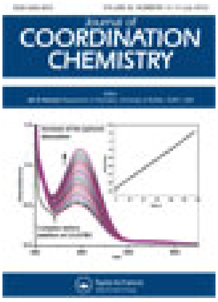

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Crystal structure and spectroscopic properties of polymeric adducts of the tetra-μ-haloaspirinate-dicopper(II)

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Crystal structure and spectroscopic properties of polymeric adducts of the tetra-μ-haloaspirinate-dicopper(II)[⊥]

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Eight new copper(II) complexes with halo-aspirinate anions have been synthesized: $[Cu_2(Fasp)_4(MeCN)_2]\cdot 2MeCN$ (**1**), $[Cu_2(Clasp)_4(MeCN)_2]\cdot 2MeCN$ (**2**), $[Cu_2(Brasp)_4(MeCN)_2]\cdot 2MeCN$ (**3**), $\{[Cu_2(Fasp)_4(Pyrz)]\cdot 2MeCN\}_n$ (**4**), $\{[Cu_2(Clasp)_4(Pyrz)]\cdot 2MeCN\}_n$ (**5**), $[Cu_2(Brasp)_4(Pyrz)]_n$ (**6**), $[Cu_2(Clasp)_4(4,4'\text{-Bipy})]_n$ (**7**), and $[Cu_2(Brasp)_4(4,4'\text{-Bipy})]_n$ (**8**) (Fasp: fluor-aspirinate; Clasp: chloro-aspirinate; Brasp: bromo-aspirinate; MeCN: acetonitrile; Pyrz: pyrazine; 4,4′-Bipy: 4,4′-bipyridine). The crystal structure of two **2** and **4** have been determined by X-ray diffraction methods. All compounds have been studied employing elemental analysis, IR, and UV-Visible spectroscopic techniques. The results have been compared with previous data reported for complexes with similar structures.

Keywords: Copper(II) complexes; Haloaspirinate anions; Crystal structures

1. Introduction

Copper(II) aspirinate complexes have been used as analgesic, antipyretic, anti-inflammatory, and platelet anti-aggregating agents [1–3]. They also have antioxidant activity and protect against some harmful consequences of UV exposure [4]. Complexes like $Cu_2(asp)_4$ exert additional activities including antiulcer, anticancer, anti-mutagenic, cardiovascular dysfunction associated with aging and anticonvulsant effects [2, 4–7]. Several binuclear and mononuclear copper–aspirin adducts have been prepared and structurally and catalytically characterized [8–10].

In contrast with the large number of experimental and theoretical studies about aspirin [2, 8, 11], much less is known about its 5-halogenated derivatives. There only

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[⊥] In Memory of Prof. Oscar V. Quinzani.

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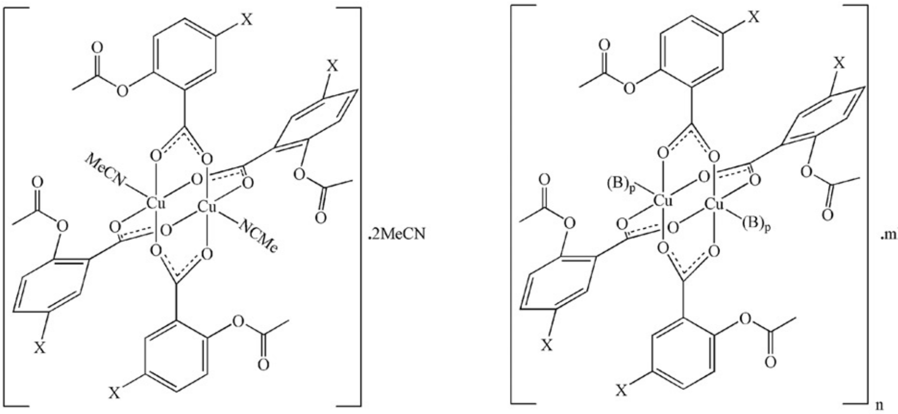

1: X = F
2: X = Cl
3: X = Br

4: X = F, B = Pyrz, m = 2
5: X = Cl, B = Pyrz, m = 2
6: X = Br, B = Pyrz, m = 0
7: X = Cl, B = 4,4′-bipy, m = 0
8: X = Br, B = 4,4′-bipy, m = 0
4-8 p = 1/2

Scheme 1. Structures of **1–8**.

exists the report of Meier *et al.* [12] about the synthesis and ESR spectra of the complete series of binuclear copper-5-haloaspirinate anions (halo = fluoro, chloro, bromo, iodo) and our own study on the thermal stability of the same series of complexes and of the mononuclear bis(pyridine) haloaspirinate-copper(II) adducts [13].

Due to the various coordination modes that carboxylates can adopt, different structures with copper(II) have been resolved by X-ray diffraction methods [14 and references therein, 15, 16], ranging from binuclear tetrakis μ-carboxylate complexes, which exhibit well-characterized paddle-wheel cage-like structures [17, 18], to mononuclear dicarboxylate complexes [9], involving diverse stereochemistries with different numbers of bridging bidentate carboxylates [14].

