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Dinuclear alkoxo-bridged copper(II) coordination polymers: Syntheses, structural and magnetic properties

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1. Introduction

Coordination compounds forming metal–organic frameworks via self-assembly have received great attention due to their interesting architectures and potential applications in the field of catalysis, conductivity, porosity, chirality, luminescence and magnetism [1–16]. Metal–organic frameworks are infinite systems constructed from metal ions (and metal clusters) functioning as nodes and organic ligands as bridges. Andruh et al. have successfully used alkoxo-bridged dinuclear Cu(II) units as nodes in the design of framework polymers [17–24]. The alkoxo-bridged dinuclear copper(II) nodes are formed spontaneously from the reaction of copper(II) salts with aminoalcohol. The lower the denticity of the aminoalcohol ligand the higher dimensionality of the metal–organic framework can be expected [23].

The magnetic behavior of polynuclear transition metal coordination compounds have been widely studied [25,26]. The magnetic behavior of hydroxy- and alkoxy-bridged dinuclear Cu(II) units are well known [23,27–35]. The primary geometric factor determining the magnitude of the exchange coupling for the hydroxy- and alkoxy-bridged dinuclear Cu(II) complexes, the Cu–O–Cu bridging angle (θ), was established by Hatfield and co-workers [27]: the larger the angle θ the stronger the antiferromagnetic coupling between the copper(II) ions. There are several other geometric parameters found by theoretical studies [36–42], which affect the magnetic

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ABSTRACT

The alkoxo-bridged dinuclear copper(II) complexes $[Cu_2(ap)_2(NO_2)_2]$ (1), $[Cu_2(ap)_2(C_6H_5COO)_2]$ (2) and $[Cu_2(ap)_2\mu-1,3-C_6H_4(COO)_2(dmso)_2]$ -dmso (3) (ap = 3-aminopropanolato and dmso = dimethyl sulfoxide) have been synthesized via self-assembly from copper(II) perchlorate, 3-aminopropanol as main chelating ligand and nitrite and isophthalate anions as spacers and benzoate anion as auxiliary ligand. Complexes 1 and 3 crystallize as 2D and 1D coordination polymers, respectively, and their structures consist of dinuclear $[Cu_2(ap)_2]^{2+}$ units connected with nitrite and isophthalate ligands. The adjacent dinuclear units of 2 and 1D polymers of 3 are further connected by hydrogen bonds resulting in the formation of 2D layers. The variable temperature crystallographic measurements of 1 at 100, 173 and 293 K indicate the static Jahn–Teller distortion with librational disorder in the nitrite group. Experimental magnetic studies showed that complexes 1–3 exhibit strong antiferromagnetic couplings. The values of the magnetic exchange coupling constant for 1–3 are well reproduced by the theoretical calculations.

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coupling between copper(II) ions. For example, the planarity of the coordination sphere around copper(II) ions, the out-of-plane shift of the carbon atom of the bridging alkoxo group (H atom for hydroxo complexes). Ruiz et al. [38] showed that the antiferro-magnetic coupling diminished for hydroxy- and alkoxo-bridged dinuclear Cu(II) coordination compounds as the out-of-plane shift of the carbon atom increased.

Although the majority of coordination polymers are formed from metal ions connected by oxygen atoms of carboxylate anions and/or nitrogen atoms of pyridines [11], there are only a few coordination structures constructed from alkoxo-bridged dinuclear Cu(II) units (chelated with different aminoalcohols) with aromatic carboxylate ligands [43–52]. The only reported metal–organic frameworks derived from these dinuclear Cu(II) units with aromatic polycarboxylate ligands are obtained by using aminopolyalcohols [34,53–55].

We have earlier studied experimentally and theoretically the charge densities in polymeric $[Cu_2(ap)_2(NO_2)_2]$ (1) (ap = 3-aminopropanolato) at 100 K [35], in which a dinuclear Cu(II) unit with a *pseudo*-Jahn–Teller distorted 4 + 1 + 1 coordination was found. Now we have determined the crystal structure of 1 at 173 and 293 K to explore the nature of this *pseudo*-Jahn–Teller phenomenon.

Also the syntheses and crystal structures of two new alkoxobridged dinuclear copper(II) complexes derived from using 3-aminopropanol (Hap) as chelating ligand and aromatic mono- or polycarboxylic acid, benzoic acid or isophthalic acid, as auxiliary or bridging ligand $[Cu_2(ap)_2(C_6H_5COO)_2]$ (2) and $[Cu_2(ap)_2\mu-1,3-C_6H_4(COO)_2(dmso)_2]$ ·dmso (3) (dmso = dimethyl sulfoxide) are presented in this study. The structural properties of the extended



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2D coordination polymers of **2** and **3** are compared to the polymeric structure of **1**. Finally the magnetic properties (experimental and theoretical) of these alkoxo-bridged dinuclear copper(II) complexes **1–3** are presented and discussed.

