From Mononuclear to Tetranuclear Oxalate- or Chloranilate-Based Complexes of Copper(II) with Halogen Atoms and *N*-donor Ligands

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─── THIS PAPER IS DEDICATED TO PROF. BRANKO KAITNER ON THE OCCASION OF HIS 80TH BIRTHDAY ───

Abstract: Four novel copper(II) complexes were prepared and characterised by single-crystal X-ray diffraction and IR spectroscopy: $[Cu(bpy)(H_2O)(C_6O_4Cl_2)]\cdot H_2O$ (**1**), $[Cu_2(phen)_2(C_2O_4)I_2]$ (**2**), $[Cu_2(bpy)_2(C_2O_4)Br_2]$ (**3**), and $[Cu_4(bpy)_4(C_2O_4)_3(I_3)_2]$ (**4**). Three types of ligands were varied to assess their effects on the structure, nuclearity and topology: the bridging *O*-donor ligand (oxalate and chloranilate), the terminal *N*-donor ligand (2,2'-bipyridine and 1,10-phenanthroline) and the halogen anion present in the solution (Cl, Br, I). Compound **4** is a rare example of a triiodide anion coordinated to a copper(II) metal centre.

**Keywords:** oxalate, coordination compounds, chloranilate, crystal structure.

INTRODUCTION

THE oxalate group has proven to be one of the most versatile ligands used in the preparation of functional materials. Because of its multiple coordination possibilities to the metal centres and its ability to mediate magnetic interactions between paramagnetic metal ions, a large number of oxalate-based transition-metal species of different nuclearity[1,2] and dimensionality[3–6] have been synthesized and characterized, many of them exhibiting tunable magnetic frameworks.[7,8] Most of the oxalate-based molecular magnets described to date have been obtained by the "complex-as-ligand approach". In this synthetic strategy, a molecular building block, the tris(oxalato)metalate $[M^{III}(C_2O_4)_3]^{3-}$ anion (M^{III} = Cr, Fe, Ru, Rh, Mn or V) is used as a ligand towards other metal cations in the preparation mostly of two- (2D) and three-dimensional (3D) extended systems.[3,5,6]

Semiquinones are a class of stable organic radicals derived from quinones and are therefore very promising candidates for the development of functional materials, not only because of their stability, but also because of their availability, low cost and easy preparation.[9–12] Methods of preparation, stabilization (crystallization) and X-ray measurement of crystals containing semiquinones have already been developed.[13,14] Therefore, it has been logical to extend the research to crystal engineering and design of metal-organic frameworks that would exhibit exceptional magnetic and electric properties. Following these previous investigations and the gained knowledge, we have now focused on the preparation of novel heterometallic compounds by the layering technique, combining the building block $[M^{III}(C_2O_4)_3]^{3-}$ (M^{III} = Cr and Fe) in reaction with copper(II) ions and bidentate *N*-donor ligands, such as 2,2'-bipyridine and 1,10-phenathroline, and semiquinone radicals. It is well known that the use of the capping ligands can control and influence the dimensionality of coordination systems in addition to the stabilization of the solid-state structures.

Further, the 2D and 3D homo- and heterometallic lattices, also obtained in the oxalate family, have been prepared using tris(anilato)metallate building blocks $[M^{III}(C_6O_4X_2)_3]^{3-}$ (M^{III} = Cr and Fe; X = Cl and Br). A new family of heterometallic 2D honeycomb lattices exhibiting chirality and porosity or long-range magnetic order has
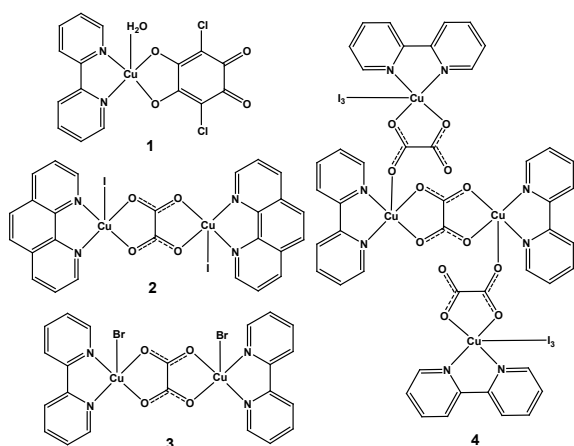
Scheme 1. Compounds studied in this work.

been studied.[15–18] Motivated by these interesting results we have also extended our research to the preparation of novel compounds using $[Cr(C_6O_4Cl_2)_3]^{3-}$ as ligand toward copper(II) ions, adding 2,2'-bipyridine and reactants to obtain semiquinone radicals.

This effort yielded four homometallic novel compounds: a mononuclear, $[Cu(bpy)(H_2O)(C_6O_4Cl_2)]\cdot H_2O$ (**1**), two dinuclear oxalate-bridged, $[Cu_2(phen)_2(C_2O_4)I_2]$ (**2**) and $[Cu_2(bpy)_2(C_2O_4)Br_2]$ (**3**), and one tetranuclear also oxalate-bridged, $[Cu_4(bpy)_4(C_2O_4)_3(I_3)_2]$ (**4**) (Scheme 1). Unfortunately, during the crystallization process, oxalate or chloranilate groups were released as a result of the decomposition of the used building blocks and are coordinated to copper(II) ion leading to the crystallization of these four oxalate- or chloranilate-based compounds.[5,6,19–21] It is evident that the halide anions added to the reaction mixture to form semiquinone radicals from tetrahalogenoquinones were coordinated to copper ions. IR spectroscopy and single-crystal X-ray diffraction were used to characterize the prepared compounds.

