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† Electronic supplementary information (ESI) available: selected bond distances and angles for **1**–**3** (Tables S1–S4), fragments of 1D coordination polymers **1** and **2** (Fig. S1), hydrogen bonding geometry (Fig. S2, Table S5), structural overlay between **1** and **2** (Fig. S3),coordination of the metal centers in **3a** (Fig. S4), TG/DTA curves of **3b** (Fig. S5). CCDC 1939829–1939832. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x

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# Dimensionality controlled by light exposure: 1D *versus* 3D oxalate-bridged [CuFe] coordination polymers based on [Fe(C2O4)3]3− metallotecton

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The heterodimetallic [CuIIFeIII] one-dimensional (1D) coordination polymers {NH4[{Cu(bpy)}2(C2O4)Fe(C2O4)3]·H2O}*n*(**1**) and {K[{Cu(bpy)}2(C2O4)Fe(C2O4)3]·H2O}*n* (**2**) (bpy = 2,2*'*-bipyridine) were obtained using a building block approach by layering technique, from the reaction of aqueous solution of [Fe(C2O4)3]3– and methanol solutions of Cu2+ and bpy. In a test tube without the presence of light partial decomposition of the tris(oxalato)ferrate(III) anion occurred yielding oxalate-bridged dinuclear [Cu(bpy)(C2O4)Cu(bpy)]2+ units. These cationic species are mutually connected through oxalate groups from [Fe(C2O4)3]3–, thus forming ladder-like topologies in compounds **1** and **2**. When the same reaction mixture was exposed to daylight, initial building block [Fe(C2O4)3]3– undergoes [photoreduction](https://en.wikipedia.org/wiki/Photoreduction) producing [CuIIFeII] three-dimensional (3D) coordination polymer {[Cu(bpy)3][Fe2(C2O4)3]·H2O}*n* (**3a**). In addition, under hydrothermal conditions, the same reduction occurs giving compound {[Cu(bpy)3][Fe2(C2O4)3]}n (**3b**), that crystallizes without water molecule. The molecular structure of **3a** and **3b** consist of a 3D anionic network {[Fe2(C2O4)3]}*n*2*n*– and tris-chelated cations [Cu(bpy)3]2+ occupying the vacancies in the framework. Very strong antiferromagnetic coupling between two copper(II) ions from [Cu(bpy)(C2O4)Cu(bpy)]2+ species transferred through oxalate bridge was determined in **1** and **2** from the magnetization measurements. In **3a** and **3b** strong exchange interaction is present in Fe-oxalate network, {[Fe2(C2O4)3]}*n*2*n*–, and the ground state of compounds tends to zero-magnetization at the lowest temperature. Additionally, the ability of compound **3a** (or **3b**) to act as a single-source precursor for the formation of spinel oxide was investigated by thermal analysis (TG and DTA) and powder X-ray diffraction (PXRD).

Introduction

In the field of molecular magnetism, coordination polymers have been extensively used to generate magnetic materials exhibiting cooperative properties. The majority of molecule-based magnets reported so far are exclusively based on linkers with a small size (constituted by a low number of atoms) providing an effective pathway for the super-exchange interactions.1–3 The oxalate group has been demonstrated to be one of the most versatile ligands used in the preparation of these materials. Due to its various possibilities of coordination to metal centres as well as its ability to mediate magnetic interactions between paramagnetic metal ions, a large number of oxalate-based transition-metal species of different nuclearity and dimensionality have been synthesized and characterized, many of them having tunable magnetic frameworks.4 Furthermore, these systems are negatively charged and therefore can be combined with functional molecular cations in order to afford complex salts combining cooperative magnetism with a second property of interest.1–4

Most of the oxalate-based molecular magnets described to date have been obtained by "complex-as-ligand approach". In this synthetic strategy a molecular building block, the tris(oxalato)metalate [MIII(C2O4)3]3– anion (MIII = Cr, Fe, Ru, Rh, Mn or V) is used as a ligand towards other metal cations.The topology of these oxalate-bridged heterobimetallic compounds are controlled by a templating counterion. Therefore, layered 2D honeycomb structures with the formulae {[MIIMIII(C2O4)3]}*nn*– are obtained using bulky organic cations [XR4]+ (X = N and P; R = aryl and alkyl) or even the decamethylmetallocenium unit [A(Cp\*)2]+ (A = Fe and Co; Cp\* = pentamethylcyclopentadienyl) as a cation, showing ferro-, ferri- or antiferromagnetic ordering. The use of the tris-chelated [M(bpy)3]2+ or [M(bpy)3]3+ (bpy = 2,2′-bipyridine) entities provides 3D networks of the formulas [MII2(C2O4)3]*n*2*n*–, [MIMIII(C2O4)3]*n*2*n*–, and [MIIMIII(C2O4)3]*nn*–. The homochiral 3D anionic networks have lower critical temperatures than their 2D analogues, although the pathway for magnetic interaction is mainly the same. The templating complexes with the intrinsic *D*3 symmetry force the [MIII(C2O4)3]3– building blocks to adopt a homochiral configuration (ΔΔ or ΛΛ) leading to different relative orientation of the magnetic orbitals and to longer metal-to-metal distances.1,2,5

All of these and other similar 2D and 3D systems are examples of multifunctional molecular-based materials in which the magnetic properties are often complemented by additional feature such as electrical conductivity, prefixed chirality, and nonlinear optical activity. One step further in the control of the dimensionality of these systems can be accomplished through the use of capping ligands, which can restrict the growth of the bimetallic complexes, yielding for example 1D oxalate-bridged chains or discrete polynuclear complexes such as dimers, trimers, or tetramers.1

