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HALIDE COPPER(II) COMPLEXES OF AROMATIC N-DONOR CONTAINING LIGANDS: STRUCTURAL, MAGNETIC AND REACTIVITY STUDIES

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The preparation of four new copper(II) complexes with different N-donor ligands [$CuBr_2\cdot$(2-benzylpyridine)$_2$] (**1**), [$CuBr_2$(2-benzylpyridine)(2,2′-bipyridine)]$\cdot H_2O$ (**2**), [$CuBr_2$(3-methyl-2-phenylpiridine)$_2$] (**3**), [Cu(picolinate)$_2$]$\cdot$KI (**4**) from copper(I) halides as starting material is described. During the preparation of compound **4** a ligand oxidation reaction took place to give the picolinate ligand starting from 2-(2-methylaminoethyl)pyridine. The complexes were characterized by elemental analyses, IR spectroscopy and crystallographic studies. Single crystal X-ray diffraction analysis of the complexes reveals their monomeric penta- and tetracoordinated nature. For all compounds, the copper(II) present a common square planar coordination except for compound **2** which is five coordinated in a quasi-square pyramidal configuration with τ of 0.29. The Cu—N distances for these compounds are in the range of 1.959(4)—2.041(3) Å, Cu—O distance was 1.961(3) Å and Cu—Br distances were in the range of 2.4052(4)—2.4381(6) Å for the square base configuration while for apical distance it was 2.6745(7) Å. Magnetic properties have been investigated for all compounds in the temperature range 2—300 K. Compound **1** shows weak antiferromagnetic intermolecular interaction.

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Keywords: copper, structures, halides, magnetism.

INTRODUCTION

Halide copper(II) complexes have been extensively studied [1—7] especially those containing chloro and bromo ligands. This family of compounds exhibit a wide variety of structural types and a broad range of Cu—X distances.

The structures of these compounds are influenced by various factors such as the ligands and solvents used, reaction temperature, metal-ligand ratio, thus producing a variety of coordination geometries. Studies to explore the relationship between the oxidation state of the copper(II) centre and the geometry of the complex as well as the coordinating atoms have been carried out [8—12]. As a result it has become possible to control the oxidation/reduction behaviour using certain ligands.

A significant amount of research has been centered in relatively simple copper(II) complexes which may display some of the properties of the metalloproteins. One of such system of potential im-

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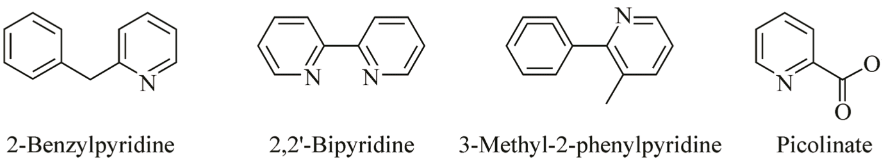
portance is that formed by copper(II) halides with pyridine and substituted pyridines [13]. Copper(II) coordination complexes with N-donor ligands have frequently been used to model the active site in copper proteins with the aim of obtaining insight into the correlation between structure and the spectroscopic and magnetic behavior [14—16].

The biological and medicinal relevance of copper(II) complexes containing aromatic N-containing ligands have been reported. Several reports have appeared describing the anticancer activity of copper(II) derivatives of many classes of nitrogen donors including thiosemicarbazone and imidazole [17]. One such system of potential importance is that formed by copper(II) halides with pyridine and substituted pyridines. Our group recently reported a lawsonate-copper(II) complex showing citotoxicity [18].

Copper(II) complexes were equally used as catalysts for aerial oxidation of primary alcohols in aldehydes under ambient conditions [19, 20]. Thus, [$CuBr_2$(bpy)] in association with 2,2,6,6-tetramethylpiperidyl and a base are good catalysts for the aerobic oxidation of primary alcohols under mild conditions [21]. In this regard it is also interesting to mention the work about biomimetic oxidations catalysed by mononuclear copper complexes carried out by Que Jr. and Tolman [22]. In the present work we have observed the oxidation of the ligand 2-(2-methylaminoethyl)pyridine used for the preparation of compound **4** into picolinate. This oxidation is likely to be promoted by copper(II). Considering the similarities between our complexes and [$CuBr_2$(bipy)], which has been proved to show catalytic activity, alongside the medicinal importance of copper(II) complexes with N-donor heterocycles, this results open the possibility to explore both the catalytic and the medicinal properties of such complexes in a future work.

In this paper we report the synthesis, structural characterisation and magnetic properties of four new copper(II) coordination complexes of general formula [CuL_2X_2] (where L = 2-benzilpyridine, 2-(2-methylaminoethyl)pyridine (Py—CH_2CH_2NHMe), 3-methyl-2-phenyl-pyridine, 2,2′-bipyridine (bpy) and X = I or Br, see the structures of the ligands in Scheme 1).