EXPERIMENTAL

Materials and Physical Measurements

All chemicals were purchased from commercial sources and used without further purification. The starting species $K_3[Cr(C_2O_4)_3]\cdot 3H_2O$, $K_3[Fe(C_2O_4)_3]\cdot 3H_2O$ and $[(C_4H_9)_4N]_3[Cr(C_6O_4Cl_2)_3]$ were prepared according to the method described in the literature.[22,23] The infrared spectra were recorded with samples as KBr pellets with a Bruker Alpha-T spectrometer in the 4000–350 cm^{-1} region.

SYNTHESIS OF [Cu(bpy)(H₂O)(C₆O₄Cl₂)]·H₂O (1)

A mixture of aqueous solutions (4 mL) of CuCl₂·2H₂O (0.009 g; 0.050 mmol) and 2,2'-bipyridine (0.008 g; 0.050 mmol) is

layered with a mixture of acetonitrile solutions (6 mL) of tetrachloroquinone, $C_6O_2Cl_4$, (0.010 g; 0.041 mmol) and KI (0.020 g; 0.012 mmol). Then, the acetonitrile solution (5 mL) of precursor $[(C_4H_9)_4N]_3[Cr(C_6O_4Cl_2)_3]$ (0.067 g; 0.100 mmol) is slowly added as the top layer in the test tube. After several days black rod-like single-crystals of compound $[Cu(bpy)(H_2O)(C_6O_4Cl_2)]\cdot H_2O$ (**1**) were formed, isolated, washed with water and dried in air. (Yield 25 %). IR (KBr, cm^{-1}): 3444 (m), 1648 (vm), 1611 (m), 1539 (vs), 1478 (s), 1351 (s), 1300 (m), 999 (w), 845 (m), 774 (w), 604 (m), 576 (m), 509 (w), 416 (w) cm^{-1}.

SYNTHESIS OF [Cu₂(phen)₂(C₂O₄)I₂] (2)

An aqueous solution (7 mL) of CuCl₂·2H₂O (0.017 g; 0.100 mmol), 1,10-phenanthroline (0.020 g; 0.100 mmol) and K₃[Cr(C₂O₄)₃]·3H₂O (0.050 g; 0.100 mmol) was carefully layered with an acetonitrile solution (6 mL) of tetrachloroquinone, $C_6O_2Cl_4$ (0.010 g; 0.0408 mmol) and KI (0.020 g; 0.012 mmol). Blue rod-like single-crystals of compound $[Cu(H_2O)(phen)(C_2O_4)]\cdot H_2O^{[24–26]}$, together with yellow crystals of tetrachloroquinone, $C_6O_2Cl_4$, crystallized within a few of weeks. By prolonged standing in solution (about a month) black crystals of $[Cu_2(phen)_2(C_2O_4)I_2]$ (**2**) were formed and isolated, washed with water and dryed in air. Yield: 24 %. IR (KBr, cm^{-1}): 3465 (m), 1709 (m), 1678 (s), 1638 (vs), 1620 (sh), 1518 (m), 1426 (m), 1395 (m), 1342 (m), 1307 (w), 1256 (m), 1140 (w), 1107 (m), 905 (m), 873 (m), 854 (m), 813 (m), 800 (m), 787 (m), 721 (m), 548 (w), 505 (w), 482 (w), 422 (w) cm^{-1}.

SYNTHESIS OF [Cu₂(bpy)₂(C₂O₄)Br₂]·H₂O (3)

A mixture of aqueous solutions (7 mL) of CuCl₂·2H₂O (0.017 g; 0.100 mmol), 2,2'-bipyridine (0.016 g; 0.100 mmol) and K₃[Fe(C₂O₄)₃]·3H₂O (0.0496 g; 0.100 mmol) is layered with a mixture of an acetonitrile solution (4 mL) of tetrachloroquinone, $C_6O_2Cl_4$, (0.010 g; 0.041 mmol) and an aqueous solution of KBr (0.020 g; 0.012 mmol) in an open test tube. After several weeks blue prismatic single-crystals of compound **3** were formed, isolated, washed with water and dried in air (yield 25 %). IR (KBr, cm^{-1}): 3458 (m), 3069 (w), 3029 (w), 2921 (w), 1658 (vs), 1497 (w), 1475 (w), 1450 (m), 1404 (w), 1383 (w), 1355 (w), 1317 (m), 1257 (w), 1240 (w), 1171 (w), 1159 (w), 1110 (w), 1057 (w), 1035 (w), 1022 (w), 780 (s), 730 (m), 665 (w), 648 (w), 542 (w), 518 (w), 482 (w), 417 (w) cm^{-1}.

SYNTHESIS OF [Cu₄(bpy)₄(C₂O₄)₃(I₃)₂] (4)

A mixture of aqueous solutions (7 mL) of CuCl₂·2H₂O (0.017 g; 0.100 mmol), 2,2'-bipyridine (0.016 g; 0.100 mmol) and K₃[Fe(C₂O₄)₃]·3H₂O (0.0496 g; 0.100 mmol) is layered with a mixture of acetonitrile solutions (6 mL) of tetrachloroquinone, $C_6O_2Cl_4$, (0.010 g; 0.041 mmol) and KI (0.020 g; 0.012 mmol) in an open test tube. After several

weeks black prismatic single-crystals of compound **4** were formed, isolated, washed with water and dried in air (yield 32 %). IR (KBr, cm^{-1}): 3437 (m), 3113 (w), 3080 (w), 3057 (w), 3029 (w), 2957 (w), 2923 (w), 2852 (w), 1708 (m), 1676 (vs), 1654 (vs), 1618 (vs), 1597 (sh), 1567 (m), 1499 (w), 1474 (w), 1447 (w), 1409 (m), 1385 (m), 1351 (w), 1317 (w), 1264 (w), 1253 (w), 1164 (w), 1151 (w), 1108 (w), 1099 (w), 1056 (w), 1035 (m), 1021 (w), 896 (w), 786 (m), 766 (s), 727 (m), 665 (w), 643 (w), 546 (w), 480 (m), 458 (m), 417 (m), 386 (w), 369 (w) cm^{-1}.