****In this publication we report, as a continuation of our magneto-structural studies concerning the heteropolynuclear oxalate-based compounds, the preparation, crystal structures and magnetic properties of novel heterometallic [CuFe] oxalate-bridged coordination polymers: one-dimensional (1D) ladder-like chains {A[{CuII(bpy)}2(C2O4)FeIII(C2O4)3]·H2O}*n* [A = NH4+ (**1**) and K+ (**2**)] and three-dimensional (3D) networks {[CuII(bpy)3][FeII2(C2O4)3]·*m*H2O}*n*[*m* = 1 (**3a**) and *m* = 0 (**3b**)]. The most interesting, dimensionality and topology (1D *versus* 3D) of the investigated [CuFe] polymers could be controlled by exposure to light of the same reaction mixture, or by hydrothermal conditions. In 1D coordination polymers **1** and **2**, [FeIII(C2O4)3]3– bridges four copper(II) ions in an unusual fashion, thus creating ladder-like topology, while in compounds **3a** and **3b** all oxalate groups from building blocks repeatedly bridge adjacent iron(II) ions in all three dimensions, in usual bidentate mode.

Further, in the present work we also explore the ability of the 3D polymers {[CuII(bpy)3][FeII2(C2O4)3]·*m*H2O}*n*(**3a** and **3b**) due to its appropriate stoichiometry of metal ions to act as a single-source precursor for the formation of spinel CuFe2O4 oxide by heat treatment.5–7 It has been observed that the use of a well-defined heterometallic precursor can produce crystalline oxide materials under conditions that are significantly milder than those applied in traditional solid-state synthesis. Also, the single-source precursors provide better control over the stoichiometry of the metal ions in the final products as well as the homogeneity of the materials due to the mixing of the metals at the molecular level. Further, the existence of bridging or chelating ligands in the precursors prevents metal separation during oxide formation.8–12 An effective *molecular precursor-to-material* conversion requires a reasonable choice of ligands. The nature of the ligand employed endows the precursor with a clean, low-temperature thermolysis leading to the phase-pure target material. Importantly, low cost of the ligand makes heterometallic precursor highly attractive for practical applications.13–15 One of the suitable ligands for the synthesis of molecular precursors is the oxalate dianion, since it easily decomposes to gaseous CO2 and CO at low temperatures and is economical.5,7,10,12

**Results and discussion**

**Synthesis**

The title compounds {NH4[{Cu(bpy)}2(C2O4)Fe(C2O4)3]·H2O}*n*(**1**), K[{Cu(bpy)}2(C2O4)Fe(C2O4)3]·H2O}*n* (**2**) and {[Cu(bpy)3][Fe2(C2O4)3·H2O]}*n* (**3a**) were obtained using building block approach, from the reaction of aqueous solution of [Fe(C2O4)3]3– and methanol solutions of Cu2+ and 2,2'-bipyridine in the molar ratio of 1:1:1 by the layering technique (Scheme 1). In a test tube without the presence of the daylight partial decomposition of the tris(oxalato)ferrate(III) anion leads to the release of oxalate ligand from the coordination sphere of iron(III). During the crystallization process this oxalate ligand is consequently coordinated to copper(II) ions in reaction mixture, yielding oxalate-bridged dinuclear [Cu(bpy)(C2O4)Cu(bpy)]2+ cationic units of blue-green crystals of **1** and **2** (Scheme 1). Most of the bis(oxalato) and tris(oxalato) anionic species of iron(III) are quite stable, and they usually do not serve as a source of oxalate ligands for other oxalate-bridged complex ions in the reaction mixture .16–19

**Scheme 1** Schematic representation of the synthesis of compounds **1**, **2** and **3a**

When the test tube with same reaction mixture was exposed to daylight, initial building block [Fe(C2O4)3]3– undergoes [photoreduction](https://en.wikipedia.org/wiki/Photoreduction); iron(III) is reduced to the divalent state producing {[FeII2(C2O4)3]}*n*2*n*– network of reddish compound **3a** (Scheme 1). In addition, using identical building block of iron(III) in the hydrothermal conditions, the same reduction occurs yielding equivalent network of iron(II) in compound {[Cu(bpy)3][Fe2(C2O4)3]}n (**3b**), crystallizing without a water molecule.20 Interestingly, thisremarkable structure of 3D anionic network of iron(II) was for the first time also synthesized by a photoreaction.21

When test tubes containing blue-green rod-like crystals of compounds **1** or **2** were moved from darkness to daylight, the crystals stared to decompose. At the same time reddish crystalline compound **3a** started to appear. After 5 days compounds **1** and **2** were completely decomposed, and very soon compound **3a** began to degrade.

Compounds **1**–**3** are not soluble in common organic solvents; **1** and **2** are poorly soluble in water.