Scheme 1

EXPERIMENTAL

Materials and methods. All syntheses were carried out at room temperature (except for compound **4**) under aerobic conditions in commercial-grade solvents. Reagents were used as purchased (ALDRICH) without further purifications. Elemental analyses were performed on Elemental CNHS FLASH EA 1112 Elemental analyzer. IR spectra were recorded on a Nicolet IR spectrophotomer. X-ray analysis was performed with an Agilent SuperNova diffractometer with micro-focus X-ray. Variable-temperature direct current (dc) magnetic susceptibility measurements were carried out on powdered samples with a Quantum Design SQUID magnetometer in the range 2—300 K under an applied magnetic field of 1 T. The susceptibility data were corrected for the diamagnetism of the constituent atoms and the sample holder [23].

Synthesis of the compounds. Synthesis of [$CuBr_2$(2-benzylpyridine)$_2$] (1). CuBr (0.2 g, 1.39 mmol) was dissolved in a mixture of dichloromethane (30 ml) and acetonitrile (30 ml) and then 2-benzylpyridine (0.23 g, 1.39 mmol) dissolved in dichloromethane (20 ml) was added. The mixture was stirred for 2 h at room temperature and allowed to stand overnight. The next day the colour of the solution was green indicating the oxidation of Cu(I) to Cu(II) and the green solid was filtered off and recrystallized from methanol. Yield (70 %). Single crystals suitable for X-ray diffraction were grown by slow evaporation of the solvent after a few days. Elemental analysis calc. for $C_{24}H_{22}Br_2CuN_2$ (**1**) (M = 531.53) (%): C 51.29, H 3.95, N 4.99. Found (%): C 51.50, H 4.12, N 5.05. IR (KBr, cm^{-1}): 3432, 3023, 2353, 2336, 1601, 1482, 1025, 755, 706. The bands at 1601 cm^{-1} and 1482 cm^{-1} are due to the pyridine groups.

Compound **1** can be also prepared by mixing an equimolar solution of $CuBr_2$ (0.20 g, 0.89 mmol) with 2-benzylpyridine (0.136 mg, 0.89 mmol) in acetonitrile. The mixture was stirred for 30 minutes and allowed to stand overnight, after that crystals of the compound **1** were obtained. Yield based on $CuBr_2$ 70 %.

Synthesis of [$CuBr_2$(2-benzylpyridine)(2,2′-bipyridine)]·H_2O (2). CuBr (0.20 g, 1.39 mmol) was dissolved in dichloromethane (30 ml) and acetonitrile (30 ml), then 2-benzylpyridine (0.23 g, 1.39 mmol) and 2,2′-bipyridine (0.05 g, 0.35 mmol) dissolved in dichloromethane (20 ml) were added. The mixture was stirred for 2 h at room temperature, and after a few hours the colour of the solution turned green indicating the oxidation of Cu(I) to Cu(II). The compound was recrystallized from a mixture of toluene/methanol. Single crystals suitable for X-ray diffraction were grown by slow evaporation of the solvent after a few days. Yield based on CuBr (0.504 g). Elemental analysis calc. for $C_{22}H_{21}Br_2CuN_3O$ (**2**) ($M = 566.52$) (%): C 46.60, H 3.74, N 7.42. Found (%): C 46.32, H 4.07, N 7.17. IR (KBr, cm^{-1}): 3521, 3032, 1609, 1573, 1490, 1436, 1158, 852, 696. The bands at 1609 cm^{-1}, 1573 cm^{-1} and 1490 cm^{-1} are assigned to benzyl and pyridine groups.

Alternatively, compound **2** can be obtained by mixing together equimolar amounts of $CuBr_2$ (0.20 g, 0.89 mmol), 2-benzylpyridine (0.136 mg, 0.89 mmol) and 2,2′-bipyridine (0.139 g, 0.89 mmol) in acetonitrile. After standing overnight crystals of the compound were obtained. Yield 60 % based on $CuBr_2$.

Synthesis of [$CuBr_2$(3-methyl-2-phenylpyridine)$_2$] (3). CuBr (0.2 g, 1.39 mmol) dissolved in methanol (60 ml) was mixed with 3-methyl-2-phenyl pyridine (0.23 g, 1.39 mmol) dissolved in methanol (20 ml). The mixture was stirred for 3 h at room temperature. After three hours, the colour of the solution turned green indicating the oxidation of Cu(I) to Cu(II). Single crystals suitable for X-ray diffraction were grown by slow evaporation of the solvent. Elemental analysis calc. for $C_{24}H_{22}BrCuN_2$ (**3**) ($M = 481.63$) (%): C 59.80, H 4.60, N 5.81. Found (%): C 60.06, H 4.21, N 5.58. IR (KBr, cm^{-1}): 3038, 1981, 1879, 1584, 1432, 1121, 999, 785, 747, 702. The bands at 1584 cm^{-1} and 1432 cm^{-1} are due to benzyl and pyridyl.