Single-Crystal X-Ray Structural Study

Single crystal measurements for compounds **2**, **3** and **4** were performed on a dual-source (Cu/Mo) Rigaku Oxford Diffraction Synergy S diffractometer. Data reduction and absorption correction were performed using the program package CrysAlis PRO.[27]

Single crystal of **1** was measured on an Enraf-Nonius CAD4 diffractometer using Mo$K\alpha$ radiation. The WinGX standard procedure was applied for data reduction.[28] Three standard reflections were measured every 120 minutes as an intensity control. Since the absorption coefficient of the sample was 1.6 mm^{-1}, no absorption correction was applied.

The structures were solved using SHELXS97 or SHELXT[29] and refined with SHELXL-2017.[30] Models were refined using the full-matrix least squares refinement; all non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located in a difference Fourier map and refined as riding entities.

Molecular geometry calculations were performed by PLATON[31] and molecular graphics were prepared using ORTEP-3[32] and Mercury.[33] Crystallographic and refinement data for the structures reported in this paper are shown in Table 1. Crystal structures have been deposited in the Cambridge Structural Database[7] as entries no. 2215191–2215194.

RESULTS AND DISCUSSION

Synthesis of Compounds 1–4

Compounds **1**–**4** were obtained applying the building block approach using the layering technique, with the intention of preparing heterometallic oxalate- or chloranilate-based compounds containing a semiquinone radical, thus improving the magnetic and electrical properties of these systems. Black crystals of the compound [Cu$_2$(phen)$_2$(C$_2$O$_4$)I$_2$] (**2**) were formed by evaporation of the solvent from the reaction mixture when an aqueous solution of the compounds CuCl$_2$·2H$_2$O, K$_3$[Cr(C$_2$O$_4$)$_3$] · 3H$_2$O and 1,10-phenanthroline ligand was carefully layered with an acetonitrile solution containing C$_6$O$_2$Cl$_4$ and KI, which are the reactants used to

prepare the mentioned radical. The partial decomposition of the [Cr(C$_2$O$_4$)$_3$]$^{3-}$ anion enabled the release of the oxalate ligand from the coordination sphere of chromium(III), which was consequently coordinated to copper(II) ions in the reaction mixture during the crystallization process, forming a homodinuclear oxalate-bridged compound of copper(II). The present iodide ions were coordinated to the metal centers, and no radical species were formed. This occurrence in which the building block serves as a suitable, additional oxalate source has been recently observed for the tris(oxalato)metalate(III) precursors,[5,6,19–21] bis(oxalato)-chromate(III)[1,34] and oxotris(oxalato)niobate(V).[35,36] Interestingly, by changing tris(oxalato)chromate(III) and 2,2'-bi-pyridine with tris(oxalato)ferrate(III) and bulkier phen-anthroline ligand, respectively, a crystallization of the homo-tetranuclear oxalate-bridged compound [Cu$_4$(bpy)$_4$(C$_2$O$_4$)$_3$(I$_3$)$_2$] (**4**) with coordinated triiodide occurred. Based on these results, it was further investigated how the final product would be affected when KI is replaced by KBr; a homodinuclear oxalate-bridged with coordinated bromide ions [Cu$_2$(bpy)$_2$(C$_2$O$_4$)Br$_2$]·H$_2$O (**3**) was formed.

In the similar reaction in which the larger chloranil-ate building block was used together with a copper salt, a bipyridine ligand and the reactants necessary to obtain the semiquinone ligand, the decomposition of the used tris(chloranilato)chromate(III), [(C$_4$H$_9$)$_4$N]$_3$[Cr(C$_6$O$_4$Cl$_2$)$_3$], leads to the release of the chloranilate ligand from the metal coordination sphere.[21] During the crystallization process, the released chloranilate group of chromium(III) is consequently coordinated to the copper(II) ion in the reaction mixture, yielding the mononuclear compound [Cu(bpy)(H$_2$O)(C$_6$O$_4$Cl$_2$)]·H$_2$O (**1**). A methanol solvate of this compound is known from the literature, [Cu(bpy)(H$_2$O)-(C$_6$O$_4$Cl$_2$)]·CH$_3$OH, where molecules of crystalline methanol are incorporated into the structure.[37]

In this research, various combinations of molar ratios of reactants, different *N*-ligands and solvents, number and arrangement of layers in a test tube, etc., were investi-gated, but only single crystals of the above compounds were successfully isolated.

Crystal Structures of Compounds 1–4

The asymmetric unit of **1** consists of a neutral molecule [Cu(bpy)(H$_2$O)(C$_6$O$_4$Cl$_2$)] and a crystal water molecule (Fig. 1). Coordination around copper(II) atoms can be described as square-pyramidal, consisting of two oxygen atoms of the chelating chloranilate group (mean Cu1−O = 1.950 Å) and two nitrogen atoms of the 2,2'-bipyridine molecule (mean Cu1−N = 1.978 Å) in the equatorial plane, while the apical position is occupied by an oxygen atom of the coordinated water molecule [Cu1−O5 = 2.325(7) Å]. The bond lengths in the equatorial positions are approximately equal in both solvates, while it is somewhat longer in the apical position

