Graphical abstract

Synthesis, structure, magnetic properties and EPR spectroscopy of a copper(II) coordination polymer with ditopic hydrazone ligand and acetate bridges

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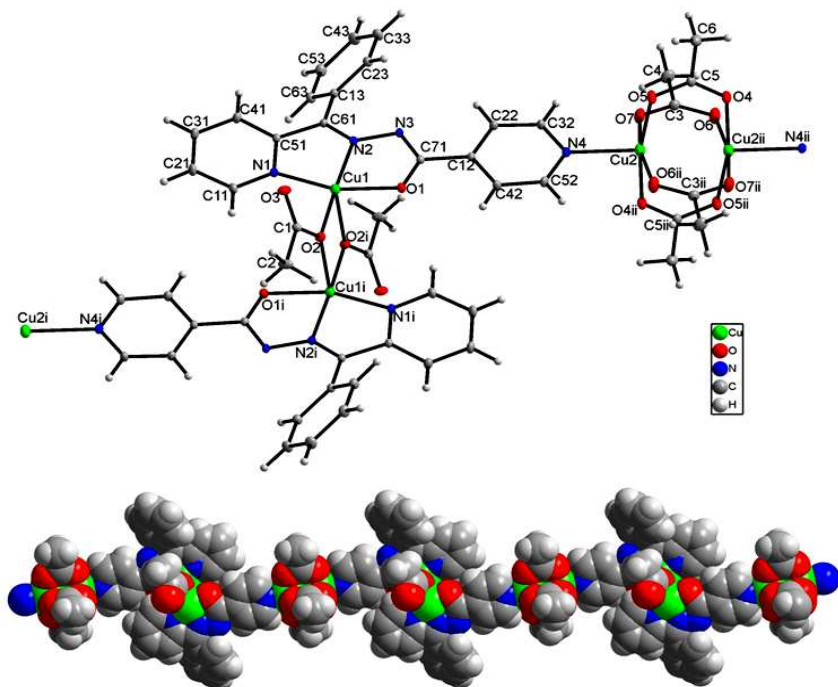
Highlights

- ✓ Synthesis and structure of a 1D coordination polymer of Cu(II) with ditopic hydrazone ligand is reported.

- ✓ The structure of copper(II) coordination polymer containing two kinds of acetate bridged dimers is reported.

- ✓ Magnetic properties and single crystal EPR spectroscopy of acetato bridged Cu(II) coordination polymer are studied.

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ARTICLE TYPE

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Abstract

20 A new one dimensional coordination polymer of copper(II), $[Cu_4(L)_2(\mu_2\text{-}1,1\text{-}OAc)_2(\mu_2\text{-}1,3\text{-}OAc)_4]_n$ (**1**), has been synthesized and characterized by spectroscopic methods and single crystal X-ray analysis [HL = (*E*)-*N'*-(phenyl(pyridin-2-yl)methylene)isonicotinhydrazide, OAc = acetate anion]. The coordination polymer contains two kinds of Cu(II) dimers which are connected by two types of acetate ($\mu_2\text{-}1,1\text{-}$ and $\mu_2\text{-}1,3\text{-}$) bridging groups. The ditopic isonicotinhydrazone ligand coordinates to the Cu1
25 center through N_2O-donor set and connects to the Cu2 center by pyridine group of isonicotine part. The EPR and magnetic susceptibility measurements confirm the existence of two kinds of Cu(II) dimers. The intradimer isotropic exchange was estimated to be $+0.80(1)$ cm^{-1} for ferromagnetic Cu1···Cu1 dimeric unit and -315 (1) cm^{-1} for antiferromagnetic Cu2···Cu2 dimeric unit.

30 *Keywords*: Ditopic ligand; Cu(II) coordination polymer; EPR spectroscopy; Magnetic properties; Crystal structure; Acetate bridges

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Introduction

The design and synthesis of novel coordination polymers and metal–organic frameworks (MOFs) have attracted great attention
[5] in the fields of inorganic and coordination chemistry.[1] Several effective synthetic strategies have been employed to construct coordination polymers in the past several decades.[2] The most useful strategy to construct such compounds is to employ suitable bridging groups,[3] or multitopic organic ligands (with specific
[10] structure and several donor atoms) which simultaneously bind to several metal ions.[4] The controlled preparation of coordination polymers with pre-established structures, properties and functions is one of the challenges in synthetic coordination chemistry.