2. Experimental

2.1. Materials and physical measurements

All chemicals and solvents were purchased from commercial sources and were used without further purification.

CAUTION: Although we have experienced no difficulties, perchlorate salts of metal complexes with organic ligands are potentially explosive and should be handled with care even in small quantities.

Elemental analyses were performed using a VarioEl III elemental analyzer. Variable temperature (1.9–300 K) magnetic susceptibility measurements on polycrystalline samples were carried out with a Quantum Design SQUID MPMS XL-5 device operating at 1 T from room temperature to 50 K and at 0.05 T from this latter temperature to 2 K. The experimental susceptibilities were corrected for the diamagnetism of the constituent atoms by using Pascal's tables.

2.2. Syntheses

2.2.1. Preparation of $[Cu_2(ap)_2(NO_2)_2]$ (1)

Cu(ClO₄)₂·6H₂O (186.7 mg, 0.50 mmol) was dissolved in methanol (65 ml). To this solution Hap (98.8 μ l, 1.28 mmol) in methanol (10 ml) and NaNO₂ (42.0 mg, 0.61 mmol) in methanol (25 ml) were added. The dark green solution was allowed to stand at room temperature for overnight. The dark blue crystalline product was filtered and washed with ethanol and diethyl ether and dried in air. Yield 59.6 mg (64%).

Anal. Calc. for $C_6H_{16}Cu_2N_4O_6$: C, 19.62; H, 4.39; N, 15.25. Found: C, 19.56; H, 4.21; N, 15.12%.

2.2.2. Preparation of $[Cu_2(ap)_2(C_6H_5COO)_2]$ (2)

Cu(ClO₄)₂·6H₂O (184.3 mg, 0.49 mmol) was dissolved in methanol (5 ml) and Hap (91.2 μ l, 1.20 mmol) was added. To this solution, benzoic acid (148.6 mg, 1.22 mmol) and N(Et)₃ (194.2 μ l, 1.40 mmol) in methanol (17.5 ml) was added. Violet crystals were formed after standing at room temperature for overnight. The violet crystalline product was filtered and washed with ethanol and diethyl ether and dried in air. Yield 70.4 mg (55%).

Anal. Calc. for C₂₀H₂₆Cu₂N₂O₆: C, 46.42; H, 5.06; N, 5.41. Found: C, 46.50; H, 4.81; N, 5.33%.

2.2.3. Preparation of $[Cu_2(ap)_2\mu - C_6H_4(COO)_2 - 1,3(dmso)_2] \cdot dmso$ (**3**)

Cu(ClO₄)₂·6H₂O (187.8 mg, 0.51 mmol) was dissolved in dmso (5 ml) and Hap (152.0 μ l, 2.00 mmol) was added. To this solution isophthalic acid (101.3 mg, 0.61 mmol) in dmso (7 ml) was added. The dark blue solution remained clear at room temperature, but when the solution was transferred to refrigerator (7 °C), dmso solidified (mp. 18.6 °C) and small blue crystals started to form. After melting of dmso, the crystals were filtered and washed with ethanol and diethyl ether and dried in air. Yield 143.3 mg (92%).

Anal. Calc. for $C_{20}H_{38}Cu_2N_2O_9S_3$: C, 35.65; H, 5.68; N, 4.18. Found: C, 35.25; H, 5.91; N, 4.09%.

2.3. X-ray data collection and structure refinement

Crystallographic data were collected at 173 K for **1–3** and also at 293 K for **1** with a Nonius-Kappa CCD area-detector diffractometer using graphite monochromatized Mo K α radiation (λ = 0.71073 Å).

The data were collected by φ and ω rotation scans and processed with the DENZO-SMN v0.93.0 software package [56]. Empirical absorption corrections were performed with sADABS program [57]. The structures were solved by direct methods using the SHELXS-97 program [58] and full-matrix, least-squares refinements on F^2 were performed using the SHELXL-97 program [58] with the WinGX graphical user interface [59]. Mean-square displacement parameters for **1** were calculated using the THMA11 program [60]. Thermal ellipsoid plots were obtained by using the DIAMOND program [61]. The partial packing diagrams were drawn with the MERCURY program [62]. For complexes 1 and 2 the heavy atoms were refined anisotropically. The NH hydrogen atoms of 1 and 2 were located from the difference Fourier map and were refined isotropically while other hydrogen atoms were constrained to ride on their parent atoms. In 3, one dmso molecule was disordered over two sites (C11, C12, O5 and S2) with equal occupancies, thus accounting for the residual electron density in 3. The S2-C11 and S2-C12 distances of the disordered dmso molecule were fixed to 1.8 Å. The disordered C11 and C12 atoms were refined isotropically while other heavy atoms were refined anisotropically. Anisotropic refinement of the C11 and C12 atoms did not improve the structure model of 3. The NH hydrogen atoms of 3 were located from the difference Fourier map and were refined isotropically with fixed distances of 0.87 Å while other hydrogen atoms were constrained to ride on their parent atoms. The crystal data for 1-3 along with other experimental details are summarized in Table 1.

