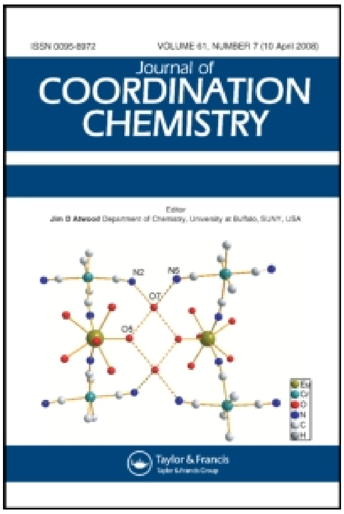

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Copper(ii) halogenopropionates: low-temperature crystal and molecular structure of bis(2,2-dichloropropionato)-di(methyl-3-pyridylcarbamate)copper(ii) and bis(2-bromopropionato)-di (2-pyridylmethanol)copper(ii)

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COPPER(II) HALOGENOPROPIONATES: LOW-TEMPERATURE CRYSTAL AND MOLECULAR STRUCTURE OF BIS(2,2-DICHLOROPROPIONATO)-DI(METHYL-3-PYRIDYLCARBAMATE)COPPER(II) AND BIS(2-BROMOPROPIONATO)-DI (2-PYRIDYLMETHANOL)COPPER(II)

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The synthesis and characterization of $[Cu(CH_3CCl_2CO_2)_2(3\text{-mpyc})_2]$ (**1**) (3-mpyc = methyl-3-pyridylcarbamate) and $[Cu(CH_3CHBrCO_2)_2(2\text{-pyme})_2]$ (**2**) (2-pyme = 2-pyridylmethanol) are reported. The compounds under study were characterized by IR, electronic spectroscopy and X-ray analysis. The molecular structure of both Complexes **1** and **2** is mononuclear. The coordination environment around each copper(II) atom is a distorted tetragonal bipyramid.

Keywords: Cu(II); Chloropropionate; Bromopropionate; Crystal structure; Hydrogen bonds; Methyl-3-pyridylcarbamate; 2-Pyridylmethanol; Jahn–Teller effect

INTRODUCTION

Crystal engineering, a subdiscipline of supramolecular chemistry, represents an important and rapidly developing area of chemical research. Metal-containing supramolecular systems constructed from intermolecular forces by weak, as well as strong, hydrogen bonds, and also hydrophobic and electrostatic forces and covalent bonds, have potential applications in heterogeneous catalysis and molecular electronics, and in magnetic, nonlinear optical and nanoporous materials [1]. Interesting, metal-containing supramolecular systems consist of coordination and organometallic complexes connected

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by strong hydrogen-bonding motifs [2,3]. Biological derivatives of pyridine, such as pyridinecarboxylic acids and their amides, form strong directional hydrogen-bonded motifs. Crystal engineering studies using transition metal-coordinated pyridinecarboxamides or pyridinecarboxylic acids in hydrogen-bonding supramolecular synthons have been reported [4–21].

Carboxylato-copper(II) complexes are interesting from both chemical and biological points of view. Different coordination of the carboxyl group to the central atom has led to compounds with distinct crystal structures. Propionic acid and its derivatives, in particular, possess very interesting pharmaceutical properties and constitute an important group of nonsteroidal antirheumatic drugs [22–24]. Some drugs act via chelation [25] or inhibition of metalloenzymes [26], but little is known about the modification of activity of most drugs when their ligating potential is utilized. Syntheses, structures, spectral and magnetic properties of various $CuX_2 \cdot nL$ (where X is propionate or halogenopropionate and L is water, triphenylphosphine oxide, pyridine or its derivatives) complexes have been reported [27–41].

The present paper reports, as part of our investigation of metal–drug interactions, compounds of composition $[Cu(CH_3CCl_2CO_2)_2(3\text{-mpyc})_2]$ (**1**) (3-mpyc = methyl-3-pyridylcarbamate) and $[Cu(CH_3CHBrCO_2)_2(2\text{-pyme})_2]$ (**2**) (2-pyme = 2-pyridylmethanol), which were prepared and studied by spectral methods, as well as by X-ray analysis.

