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Effect of N-Donor Ancillary Ligands on Structural and Magnetic Properties of Oxalate Copper(II) Complexes

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Through varying the auxiliary N-donor ligands under similar synthetic conditions nine new compounds: [Cu(C₂O₄)(pz)₄] (1), [Cu(C₂O₄)(apz)₂] (3) [Cu(C₂O₄)(mpz)₂] (4), [Cu(C₂O₄)(mpz)₂] (5), [Cu(C₂O₄)(bpzm)₂] (6), [Cu(C₂O₄)(ampy)(H₂O)] (7) ([Cu(C₂O₄)(aepy)₂][Cu(C₂O₄)(H₂O)] (8) and [Cu(C₂O₄)(aepy)₄(H₂O)₄]Cl₂ (9) (pz = pyrazole, apz = 3(5)-aminopyrazole, mpz = 3(5)-methylpyrazole, ampz = 3(5)-amino-5(3)-methylpyrazole, aepy = 7-azaindole, bpzm = bis(pyrazol-1-yl)methane, ampy = 2-aminomethylpyridine and aepy = 2(2-pyridyl)ethylamine) have been synthesized and characterised structurally (by single X-Ray analysis) and spectroscopically. On the basis of structural data, the influence of neutral N-donor ligands on the control of the final complex structures and the role of weak intermolecular interactions in the creation of molecular architectures have been discussed in detail. The two independent oxalate anions in 1, adopting μ₁-oxalato–1κO',O':2κO;3 κO'2 coordination modes, connect the Cu centers into two-dimensional net extending along crystallographic plane (100). Simultaneous existence of both amino and methyl group in ampy ligand results in formation of and D₄ dimeric structure of 3. Compounds 2 and 4-8 display one-dimensional coordination structures, and the most significant differences between these structures concern the geometry around the copper(II) center and coordination mode of the oxalate bridge. The structures of 2-9 are stabilized by the extensive hydrogen-bonding interactions that give rise to the supramolecular architectures. Additionally, the magnetic properties of the complexes 1-9 have been investigated and discussed in context their structures.

Introduction

The crystal engineering of inorganic–organic hybrid coordination polymers is currently one of the most active fields in coordination chemistry, supramolecular and materials chemistry. These compounds attract significant attention for their intriguing architectures and topologies and due to the diverse promising applications. The inorganic component is a source of useful magnetic or optical properties, mechanical hardness, and thermal stability, while the organic component may offer processability, structural diversity and luminescent properties. The combination of the characteristics of the organic and inorganic components allows to obtain new materials with potential applicability to catalysis, separation, sorption, luminescence, biological chemistry etc. 1.

The common strategy for synthesis of inorganic–organic hybrid coordination polymers is based upon the self-assembly strategy of organic ligands and metal ions. In this method a final structure and topology of a coordination polymer is a result of combination of various forces including strong and directional interactions (metal–ligand coordination bond) and much weaker interactions such as hydrogen bonds, π–π stacking, halogen–halogen and C–H–X (X= O, N, Cl or I etc.) contacts. To some extent, the coordination network assembly process can be also affected by counter anions, ligand–metal molar ratio, coexisting neutral ligands, temperature, pH, and solvents used for crystallization. So far a variety of metal coordination frameworks with various topologies and properties have been synthesized and notable advances have been made in understanding the factors that influence network topology.

However, rational control in the construction of polymeric networks remains a great challenge in crystal engineering and much more work is required to extend our knowledge of cooperative interactions between metal atoms and organic ligand moieties. 2.

Oxalate ions have been proven to be good connectors to bind to metal joints and play a key role in design of new functional coordination networks. They have presented highly versatile binding modes (Scheme 1) and also serve as a good hydrogen-bonding participant to give rise to higher dimensional structures. On the other hand, oxalate bridges act as an efficient mediator for the magnetic interaction between the paramagnetic transition metal centers providing a great opportunity to develop new magnetic materials and explore systematically magneto-structural correlations. 3

The aim of this research was to examine the role of N-donor ligands in structure formation of oxalate copper(II) complexes. For the study, we choose pyrazole derivatives and chelating ligands with aromatic N-heterocycle ring and aliphatic amine donor (Scheme 2). Except for bis(pyrazol-1-yl)methane, all these ligands contain hydrogen-bonding functionalities which can arise to a broad variety of supramolecular networks.
Herein, nine oxalate copper(II) complexes, namely [Cu(C₂O₄)(pz)]₆ (1), [Cu(C₂O₄)(apz)]₆(3H₂O)₆ (2), [Cu₂(C₂O₄)₂(H₂O)₂](apz)₆ (3), [Cu(C₂O₄)(mpz)]₆ (4), [Cu(C₂O₄)(aind)]₆ (5), [Cu₂(C₂O₄)(bpzm)]₆(3.5H₂O)₆ (6), [Cu(C₂O₄)(ampy)]₆(H₂O)₆ (7), [[Cu₂(μ-C₂O₄)(apz)]₆[[Cu(C₂O₄)₂(H₂O)₆]]₄(2H₂O)₆ (8) and [Cu₂(μ-C₂O₄)(apz)]₆(ampz)₆(3H₂O)₄Cl₂ (9) (pz = pyrazole, apz = 3-(5)-aminopyrazole, mpz = 3(5)-methylpyrazole, ampy = 3(5)-aminomethylpyrazole, aind = 7-azaindole, bpzm = bis(pyrazol-1-yl)methane, ampy = 2-aminomethylpyridine and aepy = 2-(2-pyridyl)ethylamine), are reported. On the basis of synthesis and structural characterization, the influence of neutral N-donor ligands on the control of the final complex structures and the role of weak intermolecular interactions in the creation of molecular architectures are discussed. Moreover, the magnetic properties of the complexes 1-9 have been investigated and discussed in context their structures.

Result and discussion

Preparation and General Characterization

Synthesis and isolation of Cu(C₂O₄)(pz)₆ (1), [Cu(C₂O₄)(apz)]₆(3H₂O)₆ (2), [Cu₂(C₂O₄)₂(H₂O)₂](apz)₆ (3), [Cu(C₂O₄)(mpz)]₆ (4), [Cu(C₂O₄)(aind)]₆ (5), [Cu₂(C₂O₄)(bpzm)]₆(3.5H₂O)₆ (6), [Cu(C₂O₄)(ampy)]₆(H₂O)₆ (7), [[Cu₂(μ-C₂O₄)(apz)]₆[[Cu(C₂O₄)₂(H₂O)₆]]₄(2H₂O)₆ (8) and [Cu₂(μ-C₂O₄)(apz)]₆(ampy)(3H₂O)₄Cl₂ (9) were carried out through the self-assembly reactions of aqueous solution of (NH₄)₂C₂O₄ with methanolic solution of copper salt and suitable N-donor ligand (pz = pyrazole, apz = 3(5)-aminopyrazole, mpz = 3(5)-methylpyrazole, ampy = 3(5)-amino-5(3)-methylpyrazole, aind = 7-azaindole, bpzm = bis(pyrazol-1-yl)methane, ampy = 2-aminomethylpyridine and aepy = 2-(2-pyridyl)ethylamine), followed by a solvent evaporation at room temperature. The reactions with pyrazole, 3(5)-aminopyrazole, 3(5)-methylpyrazole, 3(5)-amino-5(3)-methylpyrazole and 7-azaindole were carried out in molar ratio of copper(II) chloride to ligand equal 1:2. In the reactions with potentially chelating ligands, the metal-to-ligand ratio was equal 1:1. Interestingly, the choice of copper(II) salt (CuCl₂ and Cu(NO₃)₂) turned out to be crucial only in complex formation with 2(2-pyridyl)ethylamine. Cu(NO₃)₂ reacted with apy and (NH₄)₂C₂O₄ to give [[Cu₂(μ-C₂O₄)(apy)]₆[[Cu(C₂O₄)₂(H₂O)₆]]₄(2H₂O)₆ (8), whereas the reaction of CuCl₂ with apy and (NH₄)₂C₂O₄ yielded [Cu₂(μ-C₂O₄)(apy)]₆(H₂O)₄Cl₂ (9). To confirm the phase purity of the synthesized complexes, the PXRD patterns of these compounds were recorded. As shown in the Figure S1-S9 (Supporting Information), all the XRPD patterns measured for the as-synthesized samples were in good agreement with the XRPD patterns simulated from the respective single-crystal X-ray data using the Mercury 2.4 program, demonstrating that the crystal structures are truly representative of the bulk materials.

The IR spectra of 1-9 show features attributable to each component of the complexes. In high frequency region the IR spectra of 1-9 show strong absorptions assignable to N–H and O–H stretching vibrations (3480 – 3100 cm⁻¹). Coordination of the oxalate group was confirmed by absorptions in the region 1710–1630 and 1430–1270 cm⁻¹ assigned to the asymmetric and symmetric stretching vibration of C₂O₄²⁻ group, respectively. These values agree well with those reported for the related oxalate complexes. The characteristic bands assignable to ν(C=C) and ν(C=N) vibration of coordinated N-heterocyclic ligands are observed in the range 1610–1500 cm⁻¹.