2.4. Computational details

All theoretical calculations were carried out with the hybrid B3LYP method [63–65], as implemented in the GAUSSIAN 03 program [66]. A quadratic convergence method was employed in the SCF process [67]. Triple- ζ quality basis set proposed by Ahlrichs and co-workers has been used for all atoms [68]. The calculations were performed on the complexes built from the experimental geometries. More detailed about the models can be found in the discussion of the results. The electronic configurations used as starting points were created using the JAGUAR 7.5 program [69].

The *J* value of the dinuclear complexes have been determined by calculating the energy difference between the high spin state (E_{HS}) and the broken symmetry state (E_{BS}), according to the following equation:

$$E_{\rm HS} - E_{\rm BS} = -S_{\rm HS}(S_{\rm HS} + 1)J/2 \tag{1}$$

using the Heisenberg Hamiltonian $\hat{H} = -J\hat{S}_1\hat{S}_2$. Here S_1 and S_2 are the spin of the paramagnetic centers.

The approach that we used herein to determine the exchange coupling constants for polynuclear complexes has been described in detail elsewhere [70–73].

3. Results and discussion

3.1. Syntheses

Complexes **1–3** have been synthesized via the self-assembly of copper(II) perchlorate, 3-aminopropanol as chelating ligand, nitrite and isophthalate anions as spacers, and benzoate anion as auxiliary ligand. The alkoxo-bridged dinuclear $[Cu_2(ap)_2]^{2+}$ units are easily formed after deprotonation of the OH group of the 3-aminopropanol ligand with presence of copper(II) ions. The addition of sodium nitrite for **1**, benzoic acid for **2** and isophthalic acid for **3** leads to formation of three coordination compounds $[Cu_2(ap)_2(NO_2)_2]$ (**1**), $[Cu_2(ap)_2(C_6H_5COO)_2]$ (**2**) and $[Cu_2(ap)_2\mu-1,3-C_6H_4(COO)_2(dm-so)_2] dmso ($ **3**).

Table I

Summary of crystallographic data for 1 at three different temperatures and for 2 and 3 at 173 K.

Complex	1 (100 K) ^a	1 (173 K)	1 (293 K)	2	3
Formula	$C_6H_{16}Cu_2N_4O_6$	$C_6H_{16}Cu_2N_4O_6$	$C_6H_{16}Cu_2N_4O_6$	C20H26Cu2N2O6	C20H38Cu2N2O9S3
M _r	367.31	367.31	367.31	517.51	673.78
Crystal system	orthorhombic	orthorhombic	orthorhombic	monoclinic	monoclinic
Space group (No.)	Pbca (61)	Pbca (61)	Pbca (61)	$P2_1/c$ (14)	$P2_1/m$ (11)
a (Å)	8.3395(3)	8.3598(2)	8.3644(2)	12.7444(3)	7.7639(3)
b (Å)	8.5023(3)	8.5416(2)	8.6348(2)	8.3887(2)	21.6931(9)
c (Å)	17.1507(5)	17.1799(5)	17.2222(5)	10.1696(2)	8.7016(4)
α (°)	90	90	90	90	90
β(°)	90	90	90	103.579(2)	96.731(3)
γ (°)	90	90	90	90	90
$V(Å^3)$	1216.07(7)	1226.75(5)	1243.87(5)	1056.83(4)	1455.45(11)
Ζ	4	4	4	2	2
D_{calc} (g mm ⁻³)	2.01	1.989	1.961	1.626	1.537
$\mu(Mo K\alpha) (mm^{-1})$	3.524	3.493	3.445	2.051	1.723
Number of collected data	227 269	25 744	16 284	11 832	13 426
Number of unique data	8930	1863	1980	2600	3648
R _{int}	0.0421	0.0593	0.0514	0.0385	0.0615
Parameters	82	90	91	144	193
R_1^{b}	0.0355 (0.0251) ^c	0.0422 (0.0296)	0.0514 (0.0337)	0.0394 (0.0311)	0.0910 (0.0552)
wR_2^d	0.0641 (0.0620)	0.0591 (0.0562)	0.0725 (0.0669)	0.0727 (0.0697)	0.1224 (0.1103)
Goodness of fit (GOF) on F^2	1.096	1.067	1.033	1.039	1.032
Largest difference in peak and hole (e ${\rm \AA}^{-3})$	1.154 and –1.180	0.368 and -0.417	0.376 and -0.343	0.286 and -0.463	1.500 and -0.710

^a Data from Ref. [35].