EXPERIMENTAL

Preparation of the Complexes

The violet complex $[Cu(CH_3CCl_2CO_2)_2(3\text{-mpyc})_2]$ (**1**) was prepared as described previously [28]. The pH of a solution of the sodium salt of 2,2-dichloropropionic acid was adjusted to 4.5 and an aqueous solution of copper(II) sulfate in the molar ratio 1 : 2 was added. This was left to stand at room temperature and a green product of composition $Cu(CH_3CCl_2CO_2)_2$ was isolated. Complex **1** was prepared by reaction of a methanol solution of methyl-3-pyridylcarbamate (0.005 mol 3-mpyc, 30 cm^3 acetone) with a methanolic solution of $Cu(CH_3CCl_2CO_2)_2$ (0.002 mol, 50 cm^3 acetone). The resultant blue solution was concentrated to 50 cm_3 and cooled to room temperature. Crude product was recrystallized from acetone. Fine crystals were isolated and washed with cold methanol. Anal. Calcd. $C_{20}H_{22}N_4O_8Cl_4Cu$(%): C, 36.86; H, 3.40; N, 8.60; Cu, 6.75. Found: C, 36.91; H, 3.50; N, 8.52; Cu, 9.72.

$Cu(CH_3CHBrCO_2)_2 \cdot H_2O$ was prepared similarly, as described by Melnik [42]. An aqueous solution (10 cm^3) of the 2-bromopropionic acid and an equimolar quantity of sodium hydroxide (10 mmol) were added to 30 cm^3 of an aqueous solution of copper(II) sulfate (5 mmol), and the reaction mixture was then refluxed for 15 min. The blue–green precipitate was filtered off in nearly quantitative yield (95%).

The blue complex $[Cu(CH_3CHBrCO_2)_2(2\text{-pyme})_2]$ (**2**) was formed in a methanolic solution (30 cm^3) of $Cu(CH_3CHBrCO_2)_2 \cdot H_2O$ (1.25 mmol) by adding 2-pyridylmethanol (in the molar ratio of 1 : 2). The mixture was stirred, filtered and left to cool at ambient temperature. Well-shaped crystals, suitable for X-ray structure analysis, were collected after a few hours by filtration, washed with cold methanol and finally dried at ambient temperature (yield 75%). Anal. Calcd. $C_{18}H_{22}N_2O_6Br_2Cu$(%): C, 36.91; H, 3.79; N, 4.78; Cu, 10.85. Found: C, 36.86; H, 3.88; N, 4.82; Cu, 10.72.

Physical Measurements

Electronic spectra (9000–50 000 cm^{-1}) of the complexes in nujol mull were recorded at room temperature on a Specord 200 instrument. IR spectra in the region 400–4000 cm^{-1} were recorded on a Philips Analytical PU 9800 FTIR spectrometer and on a Magma 750 spectrometer at ambient temperature.

X-ray Crystallography

Data collection and cell refinement for the [Cu($CH_3CCl_2CO_2$)$_2$(3-mpyc)$_2$] (**1**) complex were carried out using an Oxford-Diffraction Xcalibur CCD κ-axis diffractometer with graphite-monochromated Mo Kα radiation at 100 K. The data were corrected for Lorentz and polarization effects. The structure was solved by Patterson methods using XFPS-94 [43] and refined by the full-matrix least-squares method on all F^2 data using the SHELXL-97 program [44]. Empirical absorption corrections were applied by using XABS-2 [45]. Geometrical analysis was performed using SHELXL-97. Two chlorine atoms and the methyl carbon atom of –CCl_2CH_3 are disordered, occupying three statistical positions, presented by C3, Cl2X and Cl1Y in position 1, with site occupancy factors of 0.48, 0.26 and 0.26, respectively; further by Cl1, C3X and Cl2Y in position 2, with site occupancy factors of 0.40, 0.20 and 0.40, respectively; and finally by Cl2, Cl1X and C3Y in position 3 with site occupancy factors of 0.34, 0.34 and 0.32, respectively. The –CCl_2CH_3 fragment was modeled using EXYZ and EADP constraints of SHELXL-97, respectively. The hydrogen atoms of –CCl_2CH_3 groups were positioned geometrically and refined using a riding model by HFIX 33 of SHELXL-97. Complex **1** has also been studied by X-ray diffraction at 293 K, but the –CCl_2CH_3 group was not modeled completely [28].