Crystal Structure Analysis

The crystallographic data of 1–9 are summarized in Tables 1 and 2. The intra- and intermolecular contacts detected in the structures 1–9 are collected in Table S1. The selected bond distances and angles and of 1-9 are listed in Tables S2–S10 (Supplementary Materials).

Structure of [Cu(C₂O₄)(pz)]₆ (1)

The complex 1 crystallizes in the monoclinic space group P2₁/c. The asymmetric unit contains a metal ion, pyrazole molecule and two halves of oxalate anions (Figure 1a). The mid points of the C(4)—C(4A) and C(5)—C(4C) bonds (symmetry codes as in Fig. 1) exist on the inversion centres (respectively the special positions and of the P2₁/c space group with the multiplicity 2). The pyrazole ligand is disordered over three positions with the 0.4:0.3:0.3 participation of partially occupied domains. The anisotropic displacement parameters (ADPs) of these disordered atoms show prolation and oblation effects, thus the atoms possessing...
most different ADPs (C(2) C(1A) N(2A) C(2A) C(1B) N(2B)) were restrained to be equal with effective standard deviation 0.01, and with the corresponding equivalent displacement parameters $U_{eq}$ free to refine. The one potential hydrogen bond donor (the N$-$H group) and one type of acceptor group (oxalate oxygen atoms) exists in the asymmetric unit of compound 1, however the restraints imposed by the rigid polymer net disallow formation of close contact between these group. The lack of hydrogen bonding and relative rotation freedom about Cu$-$N coordination bond favours the disorder of the neutral ligand of the 1. The two independent oxalate anions, situated on centers of inversion, adopt different coordination modes μ$-$oxalato$-\kappa_{1}$O:$\kappa_{2}$O$^\prime$:2κ$^\prime$O$^{\prime\prime}$,O$^{\prime\prime\prime}$ and μ$-$oxalato$-\kappa_{1}$O:$\kappa_{2}$O$^\prime$:2κ$^\prime$O$^{\prime\prime}$,O$^{\prime\prime\prime}$,O$^{\prime\prime\prime\prime}$ (Figure 1b) and connect the Cu centers into two-dimensional net extending along crystallographic plane (100) with Cu$-$Cu separations equal to 4.237(2), 5.546(2) and 5.553(2) Å (Figure 1b and Figure 1c). The pyrazole ligands alternately extrude above and below the [Cu(C$_2$O$_4$)$_2$]$_n$ layer.

To get better insight into the framework structure of 1, topological analysis was carried out and revealed that the metal centres create the 7-c unimodal net (Fig. 1e), described by $\{3^9\}$ Schlafli symbol and $[3.3.3.3.3.3.4.4.4.4.4.4.5(2).5(2)]$ extended point vertex symbol $^8$. This means that the net if formed by alternating hexa- and tetra-functional oxalate ions (coordinating to four metal ions in two bidentate-chelating modes and two monodentate modes, and to two metal ion in two bidentate-chelating modes, Fig. 1c).

**Structure of [Cu(C$_2$O$_4$)(apz)$_2$](3H$_2$O)$_2$ (2)**

The structure 2 consists of [Cu(C$_2$O$_4$)(apz)$_2$] units and solvated water molecules. The [Cu(C$_2$O$_4$)(apz)$_2$]$_n$ units are linked by alternating amino nitrogen atoms of apz ligand and oxygen atoms of oxalate ion to give an infinite one-dimensional zig-zag chain propagated along the [010] direction (Figure 2).
oxalate groups also act in a monodentate–bidentate mode. According to Hathaway’s criterion the axial oxalate oxygen atom is in the borderline to be considered as semicoordinated. The pyrazole rings are close to planarity (maximum deviation of methylpyrazole/oxalato moieties. A view of dimeric unit \[\text{Cu} \text{hydrogen bonds involving water molecules and 5$Š$amin o$Š$3$Š$ atoms were omitted. (a) The perspective drawing of the coordination entity of the compound 2, the symmetry generated atoms are indicated by A and B letters (symmetry codes $-x$, $-y+2$, $-z+1$ and $-x$, $-y+1$, $-z+1$ respectively); b) the part of the 1D coordination network, the ligand molecules not involved into formation of the chain and hydrogen atoms were omitted.

Figure 3. The perspective drawing of the dimeric coordination unit of the compound 3, the symmetry generated atoms are indicated by A letter (symmetry code $-x+1$, $-y$, $-z$).

The dinuclear complex results from the pairing of two mononuclear units [Cu(C$_2$O$_4$(H$_2$O)(ampz)]$_2$ related by a crystallographic center of inversion. Two centroymmetrically related copper(II) centers are bridged by two oxalate groups which act in a monodentate–bidentate mode. The resulting intradimensional Cu–Cu separation of 5.424(2) Å falls in the range reported for the related Cu(II) species. Taking the semi-coordinated oxygen atom into consideration, the coordination about the copper(II) ions can be described as an elongated octahedron. The equatorial plane is comprised of two oxygen atoms belonging to an oxalate group and two nitrogen atoms from two ampz molecules. The four equatorial atoms are nearly coplanar within ± 0.002(12) Å, and copper atom is displaced 0.100(2) Å in the least-squares plane towards the ligand in apical site. The pyrazole mean planes make dihedral angles of 56.26(10) º and 52.12(10) º with the equatorial plane, and the dihedral angle between the two pyrazole rings is 74.52(13) º. The oxalate group is approximately planar with deviations up to 0.064(4) Å from the least-squares plane and makes a dihedral angle of 7.71(15) ° with the equatorial plane of Cu(1) center formed by N(1), N(4), O(1) and O(3) atoms. The C(7)–C(8) bond distance of 1.543(4) Å reflects carbon–carbon single bond character. The C–O bond lengths satisfy the trend C–O$_\text{semicoord} > C–O_{\text{coord}} > C–O_{\text{seacord}}$, as expected from the polarization of the compound structure due to the metal–bonded oxygen atoms. The presence of multiple N–H (complex molecule) and O–H (water molecules) hydrogen bond donors in different environment leads to the complex scheme of intramolecular interactions. The unitary basic graph set is composed from DDDDC(11)[R$_2$($\pi$14)DDDDe(5)S(8)]DD basic motifs, respectively for bonds listed in Table S1. These interactions expand the molecules to the three-dimensional supramolecular network.

Structure of [Cu$_2$(µ-C$_2$O$_4$)$_2$(H$_2$O)$_2$(ampz)$_2$] (3)

The structure 3 is built up of centrosymmetric dimeric [Cu$_2$(µ-C$_2$O$_4$)$_2$(H$_2$O)$_2$(ampz)$_2$] entities which are linked through hydrogen bonds involving water molecules and 5-amino-3-methylpyrazole/oxalato moieties. A view of dimeric unit [Cu$_2$(µ-C$_2$O$_4$)$_2$(H$_2$O)$_2$(ampz)$_2$] is depicted in Figure 3, and its relevant bond distances and angles are reported in Table S4. The dinuclear units are constructed via oxalate ions analogously to linkage observed in compound 2, i.e. the two tri-functional bridging oxalate ions (coordinating to two metal cations in bidentate-chelating and monodentate mode, Fig. 3) join two copper ions.

Structure of [Cu(C$_2$O$_4$)(mpz)$_2$]$_n$ (4)
The crystal structure of 4 is built of \([\text{Cu(mpz)}_2]_2^{2+}\) units joined sequentially by \(\mu\)-oxalato–\(\mu\)\(^{-1}\)\(O^2-\) \(2\times\) \(O^2-\) \(2\times\) \(\mu\)-ligands to \(\text{zig-zag}\) chains parallel to [010] direction with intrachain separations \(\text{Cu}^{\text{II}}\text{–Cu}^{\text{II}}\) of 6.300(2) Å (Figure 4). The three tri-functional bridging oxalate ion coordinate to two metal ions (in bidentate-chelating and monodentate mode, Fig. 4b) forming the 1D coordination polymer, with intra-chains linkage the same as in compound 3. Each copper(II) is five-coordinate by two oxygen atoms (\(\text{Cu}(1)\text{–O}(1), 1.9345(16)\) Å; \(\text{Cu}(1)\text{–O}(3), 1.9651(15)\) Å) from the oxalate ligand and two nitrogen atoms (\(\text{Cu}(1)\text{–N}(1), 1.9708(19)\) Å; \(\text{Cu}(1)\text{–N}(2), 1.9766(19)\) Å) of \(\text{mpz}\) ligands to form the basal plane and the coordination sphere is completed by an apical oxygen atom from another oxalate with a longer bond \(\text{Cu}(1)\text{–O}(4), 2.4157(17)\) Å (Table S5).