To further explore the chemical and structural properties of haloaspirinate–copper complexes we started a complete study of ternary poly- and mono-nuclear derivatives, including different nitrogenate bases as additional ligands. Here we report the synthesis and spectroscopic characterization of binuclear copper(II) complexes $[Cu_2(Xasp)_4(MeCN)_2] \cdot 2MeCN$ (Xasp = haloaspirinate anion; X = F, Cl, Br; MeCN = acetonitrile) and $\{[Cu_2(Xasp)_4](B)] \cdot yMeCN\}_n$ (B = pyrazine [Pyrz] ($y = 2$) or 4,4′-bipyridine [4,4′-Bipy] ($y = 0$)) (scheme 1).

We also report the molecular and crystal structures of {bis(acetonitrile-*N*)tetrakis{μ-chloroaspirinate(η^2-O,O′)}dicopper(II) diacetonitrile and of poly[μ-pyrazine(η^2-*N*,*N′*)tetrakis{μ-fluoraspirinate(η^2-O,O′)}dicopper(II).

2. Experimental

2.1. *Reagents and materials*

All chemicals were of high purity grade and used without purification. The 5-haloacetylsalicylic acids (halo = fluoro, chloro, bromo) were prepared from the corresponding 5-halosalicylic acids (Aldrich) by modification of the reported procedure [18]. The binuclear copper starting materials $[Cu_2(Fasp)_4]$, $[Cu_2(Clasp)_4(H_2O)_2] \cdot 2H_2O$, and $[Cu_2(Brasp)_4(H_2O)_2]$ (Fasp = 5-fluoraspirinate, Clasp = 5-chloroaspirinate and Brasp = 5-bromoaspirinate anions) were prepared following published methods [12, 13].

2.2. *Synthesis of new copper complexes*

2.2.1. *μ*-Tetrakis(fluoraspirinate[η^2-O,O′])bis(acetonitrile-*N*)dicopper(II)diacetonitrile, $[Cu_2(Fasp)_4(MeCN)_2] \cdot 2MeCN$ (1). This compound was prepared by adding 0.150 g (0.160 mmol) of $[Cu_2(Fasp)_4]$ to 45 mL of hot (80°C) acetonitrile. The solution was stirred for 20 min and cooled to room temperature. The blue-green microcrystalline powder was filtered by vacuum, washed with diethyl ether, and dried at 40°C. Yield: 0.095 g (55.0%). Anal. Calcd for $C_{44}H_{36}Cu_2F_4N_4O_{16}$ (%): C, 48.94; H, 3.36; N, 5.19; Cu, 11.77. Found (%): C, 48.89; H, 3.39; N, 5.18; Cu, 11.76.

2.2.2. *μ*-Tetrakis(chloroaspirinate[η^2-O,O′])bis(acetonitrile-*N*)dicopper(II)diacetonitrile, $[Cu_2(Clasp)_4(MeCN)_2] \cdot 2MeCN$ (2). This bluish-green complex was prepared as a microcrystalline powder by the method described for **1** using 0.150 g (0.140 mmol) of $[Cu_2(Clasp)_4] \cdot 2H_2O$ and 20 mL of acetonitrile. Yield: 0.098 g (60.1%). Anal. Calcd for $C_{44}H_{36}Cl_4Cu_2N_4O_{16}$ (%): C, 46.13; H, 3.17; N, 4.89; Cu, 11.09. Found (%): C, 46.11; H, 3.13; N, 4.96; Cu, 11.07%. Single-crystals suitable for structural X-ray diffraction analysis were obtained by slow evaporation of cold acetonitrile solution.

2.2.3. Tetrakis(*μ*-bromoaspirinate[η^2-O,O′])bis(acetonitrile-N)dicopper(II)diacetonitrile, $[Cu_2(Brasp)_4(MeCN)_2] \cdot 2MeCN$ (3). The green complex was prepared by the method described for **1** using 0.150 g (0.130 mmol) of $[Cu_2(Brasp)_4] \cdot 2H_2O$. Yield: 0.098 g (60.1%). Anal. Calcd for $C_{44}H_{36}Br_4Cu_2N_4O_{16}$ (%): C, 39.93; H, 2.74; N, 4.23; Cu, 9.60. Found (%): C, 39.94; H, 2.73; N, 5.02; Cu, 9.58.

2.2.4. Poly-*μ*-pyrazine(η^2-*N*,*N*′)-[*μ*-tetrakis(fluoraspirinate[η^2-O,O′])dicopper(II)-diacetonitrile, $\{[Cu_2(Fasp)_4(Pyrz)] \cdot 2MeCN\}_n$ (4). Compound **4** was prepared by adding 0.160 g (0.174 mmol) of $[Cu_2(Fasp)_4]$ to a hot (80°C) solution of 0.28 g (0.35 mmol) of pyrazine in 45 mL of acetonitrile. The solution was stirred for 20 min and cooled to room temperature. After 2 h a green microcrystalline solid was obtained. The solid was collected by vacuum filtration, washed with anhydrous diethyl ether, and dried at 70°C. Yield: 0.143 g (76.0%). Anal. Calcd for $C_{44}H_{34}Cu_2F_4N_4O_{16}$ (%): C, 49.03; H, 3.18; N, 5.20; Cu, 11.79. Found (%): C, 49.11; H, 3.11; N, 5.21; Cu, 11.87. Single-crystals for X-ray diffraction analysis were obtained by slow evaporation of cold acetonitrile solution.