Table 1. Crystallographic, data collection and refinement data

Compound	1	2	3	4
Empirical formula	$C_{16}H_{12}Cl_2Cu N_2O_5$	$C_{16}H_{16}Cu_2I_2N_4O_2$	$C_{22}H_{18}Br_2Cu_2N_4O_5$	$C_{23}H_{16}Cu_3I_3N_4O_6$
Formula wt. / g mol^{-1}	462.72	829.33	705.30	952.18
Colour	brown	black	blue	black
Crystal dimensions / mm	0.20 × 0.15 × 0.10	0.20 × 0.16 × 0.12	0.24 × 0.11 × 0.09	0.20 × 0.16 × 0.12
Space group	$P\,2_1/c$	$P\,\bar{1}$	$C\,2/c$	$P\,\bar{1}$
a / Å	7.3741(13)	8.5665(3)	18.9220(3)	8.6437(2)
b / Å	9.749(2)	9.1081(3)	6.91040(10)	10.7793(2)
c / Å	24.238(6)	9.5173(3)	18.4251(3)	16.1402(3)
α / °	90	72.110(2)	90	97.574(2)
β / °	96.333(16)	69.006(3)	94.8660(10)	104.331(2)
γ / °	90	66.132(3)	90	103.462(2)
Z	4	1	4	2
V / Å^3	1731.9(6)	622.45(4)	2400.56(6)	1388.07(5)
D_{calc} / g cm^{-3}	1.775	2.213	1.952	2.278
λ / Å	0.71073 (Mo$K\alpha$)	0.71073 (Mo$K\alpha$)	1.54179 (Cu$K\alpha$)	0.71073 (Mo$K\alpha$)
μ / mm^{-1}	1.608	4.231	6.455	4.913
Θ range / °	1.69–24.99	3.72–32.27	4.69–79.16	3.45–32.28
T / K	293(2)	293(2)	293(2)	293(2)
Diffractometer type	CAD4	Synergy S	Synergy S	Synergy S
Range of h, k, l	−8 < h < 0; −11 < k < 0; −28 < l < 28	−10 < h < 12; −12 < k < 13; −11 < l < 14	−24 < h < 22; −8 < k < 7; −23 < l < 23	−11 < h < 12; −15 < k < 14; −23 < l < 21
Reflections collected	3577	9295	9252	23700
Independent reflections	3036	3667	2568	8194
Observed reflections ($I \geq 2\sigma$)	1734	3185	2386	6578
Absorption correction	None	Multi-scan	Multi-scan	Multi-scan
T_{min}, T_{max}	−	0.5687; 1.0000	0.6492; 1.0000	0.6507; 1.0000
R_{int}	0.2485	0.0349	0.0349	0.0233
$R\,(F)$	0.0726	0.0300	0.0374	0.0291
$R_w\,(F^2)$	0.1672	0.0819	0.1048	0.0737
Goodness of fit	1.108	0.977	1.059	1.059
H atom treatment	Mixed	Constrained	Mixed	Constrained
No. of parameters	260	172	162	343
No. of restraints	6	0	2	0
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (eÅ^{-3})	0.680; −0.587	1.118; −0.870	1.506; −0.706	1.579; −1.320

of compound **1**. The chloranilate ligand is coordinated as a terminal bidentate ligand, and has an *o*-quinoid structure (Scheme 1) typical for this type of coordination.[37–40]

Crystal packing of **1** (Fig. 2) is similar to the methanol solvate [Cu(bpy)(H$_2$O)(C$_6$O$_4$Cl$_2$)]·CH$_3$OH;[37] however, the smaller water molecule is a donor of two hydrogen bonds.

There are four symmetry-independent O−H···O hydrogen bonds (Table 2) which form centrosymmetric chains parallel to [010]. Two molecules of [Cu(bpy)(H$_2$O)(C$_6$O$_4$Cl$_2$)] are linked by two uncoordinated water molecules which are donors of two and acceptors of one hydrogen bond. These chains are stacked by π-interactions (Table 3)

between the aromatic rings of bipyridine and chloranilate rings, forming layers parallel to (001). 3D packing is achieved by C−H···O hydrogen bonds (Table 2).

During the crystallization of the compound $[Cu_2(phen)_2(C_2O_4)I_2]$ (**2**), the starting precursor $K_3[Cr(C_2O_4)_3]$ decayed; one oxalate group was released from the chromium(III) coordination sphere and bridged the
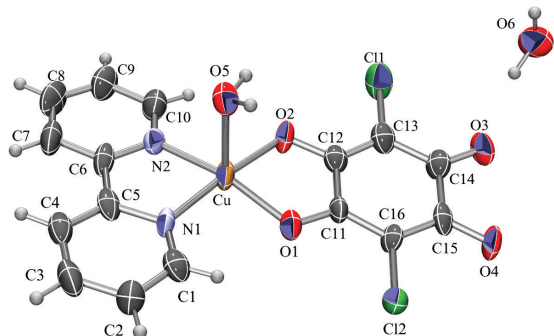

Figure 1. ORTEP-3[32] drawing of an asymmetric unit of compound $[Cu(bpy)(H_2O)(C_6O_4Cl_2)]\cdot H_2O$ (**1**). Displacement ellipsoids are drawn at 50 % probability and hydrogen atoms are shown as spheres of arbitrary radii.
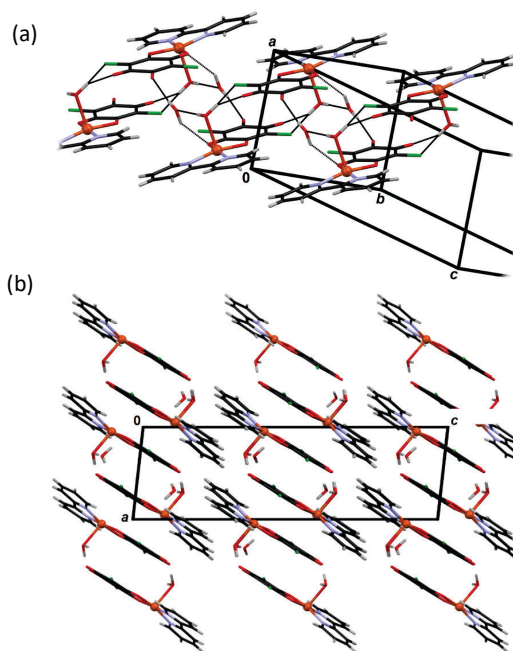

Figure 2. Crystal structure of compound $[Cu(bpy)(H_2O)(C_6O_4Cl_2)]\cdot H_2O$ (**1**): (a) hydrogen bonded chain extending in the direction [010] (hydrogen bonds shown as dashed lines) and (b) packing of chains by π-interactions.