Data collection and cell refinement for [Cu($CH_3CHBrCO_2$)$_2$(2-pyme)$_2$] (**2**) were carried out using a Siemens SMART CCD diffractometer with graphite-monochromated Mo Kα radiation at 208 K. The data were corrected for Lorentz and polarization effects. Absorption corrections were applied using the program SADABS [46]. The structure was solved by direct methods using SHELXS-97 [47] and refined by the full-matrix least-squares method on all F^2 data using the SHELXL-97 program [44]. Geometrical analysis was performed using SHELXL-97.

The structures of Complexes **1** and **2** have been drawn using ORTEP-3 for Windows [48]. The Single Crystal Suite of WINGX [49] was used as an integrated system for all the crystallographic programs and software to prepare material for publication. The crystal data and final parameters after refinement are summarized in Table I. Selected bond distances and angles are given in Table II. The hydrogen-bonding geometry of **1** and **2** is summarized in Table III.

CSD Search

Searches of CSD [50] version 5.25 (November 2003 plus updates January 2004) were conducted using the CONQUEST software based on structures with a conventional R-value less than 10.0%.

TABLE I Crystal data and structure refinement details for [Cu($CH_3CCl_2CO_2$)$_2$(3-mpyc)$_2$] (**1**) and [Cu($CH_3CHBrCO_2$)$_2$(2-pyme)$_2$] (**2**)

	Complex **1**	*Complex* **2**
Empirical formula	$C_{20}H_{22}Cl_4CuN_4O_8$	$C_{18}H_{22}Br_2CuN_2O_6$
Mr	651.76	585.74
T (K)	100(2)	208(2)
λ (Å)	0.71069	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$C2/c$
Unit cell dimensions		
a (Å)	12.8160(12)	16.557(4)
b (Å)	6.1520(5)	8.1147(14)
c (Å)	17.1310(14)	16.826(3)
β (°)	109.730(8)	106.305(6)
V (Å^3)	1271.38(19)	2169.7(7)
Z, D_{calc}(Mg/m^3)	2, 1.703	4, 1.793
μ (mm^{-1})	1.333	4.726
F(000)	662	1164
Crystal size (mm)	$0.25 \times 0.10 \times 0.08$	$0.35 \times 0.35 \times 0.15$
θ (°)	3.54–25.00	2.52–29.20
Index range	$-15 \le h \le 15$, $-5 \le k \le 7$, $-20 \le l \le 20$	$-20 \le h \le 21$, $-9 \le k \le 11$, $-22 \le l \le 17$
Reflections collected	6978/2232	6791/2649
Absorption correction	XABS-2	SADABS
T_{max}, T_{min}	0.9008, 0.7317	0.5375, 0.2885
Refinement method	Full-matrix least-squares on F^2	
S	1.078	1.026
R, wR [$I < 2\sigma$ (I)]	0.0348, 0.0930	0.0342, 0.0873
R, wR (all data)	0.0361, 0.0939	0.0392, 0.0906
$\Delta\rho_{max}/\Delta\rho_{min}$ (e Å^{-3})	0.543/−0.476	0.786/−1.106

TABLE II Selected bond distances (Å) and angles (°) for [Cu($CH_3CCl_2CO_2$)$_2$ (3-mpyc)$_2$] (**1**) and [Cu($CH_3CHBrCO_2$)$_2$(2-pyme)$_2$] (**2**)

	Complex **1**	*Complex* **2**
Cu–N1	1.969(2)	1.984(2)
Cu–O1	1.996(2)	2.003(2)
Cu–O2	2.664(2)	2.404(2)
O1^a–Cu–O1	180.0(1)	180.00(9)
O1–Cu–N1^a	90.58(7)	90.34(7)
O1–Cu–N1	89.42(7)	89.66(7)
N1^a–Cu–N1	180.0(1)	180.0(1)
N1–Cu–O2^a	92.41(7)	103.03(7)
O1^a–Cu–O2	125.34(6)	96.13(7)
O1–Cu–O2	54.66(6)	83.87(7)
N1–Cu–O2	87.59(7)	76.97(7)
O2^a–Cu–O2	180.00(6)	180.00(9)

Symmetry code: $^a -x+1, -y+1, -z$ for **1** and $-x+1/2, -y+1/2, -z$ for **2**.