The acetate anion (OAc$^-$) is a versatile bridging ligand for
[15] obtaining multinuclear complexes and 1D, 2D or 3D coordination networks. When the acetate anion acts as bridging ligand, it can bind to metal ions in different coordination modes such as common μ_2-1,1-OAc,[5] μ_2-1,3-OAc,[6] μ_3-1,1,3-OAc,[7] and rare μ_3-1,1,1-OAc,[8] μ_4-1,1,1,3-OAc,[9] μ_4-1,1,3,3-OAc,[10] μ_5-1,1,1,3,3-
[20] OAc[11] modes (Scheme 1). Additionally, the acetate anion plays an important role in the magnetic exchange pathways between paramagnetic centers and depending to the coordination mode, shows various magnetic interactions.[12]
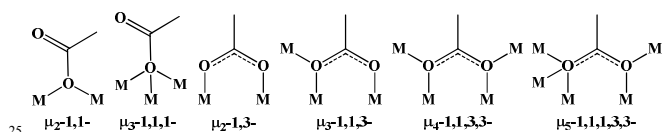

[25]
Scheme 1. The known metal ion bridging modes of acetate ion

Copper(II) complexes with acetate bridging groups have been of interest for some decades and a huge number of acetate bridged
[30] Cu(II) complexes with various ligands have been reported in literature.[13] It is well known that the copper(II) acetate in the presence of ligands containing monodentate N-donor pyridine groups forms dinuclear μ_2-1,3-OAc bridged complexes with general formula of Cu$_2$(OAc)$_4$L$_2$ (L is monodentate N-donor
[35] ligands) (Scheme 2a).[14] These dinuclear units have short Cu···Cu distances (≈ 2.6 Å). On the other hand, the reaction of copper(II) acetate with tridentate ligands usually produces dinuclear complexes containing μ_2-1,1-OAc bridging groups (Scheme 2b).[15]
[40] The hydrazone ligands obtained from the reaction of aliphatic/aromatic acid hydrazides with 2-alkyloyl-/2-aryloyl-pyridines are one of the most important classes of tridentate N$_2$O-donor ligands,[16] as they form only μ_2-1,1-OAc bridged dinuclear Cu(II) complexes.[17] The hydrazone ligand obtained from the
[45] reaction of 4-pyridine carboxylic acid hydrazide with 2-benzoylpyridine (Scheme 2c) is an interesting ditopic ligand which can coordinate to metal ions via two different donor sets: i) from the N$_2$O-donor tridentate pocket ii) from the N-atom of 4-pyridine group.[18] This ligand can coordinate to the metal ions as
[50] neutral (in the keto form) or mononegative (in the enol form) to modify the number of negative charges and the oxidation state of metal core.[18] Although many acetato bridged Cu(II) complexes have been reported until now, searching the literature indicates that the Cu(II) complexes with both μ_2-1,1-OAc and μ_2-1,3-OAc
[55] bridging groups are abnormally rare and only three structures

have been reported.[19] The advantages of the coordination ability of ditopic isonicotinhydrazone ligand (HL) and its potential to form μ_2-1,1-OAc and μ_2-1,3-OAc bridged Cu(II) complexes prompted us to employ HL for a preparation of a new Cu(II)
[60] coordination network. In this study we report the synthesis, characterization, EPR spectroscopy and magnetic properties of a new Cu(II) coordination polymer containing both μ_2-1,1-OAc and μ_2-1,3-OAc bridged dinuclear units.
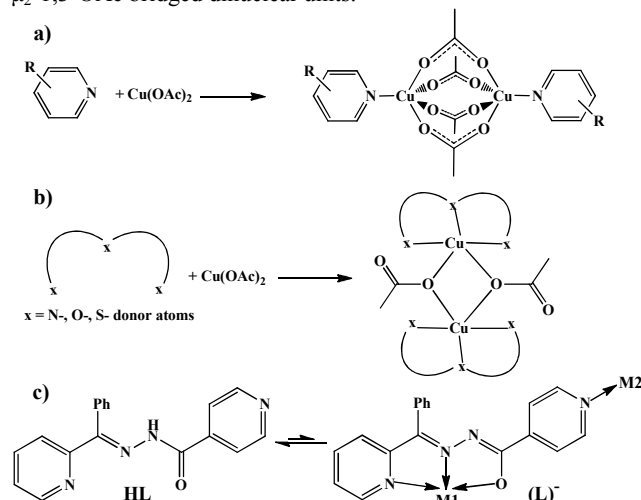
[65]
Scheme 2. a) schematic structure of the most of the copper complexes with monodentate pyridine donor ligands and acetate anion; b) schematic structure of the most of the copper complexes with tridentate ligands and acetate anion; c) the structure of ditopic isonicotinhydazone ligand with two different donor sites
[70]