2.2.5. Poly-[*μ*-pyrazine(η^2-*N*,*N*′)-[*μ*-tetrakis(chloroaspirinate[η^2-O,O′])dicopper(II)]-diacetonitrile, $\{[Cu_2(Clasp)_4(Pyrz)] \cdot 2MeCN\}_n$ (5). The complex was prepared by the same method described for **4** except that 0.185 g (0.180 mmol) of $[Cu_2(Clasp)_4] \cdot 2H_2O$ and 25 mL of acetonitrile were used. Yield: 0.117 g (73.9%). Anal. Calcd for

$C_{44}H_{34}Cu_2Cl_4N_4O_{16}$ (%): C, 46.21; H, 3.00; N, 4.90; Cu, 11.11. Found (%): C, 46.20; H, 3.10; N, 4.87; Cu, 11.20.

2.2.6. Poly-[*μ*-pyrazine(η^2-*N*,*N*′)-[*μ*-tetrakis(bromoaspirinate[(η^2-O,O′])dicopper(II)], $[Cu_2(Brasp)_4(Pyrz)]_n$ (6). The compound was prepared by the method described for **4** using 0.203 g (0.180 mmol) of $[Cu_2(Brasp)_4]\cdot 2H_2O$. Yield: 0.199 g (86.1%). Anal. Calcd for $C_{40}H_{28}Br_4Cu_2N_2O_{16}$ (%): C, 38.76; H, 2.28; N, 2.26; Cu, 10.09 %. Found (%): C, 38.74; H, 2.20; N, 2.32; Cu, 10.17.

2.2.7. Poly-[*μ*-4,4′-bipyridine(η^2-*N*,*N*′)-*μ*-tetrakis(chloroaspirinate[(η^2-O,O′])dicopper(II)], $[Cu_2(Clasp)_4(4,4'\text{-}Bipy)]_n$ (7). A solution of 0.023 g (0.150 mmol) of 4,4′-bipyridine in 3 mL of acetonitrile was added to a hot (80°C) solution of 0.154 g (0.150 mmol) of $[Cu_2(Clasp)_4]\cdot 2H_2O$ in 22 mL of acetonitrile. The mixture was stirred until a green homogeneous solution was obtained and then cooled to room temperature. After 1 h the green precipitate formed was separated with vacuum, washed with diethyl ether, and air dried. Yield: 0.090 g (49.6%). Anal. Calcd for $C_{46}H_{32}Cl_4Cu_2N_2O_{16}$ (%): C, 48.56; H, 2.84; N, 2.46; Cu, 11.17. Found (%): C, 48.57; H, 2.83; N, 2.42; Cu, 11.18.

2.2.8. Poly-[*μ*-4,4′-bipyridine(η^2-*N*,*N*′)-*μ*-tetrakis(bromospirinate[(η^2-O,O′])dicopper(II)], $[Cu_2(Brasp)_4(4,4'\text{-}Bipy)]_n$ (8). The green compound was synthesized by the method described for **7** adding a solution of 0.020 g (0.130 mmol) of 4,4′-bipyridine in 3 mL of acetonitrile to a hot (80°C) solution of 0.150 g (0.130 mmol) of $[Cu_2(Brasp)_4]\cdot 2H_2O$ in 45 mL of acetonitrile. Yield: 0.083 g (52.6%). Anal. Calcd for $C_{46}H_{32}Br_4Cu_2N_2O_{16}$ (%): C, 42.00; H, 2.45; N, 2.13; Cu, 9.66. Found (%): C, 41.94; H, 2.43; N, 2.10; Cu, 9.61.

2.3. *Physical measurements*

Infrared (IR) spectra (KBr pellets and Nujol mulls) were recorded in a Nicolet Nexus FT-IR spectrometer. Electronic spectra (solution, Nujol mulls, and KBr pellets) were recorded using a GBC Cintra 20 UV-Visible spectrophotometer. Elemental analyses (C, H, and N) were obtained in a Carlo Erba EA1108 analyzer. Spectrophotometric determination of copper(II) was carried out according to modification of two literature methods [19, 20].

2.4. *X-ray diffraction for 2 and 4*

The measurements were performed at low temperature on an Enraf-Nonius Kappa-CCD diffractometer with graphite-monochromated Mo-Kα ($\lambda = 0.71073$ Å) radiation. Diffraction data were collected (φ and ω scans with κ-offsets) with COLLECT [21]. Integration and scaling of the reflections was performed with HKL DENZO-SCALEPACK [22] suite of programs. The unit cell parameters were obtained by least-squares refinement based on angular settings for all collected reflections using HKL SCALEPACK [22]. The data were corrected empirically for absorption with the multi-scan procedure [23].