Compound **3** was also prepared by mixing an equimolar amount of $CuBr_2$ (0.20 g, 0.89 mmol) with 3-methyl-2-phenyl pyridine (0,138 g, 0.89 mmol) in methanol. The reaction mixture was left to stand overnight, yielding green crystals.

Synthesis of [Cu(picolinate)$_2$]·KI (4). CuI (0.10 g, 0.52 mmol) was dissolved in acetonitrile (20 ml) and mixed with a saturated solution of KI in 45 ml of acetonitrile. To this mixture 2-(2-methylaminoethyl)pyridine (Py—CH_2CH_2NHMe) (0.07 g, 0.52 mmol) dissolved in dichloromethane (15 ml) was added. The reaction mixture was stirred for 3 h at 75°C. The colour of the solution gradually turned green indicating the oxidation of Cu(I) to Cu(II). Single crystals suitable for X-ray diffraction were grown by slow evaporation of the solvent after a few days. Yield 55 %. Elemental analysis: calc. for $C_{12}H_{12}CuN_2O_4KI$ (**4**) ($M = 473.98$) (%): C 30.41, H 1.70, N 5.91. Found (%): C 30.62, H 1.86, N 5.69. IR (KBr, cm^{-1}): 3432, 2921, 2847, 2357, 2336, 1634, 1589, 1429, 1119, 796, 775, 743, 698, 669. The bands at 1634 cm^{-1}, 1589 cm^{-1} and 1429 cm^{-1} are due to the carboxylate groups of the picolinate ligand.

Single crystal X-ray crystallography. The XRD data for all compounds were collected at 293(2) K with an Agilent SuperNova diffractometer with micro-focus X-ray using Cu radiation ($\lambda = 1.5418$ Å) at X-ray Service of La Laguna University (SIDIX). *CrysAlisPro* [24] software was used to collect, index, scale and apply numerical absorption corrections based on Gaussian integration over a multifaceted crystal model. All structure solutions were obtained by application of the charge-flipping algorithm using the SuperFlip program [25], and Fourier recycling and least-squares refinement were used for the model completion with Shelxl software [26]. All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms have been placed in geometrically suitable positions and refined riding with isotropic thermal parameter related to the equivalent isotropic thermal parameter of the parent atom. The methyl-H atoms were refined as rigid groups, which were allowed to rotate but not to tip, with $U_{iso}(H) = 1.5U_{eq}(C)$ and the other hydrogen atoms were allowed to ride on their parent atoms with $U_{iso}(H) = 1.2U_{eq}(C)$ and restraints for water hydrogens distance was apply on com-

Table 1

Summary of the crystal data for **1—4** *compounds*

Parameter	**1**	**2**	**3**	**4**
Empirical formula	$C_{24}H_{22}Br_2CuN_2$	$C_{22}H_{21}Br_2CuN_3O$	$C_{24}H_{22}Br_2CuN_2$	$C_{12}H_8N_2O_4CuIK$
Formula weight	561.79	566.78	561.79	473.74
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	$C2/c$	P-1	P-1	$C2/c$
a, Å	21.8604(15)	8.3700(6)	8.2718(3)	12.0401(4)
b, Å	5.8964(4)	10.6039(7)	8.5429(3)	13.9506(4)
c, Å	18.0076(10)	12.06054(9)	9.2854(4)	8.7790(3)
α, deg.		96.101(6)	114.965(4)	
β, deg.	97.883(6)	97.193(6)	90.535(3)	101.219(3)
γ, deg.		102.746(6)	109.258(3)	
V, Å^3	2299.2(3)	1072.22(13)	553.04(4)	1446.40(8)
Z	4	2	1	4
D_{calc}, mg/mm^3	1.623	1.755	1.687	2.176
$\mu(\text{Cu}K_\alpha)$, mm^{-1}	5.496	5.947	5.712	21.630
$F(000)$	1116	562	279	908
Crystal dimensions, mm	0.123×0.085×0.055	0.155×0.115×0.034	0.264×0.125×0.098	0.108×0.067×0.059
2θ range for data collection, deg.	8.2—133.2	7.2—133.2	10.6—133.2	9.8—133.2
Limiting indices	$-25 \le h \le 26$	$-9 \le h \le 8$	$-9 \le h \le 9$	$-14 \le h \le 14$
	$-7 \le k \le 7$	$-8 \le k \le 12$	$-10 \le k \le 10$	$-16 \le k \le 16$
	$-21 \le l \le 20$	$-14 \le l \le 14$	$-11 \le l \le 11$	$-10 \le l \le 10$
Reflections collected / unique, (R_{int})	6524 / 2021 (0.019)	6486/3761 (0.027)	7619/1953 (0.015)	4457/1275 (0.026)
Data / restraints / parameters	2021 / 0 / 133	3761 / 3 / 262	1953 / 0 / 134	1275 / 0 / 99
R_1[a], wR_2[b] $[F^2 > 2\sigma(F^2)]$	0.0252, 0.0644	0.0376, 0.1041	0.0298, 0.0915	0.0334, 0.0863
Goodness-of-fit on F^2	1.05	1.05	1.08	1.10
Largest diff. peak/hole, e/Å^3	0.45 / –0.51	0.77 / –0.58	0.41 / –0.71	1.95 / –1.71
CCDC	949469	949470	949471	949472