**Molecular and crystal structure of compounds 1 and 2**

Compounds **1** and **2** crystalize in a triclinic space group and contain the same constituting units – [Cu(bpy)2(*μ*-C2O4)Cu(bpy)]2+ cations bridged with [Fe(C2O4)3]3– anions and one water molecule of crystallization. Difference in these compounds is the additional cation; in compound **1** it is ammonium, and in **2** potassium. These anions are located between 1D ladder-like coordination polymers formed by [{Cu(bpy)}2(C2O4)]2+ and [Fe(C2O4)3]3– (Figs. 1 and S1†), which have the same topology as previously described compounds {A[CrCu2(bpy)2(C2O4)4]·H2O}*n*.19 The ammonium and potassium cations interconnect the 1D ladder-like coordination polymers into overall 2D arrangement (Fig. 1b). The coordination sphere of potassium atom in **2** includes seven O atoms, six from three oxalate groups and one from water molecule of crystallization. The values of the K···O distances vary between 2.667(3) and 2.991(6) Å (Table S2†). The sum of covalent radii of the K and O atoms is 2.69 Å.22 The mean length of the K–O contacts from the Cambridge Structural Database (CSD) is 2.83(12) Å.4 In compound **1** NH4+ cations and water molecules of crystallization connect neighbouring 1D coordination polymers *via* hydrogen bonding into similar sheet-like supramolecular assembly. Hydrogen bonding geometry is given in ESI (Fig. S2†, Table S5). Comparison between two structures reveals very good overlap between all constituting units (Fig. S3†) pointing that the larger cation only slightly disturbs the crystal structure in terms of changing the unit cell parameters rather than crystal packing itself. Bond lengths and angles for **1** and **2** are given in Tables S1 and S2†. Their values fall within the range of common coordination geometries found in other octahedral complexes of Cu and Fe with corresponding ligands.4 Coordination octahedra of copper(II) in [{Cu(bpy)}2(*μ*-C2O4)]2+ cation are quite elongated, which is not surprising considering monodentantly coordinated oxalate groups of the [Fe(C2O4)3]3– anion in the apical positions (Figs. 1a, 1b and S1†; Tables S1 and S2†) compared to more stronger chelation of bpy molecule and bridging bis(bidentate) oxalate group in the basal plane. Magnetic interaction could be established between copper(II) centres through oxalate bridge; CuII···CuII separation is 5.140(2) Å in both compounds. Additionally, distances between CuII and FeIII metal centres bridged by oxalate ligands are in the range for effective transmission of magnetic exchange interaction [4.088(2)–5.505(2) Å in **1**, and 4.047(1)–5.553(1) Å in **2**].

**Fig. 1** (a) The ladder-like 1D chain motif in {NH4[{Cu(bpy)}2(C2O4)Fe(C2O4)3]·H2O}*n* (**1**); (b) 2D sheet formation in crystal packing of [K{Cu(bpy)}2(C2O4)Fe(C2O4)4]·H2O}*n* (**2**).

Tris(oxalato)metalates have been widely studied and many coordination modes are already reported. Search of the CSD4 shows that polynuclear compounds with tris(oxalato)metalates belong mainly to chromates, followed by cuprates, ferrates and manganates. Herein presented compounds reveal new coordination modes for tris(oxalato)ferrate(III); in **1** [Fe(C2O4)3]3– anion connects four copper(II) centres – one oxalate group bridges two metal centres with uncoordinated O atoms [bidentate-bis(monodentate) mode] and two other oxalate groups each with one of the coordinated O atoms [bidentate-monodentate mode] (Fig. 2a).19 Additionally, in compound **2** one oxalate group is bis(bidentatly) connected to the potassium cation, giving total five metal atoms in the [Fe(C2O4)3]3– coordination sphere (Fig. 2b).

**Fig. 2** New bridging coordination of oxalate groups from tris(oxalato)ferrate(III) anions: (a) monodentate and bis(monodentate) in compounds **1** and **2**; (b) one more bidentante in compound **2**.

In general, just a few heterometallic tri-23,24 and dinuclear25,26 units are obtained using [Fe(C2O4)3]3– as building blocks in which oxalate groups act as bidentate bridging ligands towards other transition metals. Also, only two heterodimetallic oxalate-bridged chains are formed using same building block in which oxalate groups act as bidentate, but also as monodentate ligand.27,28

**Molecular and Crystal Structure of Compounds 3a and 3b**

Compounds {[Cu(bpy)3][Fe2(C2O4)3]·H2O}*n* (**3a**) and {[Cu(bpy)3][Fe2(C2O4)3]}*n* (**3b**), prepared at ambient conditions and hydrothermally, respectively, belong to a family of oxalate-based chiral 3D frameworks. These compounds crystallize as racemic conglomerates, containing enantiomeric crystals belonging to the space groups *P*4132 and *P*4332. In herein presented structures, an absolute configuration was determined in the *P*4132 space group with *Λ* configuration of Cu and Fe octahedral stereogenic centres. The molecular structures of **3a** and **3b** consist of known 3D anionic [FeII2(C2O4)3]*n*2*n*− network21,29 and tris-chelated cations [Cu(bpy)3]2+ occupying the vacancies of the framework (Fig. 3). In both compounds, the FeII and CuII atoms are coordinated by three chelating ligands (oxalate and bipyridine, respectively), displaying approximately octahedral coordination geometry (Fig. S4†). The bis(bidentate) oxalate ligands repeatedly bridge adjacent FeII ions in all three dimensions, which finally leads to a polymeric net. Selected bond lengths and angles for **3a** and **3b** are given in Tables S3 and S4†. The values of the Fe–O and Cu–N bond lengths are in good agreement with the literature data.6,21,29 Compound **3a** due to different way of preparation than **3b** additionally contains water molecule of crystallization located at a 3-fold axis, which is surrounded with three [Cu(bpy)3]2+ molecules and forms weak electrostatic interactions with *π*-systems of the bpy molecules.