The coordination geometry at the copper center can be described as a distorted square pyramid with a parameter \(\tau\) equal 0.22(1) \(^\text{13}\). The pyrazole rings are close to planarity (maximum deviation of 0.0032(14) Å for N(1) atom in one of the plane and 0.0024(18) Å for atom C(5) in the second plane) and are inclined at 61.50(8) \(^\circ\). The oxalate group is approximately planar with deviations up to 0.024(3) Å from the least-squares plane and makes a dihedral angle of 5.83(12) \(^\circ\) with the equatorial plane of Cu(1) center formed by N(1), N(3), O(1) and O(3) atoms. The C(9)–C(10) bond distance of 1.554(3) Å reflects carbon-carbon single bond character.

The C–O bond lengths satisfy the trend \(\text{C–O}_{\text{eq}} < \text{C–O}_{\text{semico}} < \text{C–O}_{\text{uncoord}}\) as expected from the polarization of the charge density toward the metal-bonded oxygen atoms.

The chains of 4 are internally linked by \(\text{N}–\text{H}\cdots\text{O}\) hydrogen bonds. Such type of bond also interlinks the neighboring chains to the C(5) unitary graph motif of lowest degree and C(7+2n) motif of higher degrees (where \(n < \text{N}_0\)). These interactions forms a layer extending along crystallographic (001) plane. In the structure of 4 exists also two types of \(\text{C}–\text{H}\cdots\text{O}\) short contacts (one intra-chain and one intra-chain, Table S1), which can be classified as weak hydrogen bonds.

**Structure of \([\text{Cu}_2\text{C}_4\text{O}_4](\text{aind})_2\text{]}_n\) (5)**

The structure 5 consists of \(\text{cis-}[\text{Cu}(\text{aind})_3]^{2+}\) units bridged sequentially by bis-bidentate, oxalate ligands to form \(\text{zig-zag}\) polymeric chain parallel to [001] (Figure 5). The mid point of the C(8)–C(8A) bond (symmetry code as in Fig. 5) exists on the inversion centre (the special positions \(b\) of the \(C2/c\) space group with the multiplicity \(4\)). The each tetra-functional bridging oxalate ion coordinate to two metal ions (each in bidentate-chelating mode, Fig. 5b) forming the 1D coordination polymer, with in-chain linkage the same as in compounds 6 and 8. The Cu–Cu separation across the bridging oxalate group is 5.541(2) Å, typical of bis-bidentate oxalate-bridged copper(II) complexes, namely 5.411(2) Å in \([\text{Cu}(\text{mpz})_2\text{O}_2(\text{ampy})]_n\) \(^\text{14}\) and in 5.419(2) Å and 5.544(2) Å in \([\text{Cu}(\text{mpz})_2\text{O}_2(\mu\text{-4,4’-bipy})_2(4,4\text{-bipy})]_n\) \(^\text{15}\). The Cu(II) centres, placed on a crystallographic 2-fold axis (the special positions \(e\) of the \(C2/c\) space group with the multiplicity \(4\)), are coordinated to four oxygen atoms from two symmetry related bridging oxalate ligands and the pyridine-type nitrogen atoms of two symmetry related, \(\text{cis}\)-arranged 7-azaindole ligands. The metal coordination geometry is well described as Jahn–Teller distorted octahedral with four short bonds formed by the imine nitrogen atoms, from two crystallographically related \(\text{aind}\) molecules (Cu(1)–N(1) 2.0254(18) Å) and two oxygen atoms from two asymmetrically ligated oxalate ions (Cu(1)–O(1) 1.9936(15) Å). The axial coordination sites are occupied by the two remaining oxalate oxygen atoms, with C–O bond length (2.3053(15) Å) that is significantly longer than the equatorial one (Table S6). The difference between the Cu–O\(_\text{eq}\) and Cu–O\(_\text{uncoord}\) distances (0.31(1) Å) correlates with those observed in the related \([\text{Cu}(\text{mpz})_2\text{O}_2(\text{ampy})]_n\) \(^\text{14}\) and \([\text{Cu}(\text{mpz})_2\text{O}_2(\mu\text{-4,4’-bipy})_2(4,4\text{-bipy})]_n\) \(^\text{15}\). The oxalate and \(\text{aind}\) ligands form dihedral angles of 79.29(3) \(^\circ\) and 68.7(3) \(^\circ\), respectively, with the equatorial coordination plane.
b) Figure 5. a) The perspective drawing of the coordination entity of the compound 5, the symmetry generated atoms are indicated by A, B and C letters (symmetry codes $-x$, $-y+1$, $-z+1$; $-x$, $y$, $-z+1/2$ and $x$, $-y+1$, $z-1/2$ respectively); b) the part of the 1D coordination network, the ligand molecules not involved into formation of the chain were omitted.

Similarly to 4, the chains of 5 are internally linked by N—H···O hydrogen bonds, but, in opposition to 4, there are no hydrogen bonds between the chains (even the weak ones).

Structure of $[\text{Cu}_2(\text{C}_2\text{O}_4)_2(\text{bpzm})]_n(3.5\text{H}_2\text{O})_n$ (6)

The asymmetric unit of 6 (Figure 6a) contains of noncentrosymmetric dinuclear units $[\text{Cu}_2(\text{C}_2\text{O}_4)_2(\text{bpzm})]_n$ and crystallization water molecules. The dinuclear $[\text{Cu}_2(\text{C}_2\text{O}_4)_2(\text{bpzm})]_n$ entities are further linked into zigzag polymeric chain parallel to [1-1-1] (Figure 6b). The each tri-functional bridging oxalate ion coordinate to two metal ions (each in bidentate-chelating mode, Fig. 6b) forming the 1D coordination polymer, with in-chain linkage the same as in compounds 5 and 8. The coordination environment around ions Cu(1) and Cu(2) is a tetragonally elongated octahedron with four short bonds formed by nitrogen atoms of bpzm ligand and two oxygen atoms from oxalate ions. The axial coordination sites are occupied by the two remaining oxalate oxygen atoms, with C–O bond lengths longer than the equatorial ones (Table S7). The Cu(1)−Cu(1) and Cu(1)−Cu(2) separations through the bidentate oxalate bridges are 5.507(4) and 5.464(4) Å, respectively.

Figure 6. a) The perspective drawing of the coordination entity of the compound 6, the symmetry generated atoms are indicated by A and B letters (symmetry codes $-x$, $-y+1$, $-z+1$ and $-x+1$, $-y$, $-z$ respectively), the hydrogen atoms and water molecules were omitted for clarity; b) the part of the 1D coordination network, the ligand molecules not involved into formation of the chain were omitted.

In the structure 7, the molecules $[\text{Cu}((\text{C}_2\text{O}_4)\text{ampy})(\text{H}_2\text{O})]_n$ are associated through Cu–O semi-coordination bond of 2.830(2) Å to form zig-zag chains running along [100] direction with intrachain $\text{Cu}^{2+}$–Cu separation of 5.085(2) Å (Figure 7). The each tri-functional bridging oxalate ion coordinate to two metal ions (in bidentate-chelating and monodentate mode, Fig. 7b) forming the 1D coordination polymer, with in-chain linkage the same as in compound 4. These chains are internally stabilized by two hydrogen bonds, one N—H···O and one O—H···O, both forming C(4) motifs of basic unitary graph set composed from molecules considered as separated ones (Table S1). Taking the semi-coordinated oxygen atom into consideration, the copper(II) ion of 7 displays a tetragonally elongated octahedron. The equatorial coordination positions involve two oxalate oxygen atoms and two nitrogen atoms of ampy coordinated to the central ion in chelating way. The axial coordination sites are occupied by the oxalate and water oxygen atoms with Cu–O bond length of 2.830(2) and 2.487(2) Å which are significantly longer than the equatorial ones 1.9438(18) and 1.9549(18) Å (Table S8).

Figure 7. a) The perspective drawing of the coordination entity of the compound 7, the symmetry generated atoms are indicated by A and B letters (symmetry codes $x+0.5$, $y$, $-z+0.5$ and $x+0.5$, $y$, $-z+0.5$ respectively); b) the part of the 1D coordination network, the ligand molecules not involved into formation of the chain were omitted.