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[a] $R_1 = \sum||F_0| - |F_c|| / \sum|F_c|$.

[b] $wR_2 = \{\sum[w(F_0^2 - F_c^2)^2] / \sum[w(F_0^2)^2]\}^{1/2}$.

pound **2**. Graphics were generated using Olex2 [27] program. Crystal data, collection procedures and refinement results are summarized in Table 1 where selected bonds lengths and angles are listed in Table 2.

Crystallographic data for structures reported in this paper have been deposited in the Cambridge Crystallographic Data Centre with reference numbers 940469-949472. Copies of the data can be obtained free of charge on application to the CCDC, Cambridge, U.K. (http://www.ccdc.cam.ac.uk/).

RESULTS AND DISCUSSION

Synthesis of the complexes. For the synthesis of compounds **1—3** CuBr was used as metal source since our initial objective was to prepare Cu(I) complexes in order to study their photophysical properties. However, in the course of the reaction partial or total oxidation of the Cu(I) to Cu(II) took

Table 2

Selected bonds and angles for **1—4**

Distances, Å		Angles, deg.			
Complex **1**					
Br(1)—Cu(1)	2.4052(4)	Br(1)—Cu(1)—N(1)	89.63(6)	Br(1)—Cu(1)—Br(1)$^{\rm i}$	180.00
Cu(1)—N(1)	1.9805(18)	Br(1)—Cu(1)—N(1)$^{\rm i}$	90.37(6)	N(1)—Cu(1)—N(1)$^{\rm i}$	180.00
Complex **2**					
Br(1)—Cu(1)	2.6745(7)	Br(1)—Cu(1)—Br(2)	96.99(2)	Br(2)—Cu(1)—N(2)	95.98(9)
Br(2)—Cu(1)	2.4381(6)	Br(1)—Cu(1)—N(1)	89.99(8)	Br(2)—Cu(1)—N(3)	88.41(6)
Cu(1)—N(1)	2.041(3)	Br(1)—Cu(1)—N(2)	99.37(8)	N(1)—Cu(1)—N(2)	80.04(11)
Cu(1)—N(2)	2.028(3)	Br(1)—Cu(1)—N(3)	104.47(8)	N(1)—Cu(1)—N(3)	92.58(9)
Cu(1)—N(3)	2.038(3)	Br(2)—Cu(1)—N(1)	172.47(8)	N(2)—Cu(1)—N(3)	155.04(11)
Complex **3**					
Br(1)—Cu(1)	2.4105(4)	Br(1)—Cu(1)—N(1)	90.43(7)	Br(1)—Cu(1)—Br(1)$^{\rm ii}$	180.00
Cu(1)—N(1)	1.981(3)	Br(1)—Cu(1)—N(1)$^{\rm ii}$	89.57(7)	N(1)—Cu(1)—N(1)$^{\rm ii}$	180.00
Complex **4**					
Cu(1)—O(2)	1.961(3)	O(2)—Cu(1)—N(1)	83.13(15)	O(1)$^{\rm v}$—K(1)—O(1)$^{\rm vi}$	62.51(10)
Cu(1)—O(2)$^{\rm iii}$	1.961(3)	O(2)—Cu(1)—N(1)$^{\rm iii}$	96.87(15)	O(1)—K(1)—O(2)$^{\rm iv}$	93.60(9)
Cu(1)—N(1)	1.959(4)	O(2)—Cu(1)—O(2)$^{\rm iii}$	180.00	O(1)—K(1)—O(2)$^{\rm vi}$	86.40(9)
Cu(1)—N(1)$^{\rm iii}$	1.959(4)	N(1)—Cu(1)—N(1)$^{\rm iii}$	180.00	O(1)$^{\rm iv}$—K(1)—O(2)$^{\rm iv}$	43.13(9)
K(1)—O(1)	2.845(3)	O(1)—K(1)—O(1)$^{\rm iv}$	62.51(1)	O(1)$^{\rm iv}$—K(1)—O(2)$^{\rm vi}$	136.87(9)
K(1)—O(1)$^{\rm iv}$	3.020(3)	O(1)—K(1)—O(1)$^{\rm v}$	180.00(13)	O(2)$^{\rm iv}$—K(1)—O(2)$^{\rm vi}$	180.00(13)
K(1)—O(1)$^{\rm v}$	2.845(3)	O(1)—K(1)—O(1)$^{\rm vi}$	117.49(10)		
K(1)—O(1)$^{\rm vi}$	3.020(3)				
K(1)—O(2)$^{\rm iv}$	3.029(3)				
K(1)—O(2)$^{\rm vi}$	3.029(3)				