The CSD4 contains only 54 cubic structures having known 3D [MII2(C2O4)3]*n*2*n*−, [MIMIII(C2O4)3]*n*2*n*− and [MIIMIII(C2O4)3]*nn*− anionic networks, in which exclusive paramagnetic metal networks are found in less than half of that number. Only two compounds based on 3D21,29 and one based on 2D30 [FeII2(C2O4)3]*n*2*n*− networks have been found, whereas three 2D31−33 and one 3D34 compounds have heterobimetallic [MnIIFeIII(C2O4)3]*nn*– networks. Therefore, study of magnetic properties of these compounds is of great value to the field of molecular magnetism. Distance between FeII metal centres bridged by oxalate ligand is 5.478(1) Å and 5.481(2) in **3a** and **3b**, respectively.

**Fig. 3** Crystal packing in compounds {[Cu(bpy)3][Fe2(C2O4)3]·H2O} (**3a**) and {[Cu(bpy)3][Fe2(C2O4)3]} (**3b**): (a) a 3D oxalate-based anionic [Fe2(C2O4)3]*n*2*n*− network and (b) remaining voids occupied by [Cu(bpy)3]2+ cations.

Infrared study

The IR spectra of the investigated complexes are in agreement with the results of the X-ray analysis and show the absorption bands that can be attributed to the vibrations of the oxalate groups, besides those originating from coordinated 2,2'-bipyridine ligands.35 The absorption bands characteristic for the different bridging modes of the oxalate group for all compounds are summarized in Table 1.5,6,19 All absorption bands observed in the IR spectra of **1**, **2**, **3a** and **3b** are given in Experimental section.

**Table 1**  Selected absorption bands (cm–1) of different bridging modes of the oxalate group observed in the infrared spectra of compounds **1**–**3**

|  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Comp. | | *bidentate-monodentate* | | | | | | *bis(bidentate) /*  *bidentate-bis(monodentate)* | | | |
| νas(CO) | | νs(CO) | *δ(OCO)* | | νas(CO) | | νs(CO) | *δ(OCO)* | |
| **1** | 1709, 1671 | | 1385 | | 794 | | 1645 | | 1356 | 781 | |
| **2** | 1706, 1667 | | 1383 | | 794 | 1647 | | | 1358 | 797 | |
| **3a**  **3b** | –  – | | –  – | | –  – | 1658, 1635  1658, 1635 | | | 1361, 1310  1361, 1310 | | 800  800 |

**Thermal analysis of 3 and characterization of the residues**

The thermal behaviour of compound {[Cu(bpy)3][Fe2(C2O4)3]}*n* (**3b**) has been studied by simultaneous thermogravimetric analysis (TG) and differential thermal analysis (DTA) performed on a crystalline sample in a stream of synthetic air, up to 1000 °C. The corresponding curves are presented in Fig. S5†. The decomposition process of **3b** undergoes several successive processes, not very well separated. The loss of mass occurs up to 550 °C, associated with the degradation of bpy ligands, conversion of the oxalate groups to CO and CO2 and the removal of all resulting products. The mass of the reddish residue corresponds to the mixture of CuO and Fe2O3 (exp. 25.89; calcd 26.35%). During the cooling of the thermal decomposition residue no mass change or DTA peaks were observed (Fig. S5†).

A very similar 3D coordination polymer {[Co(bpy)3][Mn2(C2O4)3]·H2O}*n* was successfully used as a single-source precursor for the formation of the pure mixed metal oxide CoMn2O4.5 Furthermore, it was shown that the changes in the temperature of the heat treatment (500–1000 °C) cause thermally induced cation redistribution within the spinel lattice, an increase of the particle sizes (from 8 to 40 nm), and coexistence of the superparamagnetic and ferrimagnetic behaviour in the same system.7

In the present work we have tested the ability of compound **3b** (also of compound **3a**) to act as a single-source precursor for the formation of spinel oxide CuFe2O4. Copper ferrite is one of the important spinel ferrites, MFe2O4, interesting for its phase transitions, magnetic and semiconducting properties, electrical switching and tetragonality variation when treated under different conditions.36 To our knowledge, several methods have been employed to prepare copper ferrite, such as sol–gel method, co-precipitation, solid state reaction (up to 800 °C) and auto-combustion.37

Crystalline products obtained by pyrolysis of the heterometallic 3D coordination polymer **3b** used as precursor in the range 600–1000 °C were explored by powder X-ray diffraction (PXRD) at room temperature (RT). Unfortunately, in the X-ray powder patterns of products prepared by heating up to selected temperatures the diffraction lines were indexed and attributed only to the CuO and Fe2O3 phases, not to the desired spinel CuFe2O4 phase.

Magnetization study

**Compounds 1 and 2.** The *χT*(*T*) dependences for **1** and **2** have similar behaviour, being not a straight line at high temperatures (Fig. 4). Values of the *χT* at RT are lower than expected for the spin only values for non-interacting two spins 1/2 (Cu2+) and one spin 5/2 (Fe3+) and equal to 5.125 emu K mol-1Oe-1 for **1** and **2**. With cooling down *χT*(*T*) is decreasing and reaches plateau below 50 K which corresponds to the value expected for only Fe3+ ion suggesting that Cu2+ from [Cu(bpy)(C2O4)Cu(bpy)]2+ units are strongly antiferromagnetically coupled. Small decrease of *χT*(*T*) at low temperature is ascribed to the zero-field splitting contribution of Fe3+ with spin 5/2.38

In our previous work related to [CrCu] polymers having similar structure as **1** and **2** based on DFT calculations and magnetic measurements, it was observed that the contribution of magnetic exchange interaction between Cu2+ and Cr3+ along ladder is negligible compared to those between two copper(II) ions through the oxalate bridge.19 Therefore, magnetic behaviour of **1** and **2** is modelled by a simple 0-D spin Hamiltonian:

(1),

where *S*1 and *S*2 are spins of Cu2+ and *S*3 of Fe3+, and other symbols have their usual meaning. The best fitting was obtained for parameters: *g*Cu = 2.18, *g*Fe = 2.01, *J* = –342 cm–1, |*D*Fe|= 0.035 cm–1 for **1** and *g*Cu = 2.11, *g*Fe = 2.00, *J* = –227 cm–1, |*D*Fe|= 0.034 cm–1 for **2**.