Table 1. Crystal data and structure refinement results for **2** and **4**.

	2	**4**
Empirical formula	$C_{44}H_{36}Cl_4Cu_2N_4O_{16}$	$C_{22}H_{17}CuF_2N_2O_8$
Formula weight	1145.65	538.92
Temperature (K)	116(2)	116(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Tetragonal	Triclinic
Space group	$P4_3$	P-1
Unit cell dimensions (Å, °)		
a	11.9693(2)	9.8902(2)
b	11.9693(2)	11.0855(3)
c	34.0456(8)	11.7897(3)
α	90	78.819(1)
β	90	65.294(1)
γ	90	73.048(1)
Volume (Å^3), Z	4877.5(2), 4	1119.39(5), 2
Calculated density (Mg m^{-3})	1.560	1.599
Absorption coefficient (mm^{-1})	1.164	1.044
F(000)	2328	548
Crystal size (mm^3)		$0.24 \times 0.16 \times 0.10$
θ range for data collection (°)	2.39–24.39	1.93–25.99
Limiting indices	$-13 \le h \le 13$; $-13 \le k \le 13$; $-31 \le l \le 39$	$-12 \le h \le 12$; $-13 \le k \le 13$; $-14 \le l \le 14$
Reflections collected	22,991	15,470
Independent reflections	7368 [R(int) = 0.0953]	4409 [R(int) = 0.0614]
Observed reflections [$I > 2\sigma(I)$]	5126	3987
Completeness to $\theta = 24.39°$ (%)	99.4	99.9
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.659 and 0.625	0.905 and 0.752
Refinement method	Full-matrix least-squares an F^2	Full-matrix least-squares an F^2
Data/restraints/parameters	7368/1/640	4409/0/319
Goodness-of-fit on F^2	0.979	1.039
Final R indexes[a] [$I > 2\sigma(I)$]	$R_1 = 0.0501$, $wR_2 = 0.0794$	$R_1 = 0.0375$, $wR_2 = 0.1030$
R indexes (all data)	$R_1 = 0.0945$, $wR_2 = 0.0936$	$R_1 = 0.0433$, $wR_2 = 0.1070$
Largest difference peak and hole (e Å^{-3})	0.511 and −0.500	0.697 and −0.910

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w(|F_o|^2)^2]^{1/2}$.

The structures were solved by direct methods with SHELXS-97 [24] and the molecular model refined by full-matrix least-squares procedure on F^2 with SHELXL-97 [25]. Hydrogen atoms were positioned stereochemically and refined with the riding model. The methyl hydrogen locations were optimized during the refinement by treating them as rigid bodies which were allowed to rotate around the corresponding C–CH_3 bond. Crystal data and refinement results are summarized in table 1.

3. Results and discussion

3.1. *Crystal structure of 2*

Figure 1 shows an ORTEP [26] drawing of binuclear **2** and selected bond distances and angles are listed in table 2. As usual in this kind of binuclear complex [21], the Cu(Clasp)$_4$Cu group shows a lantern-like conformation where the Cu(II) ions are