Results and discussion

### Synthesis and spectroscopy

The reaction of 4-pyridinecarboxylic acid hydrazide with 2-
[75] benzoylpyridine in methanol gave the desired ditopic Schiff base ligand, HL, in excellent yield and purity (Scheme 2c). IR and NMR spectra of ligand indicate that it is stable in the keto form.[18] Compound [Cu$_4$(L)$_2$(μ-OAc)$_2$(μ-OAc)$_4$]$_n$ (**1**) was synthesized by the reaction of HL and Cu(OAc)$_2$·H$_2$O in molar ratios of 1:2 in
[80] methanol. Dark green crystals of **1** were obtained by thermal gradient method during three days. Comparing the IR spectra of **1** with HL, it is seen that the N-H stretching vibration of the ligand eliminated in **1**. This suggests the enolization of the amide is taken place upon coordination to the copper centre and the ligand
[85] is coordinated to the copper in the enol form.[20] The band at 1609 cm^{-1} expresses the coordination of azomethine nitrogen (C=N) to the metal core.[21,22] Moreover, there is a very strong band at 1630 cm^{-1} in the IR spectrum of **1** which is due to the presence of C=O groups in **1** and confirms the presence of acetate groups.[23]
[90] Elemental analyzes is in good agreement with the obtained structure by single crystal X-ray analyzes.

X-ray structure of [Cu$_4$(L)$_2$($\mu_{1,1}$-OAc)$_2$($\mu_{1,3}$-OAc)$_4$]$_n$ (1)

[95] The structure of **1** with atom numbering scheme is shown in Fig. 1 and selected bond lengths and angles are listed in Table 1.

Compound **1** is a one-dimensional coordination polymer and contains two types of centrosymmetric dimers of Cu(II) in which the acetate anions act as bridging groups in both cases. In the first dimeric unit the two copper(II) centers (Cu1) are bridged by two [5] μ_2-1,1-OAc$^-$ to form a planar four membered Cu_2O_2 ring. The Cu1 atom is five-coordinated with CuN_2O_3 coordination environment (Fig. 2a) and has a distorted square pyramidal geometry ($\tau = 0.266$ which $\tau =$ difference between the two largest angles)/60; $\tau = 1$ for ideal trigonal-bipyramidal and $\tau = 0$ for ideal [10] square-pyramidal).[24] The hydrazonate ligand, (L)$^-$, coordinates to the Cu1 through tridentate N_2O-donor set (O_{amidic}, $N_{azomethine}$, $N_{2-pyridine}$). The amide hydrogen of HL is eliminated during the complexation and it behaves as a mononegatve ditopic ligand, (L)$^-$. In Cu1, the hydrazone ligand forms a basal plane together [15] with the oxygen atom from the one of the bridging acetate ligand. The axial position of Cu1 is occupied by the oxygen atom from the second acetate. Around Cu1, the Cu–N and Cu–O bond distances are close to those found in other Cu(II) complexes with hydrazone ligands.[25] The axial Cu1–O2^i ($i = 2-x, 1-y, 1-z$) bond [20] 2.2839(10) Å is considerably longer than the other four bonds which is consistent with the Jahn-Teller effect usually found for Cu(II) complexes with d^9 electronic configuration.[26] The Cu1···Cu1^i distance within the four membered Cu_2O_2 cyclic unit is 3.2121(7) Å. The O2–Cu1–O2^i and Cu1–O2–Cu1^i bond angles [25] are 80.88(4) and 99.12(4)°, respectively, which are close to the observed bond angles in μ_2-1,1-acetato bridged copper(II) complexes.[5,17] This dimeric unit is connected to the second dimeric unit by 4-pyridine moiety of ditopic isonicotinhydrazone ligand to form a 1D coordination polymer (Fig. 3). The Cu2 atom [30] is coordinated by nitrogen atom of isonicotinhydazone ligand and four oxygen atoms of acetate groups. The coordination environment around the Cu2 atom is $CuNO_4$ with square pyramidal geometry ($\tau = 0.0015$). Two Cu2 atoms are connected together by four μ_2-1,3-acetate bridges which are related by [35] symmetry operation ($ii = -x, 2-y, 2-z$). The Cu2···Cu2^{ii} distance is 2.6253(8) Å which is in normal range of reported complexes containing similar dinuclear unit (Fig. 2b).[14] The oxygen atoms of acetate anions occupy equatorial positions and the axial position is occupied by the nitrogen atom of (L)$^-$. The axial Cu2−N4 bond [40] length (2.1645(12) Å) is longer than the equatorial bonds (≈ 1.97 Å) which is due to the Jahn-Teller effect. The Cu2 atom deviates 0.199(1) Å from the mean plane of acetate oxygen atoms towards the axial nitrogen.
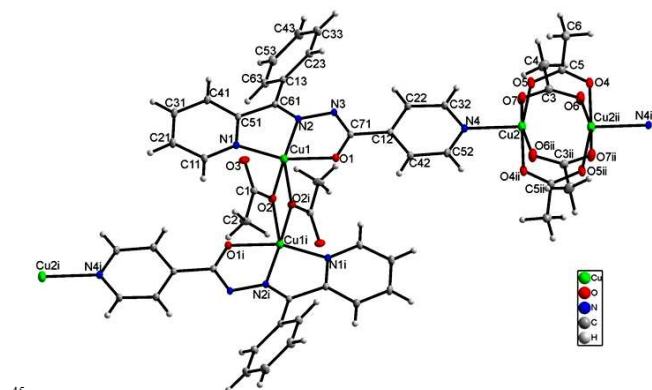