Magnetization *vs.* field curves measured at 2 K for **1** and **2**, shown in the inset of Fig. 4, are close to the saturation, reaching 27500 emu mol–1 (4.92 N*μ*B) at the highest measured field of 50 kOe. Good agreement of measured data with the plotted Brillouin function, describing the *M*(*H*) curve for spin *S* = 5/2 corresponding to Fe3+, confirms that copper(II) dimers behave as a non-magnetic entity at low temperatures due to the strong antiferromagnetic interaction between metal centres mediated trough oxalate bridge.

**Fig. 4** Temperature dependence of the product *χT* for compounds **1** and **2**. The red and blue solid lines are model curves. Inset: Field dependence of magnetization, *M*(*H*), measured at 2 K, with plotted Brillouin function of spin *S* = 5/2 as red line.

The values of *J* parameters of **1** and **2** are comparable to those of oxalate-bridged copper(II) moieties containing an entirely planar [Cu(bpy)(*µ*-C2O4)Cu(bpy)] array, pointing to a maximized antiferromagnetic interaction as a consequence of the 4 + 2 coordination of oxalate-bridged copper(II) centres observed in studied polymers.19 Somewhat lower value of *J* obtained for **2** suffers from artefact in measurements of this compound visible around 50 K and in the range 15–25 K. Despite of this we used model in whole range, so that the true value of exchange should be somewhat higher than obtained as judged from the curvature of the measured and modelled *χT*(*T*)at temperatures above 100 K.

**Compounds 3a and 3b.** Susceptibility curves for **3a** and **3b** are almost identical indicating that the crystal water does not affect the magnetic behaviour of these compounds.

Product of magnetic susceptibility and the temperature is decreasing by cooling in the whole temperature interval. Above room temperature *χT*(*T*) is still rising and the value is higher than the value for the non-interacting magnetic centres of two Fe2+ ions (*S* = 2) and one Cu2+ (*S* = 1/2) which is expected to be 6.4 emu K mol–1 Oe–1 (Fig. 5). This suggests that the interaction of spins is present even at room temperature and magnetic behaviour is determined by presence of 3D order of Fe2+ ions through oxalate bridges in the [Fe2(C2O4)3]*n*2*n*− network. To extract the character of the long-range order the *χ*(*T*) dependence is fitted with the Curie–Weiss law (inset of Fig. 5). The obtained values are *C* = 8.6 emu K mol–1 Oe–1 for the Curie constant and *θ* = –46.8 K for the Weiss parameter for **3a** and *C* = 8.7 emu K mol–1 Oe–1 and *θ* = –46.5 K for **3b**, suggesting long-range antiferromagnetic interaction. This is not unusual since in similar complexes with Fe2+ chains or frameworks antiferromagnetic interaction was observed.4

At the lowest temperatures *χT*(*T*) is sharply decreasing. Paramagnetic Cu2+ ions from tris-chelated cations [Cu(bpy)3]2+ located in the vacancies of the framework are isolated from structural point of view, and one would expect that the *χT*(*T*) would twist to the straight plateau of value 0.4 emu K mol–1 Oe–1 at low temperatures coming from the spin *S* = 1/2 (Cu2+). Quite oppositely, measurements show the extrapolation of *χT*(*T*) to zero as *T*→0,

**Fig. 5** Temperature dependence of the product *χT* for compounds **3a** and **3b**. Inset: Reciprocal susceptibility with the Curie-Weiss fitting line for compound **3a**.

pointing to the coupling of Cu2+ spins to the zero-magnetization state of the whole crystal. Confirmation of interaction of the Cu2+ spins with the overall field coming from the Fe2+ which leads to decreasing *χT*(*T*) at low temperatures is obtained from a plausible mean-field model Hamiltonian

(2)

where *S* is Cu2+ spin, approximation of the interaction of Cu2+ with Fe2+ field in the mean filed approximation, and ). The *M*(*H*) curve simulated using Hamiltonian (2) is shown in inset of Fig. 6 assuming the antiferromagnetic character of *zJ’*. Obviously, even a value of *H*eff as small as 10000 Oe which corresponds to the cm-1 only, decreases susceptibility curve at low temperatures considerably. Therefore, even the small interaction can lead to the observed lowering of the *χT*(*T*) values.

The *M*(*H*) dependences measured at 2 K for complexes **3a** and **3b** are shown in Fig. 6. Magnetization at lower fields (below 30 kOe) is lower than expected for paramagnetic Cu2+ spins, and at higher fields it increases considerably above the Brillouin function for spin 1/2 due to the influence of field on the antiferromagnetic lattice of Fe2+. This also confirms the coupling of Cu2+ ions to the zero-magnetization ground state.