The above mentioned chains are assembled via N—H···O and O—H···O bonds (both creating C(6) motifs of basic unitary graph set) to the two dimensional supramolecular network extending along crystallographic (001) plane. The one C−H···O short contact (Table S1), which can be considered as weak hydrogen bond, provides additional linkage between the chains of supramolecular network. Additionally the molecules of 7 contain the intramolecular C−H···O interactions (Table 3) which can be classified as weak intramolecular hydrogen bond.
Structure of \( [[\text{Cu}_4(\mu_2-\text{C}_2\text{O}_4)(\text{aepy})]_2[[\text{Cu}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]_2(2\text{H}_2\text{O})_n \text{Cu}(1)]_6 \text{Cu}(2) \text{Cu}(3) \text{Cu}(4) \text{Cu}(5) \text{Cu}(6)]_6 \text{Cu}(7) \text{Cu}(8)]_n \) (8)

The crystal structure of 8 is comprised of zig-zag chains built of the centrosymmetric bimolecular \([\text{Cu}(\mu_2-\text{C}_2\text{O}_4)(\text{aepy})]_2^{2-}\) cations joined sequentially by \([\text{Cu}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]^{2-}\) anions and solvated water molecules (Figure 8). The each tetra-functional bridging oxalate ion coordinate to two metal ions (each in bidentate-chelating mode, Fig. 8b) forming the 1D coordination polymer, with in-chain linkage the same as in compounds 5 and 6. There are two different copper centers in crystal structure 8, Cu(1) in the cationic unit and Cu(2) in the anionic unit. The coordination environment around both Cu(1) and Cu(2) ions is a tetragonally elongated octahedron. The equatorial coordination positions of Cu(1) involve two oxalate oxygen atoms O(1), O(10) \( (i)-x+1,y+1,z+1 \) and two nitrogen atoms of chelating aepy ligand. The axial coordination sites are occupied by the oxalate oxygen atoms with Cu–O bond length greater than the Cu–Oeq by ca. 0.3 Å (Table S9). The Cu(2) atom occupies special position (the special positions \( a \) of the \( P-1 \) space group with the multiplicity 1), and its basal plane of Cu(2) ions is defined by four oxygen atoms from two crystallographically related bidentate oxalate ligands with almost equal Cu–O bond distances 1.942(6) and 1.955(6) Å. The mid point of the C(10)–C(10A) exist on the inversion centre (the special position \( h \) of the \( P-1 \) space group with the multiplicity 1). The coordination sphere of Cu(2) is completed by two water molecules occupying axial positions and symmetrically related. As expected the Cu–Owater bond length (2.531(3) Å) is considerably greater than the Cu–Oeq. The Cu(1)–Cu(1) and Cu(1)–Cu(2) separations through the bidentate oxalate bridges are 5.576(2) and 5.365(2) Å, respectively. Two crystallographically related oxalate ligands form dihedral angles of 3.3(3)° with the equatorial coordination plane of Cu(2), whereas the dihedral angle between the oxalate ions and the equatorial plane of central ion Cu(1) are equal 88.5(3) and 87.6(3) °.

The polymeric chains and outer coordination sphere water molecules of compound 8 are linked by N—H…O and O—H…O to the three dimensional supramolecular network, and the basic unitary graph set consists of DDR \( ^2(4)\) [C(6)]DD motifs, respectively for interactions listed in Table S1. The one water molecule is involved in the O—H…O hydrogen bond formed between the O7—H7OA donor and pyridine ring acceptor (containing N1/C1/C2/C3/C4/C5 atoms), with D–A distance of 3.351(2) Å, H–D distance of 2.388 Å and D–H…A angle of 168.6 °. The supramolecular network is crosslink by two different types of C—H…O weak hydrogen bonds and the polymer chains are additionally stabilized by one C—H…O weak intramolecular hydrogen bond.

<table>
<thead>
<tr>
<th>Table 1. Crystal data and structure refinement for 1-5 complexes incorporating monodentate ligands.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Empirical formula</strong></td>
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<tr>
<td><strong>Formula weight</strong></td>
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<tr>
<td><strong>Crystal system</strong></td>
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<tr>
<td><strong>Space group</strong></td>
</tr>
<tr>
<td><strong>Unit cell dimensions [Å, °]</strong></td>
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<tr>
<td><strong>Volume [Å^3]</strong></td>
</tr>
<tr>
<td><strong>Z</strong></td>
</tr>
<tr>
<td><strong>Density (calculated) [Mg/m^3]</strong></td>
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<tr>
<td><strong>Absorption coefficient [mm^-1]</strong></td>
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<tr>
<td><strong>F(000)</strong></td>
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<tr>
<td><strong>Crystal size [mm]</strong></td>
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<tr>
<td><strong>θ range for data collection [°]</strong></td>
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<tr>
<td><strong>Index ranges</strong></td>
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<tr>
<td><strong>Reflections collected</strong></td>
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<td><strong>Independent reflections</strong></td>
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<td><strong>Completeness to 2θ [°]</strong></td>
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<td><strong>Goodness-of-fit on ( R^2 )</strong></td>
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<tr>
<td><strong>Final R indices [( I \geq 2\sigma(I) )]</strong></td>
</tr>
<tr>
<td><strong>R indices (all data)</strong></td>
</tr>
<tr>
<td><strong>Largest diff. peak and hole ( [e Å^{-3}] )</strong></td>
</tr>
</tbody>
</table>
Structure of [Cu₂{µ-C₄O₂}(apzy)(H₂O)]Cl₂ (9)

The structure of 9 consists of tetranuclear complexes [Cu₂{µ-C₄O₂}(apzy)]Cl₂ and chloride ions. The tetranuclear complex [Cu₂{µ-C₄O₂}(apzy)]Cl₂ (Figure 9) results from the pairing of two dinuclear units [Cu₂{µ-C₄O₂}(apzy)](H₂O)]Cl₂ related by a crystallographic center of inversion located in the middle of the C–C bond of this central µ-oxalato bridge.

The tetramers are constructed via oxalato ions analogously to linkage observed in compounds 5, 6 and 8, i.e. the three tetrafunctional bridging oxalato ions (coordinating to two metal ions in bidentate-chelating mode), Fig. 9) join four copper ions. The two Cu atoms of the tetramer are coordinated by two oxalate and apzy ligands, which build up an elongated octahedral surrounding around Cu(1). Both bis-chelating oxalato bridges are asymmetrically coordinated to the Cu(1) atom with one Cu–O bond distance 2.363(3) and 2.273(3) Å for Cu(1)–O(3) and Cu(1)–O(7), respectively) significantly longer than the other one [2.088(3) and 1.0986(3) Å for Cu(1)–O(1) and Cu(1)–O(6), respectively]. The oxygen atoms O(1), O(6) involved in the short bond distances and nitrogen atoms N(1) and N(2) of apzy ligand define the equatorial plane of the octahedron around Cu(1). The apical positions are filled by the O(3) and O(7) atoms involved in the longest bond distances. The dihedral angle between the two bridging oxalato ligands around the Cu(1) is 88.6(4) °, and the oxalato bridges form dihedral angles of 87.8(4) and 75.1(4) ° with the best equatorial mean plane of Cu(1) center (Table S10). The two outer Cu atoms have a square-pyramidal environment, with two oxygen atoms of the oxalate bridge and two nitrogen atoms of apzy occupying the base of the pyramid. The axial coordination site is occupied by the oxygen atom of water molecule.

In contrast to Cu(1), the coordination of the bridging oxalato ligands to Cu(2) is almost symmetric, with two very short Cu–O bond distances 1.988(3) and 1.971(3) Å for Cu(2)–O(2) and Cu(2)–O(4), respectively. The dihedral angle between the bridging oxalato ligand and the best equatorial mean plane of Cu(2) is 5.434(3) °. The metal–metal distances across the two oxalato bridges are 5.434(3) Å, [Cu(1)−Cu(2)], and 5.525(3) Å, [Cu(1)−Cu(1a)]. In the dimer, the oxalato bridge is asymmetrically coordinated to the copper atom which exhibits a tetragonally elongated CuO4N2 environment, whereas it is linked to the five-coordinated copper atom by means of two short Cu–O distances.

The tetranuclear complex cation is internally linked the four Cu-H...O weak hydrogen bonds (two bonds in each asymmetric unit). The N-H...O hydrogen bonds links cation to the supramolecular rings (R2(20)R2(24) unitary graph motifs) and the N/O–H...Cl hydrogen bonds forms the finite D motifs of the first level graph. On the higher levels all these interactions assemble the cations and anions to the two dimensional layer extending along the crystallographic (102) plane. These layer are linked by the Cu-H...O/Cl intermolecular hydrogen bonds to the three dimensional supramolecular network.

Effect of N-donor Ligand on the Structures

Through varying the auxiliary N-donor ligands under similar synthetic conditions nine new copper(II) oxalate compounds with different structures were successfully obtained. Depending on the features of the N-donor ligands (substituents and coordination groups, conformations, and flexibility), the resultant compounds differ in dimensionality, metal coordination sphere or oxalate coordination modes. The two dimensional network is formed only in case of compound containing only one monofunctional organic N-donor ligand, i.e. compound 1. In other studied compounds, two or three N-donor ligands exist the inner coordination sphere, or the one such ligand acts in the chelating mode. Thus in only in 1 the five metal coordination sites are available (instead of four less existing in compounds 2-9) after coordination of organic ligand, and 2D structure is achieved by very rare µ-oxalato coordination cation and asymmetric unit anion of the compound 9, the symmetry generated atoms are indicated by A letter (symmetry code -x, -y, -z). The hydrogen atoms were omitted for clarity, the bonds of disordered domains are drawn as hollow lines.

