the copper centres are spin coupled, exchange is likely to be weak. The magnetic moments of these complexes are more or less constant (ca. 1.87  $\mu_B$ ) within the temperature range (35–300 K), but decrease below 35 K and drop to ca. 1.74  $\mu_B$  at 10 K, suggesting weak antiferromagnetic interactions. Assuming Curie-Weiss behaviour, plots of inverse magnetic susceptibility for 8 ( $R = C_6H_5$ , p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub> and p-ClC<sub>6</sub>H<sub>4</sub>) versus temperature gave Curie–Weiss constants  $\theta = -1.35$ , -1.75 and -3.20, respectively. This magnetic behaviour can rule out the possible formation of a binuclear structure with phenoxy bridges similar to that reported for the corresponding chloride or nitrate complexes and a monomeric structure (8) can be proposed for these thiocyanate complexes. However, dimeric or polymeric structures with bridged thiocyanate cannot be ruled out, since no magnetic interactions between the copper(II) centres was observed in polymeric [Cu(bheg)NCS] $\cdot$ H<sub>2</sub>O (where Hbheg is *N*,*N* bis(2-hydroxyethylglycine)) [34]. The actual structure of these isothiocyanate complexes must remain in doubt until complete X-ray molecular structures are available.

### 2.4. Infrared spectra

The IR spectra of N-salicylidenearoylhydrazines, Table 5, show a series of bands at ca. 3200, 1670, 1600 and 1340 cm<sup>-1</sup>, respectively due to  $\nu$ (N–H),  $\nu$ (C=O) (amide I),  $\nu$ (C=N),  $\delta$ (N-H) (amide II), and  $\nu$ (C-N) (amide III). The spectra of the corresponding binuclear complexes  $[{Cu(L)}_2]$  (2) and K $[{Cu(L)(OH)}_2] \cdot nH_2O$  (4) lack any absorption which can be attributed to  $\nu$ (N–H),  $\nu$ (C=O) or  $\delta(N-H)$ , but show an intense absorption due to  $\nu(C=N-$ N=C) as well as the amide III band, implying the deprotonation of the enolimine tautomer of the hydrazone ligand [1,2,35,36]. However, the spectra of the mononuclear complexes of the types  $[Cu(HL)Cl \cdot H_2O] \cdot nH_2O$  (5),  $[Cu(HSBzH)NO_2] \cdot H_2O$ , and  $[Cu(HL)NCS] \cdot nH_2O$  (8) as well as the binuclear complexes  $[{Cu(HL)Cl}_2]$  (6),  $[{Cu(HL)H_2O}_2](NO_3)_2 \cdot nH_2O$  (7)  $[{Cu(HL)}_2]$ - $(NO_3)_2$  (7a), Table 5, show a series of bands at ca. 3180, 1615, 1600, 1540 and 1320 cm<sup>-1</sup> due to  $\nu$ (N–H),  $\nu$ (C=O),  $\nu$ (C=N),  $\delta$ (N-H) and  $\nu$ (C-N), respectively. The presence of  $\nu$ (N–H),  $\nu$ (C=O) and  $\delta$ (N–H) in the IR spectra of these complexes indicate that the hydrazone molecule reacts in the ketoamine form. Moreover, the stoichiometry of these complexes as well as the pronounced shift in both  $\nu$ (C=O) and  $\nu$ (C=N) to lower frequencies relative to those of corresponding uncoordinated hydrazones suggest that these aroylhydrazones act as mononegative ONO tridentate ligands [1,2,35,36]. The IR spectrum of the mononuclear complex  $[Cu(HSBzH)NO_2] \cdot H_2O$ , Fig. 1, displays three bands at 1510, 1290 and 1000 cm<sup>-1</sup>, respectively due to the  $\nu$ (N=O),  $\nu_{\rm asym}(\rm NO_2)$  and  $\nu_{\rm sym}(\rm NO_2)$ , in agreement with the unsymmetric bidentate nature of the coordinated nitrate. The spectra of the binuclear nitrate complexes  $[{Cu(HL)H_2O}_2]$ - $(NO_3)_2 \cdot nH_2O(7)$  and  $[{Cu(HL)}_2](NO_3)_2(7a)$ , on the other hand, show an intense band at ca. 1380 cm<sup>-1</sup> characteristic of ionic nitrate [22,37]. The spectra of the thiocyanate complexes 8 show an intense band at 2085  $\text{cm}^{-1}$  indicating that the thiocyanate group acts as monodentate ligand, most probably through the nitrogen atom [37].