RESULTS AND DISCUSSION

[Cu($CH_3CCl_2CO_2$)$_2$(3-mpyc)$_2$] (1)

The bands corresponding to $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ are present at 1610 and 1450 cm^{-1}, respectively. The value of $\Delta\nu$ ($\Delta\nu = \nu_{as} - \nu_s$) is 160 cm^{-1}, much smaller

TABLE III Hydrogen bonding geometry for **1** and **2**

D–H···A	*d(D–H)*	*d(H···A)*	*d(D···A)*	*∠(DHA)*
[Cu($CH_3CCl_2CO_2$)$_2$(3-mpyc)$_2$] (**1**)				
C8–H4···O1^{a}	1.02(4)	2.52(4)	2.991(4)	108(2)
N2–H5···O2^{b}	0.78(3)	2.02(3)	2.792(3)	168(3)
C4–H1···O2^{b}	0.96(3)	2.62(3)	3.340(3)	132(2)
C6–H2···O3^{c}	0.93(3)	2.48(3)	3.178(3)	133(2)
[Cu($CH_3CHBrCO_2$)$_2$(2-pyme)$_2$] (**2**)				
O2–H1O1···O3^{d}	0.67(4)	1.99(4)	2.630(3)	163(4)
C3–H3···O3^{e}	1.01(3)	2.51(3)	3.217(3)	126(2)
C3–H3···O3^{f}	1.01(3)	2.56(3)	3.323(3)	132(2)

Symmetry code: $^{a}-x+1, -y+1, -z$; $^{b}x, y-1, z$; $^{c}-x+2, -y, -z$; $^{d}-x+1/2, -y+1/2, -z$; $^{e}x-1/2, y-1/2, z$; $^{f}-x+1/2, -y+1/2, z$.

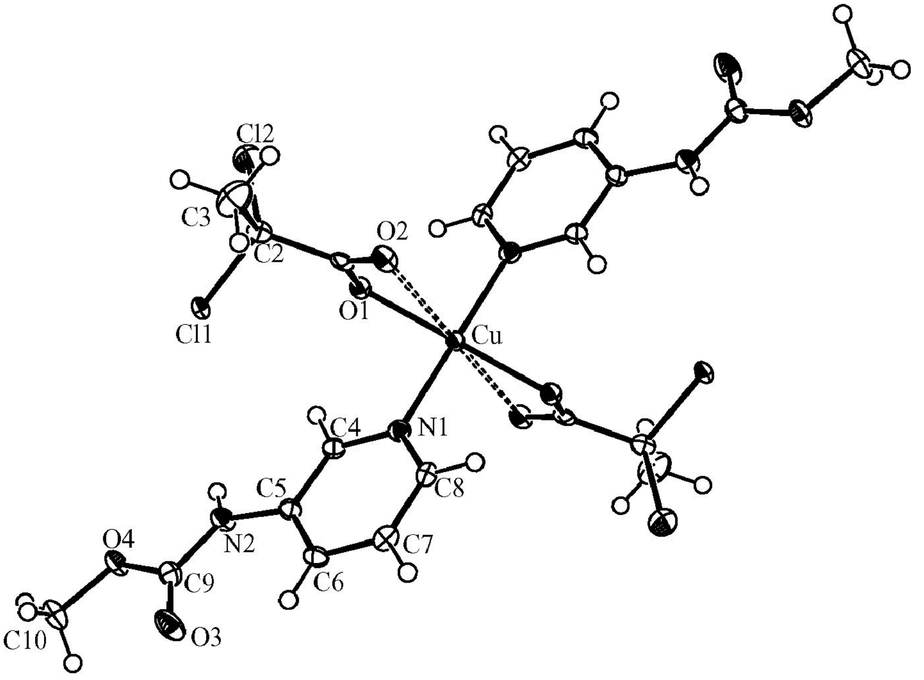

FIGURE 1 Perspective view of the complex [Cu($CH_3CCl_2CO_2$)$_2$(3-mpyc)$_2$] (**1**), with atom numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

than $\Delta\nu$ for the ionic form of 2,2-dichloropropionic acid (267 cm^{-1}), and corresponds to the bidentate mode of coordination. Frequencies at *ca* 3300, 3240 and 3144 cm^{-1} can be attributed to ν(NH). The absorption at 1290 cm^{-1} can be attributed to ν(C–N). The electronic spectrum of **1** shows a maximum at 14 900 cm^{-1} and a shoulder at 18 100 cm^{-1}, typical for tetragonal Cu(II) [28].