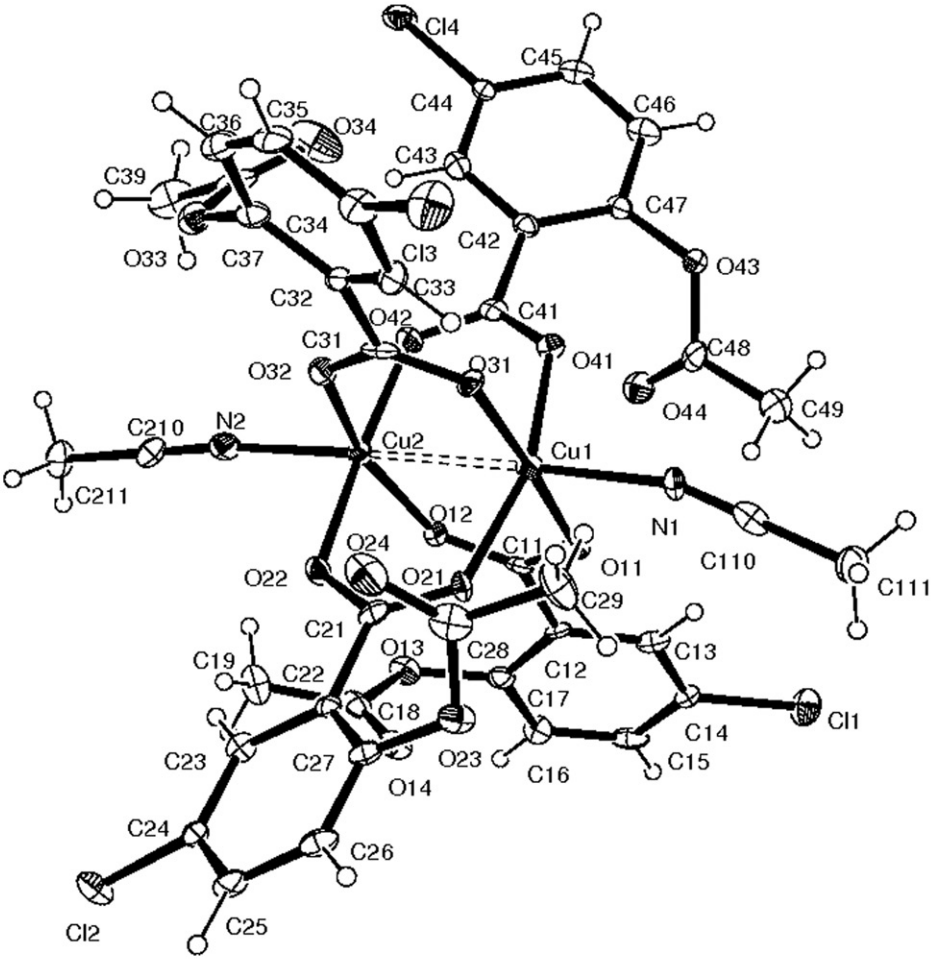

Figure 1. Drawing of **2** showing the labeling of the non-H atoms and their displacement ellipsoids at the 30% probability level. Cu···Cu bond is indicated by dashed lines.

syn–syn bridged by four Clasp groups as bidentate ligands through their carboxylic oxygen atoms. The metal environment can be described either as axially distorted octahedral or square-bipyramidal (approximate C_{4v} site symmetry), with the above-mentioned oxygen atoms conforming a square of equatorial ligands. The Cu–O distances (from 1.941(4) to 2.000(4) Å for Cu1 and from 1.938(4) to 2.001(4) Å for Cu2) are in the range of corresponding values reported for $Cu_2(asp)_4$ [8b, 27] and other bis(acetonitrile)tetra(μ-carboxylate) complexes [28]. The apical position around each copper is occupied by an acetonitrile (MeCN) [*d*(Cu1–N1) = 2.164(7) and *d*(Cu2–N2) = 2.181(7) Å]. As expected, copper is slightly shifted (*ca* 0.206 Å) out of the square of equatorial ligands toward MeCN. The remaining axial copper coordination is completed with a copper–copper bond [*d*(Cu···Cu) = 2.6641(9) Å]. This bond length is similar to the value observed for $Cu_2(asp)_4(DMF)_2$ (2.615(4) Å) [7], $Cu_2(asp)_4$ (2.621(8) Å) [8b, 27] and $Cu_2(HCO)_2(DMSO)_2$ (2.662(9) Å) [24], but shorter than in acetate dimers containing CuO_4N (2.671–2.886 Å) [29]. These results are in agreement

Table 2. Selected bond lengths (Å) and angles (°) of **2**.

Cu(1)–Cu(2)	2.6641(9)	O(21)–Cu(1)–Cu(2)	81.5(1)
Cu(1)–O(11)	1.950(4)	O(41)–Cu(1)–Cu(2)	78.9(1)
Cu(1)–O(21)	1.990(4)	N(1)–Cu(1)–Cu(2)	177.8(2)
Cu(1)–O(31)	1.941(4)	O(22)–Cu(2)–O(42)	175.7(2)
Cu(1)–O(41)	2.000(4)	O(22)–Cu(2)–O(12)	89.5(2)
Cu(1)–N(1)	2.164(7)	O(42)–Cu(2)–O(12)	89.8(2)
Cu(2)–O(12)	1.999(4)	O(22)–Cu(2)–O(32)	89.2(2)
Cu(2)–O(22)	1.940(4)	O(42)–Cu(2)–O(32)	90.0(2)
Cu(2)–O(32)	2.001(4)	O(12)–Cu(2)–O(32)	161.0(2)
Cu(2)–O(42)	1.938(4)	O(22)–Cu(2)–N(2)	91.0(2)
Cu(2)–N(2)	2.181(7)	O(42)–Cu(2)–N(2)	93.3(2)
O(11)–C(11)	1.251(8)	O(12)–Cu(2)–N(2)	100.5(2)
O(12)–C(11)	1.273(8)	O(32)–Cu(2)–N(2)	98.5(2)
O(21)–C(21)	1.265(8)	O(22)–Cu(2)–Cu(1)	86.7(1)
O(22)–C(21)	1.260(8)	O(42)–Cu(2)–Cu(1)	89.0(2)
O(31)–C(31)	1.271(8)	O(12)–Cu(2)–Cu(1)	80.1(1)
O(32)–C(31)	1.258(8)	O(32)–Cu(2)–Cu(1)	80.9(1)
O(41)–C(41)	1.264(7)	N(2)–Cu(2)–Cu(1)	177.6(2)
O(42)–C(41)	1.271(7)	C(11)–O(11)–Cu(1)	118.9(4)
O(31)–Cu(1)–O(11)	175.6(2)	C(11)–O(12)–Cu(2)	125.3(4)
O(31)–Cu(1)–O(21)	89.3(2)	C(21)–O(21)–Cu(1)	124.2(4)
O(11)–Cu(1)–O(21)	89.5(2)	C(21)–O(22)–Cu(2)	120.7(4)
O(31)–Cu(1)–O(41)	89.0(2)	C(31)–O(31)–Cu(1)	119.8(4)
O(11)–Cu(1)–O(41)	90.8(2)	C(31)–O(32)–Cu(2)	124.9(4)
O(21)–Cu(1)–O(41)	160.4(2)	C(41)–O(41)–Cu(1)	128.1(4)
O(31)–Cu(1)–N(1)	94.6(2)	C(41)–O(42)–Cu(2)	119.1(4)
O(11)–Cu(1)–N(1)	89.7(2)	C(110)–N(1)–Cu(1)	159.6(6)
O(21)–Cu(1)–N(1)	97.7(2)	C(210)–N(2)–Cu(2)	169.4(6)
O(41)–Cu(1)–N(1)	101.8(2)		
O(31)–Cu(1)–Cu(2)	87.5(2)		
O(11)–Cu(1)–Cu(2)	88.2(1)		