### 3. Experimental

### 3.1. Preparation of aroylhydrazines and N-salicylidenearoylhydrazines

Aroylhydrazines were prepared, as previously described [38], by the hydrazinolysis of aromatic carboxylic methyl esters in methanol. The corresponding *N*-salicylidene aroyl-

Table 5

Selected IR spectral bands (cm<sup>-1</sup>) for N-salicylidenearoylhydrazines and their corresponding copper(II) complexes

Compound		ν(N–H)	v(C=O) (amide I)	ν(C=N), ν(C=C)	$\delta$ (N–H)	
R	n				(amide II)	(amide III)
$[H_{2}L] (1) C_{6}H_{5} p-CH_{3}C_{6}H_{4} p-CH_{3}OC_{6}H_{4} p-ClC_{6}H_{4} p-ClC_{6}H_{4} $		3250 m 3200 m 3200 m 3205 m	I675 s 1675 s 1670 sh 1646 s	1635 s 1640 s, 1620 s 1636 s, 1604 s 1620 s	1540 s 1540 s 1555 s 1560 s	1355 m 1362 m 1355 s 1365 s
$[{Cu(L)}_2]$ (2) $C_6H_5$ p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> p-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> p-CIC <sub>6</sub> H <sub>4</sub>				1618 s, 1594 s 1619 s, 1595 s 1618 s, 1597 s 1619 s, 1593 s		1340 s 1342 m 1342 s 1342 s
$ \begin{array}{l} K_2[\{Cu(L)OH\}_2] \cdot nH_2O(\textbf{4})\\ C_6H_5\\ p\text{-}CH_3C_6H_4\\ p\text{-}CH_3OC_6H_4\\ p\text{-}ClC_6H_4\\ \end{array} $	2 2 1			1612s 1612s 1615s 1614s		1340 s 1340 m 1343 m 1338 s
$\begin{bmatrix} Cu(HL)Cl.H_2O \end{bmatrix} \cdot nH_2O (5) \\ C_6H_5 \\ p-CH_3C_6H_4 \\ p-CH_3OC_6H_4 \\ p-ClC_6H_4 \\ p-ClC_6H_4 \\ \end{bmatrix}$	1 1	3120 m 3195 m 3200 m	1620 s 1618 s 1620 s	1600 s, 1590 sh 1605 s 1605 s, 1590 s 1590 s	1545 m 1535 s 1555 s 1540 s	1340 s 1335 m 1330 m 1318 m
$[\{Cu(HL)Cl\}_2] (6)$ $C_6H_5$ $p-CH_3C_6H_4$		3125 m 3130 m	1615 s 1618 s	1595 s 1590 s	1550 s 1543 s	1344 m, 1312 m 1326 m, 1308 m
$[Cu(HL)NO_3] \cdot nH_2O$ C <sub>6</sub> H <sub>5</sub>	1	3195m	1622s	1603 s	1545 m	1335 m
$[{Cu(HL)}_2](NO_3)_2(7a)$ $C_6H_5$ p-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>		3180 m 3170 m	1618 s 1620 s	1595 s 1597 s	1545 m 1540 m	1300m 1305m
$[\{Cu(HL) \cdot H_2O\}_2](NO_3)_2 \cdot nH_2O(7)  p-CH_3C_6H_4$	1	3170 m	1620 s	1602 s, 1570	1545 m	1330 m
$ \begin{bmatrix} Cu(HL)(NCS) \end{bmatrix} \cdot nH_2O(8) \\ C_6H_5 \\ p-CH_3C_6H_4 \\ p-CH_3OC_6H_4 \\ \end{bmatrix} $	1	3146 m 3195 m 3210	1620 s 1620 s 1623 s	1605 s, 1590 s 1605 s 1605 s	1544 s 1538 s 1540 m	1327 m 1335 m 1335 s

hydrazines were prepared by the condensation of salicylaldehyde with aroylhydrazines in methanol [38–40] (H<sub>2</sub>SBzh, m.p. = 182°C; H<sub>2</sub>Sp-MeBzh, m.p. = 195°C; H<sub>2</sub>Sp-MeOBzh, m.p. = 173°C; H<sub>2</sub>Sp-ClBzh, m.p. = 208°C).