^b $R_1 = \sum ||F_0| - |F_c|| / \sum |F_0|.$

^c Values in parentheses for reflections with $I > 2.0\sigma(I)$.

^d $wR_2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$ and $w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP)]$, where $P = (2F_c^2 + F_o^2)/3$.

The crystallization of polymeric complexes **1** and **3** is very rapid, resulting in microcrystalline or amorphous powders for **1** and **3**, which are not suitable for single X-ray studies. In order to obtain X-ray quality single crystals, the crystallization process was slowed down using dilute solutions for **1** and by solidifying the solvent for **3**. Although these syntheses were optimized to obtain X-ray quality single crystals the products were isolated with moderate to high yields (based on copper(II) perchlorate).

3.2. Description of the structures

Complexes **1** and **3** crystallize as 2D and 1D coordination polymers and their structures consist of dinuclear $[Cu_2(ap)_2]^{2+}$ units connected with nitrite and isophthalate ligands. In complex **2**, dinuclear units are not connected by the benzoate anions, which act as monodentate end-cap ligands. The 2D coordination polymer layers of **1** are further stabilized by intralayer H-bonds. The adjacent dinuclear units of **2**, and 1D polymers of **3** are further connected with hydrogen bonds resulting in the formation of 2D layers. The dinuclear units and the numbering of the atoms of **1**-**3** are shown in Figs. 1–3, respectively, whereas the partial crystal packing diagrams showing polymeric chains and hydrogen bonding networks of **1**–**3** are shown in Figs. 4–6, respectively. Selected bond parameters and hydrogen bond parameters are presented in Tables 2 and 3, respectively.

As the crystal structure of **1** was reported and discussed earlier [35], we concentrate upon its variable temperature crystallographic measurements at 100, 173 and 293 K. At the three measured temperatures, the structure shows a clear *pseudo*-Jahn– Teller elongation along O3–Cu–O3ⁱⁱ axis and the Cu(II) coordination sphere is close to tetragonally distorted octahedral (4 + 1 + 1) geometry. In this description, the oxygen atoms belonging to the alkoxo bridging groups (O1 and O1ⁱ), the amine nitrogen atom (N1) and an oxygen atom of the nitrite group (O2) are coordinated in equatorial positions, whereas the O3 and O3ⁱⁱ oxygen atoms from two nitrite anions occupy the axial positions. The variable temperature crystallographic measurements also indicate that bond lengths and angles around the Cu(II) center vary only



Fig. 1. The dimeric unit of **1** (173 K) showing the atomic labeling scheme, with thermal ellipsoids drawn at the 30% probability level. Symmetry codes: (i) –*x*, 1 – *y*, –*z*; (ii) –1/2 + *x*, 3/2 – *y*, –*z*; (iii) 1/2 - x, -1/2 + y, *z*.

marginally with temperature (Table 2). Only the axial Cu–O3ⁱⁱ bond distance lengthens from 2.6042(7) to 2.682(2) Å as the temperature is increased from 100 to 293 K. The temperature-invariant Cu-ligand bond lengths and the nearly perpendicular orientation of the thermal ellipsoids of the ligand atoms towards the Cu–L bonds are indication of the static Jahn–Teller distortion [74].

Since the bond lengths and the thermal ellipsoids of Cu–L bonds of **1** at different temperatures show structural evidence of a static disorder, the presence or absence of librational disorder was determined through a mean-square displacement amplitude (MSDA) analysis [60,75]. The MSDA of a given atom is the desired meansquare displacement amplitude of the atom parallel to the direction of a given chemical bond. The difference between the MSDA values for the two atoms in a given bond (Δ MSDA or $\langle d^2 \rangle$) is proportional to the degree of interatomic libration along that bond. The Δ MSDA for metal–ligand bond is computed as MSDA(ligand)–MSDA(metal), with both MSDAs calculated for the direction



Fig. 2. The dimeric unit of **2** showing the atomic labeling scheme, with thermal ellipsoids drawn at the 30% probability level. Symmetry code: (i) 1 - x, -y, 1 - z.