with the relationship expected between the acidity of the carboxylic group and the Cu–Cu distance [30].

The chloroaspirinate $–CO_2$ groups show C–O distances from 1.251(8) to 1.273(8) Å. The torsion angles of the $–CO_2$ planes from the benzene rings are 15.7(8)–26.4(7)°, similar to those observed for $Cu(Clasp)_2Py_2$ [31].

3.2. *Crystal structure of 4*

Figure 2 shows a drawing of a monomeric unit of $[Cu(Fasp)_4Cu(Pyrz)]_n$, polymer **4**. Selected intramolecular bond distances and angles are in table 3.

$Cu(Fasp)_4Cu$ shows the same lantern-like conformation described for Cu(Clasp)Cu, but now has a crystallographic inversion center. As for the chloroaspirinate complex, Cu(II) ions are equatorially *syn–syn* bridged by four Fasp groups as bidentate ligands through their carboxylic oxygen atoms with Cu–O bond lengths from 1.964(2) Å to 1.974(2) Å, in the range of corresponding values reported for similar compounds [32]. Neighboring $Cu(Fasp)_4Cu$ groups in the lattice are axially linked by Pyrz (also on a crystal inversion center) [$d(\text{Cu–N}) = 2.233(2)$ Å] giving a $–Cu(Fasp)_4Cu–N(C_4H_4)N–Cu(Fasp)_4Cu–$ polymeric structure that extends along the crystal *a*-axis. Distorted octahedral coordination is completed by the formation of a copper–copper bond ($d(\text{Cu}\cdots\text{Cu}) = 2.6416(5)$ Å). The structure agrees with the ones reported for

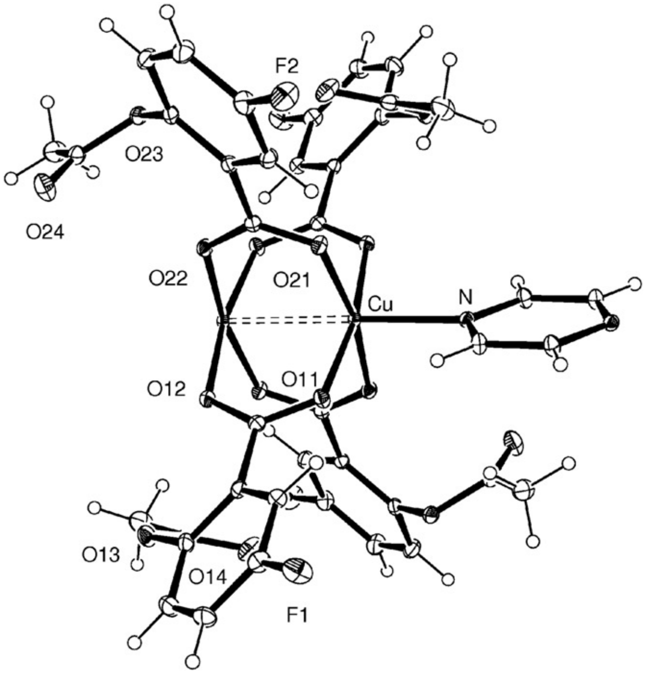

Figure 2. View of a monomeric unit of **4**. Both $Cu_2(Fasp)_4$ and pyrazine axial ligand are on crystallographic inversion centers. For clarity, only independent non-C atoms have been labeled. The carbons in Fasp ligands follow the same labeling scheme as Clasp in **2** of figure 1.

Table 3. Selected bond lengths (Å) and angles (°) of **4**.