Figure 8. a) The perspective drawing of the coordination entity of the compound 8, the symmetry generated atoms are indicated by A and B letters (symmetry codes -x+1, -y+1, -z+1 and -x, -y, -z respectively); b) the part of the 1D coordination network, the ligand molecules not involved into formation of the chain were omitted.

Figure 9. The perspective drawing of the tetranuclear coordination cation and asymmetric unit anion of the compound 9, the symmetry generated atoms are indicated by A letter (symmetry code -x, -y+1, -z+1), the hydrogen atoms were omitted for clarity, the bonds of disordered domains are drawn as hollow lines.
of the N-donor and oxalate ligands and absence of the respect species in the reaction environments disallow formation subsequent Cu–N and Cu–Oxalate bonds.

The substituents of pyrazole ring influence also the coordination modes of oxalate anions. The structures 2, 3 and 4 display rather unusual mono/bidentate coordination mode (μ–oxalato−1κ2O1,2κO2) of oxalate ligands, whereas the metal centers of 5 are typically bridged by bis-bidentate oxalate ions (μ–oxalato−1κ2O1,2κ2O1O2). The same oxalate coordination mode was confirmed for [Cu2(C6H4O2)(bpzm)] (3.5H2O) (6). In contrast to 5, however, the zigzag polymeric chain of 6 is built of dinuclear units. The structural difference of compounds 7 or 8 and 9, noticeable in the metal coordination environments and oxalate coordination modes, is mainly attributed to the effect of the spacer length and flexibility of the N-donor ligand. Compared with the ampy ligand, the aepy ligand has an additional –CH2– group. The role of coordinated and lattice water molecules as well as extensive hydrogen-bonding interactions is also important in these structures.

### Thermal Analysis

The thermal stability of compounds 1–9 was measured by TGA on polycrystalline samples in an air atmosphere with a heating rate of 20 °C/min. The TG analyses of 2, 6, 7 and 8 show the first weight loss of 14.316 % (50–113°C, calcd. 14.54 %) for 2, 9.87 % (80–148 °C, calcd. 9.52 %) for 6, 6.5 % (165–209 °C, calcd.6.49 %) for 7 and 9.43 % (55–229.1°C, calcd. 9.35 %) for 8, corresponding to the loss of coordinated or lattice water molecules per formula unit (Figure S10). After that, the weight loss occurs upon heating including three steps for 7 and 8 and four for 2 and 8. The weight losses in the range of 130–290 °C for 2, 205–289 °C for 7 and 202–298 °C for 8 correspond to the removal of the corresponding organic components, 44.91 % (calcd. 44.70 %) for 2, 37.5 % (calcd. 38.94 %) for 7 and 46.15 % (calcd.47.53 %) for 8. The anhydrous framework of 6 starts to decompose beyond 165.5 °C in a series of complicated overlapped weight losses. The final mass remnant is of 25.1 % for 2, 10.5 % for 6, 25.4 % for 7 and 28.0 % for 8 of the total sample. The complex 1 remains intact until heating to 229.3 °C, and then suffers two consecutive weight losses that end at 430 °C. The pz molecules are lost in the first step followed by degradation. Further heating to 800 °C reveals no weight loss and the final solid holds a weight of 29.9 % of the total sample. For 5, TG curve also displays two weight losses. The first weight loss of 60.89 % from 190 to 245 °C corresponds to the loss of organic components (calcd. 60.92 %), while the second weight loss of 11.93 % from 224.1 to 323.6 °C corresponds to the decomposition of copper oxalate. Complex 4 is thermally stable upon heating to ca. 180 °C followed by three stages...
of weight loss peaking at 198 °C, 277 °C and 334 °C, corresponding to the exclusion of mpz ligands and then degradation. For 9, the TG curve indicates that the coordinated water molecules and chloride anions are released in the range 75–188 °C (found 9.08 %, calcld 9.65 %). The weight loss of 50.40 % at 234 °C (in the range 190–245 °C) (calcld 44.0 %) corresponds to the loss of N-donor ligand. For 3, the TG curve indicates that the organic ligands are released in the range 140–260 °C (found 53.3 %, calcld. 53.4 %). The final mass remnant of weight loss peaking at 198 °C, 277 °C and 334 °C, corresponding to the exclusion of mpz ligands and then degradation. For 9, the TG curve indicates that the coordinated water molecules and chloride anions are released in the range 75–188 °C (found 9.08 %, calcld 9.65 %). The weight loss of 50.40 % at 234 °C (in the range 190–245 °C) (calcld 44.0 %) corresponds to the loss of N-donor ligand. For 3, the TG curve indicates that the organic ligands are released in the range 140–260 °C (found 53.3 %, calcld. 53.4 %). The final mass remnant

Magnetic properties and EPR spectra

Magnetic parameters and magnetization data as well as EPR results of the discussed compounds are presented in the Table 3. The variation of the magnetization M versus the magnetic field H have been measured for all complexes at 2 K. The EPR results of 1–9 indicated signals typical for Cu(II) centers in different coordination spheres, like single, axial or rhombic type signals.

Magnetic susceptibilities studies indicated that five of compounds 2, 4, 7, 8 and 9 revealed the one-dimensional infinite chains of copper(II) centers.

Two methods calculation of exchange parameters have been used e.g. Ising (1) and Fisher (2) models. The Ising model with molecular field correction was solved for spin S=1/2 a linear chain system and the Hamiltonian used was:

\[ H = -2J \sum_{i=1}^{N} S_i^z \sum_{j=1}^{N} S_j^z + g\beta \sum_{i=1}^{N} H S_i^z + g\beta \sum_{i=1}^{N} H_i^S S_i^z \]

where \( J \) is the exchange parameter, \( N \) is the number of magnetic atoms, \( S_i^z \) is the projection of the spin angular momentum in the direction of quantization, \( \beta \) is the Bohr magneton, \( H \) is the external magnetic field, and \( H_i^S \) is the molecular field on the i-th atom which describes the interactions between atoms in different chains.

The magnetic susceptibility for such a system is given by the relationship:

\[ \chi_M = \frac{N g^2 \beta^2 S(S+1)}{3kT} \left( 1 - \frac{u}{1 + u} \right) \]

which is the one-dimensional Ising model for S=1/2.

In order to obtain values for those exchange parameters, the present data have been fit using also Fisher's classical Heisenberg results for infinite linear chains. A molecular field approximation has been used to account for interaction between chains. Fisher's equation for the magnetic susceptibility of a classical spin S chain is:

\[ \chi_M = \frac{N g^2 \beta^2 S(S+1)}{3kT} \left( 1 - \frac{2z'J' \chi_M}{N g^2 \beta^2} \right) \]

where \( u = \coth[2JS(S+1)/kT] - kT/(2JS(S+1)) \) and \( J' \) is the interchain exchange parameter.

If there are interactions between chains, the actual observed susceptibility may then be obtained using the results of a molecular field correction:

\[ \chi_{M,corr} = \frac{\chi_M}{1 - 2z'J' \chi_M/N g^2 \beta^2} \]

where \( J' \) is the interaction between chains and \( z \) is the number of nearest neighbor chains.