$^{\rm i}$ 1/2–*x*, 3/2–*y*,1–*z*; $^{\rm ii}$ 2–*x*, 1–*y*, –*z*; $^{\rm iii}$ 1/2–*x*, 1/2–*y*, 1–*z*; $^{\rm iv}$ 1–*x*, *y*, 1/2–*z*; $^{\rm v}$ 1–*x*, –*y*, –*z*; $^{\rm vi}$ *x*, 1–*y*, –1/2+*z*.

place which could be observed from rapid colour changes from yellow to green. After slow evaporation of the solvent crystals of complexes **1—3** were obtained. Then we reproduced the syntheses under the same conditions with CuBr$_2$ as starting material instead of CuBr, and the same compounds were obtained in comparable yields which was confirmed by X-ray data. Typically, CuBr$_2$ and the corresponding N-donor ligand were mixed in equimolar ration and stirred in acetonitrile for half an hour. Then the solution was allowed to stand overnight and the next day crystals of the complexes were filtered off by suction. There are several examples reported in the literature of halides complexes prepared from CuX$_2$ as a metal source [28, 29]. The stabilisation of Cu(I) complexes using bromide as halide is more difficult than using iodide. We have observed this in the preparation of several copper(I) complexes (unpublished work), when CuI gave in all cases only Cu(I) complexes. However, the present work gives an example of a Cu(II) complex obtained from CuI as starting material. The synthetic procedure for the preparation of these Cu(II) complexes is straightforward and involves mixing together equimolar amounts of CuX and N-donor ligands in dichloromethane/acetonitrile mixtures or in methanol and stirring the solution in air for some hours at room temperature. We have no evidence that varying the solvent may result in the formation of other Cu(II) complexes such as was the case with [Cu(dipyam)$_2$I$_2$] reported in [30] (dipyam = 2,2′-dipyridylamine), where different complexes were obtained depending on whether the reaction was carried out in water or in acetonitrile.

For compound **4** the reaction mixture was heated for 3 h during which an oxidative degradation of the ligand took place to give coordinated picolinate. Slow evaporation of the solvent yielded crystals suitable for X-ray crystallography.