Cu–Cu	2.6416(5)	O(21)–Cu–O(12)	89.34(7)
Cu–O(11)	1.967(2)	O(11)–Cu–O(12)	168.61(7)
Cu–O(12)	1.974(2)	O(22)1–Cu–N	99.22(7)
Cu–O(21)	1.965(2)	O(21)–Cu–N	92.15(7)
Cu–O(22)	1.964(2)	O(11)–Cu–N	91.46(7)
Cu–N	2.233(2)	O(12)1–Cu–N	99.92(7)
O(11)–C(11)	1.264(3)	C(11)–O(11)–Cu	122.0(2)
O(12)–C(11)	1.265(3)	C(11)–O(12)–Cu	123.7(2)
O(21)–C(21)	1.267(3)	C(18)–O(13)–C(17)	116.6(2)
O(22)–C(21)	1.263(3)	C(21)–O(21)–Cu	121.2(2)
N–C(1)	1.332(3)	C(21)–O(22)–Cu	124.4(2)
N–C(2)	1.341(3)	C(1)–N–C(2)	117.0(2)
O(22)–Cu–O(21)	168.59(7)	C(1)–N–Cu	123.4(2)
O(22)–Cu–O(11)	89.09(7)	C(2)–N–Cu	119.6(2)
O(21)–Cu–O(11)	89.71(7)	N–C(1)–C(2)	121.4(2)
O(22)–Cu–O(12)	89.60(7)		

$[Cu_2(CH_3COO)_4(Pyrz)]_n$ and $[Cu_2(CCl_3COO)_4(Pyrz)]_n$ binuclear copper(II) polymeric complexes [33].

3.3. *Electronic spectra*

Table 4 shows the spectral band positions and assignments for **1**–**8**. The solid state spectra (KBr mulls) of **1** and **8** show broad unsymmetrical bands with a maximum at *ca*

Table 4. UV–Visible spectral data for binuclear Cu(II) complexes.

		Bands positions and assignments						
Compounds		$\pi \rightarrow \pi^*(\phi)$[a]	$\pi \rightarrow \pi^*(\phi)$[a]	$\pi \rightarrow \pi^*(\phi)$[a] Pz	LMCT[b]	Band II[c]	$d_{xy} \rightarrow d_{x^2-y^2}$	$d_{z^2} \rightarrow d_{x^2-y^2}$
1	KBr	198s[d]	282w	–	328sh	400vw	678w	–
	CH_3CN	(196s)	(285w)		(320sh)	(395vw)	(695w)	–
2	KBr	207s	291w	–	–	410sh	675w	767sh
	CH_3CN	(206s)	(291vw)		–	(406vw)	(698w)	–
3	KBr	208s	295vw	–	–	418vw	691w	–
	CH_3CN	(206s)	(292vw)		–	(405vw)	(700w)	–
4	KBr	199s	289sh	265w	319sh	410vw	690w	–
5	KBr	207vs	293vw	264sh	–	420vw	700w	791sh
6	KBr	213vs	297vw	271vw	–	405sh	699w	787sh
7	KBr	203s	293vw	–	–	403sh	720w	797sh
8	KBr	206s	288vw	–	–	402sh	718w	797sh

[a] ϕ: benzene ring [34] and [35].
[b] LMCT: ligand to metal charge transfer.
[c] Band II: Cu–Cu interaction [31].
[d] s: strong, m: medium, w: weak, vw: very weak, sh: shoulder.

700 nm, which can be assigned to unresolved d–d transitions under C_{4v} symmetry in dinuclear arrangements [27, 34–36]. The spectra also display two bands with different intensities due to $\pi \rightarrow \pi^*$ transitions of the benzene rings corresponding to haloaspirinate.

Very weak bands or shoulders can be observed and assigned to a characteristic band (Band II) of binuclear copper systems [12, 36]. Only spectra for fluoraspirinate complexes **1** and **4** have shoulders at wavelengths for LMCT bands of binuclear copper carboxylates [12, 37, 31].

Binuclear polymeric complexes with pyrazine and 4,4′-bipyridine were characterized only in the solid state (as KBr or Nujol mulls) because they have little solubility in most solvents and are stable in donor solvents only with excess amounts of free bases.

The positions of the bands assignable to d–d transitions of **7** and **8** indicate binuclear copper units connected by diazine bridges, as can be seen from the IR spectra (see below). The very weak bands at *ca* 290 nm in spectra of **4**–**6** are assignable to $\pi \rightarrow \pi^*$ transitions of coordinated pyrazine [38].

3.4. *Vibrational spectra*

The IR spectra of all the complexes show characteristic features related to aspirinate anions [11] coordinated to copper(II) [13, 39]. The IR frequencies for the carbonyl, acetoxy, and some benzene ring vibrations in **1**–**8** are given in table 5.

As expected from X-ray diffraction analysis, IR spectra of **2** and **4** show very strong bands assigned to ν_{as}(COO) and ν_s(COO) carboxylate vibrations. These bands are red-shifted with respect to the corresponding haloaspirins vibrations, as expected for Cu(II) carboxylates [13, 20, 35, 40]. The wavenumber differences (Δ) between ν_{as}(COO) and ν_s(COO) are typical of bidentate coordination of carboxylates [40]. Compounds **1**, **3**, and **5**–**8** show similar IR spectra, indicating that they are also built with the same binuclear tetracarboxylate units.

Table 5. IR spectral data and assignments for the binuclear Cu(II) complexes.