Compared to similar systems explored in our group, {[A(bpy)3][Mn2(C2O4)3]·H2O}*n* (A = Co2+ and Cu2+),5,6 having porous 3D (10,3) network [Mn2(C2O4)3]*n*2*n*–, compounds **3a** and **3b** do not show magnetic phase transition to ordered phase appearing across the Fe-network down to 2 K, and there is no superposition of the independent Cu-paramagnetism from complex [Cu(bpy)3]2+ cations located inside large decagonal voids. Interestingly, compound {(Me2NH2)3(SO4)}2[Fe2(C2O4)3] shows antiferromagnetic interactions between iron(II) ions from 3D network, without long-range ordering.29 Altogether, absence of the magnetic phase transition in **3a** and **3b** even in very small fields and coupling of the spins to the zero-magnetization ground state makes these compounds as prospective candidates for quantum spin liquids,39-42 whose further investigation is in progress.

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**Fig. 6** The *M*(*H*) curves measured at 2 K for complexes **3a** and **3b**. Blue line is a simulated curve of the Brillouin function with spin *S* = 1/2. Inset: Simulated curve using Hamiltonian (2) with *H*eff = 10000 Oe.

**Conclusions**

In summary, the heterometallic [CuFe] compounds containing a 3D network, {[CuII(bpy)3][FeII2(C2O4)3]·H2O}*n*(**3a**), or 1D ladder-like chains, {A[{CuII(bpy)}2(C2O4)FeIII(C2O4)3]·H2O}*n* [A = NH+ (**1**) and K+ (**2**)], have been synthesized depending on whether the test tube with the same reaction layers (aqueous containing [Fe(C2O4)3]3– and methanol with Cu2+ and bpy) has been exposed to daylight or not, respectively.

During the crystallization process in darkness the partial decomposition of the [Fe(C2O4)3]3– anion has been occurred, what is not typical for the tris(oxalato)ferrate(III) precursor although the studied compounds are prepared under mild reaction conditions, such as slightly acidic pH and room temperature. As a consequence of that, oxalate-bridged dinuclear [Cu(bpy)(μ-C2O4)Cu(bpy)]2+ cationic species have been formed yielding ladder-like chains by further bridging with [Fe(C2O4)3]3– anions. Unusually, simple counterions K+ and NH4+ from the precursors, which usually favour dissolution of tris(oxalato)metalate(III) salts, also appear as template cations in the investigated complexes **1** and **2**. Beside already known monodentate mode of coordination of the oxalate groups from [Fe(C2O4)3]3– building block,28 unfamiliar one, bis(monodentate), has been also observed in **1** and **2**. Interestingly, altogether three different bridging modes of the oxalate ligand in **1** and **2** were observed: bis(bidentante) [*μ*-1,2,3,4], bidentate-monodentate [*μ*-1,1,2], and bidentate-bis(monodentate) [*μ*3-1,2,3,4].

For the first time heterometallic [CuFe] compounds containing well-known chiral 3D [FeII2(C2O4)3]*n*2*n*− network have been synthesized and characterized; the reduction of Fe(III) from [Fe(C2O4)3]3– precursor to Fe(II) occurs not only in daylight (compound **3a**) but also under hydrothermal conditions yielding {[CuII(bpy)3][FeII2(C2O4)3]}*n* (**3b**).

Magnetization measurements indicate very strong antiferromagnetic coupling between two copper(II) ions from [Cu(bpy)(C2O4)Cu(bpy)]2+ species through oxalate bridge in **1** and **2**, whereas in **3a** and **3b** strong exchange interaction is present in Fe-oxalate network. Absence of magnetic transition down to 2 K points to zero-magnetization ground state in these [CuFe] compounds containing 3D anionic framework {[Fe2(C2O4)3]}*n*2*n*– occupied with [Cu(bpy)3]2+ cations.

Experimental

Materials and physical measurements

All chemicals were purchased from commercial sources and used without further purification. The starting species K3[Fe(C2O4)3]∙3H2O was prepared according to the method described in the literature.43 The preparation method used for the synthesis of (NH4)3[Fe(C2O4)3]·3H2O has been derived from those of the potassium salt, by replacing the potassium reactants by the ammonium homologues. Elemental analyses for C, H and N were performed with a Perkin–Elmer Model 2400 microanalytical analyzer. The infrared spectra were recorded in the 4000–350 cm–1 region with samples as KBr pellets, with a Bruker Alpha-T spectrometer. Thermal measurements were performed with a Shimadzu DTG-60H analyzer from room temperature (RT) to 1000 °C in a stream of synthetic air, at a heating rate of 10 °C min–1.

Synthetic procedures

**Synthesis of** **{A[{CuII(bpy)}2(C2O4)FeIII(C2O4)3]·H2O}n** **[A = NH4+(1) and K+ (2)]**.An aqueous solution (4 mL) of A3[Fe(C2O4)3]·3H2O (0.1 mmol) [A = NH4+ (0.043 g) or K+ (0.049 g)] was layered with a methanol solution (4 mL) of 2,2’-bipyridine (0.016 g; 0.1 mmol). Then, a methanol solution (4 mL) of CuCl2·2H2O (0.018 g; 0.1 mmol) was carefully laid above the existing layers into a test tube. The blue-green rod-like single crystals of **1** (or **2**) wereformed after the tube was standing in the dark for 30 days, washed with small amount of water and dried in air. The yields were 62% (**1**) and 57%. (**2**). Anal. calc. for C28H22FeCu2N5O17 (**1**): C, 38.07; H, 2.51; N, 7.93: Found. C, 38.10; H, 2.52; N, 7.95 %. IR data (KBr, cm–1): 3433 (m), 1709 (s), 1667 (vs), 1647 (sh), 1619 (s), 1573 (m), 1500 (w), 1477 (m), 1449 (m), 1377 (s), 1357 (m), 1316 (m), 1254 (m), 1160 (w), 1107 (w), 1060 (w), 1036 (w), 1023 (w), 905 (sh), 883 (w), 794 (s), 783 (m), 766 (m), 730 (m), 667 (w), 650 (w), 538 (m), 495 (m), 468 (w), 417 (m). Anal. calc. for C28H18FeCu2KN4O17 (**2**): C, 37.18; H, 2.01; N, 6.19: Found. C, 37.21; H, 2.05; N, 6.21 %. IR data (KBr, cm–1): 3447 (m), 1709 (s), 1671 (vs), 1645 (sh), 1616 (s), 1573 (m), 1500 (w), 1478 (m), 1449 (m), 1377 (s), 1358 (m), 1317 (m), 1255 (s), 1160 (w), 1109 (w), 1078 (w), 1060 (w), 1036 (w), 1023 (w), 902 (sh), 882 (w), 794 (s), 783 (sh), 767 (m), 730 (m), 667 (w), 649 (w), 537 (m), 495 (m), 466 (m), 416 (m).