The structure of [Cu($CH_3CCl_2CO_2$)$_2$(3-mpyc)$_2$] (**1**) is shown in Fig. 1. The copper(II) is bonded in a *trans* square-planar arrangement to two nitrogen atoms of two methyl-3-pyridylcarbamate molecules [Cu–N1 = 1.969(2) Å] and one carboxylate oxygen atom from each of two 2,2-dichloropropionate anions [Cu–O1 = 1.996(2) Å].

The remaining two carboxylate oxygen atoms of **1**, which are weakly bonded to the copper [Cu–O2 = 2.664(2) Å] in the direction of the Cu–O(2) bonds, lie at 54.66(6)° from the normal to the CuO_2N_2 plane and complete a tetragonal-bipyramidal coordination. The copper(II) atom lies in the crystallographic center of symmetry.

The structure of **1** at 293(2) K has been published elsewhere [28]. In the X-ray structure obtained at room temperature there are significant differences in the bond distances around copper(II); Cu–N1, Cu–O1 and Cu–O2 are 1.959(2), 1.981(3) and 2.677(2) Å, respectively [28]. The value of the T parameter ($T = R_s/R_L$), indicating the degree of tetragonally elongated octahedron with further rhombic distortion about the copper(II) centers of **1**, decreases with temperature increase (0.744 at 100 K and 0.736 at 293 K). A similar molecular structure to that obtained for **1** has been published, namely $[Cu(CH_3CH_2CO_2)_2(3\text{-mpyc})_2]\cdot 0.25H_2O$ (refcode: PUVJEV), with Cu–N1, Cu–O1 and Cu–O2 of 1.955(2), 1.955(2) and 2.653(2) Å, respectively [38]. The value of T for $[Cu(CH_3CH_2CO_2)_2(3\text{-mpyc})_2]\cdot 0.25H_2O$ of 0.737 is very similar to that obtained for **1** at room temperature [38].

A search of the CSD and/or literature [50] revealed a total of 53 copper(II) carboxylates [24,28,38,51–96] (Table IV) with similar molecular structures to **1**. There is a cooperative effect between the Cu–O_{ax} bond distances and four-membered metallocyclic ring (O_{eq}–Cu–O_{ax}). While the Cu–O_{ax} bond length elongates, the O_{eq}–Cu–O_{ax} bond angle decreases. A plot of the O_{eq}–Cu–O_{ax} bond angle against the axial Cu–O_{ax} bond length for the whole data set shows significant correlation between these two quantities (Fig. 2) with $R = -0.983$. The T parameter, which indicates the degree of tetragonal distortion about Cu(II), follows this trend. The degree of tetragonal distortion smoothly increases with elongation of the Cu–O_{ax} bond length and decreases with the O_{eq}–Cu–O_{ax} angle as a consequence of the Jahn–Teller effect (Table IV). A plot of the O_{eq}–Cu–O_{ax} bond angle against T for the whole data set shows significant correlation (Fig. 3).

The crystal structure of **1** consists of two-dimensional (2D) sheets (Fig. 4). The layers are situated in the *ab* plane and consist of molecules of **1** linked by strong and weak hydrogen bonds [N2–H5···O2^b, C4–H1···O2^b, C6–H2···O3^c and C8–H4···O1^a] (Table III). Some metal complexes with pyridinecarbaxamides have been studied for the construction of supramolecular hydrogen-bonding network [4–21]. The $-NHCO_2CH_3$ group of methyl-3-pyridylcarbamate is very similar to the $-CONH_2$ group for constructing supramolecular hydrogen-bonding networks.

$[Cu(CH_3CHBrCO_2)_2(2\text{-pyme})_2]$ (2)

The characteristic bands of the asymmetric and symmetric stretching vibrations for the carboxyl group of **2** were found at 1599 and 1396 cm^{-1}, respectively. The $\Delta\nu$ value is 203 cm^{-1}, which is very close to the value of $\Delta\nu$ for the ionic form of 2-bromopropionic acid [97], typical for *syn,syn*-bridging coordination or for monodentate binding, where one carboxylate oxygen is coordinated to the Cu(II) atom and the second carboxylate oxygen is connected to a hydrogen bond. The hydrogen bond vibration at 2657 cm^{-1} can be attributed to an intramolecular hydrogen bond. A similar band was found in $[Cu(clofibriato)_2(2\text{-pyme})_2]$ at 2663 cm^{-1} [98]. The vibration of the pyridine ring is shifted from 1003 cm^{-1} for the uncoordinated ligand to 993 cm^{-1}, suggesting coordination of 2-pyridylmethanol to Cu(II) through the nitrogen of the pyridine.