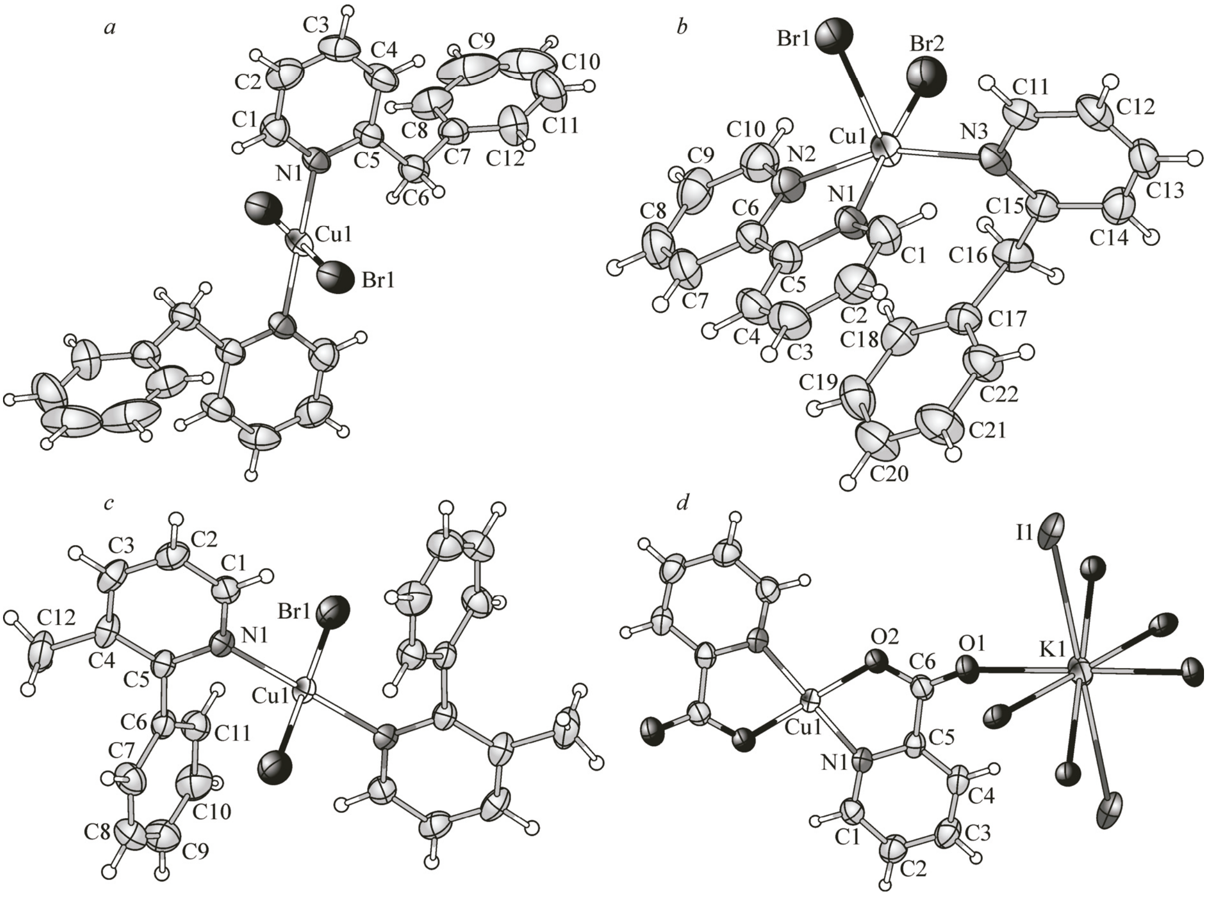

Fig. 1. View of the structures of compound **1** (*a*), compound **2** (*b*), compound **3** (*c*), compound **4** (*d*). Atom labelling is shown

Crystal structures. The crystallographic data and structure refinement parameters are summarized in Table 1, and selected bonds and angles for all compounds are listed in Table 2. In all structures Cu(II) shows a common square-planar geometry (four coordinated), except for **2**, where it has a coordination mode close to square pyramidal (five coordinated).

In compound **1** (Fig. 1, *a*) this square-planar configuration is formed by Cu—N(pyridine) and Cu—Br bonds of 1.9805(18) Å and 2.4052(4) Å, respectively, the bromide and nitrogen atoms adopting a *trans* configuration similar to other related structures [30—37]. This configuration is preferred since the 2-benzylpyridine is a bulky ligand and in this way the steric repulsion is minimized. The angle between the two rings of the organic ligand 85.9(2)°, while the aperture angle (C5—C6—C7) is 113.7(2)°. These parameters fall within the range of the values found in similar structures in the CCDC Database (version 5.33, February 2014) where we found a range of 111.34—117.93° (HEQTOO, PEFDEL) for the aperture angle and 57.73—89.66° (PEFDEL, LUHVOZ) for the angle between the respective rings. The crystal packing (Fig. 2, *a*) shows a very weak π—π interaction with Cg—Cg^{i} (Cg is the centroid of the ring formed by C7, C8, C9, C10, C11 and C12, $^{i} = -x, 1-y, 1-z$) distance of 4.042(3) Å, and a slippage of 2.110 Å with 3.447(2) Å as perpendicular distance between the centroid and the respective ring. The π—π stacking interaction between the pyridine ligands is a common feature [31]. The shortest Cu···Cu intermolecular distance is 5.8964(4) Å.

In compound **2** (Fig. 1, *b*), an N-donor ligand (bpy) replaces a 2-benzylpyridine ligand. Cu(II) atom has five fold coordination giving a quasi-square pyramidal configuration with τ = 0.29 [38]. The base of the square pyramid is defined by the N atoms of the bpy and 2-benzylpyridine (2.036(3) Å being average Cu—N distance) and the bromide atom closest to Cu(II) center (2.4381(6) Å), while the