**Synthesis of {[CuII(bpy)3][FeII2(C2O4)3]·H2O}*n* (3a).** An aqueous solution (4 mL) of K3[Fe(C2O4)3]∙3H2O (0.049 g; 0.1 mmol) was layered with a methanol solution (4 mL) of 2,2’-bipyridine (0.016 g; 0.1 mmol) and then with a methanol solution of CuCl2·2H2O (0.018 g; 0.1 mmol) in a test tube, which was left in the daylight. The red rod-like crystals of **3a** wereformed after 3 days, washed with a small amount of water and dried in air. The yield was 32%. The same crystals are obtained using (NH4)3[Fe(C2O4)3]∙3H2O as precursor by the same procedure. Anal. Calc. for C36H24CuFe2N6O13 (**3a**): C, 46.80; H, 2.62; N, 9.10: Found. C, 46.82; H, 2.61; N, 9.09 %. IR data (KBr, cm–1): 3444 (m), 1658 (s), 1635 (vs), 1611 (vs), 1460 (w), 1441 (w), 1423 (m), 1383 (m), 1361 (w), 1310 (s), 1266 (w), 1174 (w), 1157 (w), 1124 (w), 1014 (w), 973 (w), 913 (w), 800 (s), 777 (s), 735 (s), 490 (w), 383 (w).

**Synthesis of** **{[CuII(bpy)3][FeII2(C2O4)3]}n (3b).**The mixure of red rod-like crystals of **3a** and red prismatic crystals of **3b** were formed hydrothermally under autogenous pressure in a 30 mL Teflon-lined stainless steel vessel with a 60% fill factor. A mixture of K3[Fe(C2O4)3]∙3H2O (0.295 g; 0.6 mmol), 2,2’-bipyridine (0.094 g; 0.6 mmol), CuCl2·2H2O (0.102 g; 0.6 mmol) and H2O (20 mL) was heated at 180 °C for 48 h and then left to cool to RT. Reddish crystals obtained in the autoclave in were washed with a small amount of water and dried in air. Two kinds of single-crystals (**3a** and **3b**) were separated mechanically. The yield was 28% for **3b**. Anal. Calc. for C36H24CuFe2N6O12 (**3b**): C, 47.63; H, 2.66; N, 9.26: Found. C, 47.64; H, 2.66; N, 9.28 %. IR data (KBr, cm–1): 3444 (m), 1658 (s), 1635 (vs), 1611 (vs), 1460 (w), 1441 (w), 1423 (m), 1383 (m), 1361 (w), 1310 (s), 1266 (w), 1174 (w), 1157 (w), 1124 (w), 1014 (w), 973 (w), 913 (w), 800 (s), 777 (s), 735 (s), 490 (w), 383 (w).

Single-crystal X-ray structural study

The X-ray data for single crystals of compounds **1**, **3a** and **3b** were collected by ω-scans on an Oxford Diffraction Xcalibur Nova R diffractometer with mirror-monochromated Cu-Kα radiation (*λ* = 1.54179 Å, microfocus tube, CCD detector) at room temperature [293(2) K], and for compound **2** on Enraf Nonius CAD4 diffractometer with graphite-monochromated Mo-Kα radiation (*λ* = 0.71073 Å, scintillation LiI detector) at room temperature [293(2) K]. The crystal data and details of data collections and refinements for the reported structures are summarized in Table 2. Data reduction, including the multi-scan absorption correction, was performed by the CrysAlisPRO software package44 for **1** and **3**, and for compound **2** by XCAD445 within WinGX software package.46 The solution, refinement and analysis of the structures were performed using the program integrated in the WinGX system.46 The structures were solved by direct methods (SIR92)47 and refined by the full-matrix least-squares method based on *F*2 against all reflections (SHELXL-2017/1).48 All non-hydrogen atoms were refined anisotropically. The hydrogen atoms attached to the carbon atoms of aromatic ligands were treated as riding entities in idealized positions, with the C–H distances of 0.93 Å and displacement parameters assigned *U*iso(H) = 1.2*U*eq(C). One bpy molecule in compound **2** is disordered. The geometry of the water molecules was constrained to *d*(O–H) = 0.85(2) Å and *d*(H⋯H) =1.50(4) Å with displacement parameters assigned as *U*iso(H) = 1.5*U*eq(O). Geometrical calculations were carried out with PLATON49 and the figures were made by the use of the CCDC-Mercury,50 and VESTA51 programs.