Table 2. Geometric parameters of hydrogen bonding (Å, °).

	D–H/Å	H···A/Å	D···A/Å	D–H···A/°	Symm. op. on A
1					
O5–H5A···O6	0.94(6)	1.92(5)	2.837(12)	166(8)	1−x, −1−y, −z
O5–H5B···Cl2	0.94(8)	2.81(11)	3.418(7)	123(7)	1−x, −y, −z
O5–H5B···O4	0.94(8)	1.88(8)	2.730(10)	150(7)	1−x, −y, −z
O6–H6A···O2	0.95(14)	2.15(15)	2.928(11)	139(12)	1−x, −1−y, −z
O6–H6B···O3	0.95(8)	1.93(9)	2.820(12)	156(9)	x, y, z
C3–H3···O5	0.93	2.51	3.230(12)	134	−x, 1/2−y, −1/2−z
C8–H8···O4	0.93	2.40	3.281(14)	157	−1+x, −1/2−y, −1/2+z
2					
C3–H3···O2	0.93	2.54	3.371(5)	149	−x, 1−y, 1−z
C10–H10···I1	0.93	3.10	3.849(4)	139	1+x, y, z
3					
O3–H3A···Br1	0.93(4)	2.56(5)	3.4569(19)	161(4)	1−x, 1+y, 1/2−z
C7–H7···Br1	0.93	2.91	3.798(3)	161	3/2−x, 1/2−y, 1−z
C9–H9···O1	0.93	2.52	3.160(4)	126	3/2−x, 1/2+y, 1/2−z
4					
C10–H10···O1	0.93	2.60	3.330(4)	136	−x, −y, −z
C10–H10···O4	0.93	2.56	3.443(4)	159	−x, −y, −z
C12–H12···O4	0.93	2.45	3.145(4)	131	1−x, −y, −z
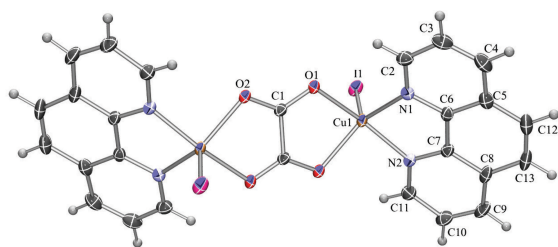
Figure 3. ORTEP-3[32] drawing of homodinuclear compound [Cu$_2$(phen)$_2$(C$_2$O$_4$)I$_2$] (**2**). Displacement ellipsoids are drawn at 50 % probability and hydrogen atoms are shown as spheres of arbitrary radii.

copper(II) ions present in the reaction mixture, to which phenanthroline molecules and iodide ions in the *trans*-position also coordinated (Fig. 3). The crystallographic center of inversion is located at midpoint of the C–C bond of the oxalate bridge. In the neutral dinuclear unit, [(phen)ICu(μ-C$_2$O$_4$)CuI(phen)], copper(II) atoms have a geometry between square pyramid and trigonal bipyramid since the parameter τ is 0.55.[41] In the case of square pyramid, the coordination sphere of copper consists of two nitrogen atoms from the molecule of phenanthroline (mean Cu–N = 2.008 Å) and two oxygen atoms from the oxalate bridge (mean Cu–O = 2.033 Å) in the equatorial plane, while the iodide ion [Cu1–I1 = 2.6541(12) Å] is in the apical position. The bond lengths between copper and iodine atoms are slightly longer than the bond lengths between copper and chlorine in the similar oxalate-bridged compound [Cu$_2$(bpy)$_2$Cl$_2$(C$_2$O$_4$)]·CH$_3$OH [2.467(3) Å and 2.449(2) Å].[20] The distance between the copper (II) atoms
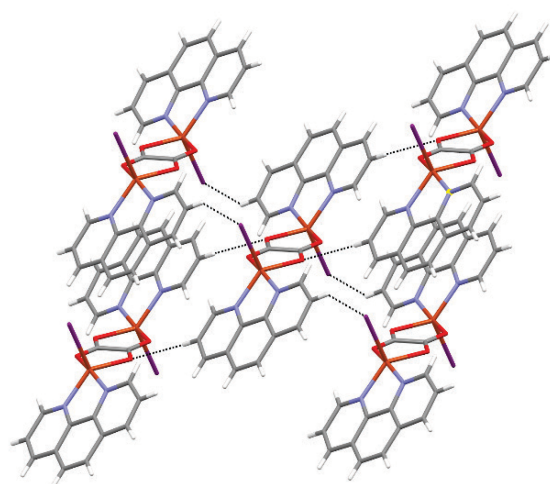

Figure 4. Representation of the hydrogen bonds (dashed lines) and π-interactions in the structure of compound [Cu$_2$(phen)$_2$(C$_2$O$_4$)I$_2$] (**2**).

bridged by the oxalate bridge is 5.279(2) Å in compound **2**, which is slightly longer than the same distance in compound [Cu$_2$(bpy)$_2$Cl$_2$(C$_2$O$_4$)]·CH$_3$OH [5.189(9) Å], where bipyridine molecules and chloride ions in the *cis*-position are coordinated to the copper(II) atoms.[20]

The dinuclear units [Cu$_2$(phen)$_2$(C$_2$O$_4$)I$_2$] are connected by hydrogen bonds C–H···I and C–H···O (Fig. 4, Table 2); each dinuclear unit is connected to four adjacent ones in a 3D network. In this compound there are also π-interactions between phenanthroline aromatic rings that connect them to pairs (Fig. 4, Table 3).