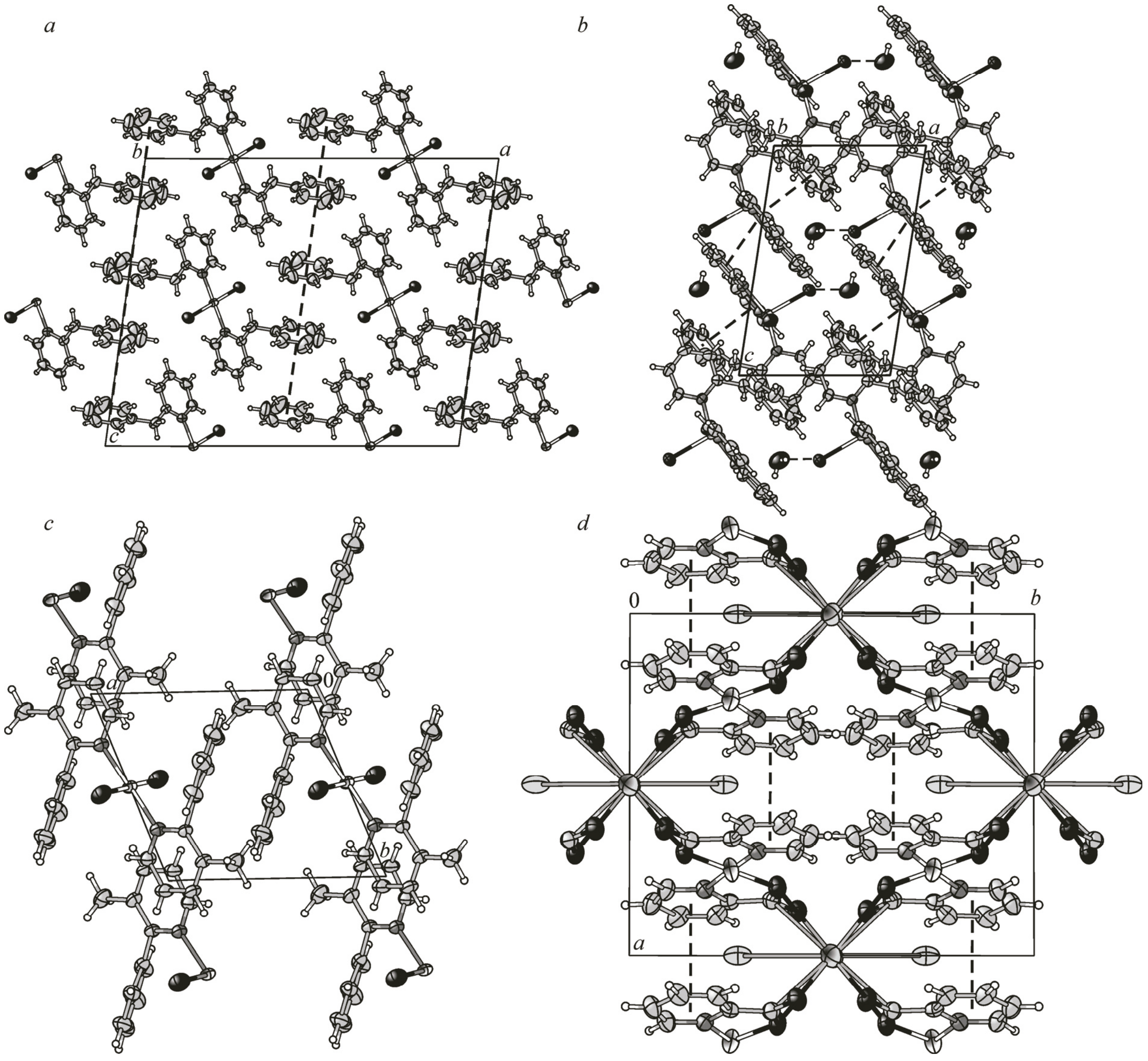

Fig. 2. Packing of the structure of compound **1** (*a*), **2** (*b*), **3** (*c*), **4** (*d*)

apical position is occupied by the other bromide atom (2.6745(7) Å). We found 44 structures with this same configuration in the CCDC (version 5.33-Feb2014) database where the τ parameter was ≤ 0.3 for 65 % of the structures. The average values of the Cu—N and Cu—Br bonds lengths that form the base of the square pyramid were 2.028 Å and 2.4306 Å, respectively, while the Cu—Br apical length was 2.6127 Å. Reported values indicates that the Cu—Br bonds in the equatorial plane are always shorter and fall in the range of 2.43—2.45 Å, in a good agreement with our data [33]. The structure has a five-membered chelate ring which gives a greater stability to this complex as compared to **1** and **3**. The angles between the rings of the 2-benzylpyridine molecule 84.3(2)° and aperture angle (C15—C16—C17) 115.6(3)° are similar to those found for **1**. The packing is dominated (Fig. 2, *b*) by π—π interactions with Cg—Cg distance of 3.796(2) Å in the case of intramolecular interaction between bpy (N1, C1, C2, C3, C4, C5) and the phenyl ring (C17, C18, C19, C20, C21, C22), and 4.027(2) Å for intermolecular interactions between the bpy ligands. Also there are C—H…π interactions at a distance of 3.655(4) Å for C…Cg^i (C21…N3, C11,C12,C13,C14,C15; $^i = -x, -y, 2-z$). Hydrogen bonding is found between the water molecule and bromide atoms with donor-acceptor distances 3.433(4) Å and 3.472(4) Å. The shortest Cu···Cu intermolecular distance is 7.9516(9) Å.