Magnetization study

The magnetization *M* of polycrystalline samples was measured with a MPMS 5 commercial superconducting quantum interferometer device (SQUID) magnetometer. Both modes of *M*(*T*) measurements were used, after zero-field cooling (ZFC) and after cooling in field (FC), but no difference was observed. *M*(*H*) curves were measured at temperature 2 K, where no magnetic hysteresis was observed. The measured magnetic moments of the samples were corrected by taking into account the sample holder, temperature-independent contributions of the core electrons in accordance with the well-known Pascal constants and temperature independent paramagnetic contribution of copper(II). Calculations of numerical fits and simulations were performed using own developed program in Python.

**Thermal synthesis of the mixed-metal CuII–FeIII oxide**

Finely ground crystalline powders of compound **3b** (or **3a**) were heated in a thermal analyser to the selected temperatures (in the range 600**–**1000 °C), in a stream of synthetic air, at a heating rate of 10 °C min-1. After thermal decomposition, the resulting oxide products were characterized by powder X-ray diffraction (PXRD).

**Powder X-ray structural study**

Products of thermal decomposition of **3b** (or **3b**) have been characterized by the means of powder XRD at RT using a Philips MPD 1880 counter diffractometer with Cu-Kα radiation. Samples were recorded in the 2Θ range 10–70° with a step of 0.02° and a fixed counting time of 10 seconds per step. Quantitative analysis and structure refinement were performed by the Rietveld method within the program X’Pert HighScorePlus, version 2.1 (PANalytical 2004), with a pseudo-Voigt function used for describing the profiles.

**Conflicts of interest**

There are no conflicts to declare.

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**Table 2** Crystallographic data and structure refinement details for compounds {NH4[{Cu(bpy)}2(C2O4)Fe(C2O4)3]·H2O}*n* (**1**), {K[{Cu(bpy)}2(C2O4)Fe(C2O4)3]·H2O}*n* (**2**), {[Cu(bpy)3][Fe2(C2O4)3·H2O]}n (**3a**) and {[Cu(bpy)3][Fe2(C2O4)3]}*n* (**3b**).

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Compound | **1** | **2** | **3a** | **3b** |
| Empirical formula | C28H22Cu2FeN5O17 | C28H16Cu2FeKN4O17 | C36H24CuFe2N6O13 | C36H24CuFe2N6O12 |
| Crystal colour, habit | Blue-green, rod | Blue-green, rod | Red, rod | Red, prism |
| *f*w (g mol–1) | 883.43 | 902.48 | 923.85 | 907.85 |
| Crystal dimensions (mm) | 0.30 × 0.06 × 0.03 | 0.40 × 0.07 × 0.04 | 0.40 × 0.05 × 0.04 | 0.15 × 0.10 × 0.07 |
| *T* (K) | 293(2) | 293(2) | 293(2) | 293(2) |
| Space group |  |  | *P*4132 | *P*4132 |
| *a* (Å) | 7.881(5) | 7.870(1) | 15.3810(3) | 15.379(5) |
| *b* (Å) | 9.879(5) | 9.680(1) | 15.3810(3) | 15.379(5) |
| *c* (Å) | 21.399(5) | 21.396(1) | 15.3810(3) | 15.379(5) |
| *α* (°) | 80.536(5) | 80.389(7) | 90 | 90 |
| *β* (°) | 88.690(5) | 88.275(11) | 90 | 90 |
| *γ* (°) | 81.763(5) | 81.506(13) | 90 | 90 |
| *V* (Å3) | 1626.4(14) | 1589.6(3) | 3638.8(2) | 3637(4) |
| *Z* | 2 | 2 | 4 | 4 |
| *Dcalc*. (g cm–3) | 1.804 | 1.885 | 1.686  1.986 | 1.658  1.986 |
| *μ* (mm–1) | 5.842 | 1.996 | 7.663 | 7.633 |
| *F*(000) | 890  902 | 902  902 | 1868  394 | 1836  394 |
| *Θ* range (°) | 4.189–76.375 | 1.931–24.980 | 4.065–75.76 | 4.065– 76.407 |
| *h*, *k*, *l* range | –8 < *h* < 9  –12 < *k* < 12  –24 < *k* < 26 | 0 < *h* < 9  –11 < *k* < 11  –25 < *l* < 25 | –19 < *h* < 13  –11 < *k* < 16  –10 < *k* < 14 | –19 < *h* < 19  –12 < *k* < 19  –14 < *l* < 18 |
| No. of measured reflections | 15164 | 6331 | 4988 | 20318 |
| No. of independent reflections | 6714 | 5594 | 1267 | 1285 |
| No. of observed reflections | 5344 | 4755 | 1184 | 1285 |
| *R*int | 0.0560 | 0.0344 | 0.0597 | 0.0597 |
| *R*, *wR* [*I* > 2σ(*I*)] | 0.0669, 0.1845 | 0.0391, 0.1020 | 0.0467, 0.1364 | 0.0593, 0.1433 |
| *R, wR* [all data] | 0.0771, 0.1997 | 0.0510, 0.1085 | 0.0502, 0.1405 | 0.0593, 0.1433 |
| Goodness-of-fit | 1.035 | 1.064 | 1.116 | 1.141 |
| No. of parameters, restraints | 496, 26 | 539, 145 | 91, 0 | 105, 0 |
| Δ*ρ*max, Δ*ρ*min (e Å–3) | 1.143, –0.585 | 0.869, –0.597 | 0.359, –0.529 | 0.444, –0.961 |