Table 3. Geometric parameters of π interactions. Symmetry operators: *i*).

π···π	Cg[a]···Cg / Å	A[b]	β[c]	Cg···plane(Cg2) / Å	Offset/ Å[d]	Symm. op. on Cg2
			2			
Cu1→N2···N1→C6	3.6146(17)	2.19(14)	16.2	3.5063(11)	1.007	1−*x*, 1−*y*, 1−*z*
N1→C6···N1→C6	3.999(2)	0.00(15)	29.1	3.4946(13)	1.945	1−*x*, 1−*y*, 1−*z*
N1→C6···N2→C11	4.0560(16)	3.28(14)	32.6	3.5117(12)	2.183	1−*x*, 1−*y*, 1−*z*
N1→C6···C5→C12	3.7392(16)	1.78(14)	21.7	3.4697(13)	1.383	1−*x*, 1−*y*, 1−*z*
N2→C11···N2→C11	3.7696(16)	0.00(13)	25.1	3.4129(11)	1.601	1−*x*, 1−*y*, 2−*z*
C5→C12··· N2→C11	4.0270(16)	2.52(13)	33.6	3.3995(11)	2.227	1−*x*, 1−*y*, 2−*z*
			3			
N1→C5···N2→C10	3.6372(18)	0.59(15)	23.4	3.3446(13)	1.444	3/2−*x*, 1/2−*y*, 1−*z*
			4			
N3→C18···N4→C23	3.7636(16)	6.53(14)	16.0	3.7109(12)	1.036	−*x*, −*y*, −*z*

[a] Cg = centre of gravity of the aromatic ring.

[b] α = angle between planes of two interacting rings.

[c] β = angle between Cg···Cg line and normal to the plane of the first interacting ring.

[d] Offset can be calculated only for the strictly parallel rings (α = 0.00°). For slightly inclined rings (α ≤ 5°) an approximate value is given.

The binuclear compound [Cu$_2$(bpy)$_2$(C$_2$O$_4$)Br$_2$]·H$_2$O (**3**) (Fig. 5) involves two oxalate-bridged copper(II) atoms and two terminal bipyridine ligands; two bromide ions are coordinated to axial positions of copper(II) atoms in a *cis*-arrangement. The molecule has a C_2 symmetry, with a twofold axis passing through a midpoint of the C–C bond of the oxalate bridge. The geometry of copper(II) atoms is square pyramidal consisting of two nitrogen atoms from the molecule bipyridine (mean Cu–N = 1.981 Å) and two oxygen atoms from oxalate bridge (mean Cu–O = 1.994 Å) in the equatorial plane, while the bromide ion [Cu1–Br1 = 2.6073(5) Å] is in the apical position. The bond lengths between copper and bromide atoms are slightly longer than the bond lengths between copper and chlorine in the already mentioned compound [Cu$_2$(bpy)$_2$Cl$_2$(C$_2$O$_4$)]·CH$_3$OH [2.467(3) Å and 2.449(2) Å],[20] and is comparable to the distance between copper and iodine in compound **2**. The distance between the copper(II) atoms bridged by the oxalate bridge is 5.185(2) Å in compound **3**, which is comparable to the analogous distance in compound **2**.

Compound **3** crystallizes as a monohydrate with a water molecule located on a twofold axis. Therefore the asymmetric unit contains a half of a [Cu$_2$(bpy)$_2$(C$_2$O$_4$)Br$_2$] and a half of a water molecule, which is a donor of one symmetry-independent hydrogen bond, O3–H3A···Br1 (Table 2). Furthermore, there are three symmetry-independent C–H···O hydrogen bonds linking the molecules
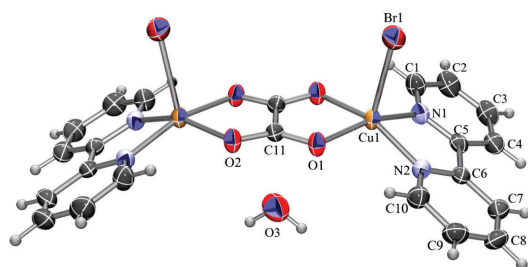

Figure 5. ORTEP-3[32] drawing of homodinuclear compound [Cu$_2$(bpy)$_2$(C$_2$O$_4$)Br$_2$] (**3**). Displacement ellipsoids are drawn at 50 % probability and hydrogen atoms are shown as spheres of arbitrary radii.
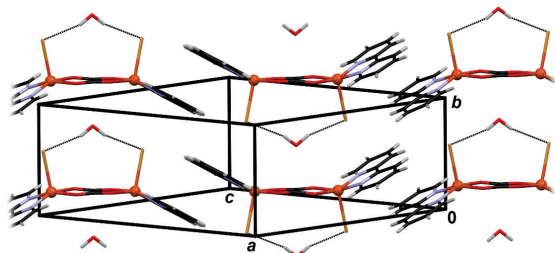

Figure 6. Crystal packing of **3** with O–H···Br hydrogen bonds shown as black dotted lines.

into a 3D network (Fig. 6, Table 2). Another feature of the crystal packing is π-stacking of bpy ligands, which form stacks of antiparallel pairs parallel to [010] (Fig. 6, Table 3).