[45] **Fig. 1.** Molecular structure of compound $[Cu_4(L)_2(\mu\text{-OAc})_2(\mu\text{-OAc})_4]_n$ (**1**); together with numbering scheme; symmetry operation: $i = 2-x, 1-y, 1-z$; $ii = -x, 2-y, 2-z$

[50] Some weak C−H···O and C−H···π interactions cooperate to stabilize the crystal packing of compound **1** (Fig. S1). Neighboring chains pack by strong π-π stacking interactions

between two pyridine rings of isonicotinhydrazone lignad (Fig. S1).[27]
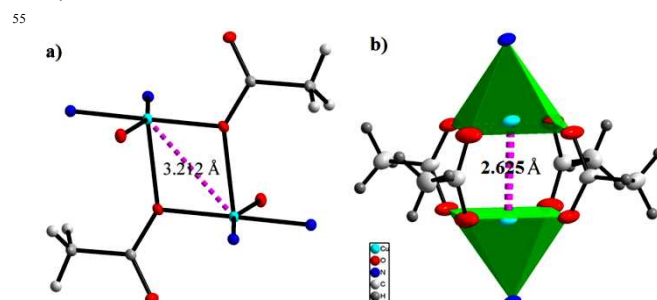
Fig. 2. Coordination environment a) around Cu1; b) around Cu2
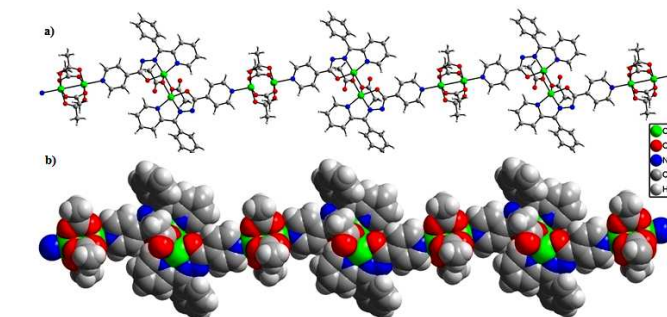
[60] **Fig. 3.** Compound **1** shown in (a) ball and stick mode and (b) spacefill mode

Table 1. Selected geometrical parameters (distances in Å, angles in deg) with s.u.'s reported in parentheses

Bond	distance/Å	Bond	Angle/°
Cu1−O1	1.9833(10)	O2−Cu1−N2	176.57(4)
Cu1−O2	1.9255(10)	O1−Cu1−N1	160.61(4)
Cu1−O2^i	2.2839(10)	O2−Cu1−O1	96.63(4)
Cu1−N1	2.0126(11)	N2−Cu1−O1	80.15(4)
Cu1−N2	1.9316(11)	O2−Cu1−N1	102.61(5)
Cu2−O4^{ii}	1.9727(12)	N2−Cu1−N1	80.56(5)
Cu2−O5	1.9758(12)	O2−Cu1−O2^i	80.88(4)
Cu2−O6	1.9658(13)	N2−Cu1−O2^i	100.34(4)
Cu2−O7^{ii}	1.9714(13)	O1−Cu1−O2^i	92.03(4)
Cu2−N4	2.1645(12)	N1−Cu1−O2^i	93.35(4)
Cu2…Cu2^{ii}	2.6253(8)	O6−Cu2−O7^{ii}	168.41(5)
N3−C71	1.3322(16)	O4^{ii}−Cu2−O5	168.32(4)
O1−C71	1.2789(15)	O6−Cu2−O4^{ii}	88.72(6)
O2−C1	1.3016(14)	O7^{ii}−Cu2−O4^{ii}	89.50(6)
O3−C1	1.2265(15)	O6−Cu2−O5	89.50(6)
O4−C5	1.2542(17)	O7^{ii}−Cu2−O5	89.94(6)
O5−C5	1.2575(17)	O6−Cu2−N4	96.16(5)
O6−C3	1.2528(18)	O7^{ii}−Cu2−N4	95.37(5)
O7−C3	1.2547(19)	O4^{ii}−Cu2−N4	93.05(5)
Cu1…Cu1^i	3.2121(7)	O5−Cu2−N4	98.61(5)