### 3.2. Preparation of copper(II) complexes of N-salicylidenearoylhydrazines

### 3.2.1. Preparation of $[{Cu(L)}_2]$ (2, $R = C_6H_5$ , $p-CH_3C_6H_4$ , $p-CH_3OC_6H_4$ and $p-ClC_6H_4$ )

To a solution of *N*-salicylidenearoylhydrazine (H<sub>2</sub>L) (1,  $R = C_6H_5$ , *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>, *p*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub> and *p*-ClC<sub>6</sub>H<sub>4</sub>) (0.01 mol) in dry methanol (30 cm<sup>3</sup>), an equivalent amount of Cu(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O (0.012 mol) in dry methanol (50 cm<sup>3</sup>) was added dropwise with constant stirring. During addition a green precipitate started to appear and after complete addition of copper acetate, the reaction mixture was refluxed, with constant stirring, for ca. 30 min. On cooling the formed green complex,  $[Cu(L)]_2$ , was filtered, washed with hot methanol and then dried in vacuo.

### 3.2.2. Preparation of $K_2[{Cu(L)OH}_2] \cdot nH_2O(4, R = C_6H_5, p-CH_3C_6H_4 and p-OCH_3C_6H_4)$

To a suspension of  $[\{Cu(L)\}_2]$  complex (2,  $R = C_6H_5$ , *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub> and *p*-OCH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>) (0.01 mol) in hot absolute ethanol (50 cm<sup>3</sup>), an excess amount of KOH (0.025 mol) was added and the reaction mixture was refluxed until complete dissolution of  $[\{Cu(L)\}_2]$  complex. The resulting solution was filtered and then evaporated to half its volume. On cooling the formed green complex K<sub>2</sub>[{Cu(L)OH}<sub>2</sub>] · *n*H<sub>2</sub>O, Table 1, was isolated and then dried over CaCl<sub>2</sub>.

### 3.2.3. Preparation of $[Cu(HL)Cl] \cdot nH_2O(5, R = C_6H_5, p-CH_3C_6H_4, p-OCH_3C_6H_4 and p-ClC_6H_4)$

A solution of  $CuCl_2 \cdot 2H_2O(0.01 \text{ mol})$  in ethanol (20 cm<sup>3</sup>) was added to a solution of salicylaldehyde (0.01 mol) in

ethanol (50 cm<sup>3</sup>). The reaction mixture was heated for a few minutes and then an equivalent amount of aroylhydrazine (0.01 mol) was added dropwise with constant stirring. The resulting mixture was then refluxed for ca. 15 min and the isolated green complex [Cu(HL)Cl·H<sub>2</sub>O]·nH<sub>2</sub>O (**5**, R = C<sub>6</sub>H<sub>5</sub>, *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>, *p*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub> and *p*-ClC<sub>6</sub>H<sub>4</sub>) which was separated on cooling, was filtered, washed with ethanol then dried in vacuo.

### 3.2.4. Preparation of $[{Cu(HL)Cl}_2] \cdot nH_2O(6, R = C_6H_5 and p-CH_3C_6H_4)$

To a solution of *N*-salicylidenearoylhydrazine (H<sub>2</sub>L) (1,  $R = C_6H_5$  or *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>) (0.01 mol) in absolute ethanol (30 cm<sup>3</sup>), an equivalent amount of CuCl<sub>2</sub> · 2H<sub>2</sub>O (0.01 mol) in hot absolute ethanol (20 cm<sup>3</sup>) was added dropwise with constant stirring, then refluxed for 1 h. On cooling the precipitated copper(II) complex (2.34,  $R = C_6H_5$  or *p*-CH<sub>3</sub>-  $C_6H_4$ ) was filtered, washed with absolute ethanol and then dried in vacuo.