Compound [Cu$_4$(bpy)$_4$(C$_2$O$_4$)$_3$(I$_3$)$_2$] (**4**) is a tetranuclear compound (Fig. 7) that crystallized during decomposition of the oxalate building block during the lengthy process of liquid diffusion. One of the released oxalate groups from the coordination sphere of chromium(III) consequentially bridged two copper(II) metal atoms with coordinated bpy, while another released oxalate group coordinated to [Cu(bpy)I$_3$]$^-$ unit and bridged Cu1 and Cu2 metal centres in a bidentate-monodentate mode. The geometry around Cu1 and Cu2 is square-pyramidal; basal planes are occupied by two *N*-atoms from bpy (mean Cu1–N = 1.981 Å; Cu2–N = 1.976 Å) and two O atoms from oxalate groups (mean Cu1–O = 1.982 Å; Cu2–O = 1.930 Å), while an oxygen atom from another oxalate ligand is located in the apical position of Cu1 [Cu1–O1= 2.2292(19) Å]; an iodine is in another apical position of Cu2 [Cu2–I1 = 3.264(4) Å]. This distance is much longer than the typical Cu–iodide bond [mean value from the Cambridge Structural Database version 2022[7] is 2.67(11) Å]; however, in this case we have a triiodide anion rather than an iodide. There are only 16 crystal structures in the CSD (version 2022[7]) with a triiodide anion coordinated to copper, and they cover a wide range of distances with a mean value of 2.9(3) Å. In three compounds, especially long Cu–I(triiodide) contacts were interpreted as coordination bonding: in bis(triiodide)-tetrakis(pyridine)-copper(II)[42] it is 3.393 Å, in [μ-5,5'-(ethene-1,2-diyl)bis(2,3,7,8,12,13,17,18-octaethylporphyrinato)]-bis(heptaiodo)-di-copper di-iodine[43] it is 3.261 Å and in catena-[bis(μ3-triodo)-bis(1,2-diaminoethane)-copper][44] it is 3.360 Å. All these distances are considerably shorter than the sum of van der Waals radii (about 4.0 Å)[45] and can be regarded as a borderline case between a coordination bond and a non-bonding contact.
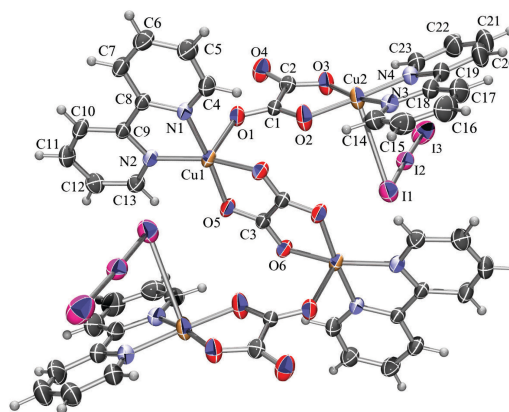

Figure 7. ORTEP-3[32] drawing of tetranuclear compound **4**. Displacement ellipsoids are drawn at 50 % probability and hydrogen atoms are shown as spheres of arbitrary radii.
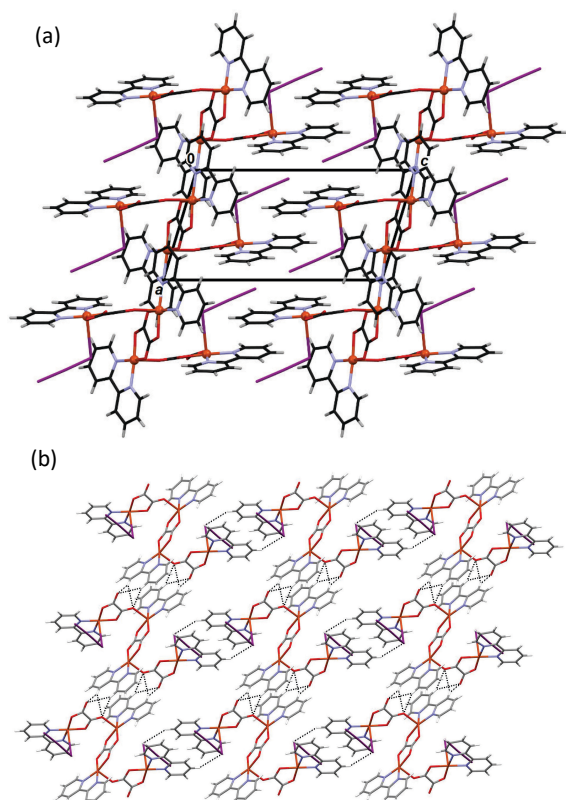
(a)

(b)

Figure 8. Crystal packing of compound **4**: (a) π-stacking viewed in the direction [010] and (b) 2D pattern of hydrogen bonds.

The distances between metal centers are Cu1···Cu2 = 5.320(5) Å and Cu1···Cu1^i = 5.153(6) Å [symmetry operator: (i) = 1−x, 1−y, −z]. π-interactions between aromatic systems of bpy ligands connect tetranuclear units to dimers in the ac plane (Fig. 8a), while 2D pattern of hydrogen bonds is represented in Fig. 8b.