TABLE IV Selected bond lengths (Å) and angles (°) for familiar complexes of **1** from CSD data

Ref.code	*Cu–N*$_{eq}$	*Cu–O*$_{eq}$	*Cu–O*$_{ax}$	O_{eq}*–Cu–*O_{ax}	*T*	*Ref.*
TEKDOS	2.003	1.995	2.450	58.41	0.816	[51]
GIHPAO	1.993	2.012	2.510	57.50	0.798	[52]
POGHOI	1.998	1.974	2.532	57.01	0.784	[53]
QALZOS	2.007	1.971	2.545	57.71	0.782	[54]
MEYVER	2.027	1.958	2.563	56.41	0.777	[55]
XEWKIT	1.987	1.975	2.570	55.83	0.771	[56]
PIWTEU	2.058	1.969	2.584	56.08	0.779	[57]
POFCES	1.964	1.978	2.587	56.19	0.762	[58]
SUBMIL	1.973	1.986	2.598	56.17	0.762	[59]
PICRUO	1.994	1.935	2.609	55.24	0.753	[60]
XAZPIX	1.995	1.994	2.614	55.49	0.763	[24]
3	2.008	1.978	2.617	55.86	0.762	[61]
CUKPED	2.002	1.949	2.622	55.25	0.753	[62]
WIBSUV	2.028	1.950	2.623	55.12	0.758	[63]
4	1.985	1.972	2.625	55.33	0.754	[64]
5	1.989	1.999	2.628	55.60	0.759	[64]
6	1.984	1.970	2.633	54.89	0.751	[65]
YAZMIV	1.987	1.969	2.638	54.76	0.750	[66]
MOXLEQ	2.008	1.955	2.643	54.89	0.750	[67]
FOWJEG	2.028	1.970	2.652	54.40	0.754	[68]
PUVJEV	2.025	1.955	2.653	54.23	0.750	[38]
1 at 100 K	1.969	1.996	2.664	54.66	0.744	
JOGNAU	2.015	1.963	2.672	54.16	0.744	[69]
QIBDEK[a]	1.981	1.959	2.677	54.00	0.736	[28]
KAFVES	1.993	1.963	2.681	53.91	0.738	[70]
NEDJAH	1.996	1.963	2.683	54.19	0.737	[71]
JUZZAF	1.986	1.943	2.688	53.45	0.731	[72]
7	1.974	1.962	2.706	53.91	0.727	[73]
CAPICU	1.989	1.974	2.707	53.94	0.732	[74]
BELZUN	2.046	1.997	2.710	52.99	0.746	[75]
CUSHON	1.977	1.970	2.731	53.58	0.723	[76]
BETLAN	1.964	1.976	2.736	52.78	0.720	[77]
ACMRCU10	2.035	1.958	2.738	52.74	0.729	[78]
CAHJAW	1.970	1.967	2.758	52.53	0.714	[79]
POGHUO	1.955	1.957	2.759	53.37	0.709	[53]
CULDIW	1.976	1.950	2.761	53.18	0.711	[80]
NOBZCU	2.062	1.939	2.764	53.70	0.724	[81]
GOLPOM	2.046	1.952	2.764	52.38	0.723	[82]
ROGWUF	2.022	1.929	2.766	52.71	0.714	[83]
FAMYOF	1.971	1.985	2.668	54.22	0.741	[84]
AGOHAF	1.954	1.971	2.776	52.02	0.707	[85]
IHUFIA	2.015	1.961	2.780	52.55	0.715	[86]
HODVUR	1.994	1.944	2.785	52.26	0.707	[87]
BEMMUB10	2.042	1.963	2.787	52.02	0.719	[88]
LOQBEY	1.983	1.949	2.788	51.97	0.705	[89]
UHERUU	1.953	1.977	2.790	52.53	0.704	[90]
CUIMAD10	2.005	1.921	2.800	52.22	0.701	[91]
MOHREG	2.018	1.937	2.804	51.91	0.705	[92]
FECHIE	1.987	1.976	2.813	51.05	0.704	[93]
WAZTOG	2.048	1.936	2.825	51.14	0.705	[94]
8	1.973	1.952	2.838	51.23	0.691	[65]
BEJGUS	1.959	1.942	2.907	49.16	0.671	[95]
FORMCU	2.033	1.948	2.978	48.40	0.668	[96]