[65] *Symmetry codes: (i) 2-x, 1-y, 1-z; (ii) -x, 2-y, 2-z*

EPR spectroscopy

The examples of resonance spectra obtained for the powdered compound **1** are shown in Fig. 4. The spectrum consists of few [70] resonance lines having different temperature behavior. To better expose the weak temperature changes, the intensity of the showed spectra was multiplied by temperature. As it is seen on Fig. 4, there is a narrow asymmetric resonance line located around 3100 Oe ($g \approx 2.16$) and having its intensity decreases upon heating. [75] There are also other resonance lines in the spectrum located at ***B*** = 250 Oe and ~4670 Oe whose intensities increase with

temperature. The opposite temperature dependence points to the presence of various magnetic interactions between Cu atoms. The obtained experimental data could be explained by the model that takes into account the presence of two different types of exchange coupled Cu···Cu pairs (dimers). This model is supported by crystallographic data. The first type of Cu···Cu pair with copper separation $d = 3.2121(7)$ Å is coupled ferromagnetically (FM). The energy spectrum of FM coupled pair consists of singlet and triplet spin states where the triplet state is the ground state. The second type of Cu···Cu pair with d = 2.6253(8) Å is coupled antiferromagnetically (AFM). The energy levels of AFM coupled pair are reversed to the FM one and the nonmagnetic singlet becomes the ground state. The zero-field separation singlet-triplet is proportional to the isotropic part of bilinear exchange interactions – J. The resonance spectra were obtained also for the single crystal of **1** at different temperatures and the data support the presence of two dimers with different intradimer exchange coupling (Fig. S2). However, the pieces of single crystals were too small to be oriented for proper qualitative EPR analysis, therefore the EPR data of powdered samples were used.

At low temperature the EPR spectrum is dominated by intense signal from the FM coupled pair, whereas triplet levels of AFM pairs are depopulated. Upon heating the signal of FM pairs decreases with a faster rate than 1/T as it is for paramagnetic isolated Cu ions, while triplet of AFM pair becomes populated giving rise to new resonance lines. The multiline structure of EPR spectra, shown in Fig. 4, indicate the presence of zero-field splitting (ZFS) within AFM triplet states and was interpreted in terms of the effective spin-Hamiltonian composed of Zeeman and zero-field splitting (ZFS) terms with fictitious spin $S = 1$:

$$\hat{\mathcal{H}} = \mu_B(\boldsymbol{B} \cdot \boldsymbol{g} \cdot \boldsymbol{S}) + D(\boldsymbol{S}_z^2 - \frac{1}{3}S(S+1)) + E(\boldsymbol{S}_x^2 - \boldsymbol{S}_y^2) \qquad (1)$$

where μ_B is the Bohr magneton, $\boldsymbol{B}$ - the external magnetic field vector, $\boldsymbol{S}$ – the spin operator, $\boldsymbol{g}$ – the g-factor tensor, D and E – the axial and rhombic ZFS parameters, respectively. The enlarged spectrum recorded at room temperature is shown in Fig. 5a. There are four well-resolved features in the spectrum attributed to the AFM dimer. Besides three allowed $\Delta M = \pm 1$ transitions at ~250, 4670, 6020 Oe, also one forbidden $\Delta M = 2$ is clearly resolved at 1490 Oe. This transition becomes partially allowed when $\boldsymbol{B}$ deviates from z direction. Adopting the Cartesian axis system (x, y, z) such that axis z is parallel to Cu···Cu direction of AFM dimer, the best matched parameters of spin-Hamiltonian (1) describing the experimental spectrum are: $|D| = 0.339 \pm 0.005$ cm^{-1}, $E \approx 0$, $g_\perp = 2.073 \pm 0.008$, $g_\parallel = 2.317 \pm 0.008$. These parameters were used to calculate splitting of the energy levels of the spin triplet as a function of $\boldsymbol{B} \parallel z$ and $\boldsymbol{B} \perp z$ (Fig. 5b,c). The energy levels were calculated for $D > 0$, and, in case of negative D, the order of energy levels need to be reverted, but the resonance positions, marked by arrows in Fig. 5(b,c), stay unchanged. The obtained value of $|D| = 0.339$ cm^{-1} falls in typical range of $0.3 – 0.45$ cm^{-1} known for Cu(II) dinuclear units.[28] The exchange coupling constants for both dimers can be estimated from the temperature dependence of magnetic susceptibility χ (T).

Magnetic susceptibility

Magnetic susceptibility measurements have been performed on the powder of **1** at $\boldsymbol{B} = 6000$ Oe in the temperature range of 2 to 300 K. The χT versus temperature plot (where χ is the molar susceptibility) is shown in Fig. 6. At 300 K, χT = 1.18 (emu·mol^{-1}), which is less than the expected value for four uncoupled Cu(II) ions (χT ≈ 1.6 cm^3·K·mol^{-1} for paramagnetic Cu$_4$ systems). The value of χT decreases upon cooling down to 70 K, then with

further cooling χT increases. The decrease indicates the presence of a quite strong antiferromagnetic coupling with the exchange coupling value $J > 300$ cm^{-1}. On the other hand, the low temperature upturn of χT indicates the presence of ferromagnetic coupling also.