Results of magnetic parameters calculated are presented in Table 4.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Intrachain parameter J (cm⁻¹)</th>
<th>Interchain interaction zJ' (cm⁻¹)</th>
<th>Factors g</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cu(C₂O₄)(apz)₂]₆(3H₂O)₉ (2)</td>
<td>-0.12 c)</td>
<td>-0.10 c)</td>
<td>2.11 c)</td>
</tr>
<tr>
<td></td>
<td>-0.11 d)</td>
<td>-0.11 d)</td>
<td>2.11 d)</td>
</tr>
<tr>
<td>[Cu(C₂O₄)(mpz)₂]₆ (4)</td>
<td>-0.36 c)</td>
<td>0.83 c)</td>
<td>2.09 c)</td>
</tr>
<tr>
<td></td>
<td>-0.37 d)</td>
<td>0.86 d)</td>
<td>2.09 d)</td>
</tr>
<tr>
<td>[Cu(C₂O₄)(ampy)(H₂O)]₉ (7)</td>
<td>0.00 c)</td>
<td>-0.19 c)</td>
<td>2.15 c)</td>
</tr>
<tr>
<td></td>
<td>0.00 d)</td>
<td>-0.19 d)</td>
<td>2.15 d)</td>
</tr>
<tr>
<td>[{Cu₂(μ-C₂O₄)(apdy)}₂] [Cu(C₂O₄)(H₂O)]₆(2H₂O)₉ (8)</td>
<td>-58.9 c)</td>
<td>0.00 c)</td>
<td>2.37 c)</td>
</tr>
<tr>
<td></td>
<td>-62.3 c)</td>
<td>0.00 d)</td>
<td>2.39 c)</td>
</tr>
<tr>
<td>[Cu₄(μ-C₂O₄)₃(apdy)(H₂O)]₃Cl₂ (9)</td>
<td>-0.35 c)</td>
<td>-2.39 c)</td>
<td>1.92 c)</td>
</tr>
<tr>
<td></td>
<td>-0.34 d)</td>
<td>-2.42 d)</td>
<td>1.92 d)</td>
</tr>
</tbody>
</table>

* a) – calculated in the temperature range 1.8 – 300 K and b) – calculated in the temperature range 120 – 300 K using Ising c) and Fisher d) models.
Magnetic behavior of compound 8 indicates overall antiferromagnetic interactions among the Cu(II) centers. Upon the compound 8 being cooled $\chi_M T$ value shows linear decrease from 0.404 cm$^{-1}$ mole$^{-1}$ K ($\mu_{\text{eff}} = 1.81$ B.M.) at 300 K up to 0.269 cm$^{-1}$ mole$^{-1}$ K ($\mu_{\text{eff}} = 1.47$ B.M.) at 120 K. The $\chi_M T$ value declines abruptly upon further cooling and reaches a minimal value of 0.058 cm$^{-1}$ mole$^{-1}$ K ($\mu_{\text{eff}} = 0.68$ B.M.) at 1.8 K. Ising and Fisher models were used for calculation of exchange parameters (Table 4).

The evaluated $J$ for compound 8 well correlates with values reported for analogous compounds, $\{[\text{Cu}_{2}(\text{C}_{2}\text{O}_{4})_{2}(\text{ampy})]_{6} \text{(ampy} = 2\text{-amino-4-methylpyridine})^{26}, [\text{dien}]\text{Cu}_{2}(\text{C}_{2}\text{O}_{4})_{2}\text{Cu}(\text{H}_{2}\text{O})(\text{nen})\text{(ClO}_{4}) \} (J = -75.0$ cm$^{-1}$; nenh = N,N,N',N'-tetramethylethlenediamine, dien = diethylenetriamine)\) and $\{[\text{Cu}_{2}(\text{C}_{2}\text{O}_{4})(\text{H}_{2}\text{O})(\text{3Meade})\text{H}_{2}\text{O}]_{6} (J = -34$ cm$^{-1}$; 3Meade = 3-methyladenine)\)\). In all these compounds, the oxalato bridging ligand forms two short Cu–O bonds at one copper atom and one short and one long at the other copper atom. As a result, one of the metal magnetic orbital ($d_{x^2}$, $d_{y^2}$ in a tetragonally elongated octahedral geometry) is coplanar with the oxalate bridge, whereas the other one is perpendicular to it. For this topology, the overlap between the magnetic orbitals occurs only via one of the two OCO fragments leading to antiferromagnetic coupling. The magnitude of magnetic coupling in such compounds is predicted to be about one-fourth of that observed for the topology with symmetric bis-bidentate bridging ligand coplanar with metal magnetic orbital and four short Cu–O$_6$ bond distances, which guarantees the strongest antiferromagnetic couplings (values of $J$ ranging from $-260$ to $-400$ cm$^{-1}$)\(^{25}\). To some extent the antiferromagnetic interactions in 8 is weakened by different coordination environments of copper of Cu(1) and Cu(2) ions\(^{27}\).

Results of magnetic measurements concern 2, 4 and 7 compounds contains infinite chains in the crystal structure and indicates a very weak intra- and interchain interactions between copper (II) centers. So far, only several $\mu$–oxalato–1$κ^2$O$^\prime$,O$^\prime$2xO$^{2\prime}$–bridged Cu(II) complexes have been magnetically characterized and in almost all previously discussed compounds, including ours, the magnetic orbitals adopt the relative geometry shown in Scheme 3. This configuration is unfavourable for transmitting exchange coupling \(^{25}\).

Scheme 4. Orbital topology found in 2, 4 and 7 and related $\mu$–oxalato–1$κ^2$O$^\prime$,O$^\prime$2xO$^{2\prime}$–bridged Cu(II) complexes.

Determination of exchange parameters of dinuclear complexes 1 and 6 were made by fitting the experimental results to the modified Bleaney-Bowers expression (4) \(^{24}\):

$$X_{\text{Cu}}^{\text{corr}} = \frac{N\beta g_{\text{av}} \frac{g}{4kT}}{1 + \frac{1}{2}(e^{-\frac{J}{kT}})} \left[1 - (1 - x) \left(\frac{N\beta g_{\text{av}} \frac{g}{4kT}}{1 + \frac{1}{2}(e^{-\frac{J}{kT}})} x\right)\right]^{-1}$$

where $X_{\text{Cu}}^{\text{corr}}$ is molar magnetic susceptibility corrected for diamagnetism and t.i.p., calculated per copper(II) magnetic center, $N$ — Avogadros number, $k$ — Boltzmann constant, $g_{\text{av}}$—average g factor, $x$—percentage of monomeric form of a complex, $\chi_{\text{imp}}$—g factor of monomeric form of complex and $J$ is the exchange parameter in the Heisenberg-Dirac-Van Vleck Hamiltonian $H = -2JS_{\uparrow}S_{\downarrow}$.

Relation of magnetic susceptibility vs. temperature for 1 and 6 compounds indicated the presence of paramagnetic impurity (Table 5).

Although the coordination structure of the compounds 1 and 6 is two- and one-dimensional respectively, from a magnetic point of view, these systems can be considered as dimers. The zig-zag polymeric chain of 6 is built up of the [[Cu$_2$(C$_2$O$_4$)$_2$(bpzm)$_2$] entities. In turn, there are two independent oxalato anions adopting different coordination modes $\mu$–oxalato–1$κ^2$O$^\prime$,O$^\prime$2xO$^{2\prime}$ and $\mu$–oxalato–1$κ^2$O$^\prime$,O$^\prime$2xO$^{2\prime}$3xO$^{4\prime}$4xO$^{3\prime}$ in the structure (1 Figure 1b). The first one, leading to almost planar Cu–C$_2$O$_4$–Cu framework with four short Cu–O, favours strong antiferromagnetic interactions, whereas the exchange coupling through out-of-plane exchange pathway $\mu$–oxalato–1$κ^2$O$^\prime$,O$^\prime$2xO$^{2\prime}$3xO$^{4\prime}$4xO$^{3\prime}$ is expected to be very weak \(^{25}\).

For calculation magnetic parameters for compound 5, Pad’e expression series (5)\(^{26}\) for the (S=1/2) Heisenberg model with a molecular field correction (3)\(^{18}\) was used:

$$X = \frac{N\beta g^2}{4kT} \left(\frac{L}{M}\right)^3$$


Relation of $\chi_M T$ vs. $T$ of compound increase cooling up to maximal value equal 0.678 cm$^{-1}$ mole$^{-1}$ K at 1.8 K.

Magnetic susceptibility data of compound 5 between 1.8-300 K to the Curie- Weiss expression, according Curie constant C=0.444 cm$^{-1}$ mole$^{-1}$ K and Weiss constant $\Theta = 0.74$ K. The positive Weiss constant confirms existence of the ferromagnetic coupling between copper(II) centers. The least-squares fit of the experimental data using these equations were limited to the temperature range from 1.8 K up to 300 K and leads $J = 1.17$ cm$^{-1}$, $2J^\prime = -0.21$ cm$^{-1}$ and $g = 2.15$ with the agreement factor R is equal 2.73×10$^{-3}$.