IR Spectra of Compounds 1–4

IR spectra of the studied complexes are in agreement with the results of the X-ray analysis and show absorption bands that can be attributed to the vibrations of the oxalate groups (**2**–**4**) or chloranilate group (**1**), besides those originating from coordinated *N*-donor ligands[46] (Figure 9). The absorption bands characteristic of the different bridging modes of the metal centres by the oxalate group [symmetric and antisymmetric vibrations of the CO groups of the bis(bidentate) and bidentate-monodentate oxalate groups] for compounds **2**–**4** and the vibrations of the bidentate chloranilate group for compound **1** are summarized in Table 4.[5,21] The effect of larger *N*-donor ligand phen in compound **2** is evident in the shift of the positions of the absorption bands of the symmetric and antisymmetric
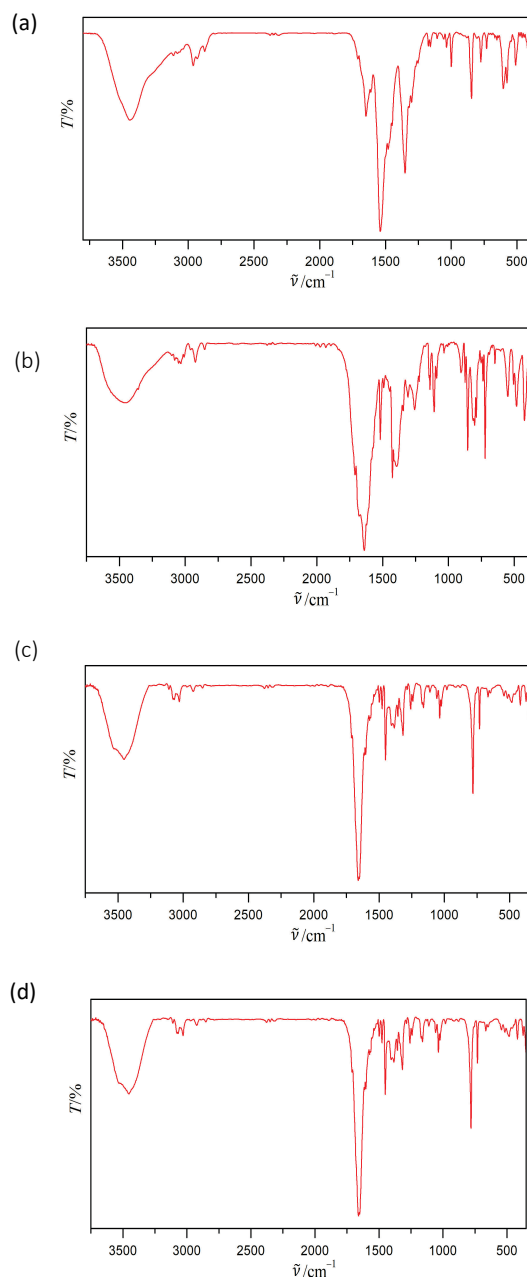

(a)

(b)

(c)

(d)

Figure 9. IR spectra of compounds: (a) [Cu(bpy)(H$_2$O)(C$_6$O$_4$Cl$_2$)]·H$_2$O (**1**), (b) Cu$_2$(phen)$_2$(C$_2$O$_4$)I$_2$ (**2**), (c) [Cu$_2$(bpy)$_2$(C$_2$O$_4$)Br$_2$] (**3**), (d) [Cu$_4$(bpy)$_4$(C$_2$O$_4$)$_3$(I$_3$)$_2$] (**4**).

vibrations of the CO groups of the bis(bidentate) oxalate groups to the lower wavelengths, compared to smaller bpy in the similar structure of **3**, where the analogous bridging mode of oxalate group is shifted to a bit larger wavenumbers, according to our results summarized in Table 4. All absorption bands observed in the IR spectra of **1**, **2**, **3** and **4** are listed in the Experimental section.

Table 4. Selected absorption bands (cm^{-1}) of the oxalate group in the infrared spectra of compounds **1**–**4**.

compound	Bidentate-monodentate oxalate group			Bis(bidentate) oxalate group		
	$\nu_{as}(CO)$	$\nu_s(CO)$	$\delta(OCO)$	$\nu_{as}(CO)$	$\nu_s(CO)$	$\delta(OCO)$
2	–	–	–	1638	1342	800
3	–	–	–	1658	1355	780
4	1708, 1676, 1654	1385	766	1618	1351	786
	Bidentate chloranilate group					
	$\nu(C=O)$	$\nu(C-O)$	$\nu(C-Cl)$	wagging C–Cl		
1	1648 vs, 1611 m, 1539 vs	1351 s, 1300 m	845 m	576 m		

CONCLUSIONS

Four novel complexes of Cu(II) with three types of different ligands, bridging *O*-donor, terminal *N*-donor and halogen, were prepared and characterised: a mononuclear containing chloranilate, [Cu(bpy)(H$_2$O)(C$_6$O$_4$Cl$_2$)]·H$_2$O (**1**), two dinuclear oxalate-bridged [Cu$_2$(phen)$_2$(C$_2$O$_4$)I$_2$] (**2**) and [Cu$_2$(bpy)$_2$(C$_2$O$_4$)Br$_2$] (**3**), and a tetranuclear oxalate-bridged [Cu$_4$(bpy)$_4$(C$_2$O$_4$)$_3$(I$_3$)$_2$] (**4**).

Using the complex-as-ligand approach, the novel Cu(II) compounds were obtained by decomposition of a precursor anion, [Cr(C$_2$O$_4$)$_3$]$^{3-}$, which was used as a ligand towards Cu(II). This unexpected source of the oxalate yielded compounds that could not be prepared by using simple oxalate salts. Also of interest is the unexpected oxidation of tetrachloroquinone to the chloranilate dianion in the preparation of **1**. It proceeded at room temperature and under relatively mild conditions, which is unusual since a strongly basic solution must be maintained under reflux at high temperature to prepare chloranilic acid. Neutral tetrachloroquinone is a very weak ligand, so it does not bind to metals, while its radical anion is apparently unstable in aqueous solutions.

It is also worth noting that two rare cases of simultaneous coordination of iodide and oxalate to copper were described, and also one of the few cases of coordination of a triiodide anion to copper. The Cu–I(triiodide) distance of 3.264(4) Å is interpreted as a borderline case between a coordination bond and a non-bonding contact.

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