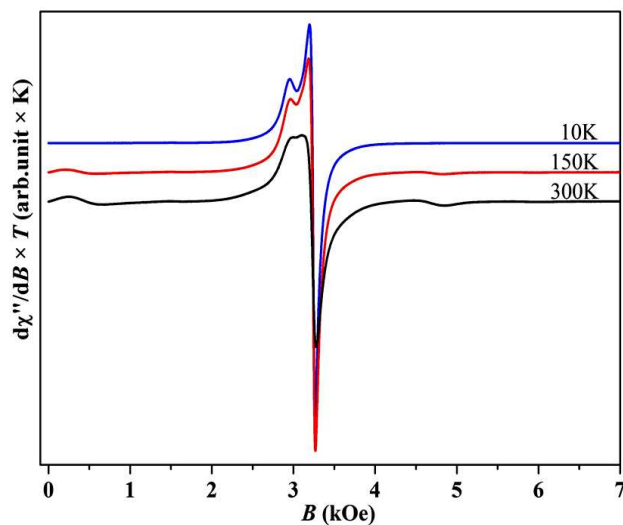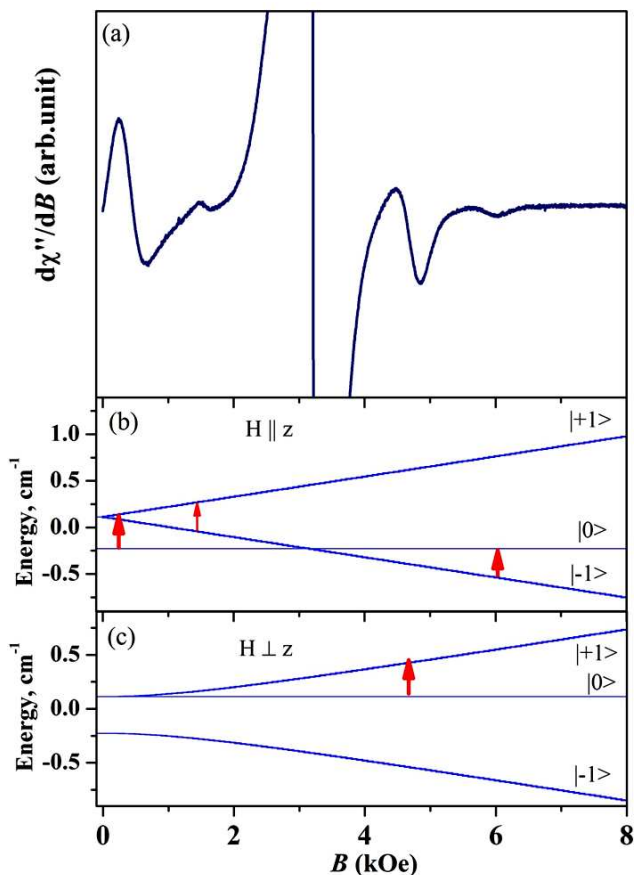**Fig. 4.** Powder experimental EPR spectra multiplied by temperature (ν=9.4 GHz).

Fig. 5. a) Powder EPR spectrum at 300K; the triplet energy level splitting as a function of the external magnetic field for $\boldsymbol{B}$ parallel to the Cu-Cu axis z (b) and $\boldsymbol{B} \perp z$ (c). The arrows of a length ν/c = 0.313 cm^{-1} show EPR transitions expected at ν = 9.4 GHz.

The 1D chains of **1** contain two active magnetic exchange-pathways which correspond to the μ_2-1,3- and μ_2-1,1-OAc bridges (Scheme 2, a and b). The coupling through the entire hydrazone ligand (Scheme 2, c) with a Cu1···Cu2 distance of 9.020(1) Å is negligible respect to the other two. Under this approach, the magnetic behaviour of **1** can be described with the isotropic Hamiltonian for two independent, FM and AFM coupled, pairs: $H = -J_1S_1S_1 - J_2S_2S_2'$, where J_1 and J_2 are exchange integrals for two types of bridges and S_i is the spin operator for the centre i. The numerical expression for such a system can be deducted from the Bleaney-Bowers equation and is given by

$$\chi = (2N\beta^2 g_1^2)/kT[3+\exp(-J_1/kT)] + (2N\beta^2 g_2^2)/kT[3+\exp(-J_2/kT)] \quad (2)$$