The weak ferromagnetic coupling observed for compound 5 is in good agreement with the magnetic results reported for related one-dimensional Cu(II) structure based on asymmetric bischelating oxalate bridges with perpendicular topology (where the metal-centered magnetic orbitals are parallel to each other and perpendicular to the oxalato) and angle $\beta$ (the bond angle C−O−C involving the apical oxalate-oxygen ) below 109.5 ° in structure 5), for example in [[Cu$_2$(C$_2$O$_4$)$_2$(bpza)$_2$]$_n$ ($J_{2\uparrow}= +2.50$ cm$^{-1}$; $\beta = 106.9$ °, bpa = 1,2-bis(4-pyridyl)ethane), [[Cu$_2$(C$_2$O$_4$)$_2$(ampy)$_2$]$_n$ ($J_{2\uparrow}= +2.00$ cm$^{-1}$; $\beta = 107.8$°, 2-ampy = 2-aminopyridine), [[Cu$_2$(C$_2$O$_4$)$_2$(bpy)$_2$]$_n$ ($J_{2\uparrow}= +2.4$ cm$^{-1}$; $\beta = 108.4$ °)\(^{25}\). Relation of $\chi_M T$ vs. $T$ of compounds 1, 5 and 6 is presented on Figure 11.
### Table 3. Magnetic parameters, magnetization data\(^a\) and EPR data

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Diamagnetic corrections(^b) (\times 10^6) (cm(^3) mol(^{-1}))</th>
<th>Effective magnetic moments(^a) (\mu_B) (B.M.)</th>
<th>Curie constant (C) (cm(^3) K mol(^{-1}))</th>
<th>Weiss constant (\Theta) (K)</th>
<th>Magnetization(^d) (B.M.)</th>
<th>Factors (g)</th>
<th>(T = 77) K</th>
<th>(T = 293) K</th>
</tr>
</thead>
<tbody>
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<td>1</td>
<td>-18</td>
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<td>-</td>
<td>-</td>
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<td>-0.24</td>
<td>0.97</td>
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<td>(g_2 = 2.07_2)</td>
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<td>-0.46</td>
<td>0.97</td>
<td>(g_1 = 2.20_3)</td>
<td>rhombic line</td>
<td>(g_2 = 2.13_2)</td>
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<td>4</td>
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<td>-0.01</td>
<td>0.98</td>
<td>(g = 2.16_4)</td>
<td>single isotropic line</td>
<td>(g = 2.14_4)</td>
</tr>
<tr>
<td>5</td>
<td>-117</td>
<td>1.88</td>
<td>0.444</td>
<td>0.74</td>
<td>1.01</td>
<td>(g_1 = 2.31_5)</td>
<td>axial line</td>
<td>(g_2 = 2.07_5)</td>
</tr>
<tr>
<td>6</td>
<td>-61</td>
<td>1.70</td>
<td>-</td>
<td>-</td>
<td>0.01</td>
<td>(g_1 = 2.31_6)</td>
<td>rhombic line</td>
<td>(g_2 = 2.10_6)</td>
</tr>
<tr>
<td>7</td>
<td>-75</td>
<td>1.90</td>
<td>0.437</td>
<td>-0.14</td>
<td>0.99</td>
<td>(g = 2.12_7)</td>
<td>single isotropic line</td>
<td>(g = 2.10_7)</td>
</tr>
<tr>
<td>8</td>
<td>-51</td>
<td>1.81</td>
<td>-</td>
<td>-</td>
<td>0.15</td>
<td>(g = 2.13_8)</td>
<td>single isotropic line</td>
<td>(g = 2.13_8)</td>
</tr>
<tr>
<td>9</td>
<td>-74</td>
<td>1.68</td>
<td>0.346</td>
<td>-2.29</td>
<td>0.56</td>
<td>(g_1 = 2.04_9)</td>
<td>axial line</td>
<td>(g_2 = 2.07_9)</td>
</tr>
</tbody>
</table>

\(a\) calculated in the temperature range 1.8 – 300 K
\(b\) \(g_a\) – factor of dimeric form
\(g_b\) – factor of monomeric form

### Table 5. Magnetic parameters of dinuclear-based compounds

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Exchange parameter (J) (cm(^{-1}))(^a)</th>
<th>Monomeric form (%)</th>
<th>Factors (g)</th>
<th>Agreement factor (R)</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Cu}(\text{C}_2\text{O}<em>4)]</em>{\text{pz}}]_n (1)</td>
<td>-156</td>
<td>0.94</td>
<td>(g_a = 2.16_b) (g_b = 2.14_d)</td>
<td>1.98(\times 10^{-5})</td>
</tr>
<tr>
<td>([\text{Cu}_2(\text{C}_2\text{O}_4)_2(\text{bpzm})<em>2]</em>{\text{H}_2\text{O}}]_n (6)</td>
<td>-41</td>
<td>0.75</td>
<td>(g_a = 2.16_b) (g_b = 2.08_d)</td>
<td>2.72(\times 10^{-5})</td>
</tr>
<tr>
<td>([\text{Cu}_2(\text{C}_2\text{O}_4)_2(\text{ampz})]_2) (3)</td>
<td>-0.45</td>
<td>0.00</td>
<td>(g_a = 2.16_b) (g_b = -)</td>
<td>1.31(\times 10^{-4})</td>
</tr>
</tbody>
</table>

\(a\) calculated in the temperature range 1.8 – 300 K

\(g_a\) – factor of dimeric form
\(g_b\) – factor of monomeric form
Figure 11. Thermal dependences of $\chi_M T$ for compounds 1 ( ), 5 ( ) and 6 ( ). Experimental magnetic data plotted as $\chi_M T$ vs. $T$. The solid line is the calculated curve for $\chi_M T$ vs. $T$.

The Bleaney- Bowers expression (4) of magnetic interaction was also used for calculation exchange parameter of semi-dimer 3.

The compound 3 indicated a very weak antiferromagnetic coupling of Cu$^{2+}$ centers $J = -0.45$ cm$^{-1}$, $zJ'=0$ and $g=2.16$ with the agreement factor $R$ is equal $1.32 \times 10^4$ and indicated lack any monomeric impurities.

Analysis of magneto-structural data of 1-9 confirmed that the value and type of the magnetic coupling is essentially governed by the magnitude of the overlap between the metal-centered magnetic orbitals ($d_{x^2-y^2}$ orbital in square pyramidal or elongated octahedral geometries) and the highest occupied molecular orbitals of the oxalate ligand. The strongest antiferromagnetic couplings occurs when the oxalato bridge is symmetrically coordinated with two short bond distances at neighboring copper(II) atoms and, it is coplanar with the magnetic orbitals. The equatorial-axial coordination mode of the oxalate bridge with long Cu-O$_{ax}$ bond substantially reduced the magnetic coupling of copper centers.

**UV-Vis properties**

Except for 3, the electronic reflectance spectra of the examined compounds are characterized by a very broad asymmetric band in the region 600 – 1000 nm typical for overlapping $d_{x^2-y^2}$, $d_{xy}$,$d_{yz}$,$d_{z2}$, $d_{2x^2-y^2}$ and $d_{2x^2}$ transitions between d orbitals in tetragonal six or five coordinate Cu(II) complexes with $d_{2x^2}$ ground state (Figure 12). The greater is tetragonality of the complex the longer the axial bonds, more shifted to the blue is the low energy absorption maximum. The electronic diffuse reflectance spectrum of 3 exhibits two bands 742 and 626 nm assigned to $d_{3z^2-r^2}$ and $d_{xy}$,$d_{yz}$,$d_{z2}$,$d_{2x^2-y^2}$, respectively, and it is also consistent the elongated tetragonal distortion. Besides the d-d bands, the spectra display bands assigned to LMCT, LLMC and IL transitions. Electronic spectral data for the compounds 1-9 are summarized in Table 6.

**Conclusions**

In summary, we have successfully synthesized and characterized nine oxalate copper(II) complexes. X-ray analysis revealed a key role of N-containing auxiliary ligand in determination of the oxalate coordination mode and final complex architecture. The two dimensional network is formed only in case of compound containing the pyrazole ligand. The introduction of substituents into pyrazole ring increases the complexation properties of N-donor ligands leading to coordination of two ligand molecules and formation of the lower dimensional networks. The exchange interaction between the copper ions via the oxalate bridge has been shown to be strongly dependent on the geometry around the Cu ions, the orientation of the magnetic orbitals in respect to the oxalate plane and the bridging mode of the oxalate group. The strongest antiferromagnetic couplings was confirmed for compound [Cu(C$_{2}$O$_{4}$)pz]$_{n}$ (1) in which the oxalato bridge is symmetrically coordinated with two short bond distances at neighboring copper(II) atoms and it is coplanar with the magnetic orbitals. The equatorial-axial coordination mode of the oxalate bridge with long Cu-O$_{ax}$ bond, detected in the other examined structures, substantially reduced the magnetic coupling of copper centers.

**Materials and General Methods**

Bis[pyrazol-1-y]methane was synthesised according to the literature method. Other reagents used to the synthesis were commercially available and were used without further purification. IR spectra were recorded on a Nicolet Magna 560 spectrophotometer in the spectral range 4000–400 cm$^{-1}$ with the samples in the form of KBr pellets. The solid reflectance spectra UV-Vis spectra were recorded on Jasco V-630 spectrophotometer in range 200-1000 nm. EPR spectra were recorded at room temperature and 77 K on a Bruker Elexsys E 500 spectrometer equipped with an NMR teslameter (ER 036TM) and frequency counter (E 41 FC) at the X-band. Powder X-ray diffraction (PXRD) measurements were performed on a PANalytical Empyrean X-ray diffractometer using Cu–Kα radiation ($\lambda = 1.5418$ Å), in which the X-ray tube was operated at 40 kV and 30 mA ranging from 5 to 80°. Thermogravimetric analysis (TGA) was performed on a Perkin Elmer Pyris1 instrument.