Compound	ν_{as}(COO) (cm^{-1})	ν_{s}(COO) (cm^{-1})	Δ[a] (cm^{-1})	ν(CO)[b] (cm^{-1})	ν_{as}(COC)[b] (cm^{-1})	ν_{as}(COC)[b] (cm^{-1})	ν(CX)[c] (cm^{-1})	ν(CC)[d] (cm^{-1})	δ(COO) (cm^{-1})
1	1629	1388	241	1762	1182	1127	1263	1437	1015
2	1631	1379	252	1770	1191	1108	688	1420	1009
3	1630	1375	255	1767	1195	1103	687	1417	1012
4	1630	1388	242	1770	1183	1050	1217	1436	1010
5	1626	1379	247	1770	1195	1051	685	1426	1012
6	1626	1377	250	1767	1195	1052	679	1425	1012
7	1634	1377	257	1766	1195	1044	697	1422	1012
8	1633	1374	259	1764	1199	1044	687	1418	1011

[a] Frequency differences between antisymmetric and symmetric carboxyl vibrations, [ν_{as}(COO)–ν_{s}(COO)].
[b] Acetoxy group vibrations.
[c] X = halogen (fluoro, chloro, bromo).
[d] Very strong benzene ring vibration.

The small increase in frequency differences from fluoro- to bromo-aspirinate indicates the existence of electronic structure modulation over the benzene rings. IR spectra of **1**–**3** show two weak bands due to C–N stretch of the coordinated-to-copper acetonitrile molecules (2300 and 2273 cm^{-1} for **1**, 2303 and 2268 cm^{-1} for **2**, 2307 and 2278 cm^{-1} for **3**).

For **2** and **3** a third weak band can be observed at lower frequencies (2249 and 2252 cm^{-1}) due to crystallization acetonitrile molecules. A similar spectroscopic observation has been reported by Agterberg *et al.* [28] for bis(acetonitrile)tetrakis(μ-diphenylacetate)dicopper(II).

Vibrations of the acetoxy groups were analyzed taking into account the reported data for the acetoxy carbonyl of the aspirinate ligand in the mononuclear complex bis(aspirinato)bis(2-methylimidazole)copper(II) and in benzoic acid ester [41–43]. Table 5 shows some strong absorption bands assigned to stretching modes of carbonyl C–O and C–O–C acetoxy bridges. The IR spectra of Nujol mulls of **1** and **3** show additional bands corresponding to different structural arrangements of acetoxy groups, some involved in intermolecular interactions.

The bands produced by C–X (X = halogen) stretching modes and other benzene ring vibrations have been assigned based on related studies of aspirin [11], metal benzoates, and halogenated benzoates [44, 45]. In IR spectra of **4** and **8** bands of medium to weak intensity due to internal modes of the pyrazine and 4,4′-bipyridine ligands (in particular: ν(CN) are at 1514, 1507, 1506, and 1608 cm^{-1}, γ(CH) at 763, 730, 724, 814, and 814 cm^{-1}, respectively). The frequency and intensity of bands for both bases are expected for center-symmetrical molecules, hence indicating their coordination as bridging bidentate ligands [46].

4. Conclusions

Eight new tetrakis(haloaspirinate)–copper(II) binuclear complexes have been prepared and characterized. The crystal structures of two have been solved by single-crystal X-ray diffraction. In **2**, four bidentate carboxylates from the chloro-aspirinate anions form *syn–syn* bridges between Cu(II) ions. The apical positions of each copper(II) are occupied by MeCN. The crystal structure of **4** reveals that the Cu(Fasp)$_4$Cu binuclear group is sited on an inversion center where Cu(II) ions are equatorially bridged by four bidentate F-aspirinate groups. The binuclear groups are axially linked by pyrazine molecules giving a polymeric structure.

The spectral data of the above two complexes can be interpreted on the basis of the respective crystal structures. The spectral behavior of the rest of the compounds suggest that all are binuclear Cu(II) units bridged by carboxylate groups of four haloaspirinate ligands.

Our structural results for **2** are in agreement with corresponding data of related *paddle-wheel* binuclear Cu(II) complexes reported, $Cu_2(\mu\text{-RCOO})_4(MePyrz)_2$, R: H, CH_3(Me), and $Cu_2(\mu\text{-MeCOO})_4(L)_2$, L: 2,3- and 2,6-$Me_2$Pyrz [47], and also [Cu($L^1$)MeCN], [Cu($L^2$)$H_2O$], and [Cu($L^4$)EtOH], where pairs of CO_2 bridging groups at *cis* positions from each other are terminal to extended L^1, L^2, and L^4 bis-chelate ring molecules [48]. The linear polymeric structure of **4** is similar to that found for $\{[Cu_2(\mu\text{-MeCOO})_4](\mu\text{-2,5-Me}_2\text{Pyrz})\}_n$ [48], demonstrating an interesting trend for dinitrogen $C_4H_4N_2$ hetero-cyclic axial ligands of *paddle-wheel* acetate and formate complexes. Steric hindrance leads to binuclear complexes for pyridazine which has two N-atoms at 1,2 positions, while pyrimidine with two nitrogen atoms at 1,3 positions afforded a *zig-zag* polymeric chain [49]. Not surprisingly, our pyrazine (having two nitrogen atoms at opposite (1,4) ring locations) leads to a linear polymer.

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