where N is the Avogadro's number, g_1 and g_2 the g-factors and k the Boltzmann constant.[29] A perfect agreement with experiment has been obtained for the parameters $g_1 = 2.16(1)$, $J_1 = +0.80(1)$ cm^{-1}, $g_2 = 2.16(1)$, $J_2 = -315(1)$ cm^{-1}. The solid line in Fig. 6 corresponds to these derived parameters. The fitted averaged value of g_1, g_2 in powder is in good correspondence with the averaged values of g-factors estimated from EPR data: $\langle g \rangle = 1/3 (g_\parallel + 2g_\perp)$.
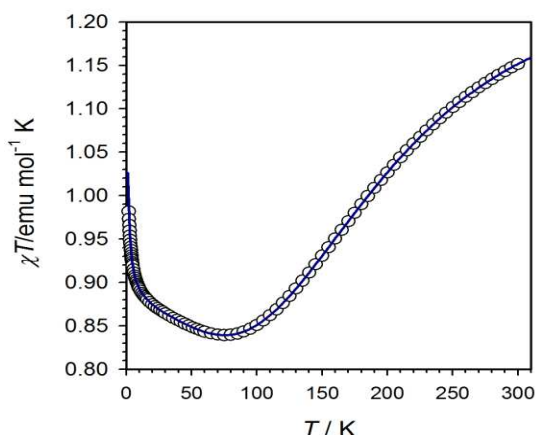
Fig. 6. χT vs. T curve for powder of **1**; the solid line corresponds to the calculated curves using eq. (2) with parameters $g_1 = 2.16(1)$, $J_1 = +0.81(1)$ cm^{-1}, $g_2 = 2.16(1)$, $J_2 = -315(1)$ cm^{-1}.

The $J_2 = -315(1)$ cm^{-1} can be assigned to the coupling through the four μ_2-1,3-carboxylate bridges (or, *syn-syn* carboxylate bridges) which are known to mediate moderate-strong antiferromagnetic couplings. The carboxylate bridge in this configuration connects very efficiently the two dx^2-y^2 orbitals of the copper(II) occupied by the unpaired electrons leading to moderate-strong antiferromagnetic coupling. The value of -315 cm^{-1} is in very good agreement with other theoretical and experimental studies.[30]

The $J_1 = +0.81$ cm^{-1} is assigned to the magnetic coupling through the μ_2-1,1-carboxylate bridge. Magneto-structural correlations in this kind of bridge have been extensively investigated and many theoretical and experimental studies have been performed. However, those studies are related to systems in which the oxygen atoms fill equatorial positions in both copper(II) ions, but for the case of the μ_2-1,1-carboxylate exchange-pathway with one oxygen in an equatorial position and the other one in an axial position just a few cases can be found and no general trends or rules are reported. The magnetic coupling through this kind of bridge tends to be weak in all cases and the J values depend on the axial Cu−O distance with ferromagnetic coupling constants in

the range 8 cm^{-1} to 0.5 cm^{-1} for Cu−O distance 2.3-2.4 Å, but other times it shows antiferromagnetic coupling constants in the range −0.5 cm^{-1} to −1.0 cm^{-1}.[31] In compound **1** the Cu$_2$O$_2$ core displays an equatorial-axial connection with a Cu1−O2 distance of 2.2839(10) Å for which a ferromagnetic coupling is expected. The small value of J can also be affected by the trigonal distortion (τ = 0.266) which increases the spin density in the z axis growing somewhat the antiferromagnetic contribution.

So, the magnetic behavior of the compound can be explained by the occurrence of the two different magnetic exchange-pathways between the two different copper(II) pairs. At high temperatures the antiferromagnetic coupling through the μ_2-1,3-carboxylate bridges predominates making the χT values to decay, at about 100K the Cu2···Cu2^{ii} pairs have almost cancel their spins and a plateau is reached. At lower temperatures the coupling through the μ_2-1,1-carboxylate bridge becomes dominant leading the χT values to increase again.

Conclusions

1D coordination polymer of Cu(II) has been synthesized using ditopic isonicotinhydrazide ligand and copper(II) acetate. The compound was characterized by single crystal X-ray analysis and spectroscopic methods. The 1D polymeric network contains two types of dinuclear Cu(II) cores with μ_2-1,1- and μ_2-1,3-OAc bridges. The Cu···Cu interactions were studied by EPR spectroscopy and magnetic susceptibility measurements. The complementary EPR and magnetic susceptibility data allowed to identify and separate two types of Cu(II) dimers contributing to magnetism with different, FM and AFM intradimer exchange coupling. The intradimer isotropic exchange was calculated as +0.80(1) cm^{-1} K for the ferromagnetic Cu1···Cu1^{i} dimeric unit and −315(1) cm^{-1} for the antiferromagnetic Cu2···Cu2^{ii} dimeric unit.

Experimental
Materials and instrumentations

All chemicals and solvents were purchased from Merck and used as received without further purification. The ligand (E)-N′-(phenyl(pyridin-2-yl)methylene)isonicotinhydrazide (HL) was synthesized by the reaction of 4-pyridinecarboxylic acid hydrazide with 2-benzoylpyridine in methanol according to the our previous reports.[18] IR spectra were recorded in KBr disks with a Bruker FT–IR spectrophotometer. The elemental analyses (carbon, hydrogen and nitrogen) were obtained from Carlo ERBA Model EA 1108 analyzer. The atomic absorption analysis was carried out using Varian Spectra AA 220 equipment. The EPR measurements were carried out using a Bruker EMX spectrometer working at fixed frequency 9.38 GHz (X-band) with Oxford Instruments helium-flow cryostat operating in the temperature range from 3.8 K to 300 K. A 100 kHz magnetic field modulation and phase sensitive detection were used to record the derivative of the absorbed microwave power. Magnetic susceptibility measurements have been performed on the powder of the coordination polymer at B = 6000 Oe by means of a Quantum Design SQUID magnetometer MPMS-XL7 in the temperature range of 2 to 300 K.