**Preparation of 1-9**

(NH$_4$)$_2$C$_2$O$_4$H$_2$O (0.085 g, 0.60 mmol) was dissolved in water (5 ml) and slowly added to the methanolic solution of CuCl$_2$·2H$_2$O or Cu(NO$_3$)$_2$·3H$_2$O and suitable N-donor ligand. The resulting solution was kept for evaporation at room temperature, and after a few weeks crystals of 1-9 were obtained, filtered off and dried. Details concerning synthesis of 1-9 are gathered in Table below.

(1) [Cu(C$_{2}$O$_{4}$)(pz)]$_{n}$: Anal. Calc. for C$_{9}$H$_{9}$N$_{2}$O$_{4}$Cu: C, 27.34; H, 1.84; N, 12.75 %. Found: C, 27.68; H,1.66; N, 12.55%. IR (KBr; cm$^{-1}$):
3291(s), 3231(m) and 3146(m) ν(NH); 1705(vs) and 1651 (vs ν(C=O); 1602(s) ν(C=O); 1358(s) and 1302(s) ν(C=O).  
2. [Cu₂(CO₃)(apz)]₃[3H₂O]; Anal. Calc. for C₂H₅NO₂Cu: C, 25.84; H, 4.34; N, 22.60 %. Found: C, 25.99; H, 4.52; N, 22.71 %. IR (KBr; cm⁻¹): 3437(s) and 3312(s) ν(NH); 1678(vs) ν(C=O); 1592 (m), 1552(m) and 1531(s) ν(C=N₃) and ν(C=O); 1429(s) and 1410(sh) ν(C=O).  
3. [Cu₂(μ-Cl)(H₂O)(apz)]₃[3H₂O]; Anal. Calc. for C₂H₅NO₂ClCu: C, 33.01; H, 4.43; N, 23.10 %. Found: C, 33.40; H, 4.55; N, 23.49 %. IR (KBr; cm⁻¹): 3417(s), 3355(s), 3200(s) and 3146(m) ν(NH) and ν(OH); 1673(vs) and 1636(s) ν(C=O); 1595(m), 1578(m) and 1502(m) ν(C=N₃) and ν(C=O); 1427(s) and 1285(s) ν(C=O).  
4. [Cu₂(CO₃)(mpz)]₃[3H₂O]; Anal. Calc. for C₂H₅NO₂Cu: C, 38.04; H, 3.83; N, 17.74 %. Found: C, 38.39; H, 3.94; N, 17.86 %. IR (KBr; cm⁻¹): 3438(m), 3246(m) and 3126(m) ν(NH); 1682(vs) 1661(s) and 1645 (s) ν(C=O); 1567(s) and 1521(w) ν(C=N₃) and ν(C=O); 1414(s) and 1097(s) ν(C=O).  
5. [Cu₂(CO₃)(aipy)]₃[3H₂O]; Anal. Calc. for C₂H₅NO₂Cu: C, 49.55; H, 3.12; N, 14.45 %. Found: C, 49.82; H, 3.24; N, 14.66 %. IR (KBr; cm⁻¹): 3235(s) ν(NH); 1670(vs) ν(C=O); 1594(s) ν(C=N₃) and ν(C=O); 1435(s) and 1335(s) ν(C=O).  
6. [Cu₂(CO₃)(bpzm)]₃[3H₂O]; Anal. Calc. for C₂H₅NO₂Cu: C, 32.63; H, 3.50; N, 16.91 %. Found: C, 32.97; H, 3.39; N, 17.05 %. IR (KBr; cm⁻¹): 3473(br) and 3137(s) ν(OH); 1666(vs) ν(C=O); 1597(s), 1522(w) and 1512(w) ν(C=N₃) and ν(C=O); 1405(s) and 1281(s) ν(C=O).  
7. [Cu₂(CO₃)(ampy)(H₂O)]; Anal. Calc. for C₂H₅NO₂Cu: C, 34.60; H, 3.63; N, 10.90 %. Found: C, 34.95; H, 3.73; N, 10.49 %. IR (KBr): 3402(s), 3290(s) and 3139(s) ν(NH) and ν(OH); 1671(vs) and 1652(vs) ν(C=O); 1607(s) and 1571(w) ν(C=N₃) and ν(C=O); 1435(s) and 1414(s) and 1270(s) ν(C=O).  
8. ([Cu(μ-CO₃)(aepy)][Cu₂(CO₃)(H₂O)]₃[2H₂O]]; Anal. Calc. for C₂H₅NO₂Cu: C, 31.15; H, 3.66; N, 7.27 %. Found: C, 31.42; H, 3.79; N, 7.51 %. IR (KBr): 3312(s), 3248(s) and 3149(s) ν(NH) and ν(OH); 1676(vs) and 1649(vs) ν(C=O); 1618(m), 1595(s) and 1565(sh) ν(C=N₃) and ν(C=O); 1444(s), 1306(s) and 1293(s) ν(C=O).  
9. [Cu₂(μ-CO₃)(aepy)][H₂O]Cl]; Anal. Calc. for C₂H₅NO₂ClCu: C, 36.80; H, 3.63; N, 10.10 %. Found: C, 37.08; H, 3.56; N, 10.43 %. IR (KBr): 3303(s), 3249(s) and 3149 ν(NH) and ν(OH); 1677(vs) and 1648(vs) ν(C=O); 1595(s) ν(C=N₃) and ν(C=O); 1444(s), 1306(s) ν(C=O).  

Crystal Structure Determination and Refinement  
The X-ray intensity data of 1-9 were collected on a Gemini A Ultra Oxford Diffraction four-circle kappa geometry diffractometer with Atlas CCD detector graphite monochromated MoKα radiation (λ = 0.71073 Å) at 293.2(2) K. The unit cell determination and data integration were carried out using the CrysAlis package of Oxford Diffraction 28. Intensity data were corrected for the Lorentz and polarization effects. The absorption correction was introduced by SCALE3 ABSPACK scaling algorithm 29. The structure was solved by direct methods using SHELXS-97 and refined by full matrix least-squares on F² with SHELXL-97 with anisotropic displacement parameters for non-hydrogen atoms 29. The hydrogen atoms were treated as ‘riding’ on their parent carbon atoms and assigned isotropic temperature factors equal 1.2 (non-methyl) and 1.5 (methyl and water) times the value of equivalent temperature factor of the parent atom. The oxygen atom of one water molecule of compound 6 occupy the inversion centre and thus the hydrogen atoms of these molecule are disordered on two positions by symmetry. Because the local electron density maximum smaller than 0.5 eÅ⁻³ cannot be reliably determined by X-ray diffraction, this water molecule disordered hydrogen atoms were not included into refinement. The Cu2 atom in compound 8 shows signs of prolation. The introduction of the multipositional disorder model to this atom does not lead improvement of the displacement parameters, i.e. all partially occupied domains also exhibits prolation with major axis pointing in the same direction as existing for non-disordered one. Thus it can be supposed that the observed disorder is dynamic in character. It must be noted that major axis of prolate ellipsoid is located along the bonds elongated as a consequence of the Jahn–Teller effect, thus the longer and consequently weaker bonds allow larger displacement in their direction. The ethylamine moiety of the one 2-(pyridyl)ethylamine ligand of compound 9 is disordered equally over two sites. Crystal data collection and refinement parameters are summarized in Table 1. The hydrogen bonds and selected bond distances and angles of 1-9 are listed in Tables S1–S10.  

Magnetic Measurements  
Magnetic measurements in the temperature range 1.8-300 K were performed using a Quantum Design SQUID-based MPMSXL-5-type magnetometer. The SQUID magnetometer was calibrated with the palladium rod sample (Materials Research Corporation, measured purity 99.9985%). The superconducting magnet was generally operated at a field strength ranging from 0 to 5 T. Measurements were made at a magnetic field of 0.5 T. Corrections were based on subtracting the sample – holder signal and contribution X₀ estimated from the Pascal constants 30. Magnetization measurements were conducted at 2 K in the magnetic field from 0 to 5 Tesla.  

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4. Department of Inorganic, Organometallic Chemistry and Catalysis, Institute of Chemistry, University of Silesia, 9th Szkolna St., 40-006 Katowice, Poland.  
5. X-ray crystallographic data in CIF format, selected bond lengths and angles, Short intra- and intermolecular contacts and PXRD patterns of the compounds 1-9. Crystallographic data for the structures reported in this article have been deposited in the Cambridge Crystallographic Data Center with CCDC 951616-951624 reference numbers for compounds 1-9.  

References  
Through varying the auxiliary N donor ligands nine new compounds have been synthesized and characterised structurally and spectroscopically. The magnetic properties of the complexes have been investigated and discussed in context their structures.