Fig. 3. The dimeric unit of **3** showing the atomic labeling scheme, with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms and disordered dmso molecule are omitted for clarity. Symmetry codes: (i) -x, 1 - y, 1 - z; (ii) x, 1/2 - y, z; (iii) x, 1/2 + y, 1 - z.

of the M–L bond. Values of $\langle d^2 \rangle$ for a bond are typically found in the range of $(10-100) \times 10^{-4} \text{ Å}^2$ [75]. At 100 and 173 K all bonds around Cu(II) center of **1** have low $\langle d^2 \rangle$ values (Table 2) and are consistent with a static molecular structure. However, at 293 K the high $\langle d^2 \rangle$ values for Cu–O3 and Cu–O3ⁱⁱ bonds, along the elongation axis, indicate that librational disorder is present involving these two bonds. Also the $\langle d^2 \rangle$ value at 100 and 173 K. The negative value of $\langle d^2 \rangle$ for the Cu1–O1ⁱ bond at 293 K arises when MSDA (O1ⁱ) < MSDA (Cu1). The librational disorder of the bonds at the elongation axis, parallel to the crystallographic *a* axis, and the $\langle d^2 \rangle$ value for Cu–O2 bond at 293 K might result from the disorder of the nitrite group along the crystallographic (*bc*) plane since the size of the unit cell becomes large primarily with the growing along the crystallographic *b* and *c* axes (Table 1) as the temperature increases.



Fig. 4. View along *c* axis of the partial crystal packing diagram of **1** (173 K) showing the 2D network and the NH \cdots O2 hydrogen bonds (black dashed lines). Hydrogen atoms are omitted for clarity.



Fig. 5. View along *a* axis of the partial crystal packing diagram of **2** showing the 2D hydrogen bonding network (black dashed lines). Hydrogen atoms are omitted for clarity.

The crystal structure of **2** shows that copper(II) ions have a square-planar coordination. The square-planar coordination sphere of Cu(II) ions in the *xy*-plane consists of two alkoxide oxygen atoms (O1, O1ⁱ), one amine nitrogen (N1) and one oxygen atom (O2) from the carboxylate anion. The Cu–X bond distances around the square-planar Cu(II) centers all lie below 1.967(2) Å, indicating the strong nature of these bonds. The shortest axial contacts [Cu···O interactions] are at 2.726(2) Å, significantly longer than the bonds in the *xy*-plane. In our recent experimental and theoretical charge density study [35] for structures of [Cu₂(ap)₂(L)₂] (L⁻ = nitrate or formate, with Cu1···O3 distances 2.6 and 2.7 Å, respectively), the charge density evidence showed no significant didentate coordination of the L⁻ anion (the Cu1···O3 interaction). Therefore, the benzoate oxygen atom did not show this axial interaction either.

On the similar basis, in the crystal structure of **3**, Cu(II) ion has a distorted square-pyramidal coordination sphere as the sixth donor atom (O3) is at the distance of 2.775(3) Å. Cu(II) ions in the *xy*-plane consists of two alkoxide oxygen atoms (O1, O1ⁱ), one amine nitrogen (N1) and one oxygen atom (O2) from the carboxylate anion. The fifth coordination position is occupied by O4 from dmso.

Within the dinuclear units in the series $[Cu_2(ap)_2(L)_2] (L^- = ni-trite, nitrate and formate) bond angles in the$ *xy*-plane are quite similar [35]. In the**1–3**series (**1** $= <math>[Cu_2(ap)_2(NO_2)_2]$), however, the bond angles in *xy*-plane vary quite a lot. For example, angles



Fig. 6. View along *c* axis of the partial crystal packing diagram of **3** showing 1D polymeric chains and the extended 2D hydrogen bonding network (black dashed lines). Hydrogen atoms and disordered dmso molecules are omitted for clarity.

Table 2

Selected bond lengths (Å) and angles (°) for 1 at three different temperatures and for 2 and 3 at 173 K. The square brackets contain values of $\langle d^2 \rangle$ (10⁻⁴Å²) calculated for 1.