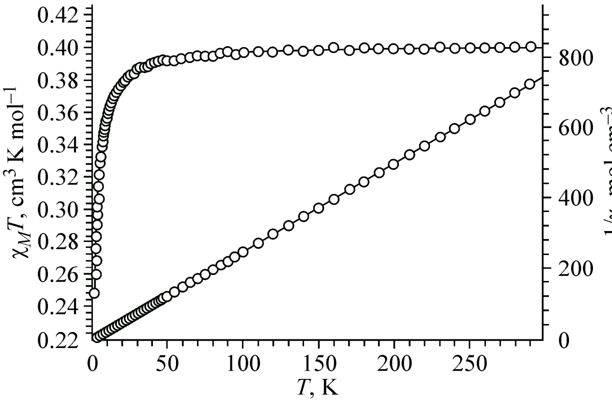

Fig. 3. $\chi_M T$ and $1/\chi_M$ vs T plots for compound **1**. The solid line represents the best fit through a Curie—Weiss law (see text)

The structure of compound **3** (Fig. 1, *c*) is similar to **1**. The square planar geometry is defined by the N atoms of the 3-methyl-2-phenylpyridine and Br atoms with bond lengths 1.981(3) Å and 2.4105(4) Å for Cu—N and Cu—Br bonds, respectively. The angle between rings is 61.37(11)°. The van der Waals interactions seem to be solely responsible for the packing of this compound (Fig. 2, *c*). The shortest Cu···Cu intermolecular distance is 8.2718(4) Å.

In **4** (Fig. 1, *d*) the square planar coordination is defined by N and O atoms of the picolinato-N,O chelating ligand, where the Cu—O and Cu—N distances are 1.961(3) Å and 1.959(4) Å, respectively. The structure has two five-membered chelate rings. The K^+ is linked with the oxygen atoms of the ligands (Fig. 1, *d*) at the distances ranging from 2.845(3) Å to 3.029(3) Å, and shows a contact with an iodine atom at 3.9136(5) Å. The crystal packing (Fig. 2, *d*) shows a square grid net topology resulting from weak coordinative interactions between the carboxylate oxygen atoms of the bis(picolinato)copper(II) anions and the potassium cations. The packing presents π—π interactions and new classical hydrogen bonds. The distance between the centroids Cg—Cg^i (N1, C1, C2, C3, C4, C5; $^i = -x, y, 1/2-z$) is 3.651(3) Å, and the bond distance is 3.748(5) Å for C—H...I interactions (Fig. 2, *d*). The shortest Cu···Cu intermolecular distance is 6.7251(2) Å.

Magnetic properties. The $\chi_M T$ product for **1** at room temperature is 0.402 cm^3·K·mol^{-1}, a value expected for a magnetically isolated spin doublet of a copper(II) ion. Upon cooling, $\chi_M T$ remains constant following Curie law up to 15 K when $\chi_M T$ starts decreasing to reach a value of 0.248 cm^3·K··mol^{-1} at 2.0 K. This magnetic behavior is consistent with the mononuclear nature of **1** as found in the crystal structure, and the decrease of $\chi_M T$ at low temperatures can be assigned to weak intermolecular antiferromagnetic interactions. A least-squares fit of the experimental magnetic data through a Curie—Weiss law where we have included a parameter to take into account these weak antiferromagnetic interactions has been carried out leading to $\theta = -1.2$ K and $g = 2.067$ with a $R = 2.0\times10^{-4}$ [$R = \sum[(\chi_M)_{obs} - (\chi_M)_{calc}]^2/\sum[(\chi_M)_{obs}]^2$] [39]. The calculated curve matches the experimental data in the whole temperature range (Fig. 3). For **2**—**4** the $\chi_M T$ value remains constant over the whole temperature range explored with the $\chi_M T$ values at room temperature being within 0.395—0.397 cm^3·K·mol^{-1}.

CONCLUSIONS

We described preparation of four new copper(II) coordination complexes from CuX (X = Br or I) and nitrogen donor ligands. Alternatively, compounds **1**, **2** and **3** can be prepared from $CuBr_2$ instead of CuBr. All the complexes are mononuclear and feature a square planar coordination except for **2** which has a quasi-square pyramidal coordination. Regarding the magnetic properties of the compounds, only **1** exhibits a weak intermolecular antiferromagnetic interaction. The intermolecular antiferromagnetic interactions observed in **1** are in agreement with those observed in other mononuclear copper(II) complexes [40]. During the synthesis of **4** a ligand degradation took place to give coordinated picolinate. The oxidative degradation of the ligand is assumed to be copper(II) or Cu(I)/O_2-catalysed.

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