### 3.2.5. Preparation of $[Cu(HSBz)NO_3] \cdot H_2O$

A solution of  $\text{CuNO}_3 \cdot 6\text{H}_2\text{O}$  (0.01 mol) in ethanol (20 cm<sup>3</sup>) was added to a solution of salicylaldehyde (0.01 mol) in ethanol (50 cm<sup>3</sup>). The reaction mixture was heated for a few minutes and then an equivalent amount of aroylhydrazine (0.01 mol) was added dropwise with constant stirring. The resulting mixture was refluxed for ca. 1 h. On cooling, the separated copper(II) complex [Cu(HL)NO<sub>3</sub>]  $\cdot$ H<sub>2</sub>O was filtered, washed with ethanol and then dried in vacuo.

### 3.2.6. Preparation of $[{Cu(HL)NO_3}_2] \cdot nH_2O(7, R = C_6H_5, p-CH_3C_6H_4, and p-CH_3OC_6H_4)$

To a solution of *N*-salicylidenearoylhydrazine H<sub>2</sub>L (1,  $R = C_6H_5$ , *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub> and *p*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>) (0.01 mol) in absolute ethanol (30 cm<sup>3</sup>), an equivalent amount of Cu(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.015 mol) in absolute ethanol (50 cm<sup>3</sup>) was added dropwise with constant stirring. The brownishgreen nitrate complex, [Cu(HL)NO<sub>3</sub>]<sub>2</sub>·*n*H<sub>2</sub>O, which was formed, was filtered off, washed with ethanol and then dried in vacuo.

### 3.2.7. Preparation of $[Cu(HL)SCN] \cdot nH_2O(8, R = C_6H_5, p-CH_3C_6H_4, p-CH_3OC_6H_4 and p-ClC_6H_4)$

To a suspension of either copper chloride or copper nitrate copper(II) complexes (0.01 mol) in methanol ( $30 \text{ cm}^3$ ), the equivalent amount of NH<sub>4</sub>SCN (0.015 mol) as a solid or in methanol ( $10 \text{ cm}^3$ ) was added dropwise and the reaction mixture was stirred at room temperature or refluxed for ca. 2 h. The green precipitate, which was formed, was isolated and washed with methanol, then dried in vacuo.

#### 3.3. Physical measurements

The IR spectra were recorded on a Perkin-Elmer 1430 data system spectrophotometer and/or Perkin-Elmer FT IR spectrometer (PARAGON 100 PC). Calibration of frequency reading was made with polystyrene film. Solid samples were examined as KBr discs. Magnetic susceptibilities of powdered dried samples were recorded on a Faraday-type magnetometer using a sensitive computer controlled D-200 Cahn RG microbalance in the temperature range 4.2–298 K. The magnetic field applied was ~ 1.5 T. Details of the apparatus have been described elsewhere [41,42]. Experimental susceptibility data were corrected for the underlying diamagnetism. The elemental analyses (C, H and N) were performed at the microanalytical laboratory, Faculty of Science, Alexandria University and/or at the Darmstadt Technical University, Germany. The copper(II) content of the prepared complexes was determined volumetrically by titration with EDTA using PAN as indicator and/or by atomic absorption technique.

#### 3.4. X-ray crystal and molecular structure

Suitable crystals were sealed in a fine focus glass capillary tube and mounted on a Nonius CAD-4 [43] diffractometer. Intensity data were collected at room temperature in the  $\omega - \theta$ scan mode, using graphite monochromatized Mo Ka radiation. Lattice constants were determined by full-matrix leastsquares refinement. The solution of the crystal structures was carried out by using both SHELXS-86 [44] and SHELXL-93 [45] programs. The SHELXL-93 program was also used for structure refinement and for the evaluation of data. The Steo-REDU4 [46] and StoeX-RED [46] programs were used for computing data reductions. The graphics plotting of the molecular and crystal structures was carried out using the PLUTON-93 [47] program as well as ORTEP [48] method. The form factors for Cu(0) were taken from the international tables [49] and those for the other atoms are included as saved values in used programs.

### Supplementary data

Atomic coordinates, equivalent isotropic displacement parameters, hydrogen coordinates, isotropic displacement parameters, anisotropic displacement parameters and complete lists of bond distances and bond angles have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk) and are available on request quoting no. CCDC 136950.

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