Complex	1 (100 K) ^a , ^b	1 (173 K) ^c	1 (293 K) ^d	2 ^e	3 ^f
Cu1–Cu1i	2.9633(2)	2.9586(5)	2.9486(5)	3.0419(5)	3.0201(8)
Cu1-N1	1.9813(4) [15(1)]	1.979(2) [26(9)]	1.980(2) [27(11)]	1.970(2)	1.976(3)
Cu1-01	1.9389(4) [12(1)]	1.9383(14) [11(7)]	1.936(2) [14(8)]	1.9227(14)	1.947(2)
Cu1-O1 ⁱ	1.9368(4) [7(1)]	1.9369(13) [7(7)]	1.9313(15) [-16(8)]	1.9310(14)	1.938(2)
Cu1-02	2.0197(6) [25(2)]	2.0230(14) [34(7)]	2.034(2) [63(10)]	1.9628(14)	1.990(2)
Cu1-03	2.4762(6) [52(2)]	2.480(2) [72(10)]	2.472(2) [144(14)]	2.7253(15)	2.795(3)
Cu1–O3 ⁱⁱ	2.6042(7) [38(2)]	2.629(2) [45(9)]	2.682(2) [95(13)]	-	-
Cu1-04	-	-	-	-	2.396(3)
$Cu1-O1-Cu1^{i}(\theta)$	99.74(2)	99.54(6)	99.36(7)	104.25(6)	102.02(10)
01-Cu1-O1 ⁱ	80.26(2)	80.46(6)	80.64(7)	75.75(6)	77.98(10)
01-Cu1-N1	95.91(2)	95.75(7)	95.56(8)	97.28(7)	93.98(12)
02-Cu1-N1	90.94(2)	90.86(7)	90.72(8)	93.12(7)	94.20(12)
02-Cu1-O1 ⁱ	93.16(2)	93.20(6)	93.29(7)	93.82(6)	93.37(10)
01-Cu1-O3 ⁱⁱ	91.68(2)	91.76(6)	91.80(8)	-	-
01-Cu1-O4	-	-	-	-	96.02(9)
O1 ⁱ -Cu1-O3 ⁱⁱ	92.81(2)	92.67(6)	92.46(8)	-	-
02-Cu1-O3 ⁱⁱ	93.33(2)	92.95(6)	91.70(8)	-	-
N1-Cu1-O3 ⁱⁱ	83.71(2)	83.61(7)	83.70(9)	-	-
02-Cu1-O3	54.93(3)	54.78(6)	54.32(8)	53.69(6)	52.38(9)
01^{i} -01-C1 (τ)	31.88(5)	32.26(12)	32.46(13)	1.43(13)	27.5(3)
Cu1-O1-Cu1 ⁱ -O2 ⁱ	175.3(1)	175.56(6)	176.73(8)	179.91(7)	171.27(11)
Cu1-O1 ⁱ -Cu1 ⁱ -N1 ⁱ	176.4(1)	176.16(7)	176.05(9)	176.30(8)	177.57(14)

^a Symmetry codes for **1** (100 K): (i) 2 - x, 1 - y, -z; (ii) -1/2 + x, 3/2 - y, -z.

^b Data from Ref. [35].

^c Symmetry codes for **1** (173 K): (i) -x, 1 - y, -z; (ii) -1/2 + x, 3/2 - y, -z.

^d Symmetry codes for **1** (293 K): (i) -x, -y, 1 - z; (ii) -1/2 + x, 1/2 - y, 1 - z.

^e Symmetry code for **2**: (i) –*x*, –*y*, 2 – *z*.

^f Symmetry code for **3**: (i) -x, 1 - y, 1 - z.

Table 3	
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Iydrogen bond	parameters	(Å,	°) for	1-3 at	173(2)) K.
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Complex	$D{-}H{\cdot}{\cdot}{\cdot}A$	d(D–H)	$d(H \cdot \cdot \cdot A)$	$d(D \cdot \cdot \cdot A)$	$d(D-H\cdots A)$
1 ^a	$\begin{array}{l} N1\text{-}H01A{\cdots}O1^{i}\\ N1\text{-}H01B{\cdots}O2^{ii}\\ N1\text{-}H01B{\cdots}N2^{ii} \end{array}$	0.84(3) 0.86(3) 0.86(3)	2.41(3) 2.23(3) 2.67(3)	3.171(2) 3.087(2) 3.464(3)	150(2) 174(2) 154(2)
2 ^b	$\begin{array}{l} N1\text{-}H01A \cdots O3^i \\ N1\text{-}H01B \cdots O3^{ii} \end{array}$	0.86(3) 0.77(3)	2.20(3) 2.30(3)	3.050(2) 2.878(3)	169(2) 133(3)
3 ^c	$\begin{array}{l} N1H01A \cdots O2i \\ N1H01B \cdots O4^i \end{array}$	0.85(2) 0.86(2)	2.37(3) 2.11(3)	3.100(4) 2.883(4)	144(4) 151(4)

^a Symmetry codes for **1**: (i) 1/2 – *x*, 1/2 + *y*, *z*; (ii) –*x*, 2 – *y*, –*z*.

^b Symmetry codes for **2**: (i) -x, -1 - y, 2 - z; (ii) x, -1/2 - y, -1/2 + z.

^c Symmetry code for **3**: (i) 1 – *x*, 1 – *y*, 1 – *z*.