[a] **1** at 293 K; 3 = Cu(diclophenato)$_2$(pyridine)$_2$; 4 = Cu(heptanoato)$_2$(4-aminopyridine)$_2$; 5 = Cu(hexanoato)$_2$(4-aminopyridine)$_2$; 6 = β-Cu(benzoato)$_2$(imidazole)$_2$; 7 = Cu(benzoato)$_2$(4-aminopyridine)$_2\cdot$0.75benzene; 8 = α-Cu(benzoato)$_2$ (imidazole)$_2$.

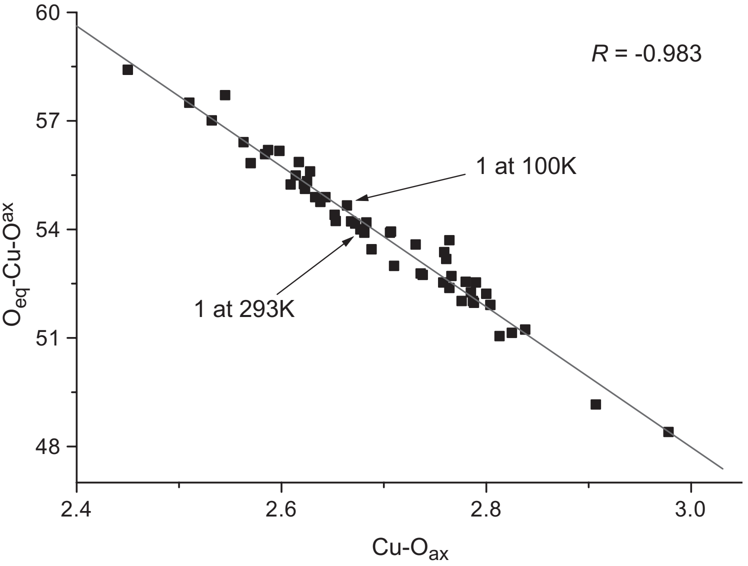

FIGURE 2 A plot of the O_{eq}–Cu–O_{ax} bond angle against the axial Cu–O_{ax} bond angle from CSD data.

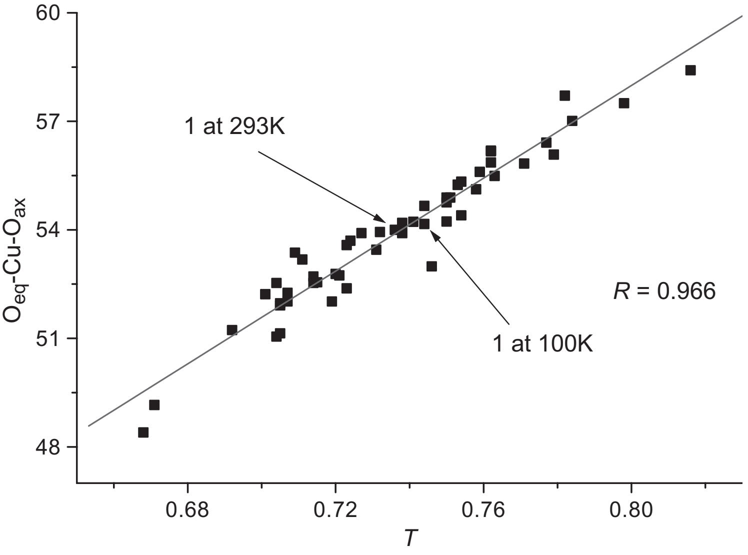

FIGURE 3 A plot of the O_{eq}–Cu–O_{ax} bond angle against the *T* parameter from CSD data.

The electronic spectrum of **2** shows a broad symmetrical band at about 16 200 cm^{-1}, typical of tetragonal copper(II), and consistent with an essentially $d_{x^2-y^2}$ orbital ground state [99].