Synthesis of [Cu$_4$(L)$_2$(μ-OAc)$_2$(μ-OAc)$_4$]$_n$ (1)

Compound **1** was synthesized by the reaction of hydrazone ligand, HL, (0.151 g, 0.5 mmol) and Cu(OAc)$_2$·H$_2$O (0.200 g, 1.00 mmol) using the thermal gradient method in a branched tube and methanol used as solvent. Mentioned amount of materials were placed in the main arm of a branched tube. Methanol was carefully added to fill the arms, the tube was sealed and the reagents containing arm immersed in an oil bath at 60 °C while

the other arm was kept at ambient temperature. After three days, dark green crystals were deposited in the cooler arm. Yield: 82.5% (0.25 g). *Anal.* Calc. for $C_{24}H_{22}Cu_2N_4O_7$ (MW = 605.54): C, 47.60; H, 3.66; N, 9.25; Cu, 20.99%. Found: C, 47.65; H,
5 3.67; N, 9.21; Cu, 21.05%. Selected FT-IR (KBr, cm^{-1}): 2937 (s), 2863 (s), 1630 (vs), 1609 (s), 1568 (s), 1556 (m), 1499 (s), 1458 (vs), 1444 (s), 1424 (s), 1376 (vs), 1312 (s), 1259 (m), 1206 (m), 1157 (m), 1149 (m), 1110 (m), 1091 (s), 1063 (m), 1017 (m), 929 (m), 887 (m), 858 (s), 785 (s), 759 (s), 742 (m), 703 (vs), 681
10 (vs), 644 (m), 624 (m), 551 (w), 508 (w), 469 (w), 453 (w), 419 (m), 402 (s). UV–Vis (in CH_3OH, c = 5×10^{-5} mol dm^{-3}, λ_{max} [nm] with ε [M^{-1} cm^{-1}]): 210 (29 500), 298 (29 400), 395 nm (6 000).

15 *X-ray crystallography*

X-ray diffraction data for **1** was collected by the ω-scan technique on KUMA-KM-4 diffractometer with a Sapphire CCD camera using graphite-monochromatized MoK$_\alpha$ radiation (λ=0.71073 Å). Data were corrected for Lorentz-polarization effects as well as for
20 absorption. Data were collected at 100(2) K using an Oxford Cryosystems cooler. Data collection, cell refinement, data reduction, analysis and absorption correction were carried out with CRYSALIS^{Pro}.[32] The structure was solved by direct methods with SHELXS[33] and refined by a full-matrix least-squares
25 technique on F^2 using SHELXL[33] with anisotropic thermal parameters for the non-H atoms (except for some positions of disordered atoms). The H atoms were found in the difference Fourier maps, but in the final refinement cycles they were repositioned in their calculated positions and refined using a
30 riding model, with C–H = 0.95 Å (for aromatic CH), 0.98 Å (for CH_3), and with $U_{iso}(H) = 1.2U_{eq}(CH)$ or $1.5U_{eq}(CH_3)$. The structure plots were prepared with DIAMOND.[34] Relevant crystal data and refinement parameters are listed in Table 2.

35 **Table 2.** Crystallographic data of **1**

	1
Formula	$[C_{24}H_{22}Cu_2N_4O_7]_n$
Formula weight	605.54
Crystal system	*Triclinic*
Space group	$P\bar{1}$
a(Å)	8.5706(17)
b(Å)	9.7965(19)
c(Å)	15.534(4)
α(°)	85.46(2)
β(°)	78.36(2)
γ(°)	74.18(2)
V(Å^3)	1228.7(5)
Z	2
D$_x$(g cm^{-3})	1.637
F(000)	616
μ(mm^{-1})	1.78
Crystal shape (color)	Block (dark green)
Crystal size (mm)	$0.40 \times 0.33 \times 0.25$
Θ range (°)	2.9–36.9
hkl range	-13→14, -13→16, -26→25
Measured reflections	23437
Reflections with $I > 2\sigma(I)$	8882
independent reflections	10658
R_{int}	0.020
$R[F^2 > 2\sigma(F^2)]$	0.035
$wR(F^2)$	0.107
Parameters/restraints	337/0
S	1.14
$\Delta\rho_{max}/\Delta\rho_{min}$ (e Å^{-3})	1.03/−0.42

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