O1–Cu1–N1 at 173 K for **1–3** are 95.56(8), 97.12(10) and 93.98(12)°, respectively and angles O1–Cu1–O1ⁱ at 173 K for **1–3** are 80.64(7), 75.90(10) and 77.98(10)°, respectively. These angle deformations of the $[Cu_2(ap)_2]^{2+}$ units depend on the nature of L⁻. Nitrite, nitrate and formate anions are similar, but when L⁻ is

a benzoate anion, it is able to modify bonding in the $[Cu_2(ap)_2]^{2+}$ unit via the change of the packing requirements. Thus varying the anionic ligand L^- in $[Cu_2(ap)_2(L)_2]$ compounds the physical properties of the dinuclear copper(II) compounds might be controlled.

In the crystal structure of **1**, $[Cu_2(ap)_2]^{2+}$ units are connected by nitrite anions as spacers leading to infinite brick wall type 2D layers. The brick wall type 2D layers are further stabilized with intermolecular hydrogen bonds (Table 3) involving the NH hydrogen atoms, the alkoxo oxygen atom (O1), the nitrite oxygen atom (O2) and the nitrite nitrogen atom (N2) within the 2D layer. In complex **2**, the neutral dinuclear $[Cu_2(ap)_2(C_6H_5COO)]$ units are connected by hydrogen bonds (Table 3) involving the NH hydrogen atoms and the carboxylate oxygen atom (O3) resulting in the formation of hydrogen bonded 2D layers. Complex **3** forms wavelike infinite 1D polymeric chains constructed from dinuclear $[Cu_2(ap)_2]^{2+}$ nodes and didentate isophthalate ligands as spacers. The formation of 2D coordination network between the $[Cu_2(ap)_2]^{2+}$ nodes and isophthalate spacers is hindered by the dmso molecule coordinated to the axial site of the Cu(II) ion. The wavelike 1D polymeric chains of **3** are connected through hydrogen bonds (Table 3) involving the NH hydrogen atoms, the dmso oxygen atom (O4) and the carboxylate oxygen atom (O2) from the adjacent polymeric chain to form 2D layers. The layers are parallel to crystallographic (*ab*) plane and stack in an AAA fashion along the crystallographic *c* axis. The space between the layers is occupied by disordered dmso molecules.

3.3. Magnetic properties

Complexes 1–3 have a similar planar $Cu(\mu-OR)_2Cu$ bridging skeleton, in which copper(II) atoms exhibit slightly distorted square-planar geometries and different weak axial interactions involving donor atoms of the counteranions. DFT calculations carried out on alkoxo-bridged model compounds [38,39], containing a planar $Cu_2(\mu$ -O₂) skeleton and a methyl group bonded to each oxygen atom of the double bridge, predicted antiferromagnetic interactions for the whole range of the Cu–O–Cu (θ) when τ values (out-of-plane displacement of the carbon atom from the Cu_2O_2 plane) were smaller than 40°. Moreover, a correlation was established between θ and τ , showing that small values of θ are associated with the largest values of τ . Therefore, the AF coupling is favored when θ increases and τ diminishes. Other theoretical studies [41] have shown that the tetrahedral distortion of the squareplanar coordination environment of the copper(II) atoms reduces the AF interaction. All these theoretical results were in good agreement with the available experimental data.

The Cu-O-Cu bridging angles in **1-3** are 99.54(6), 104.10(10) and 102.02(10)°, respectively. The τ angle of **2** is close to zero, whereas τ angles of **1** and **3** indicate a significant out-of-plane shift for the carbon atom of the alkoxo-bridge. Due to the crystallographic inversion center the $Cu_2(\mu-0)_2$ units are coplanar in all three complexes. Thus the planarity of the primary coordination sphere of the Cu atoms is quantified by the torsion angles Cu1-O1-Cu1ⁱ-O2ⁱ and Cu1-O1ⁱ-Cu1ⁱ-N1ⁱ (Table 2). Complex **2** is closest to planarity, while the complex **3** shows the greatest deviation, with the carbonyl O2 atom lying slightly out of the plane defined by the remaining three ligand atoms. Since the copper(II) coordination spheres for complexes 1-3 exhibit very similar Cu1-O1-Cu1ⁱ-O2ⁱ and Cu1–O1ⁱ–Cu1ⁱ–N1ⁱ torsion angles (Table 2), the magnetic exchange coupling will be mainly determined by the θ and τ parameters. From the θ and τ values observed for **1–3** (Table 2), strong AF interactions are expected in the order |J(2)| >|J(3)| > |J(1)|.

The magnetic properties of complex **1** in the form χ_M versus *T* (χ_M is the molar susceptibility for Cu₂ unit) are given in Fig. 7.

The plot shows a maximum at 275 K, thus indicating the existence of strong AF interactions, as expected. Below the tempera-



Fig. 7. Temperature dependence of the χ_M for complex **1**.

ture of the maximum, χ_M decreases with decreasing the temperature. At very low temperature, however, $\gamma_{\rm M}$ increases, which is typical of strong AF coupled systems, and indicates the presence of a small amount of paramagnetic impurity. As expected, the $\chi_{\rm M}T$ product at room temperature is much lower than that expected for two uncoupled copper(II) ions with g = 2 $(0.750 \text{ cm}^3 \text{ mol}^{-1} \text{ K})$. On lowering the temperature, the $\chi_M T$ rapidly decrease close to zero at 2 K. The susceptibility data for 1 were fitted to the Bleaney-Bowers equation with the Hamiltonian H = - IS_1S_2 . A ρ parameter was included in the theoretical equation to account for the percentage of paramagnetic impurity. In this complex, the dinuclear units are linked by nitrite bridging groups with long interdinuclear Cu. Cu distances of 4.39-4.43 Å at 100-293 K. The shortest interdinuclear Cu--Cu distances for 2 and **3** are 5.34 and 4.94 Å, respectively. The calculated *J* values of interdinuclear Cu...Cu interaction for similar complexes with nitrate and formate bridging groups were -0.047 and -0.156 cm⁻¹ with Cu...Cu distances of 4.42 and 4.57 Å, respectively [35]. Therefore, the magnetic interaction mediated through these long bridges is very small compared to that mediated by the alkoxo-bridge. In light of this and to avoid overparametrization, the magnetic coupling through the nitrite bridging ligand was not considered in the fitting procedure. The best-fit parameters are: $I = -302 \text{ cm}^{-1}$, g = 2.01 and $\rho = 0.05\%$ for **1**. For **2** and **3**, no maximum was observed in the χ_M versus *T* and therefore the AF interaction must be larger than -400 cm^{-1} . The uncertainty in the estimation of the J value from the fit of the susceptibility data is very large, and in consequence, these data were not fitted to the Bleaney-Bowers equation. On the other hand, for these strong antiferromag-

Table 4

Structural parameters and calculated and observed J values for 1-3 at 173 K.

Complex	Cu-O-Cu (°)	τ (°)	J_{calc} (cm ⁻¹)	$J_{\rm obs}~({\rm cm}^{-1})$
1	99.54(6)	32.26(12)	-301	-302
2	104.10(10)	1.43(13)	-941	>-400 ^a
3	102.02(10)	27.5(3)	-601	>-400 ^a

^a These values cannot be accurately determined from the magnetic susceptibility data (see text).



Fig. 8. Calculated spin density distribution for the singlet broken symmetry state of **1**. Grey shapes correspond to positive and blue shapes to negative spin densities. The isodensity surface corresponds to a cut-off value of 0.001 e bohr⁻³.

netically coupled systems, where the diamagnetic correction is of the same order of magnitude as the uncorrected molar susceptibility, the uncertainty of the corrected values is large. In view of this, we decided to perform DFT theoretical calculations to evaluate the magnetic exchange coupling constants and to check the experimental values. The *J* values were obtained as the intrinsic energy difference between the broken symmetry singlet state and the corresponding triplet state. The computed *J* values for **1**–**3** are given in Table 4 and compare reasonably well with the experimental values. In view of the above results, it seems that in the case of strong AF Cu₂ coupled systems with *J* values smaller than -400 cm^{-1} , the fit of the magnetic data still leads to relatively accurate *J* values if the diamagnetic correction is properly performed.

The spin density surfaces for **1–3** obtained from the broken symmetry singlet state (the spin density of **1** is given as an example in Fig. 8, whereas those for **2** and **3** are given as Supplementary Material) clearly show that spin density at each copper(II) atom has the shape of a $d_{x_2-y_2}$ orbital and it is σ delocalized on the donor atoms directly attached to the metal. Therefore, exchange pathway is of the σ type, involving the $d_{x_2-y_2}$ magnetic orbitals of the copper(II) atoms and the *p* orbitals of the bridging oxygen atoms.

4. Conclusions

The use of aromatic carboxylate anions in the synthesis of dinuclear copper(II) complexes with 3-aminopropanol leads to novel metal–organic frameworks. The structures of alkoxo-bridged dinuclear copper(II) complexes of the formula $[Cu_2(ap)_2(L)_2S_n]$ (L = monoanionic ligand and S = solvent, n = 0-2) depend on the nature of the anionic L. The variable temperature crystallographic measurements of $[Cu_2(ap)_2(NO_2)_2]$ (1) at 100, 173 and 293 K indicate a static *pseudo*-Jahn–Teller distortion with librational disorder in the nitrite group. Experimental magnetic studies yielded *J* values –302, >–400 and >–400 cm⁻¹ for 1–3, respectively. The theoretical calculations show that the magnetic exchange coupling will be mainly determined by the θ and τ parameters.

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Appendix A. Supplementary material

CCDC 738527, 738528, 738529, 738530 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2009.11.035.

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