In the structure of [Cu($CH_3CHBrCO_2$)$_2$(2-pyme)$_2$] (**2**) (Fig. 5) the coordination polyhedron around the Cu(II) atom is a distorted tetragonal bipyramid (4 + 2). The carboxylate oxygen atom from each of two 2-bromopropionate anions [Cu–O1 = 2.003(2) Å]

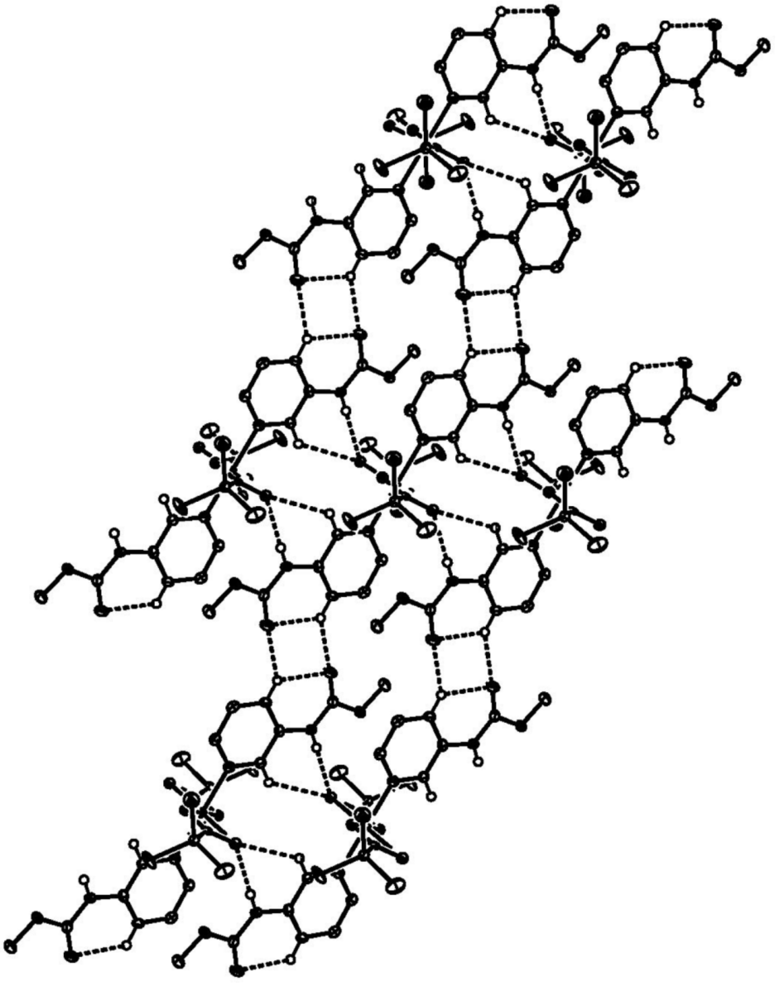

FIGURE 4 The 2D layer of molecules of [Cu($CH_3CCl_2CO_2$)$_2$(3-mpyc)$_2$] (**1**) in plane *ab*. Hydrogen atoms are omitted for clarity.

and the nitrogen atom from each of two 2-pyridylmethanol molecules [Cu–N1 = 1.984(2) Å] are bonded to the copper(II) atom in a *trans* square-planar arrangement. Two axial positions are occupied by the methanol oxygen atoms of two 2-pyridylmethanol ligands [Cu–O2 = 2.404(2) Å] and complete a tetragonal-bipyramidal coordination. The copper(II) atom lies in a crystallographic center of symmetry. The N1–Cu–O3 bond angle of the five-membered metallocycle ($CuOC_2N$) is 76.97(7)°. The uncoordinated oxygen atoms of the 2-bromopropionate anions are "fixed" to the methanol hydrogen atoms of 2-pyridylmethanol by strong hydrogen bonds O2–H1o1···O3^d ($-x+1/2, -y+1/2, -z$) with interatomic distances O3···H1o1 of 1.99(4) Å, O2–H1o1 of 0.67(4) Å and O2···O3 of 2.630(3) Å, and create six-membered metallocyclic rings (CuO_3CH).

Selected bond distances and angles for CuX_2(2-pyme)$_2$ complexes (X = clofibriate, mefenamate, salicylate and 2-bromopropionate) are given in Table V. All four complexes have similar structures in which each copper(II) atom is bonded in a

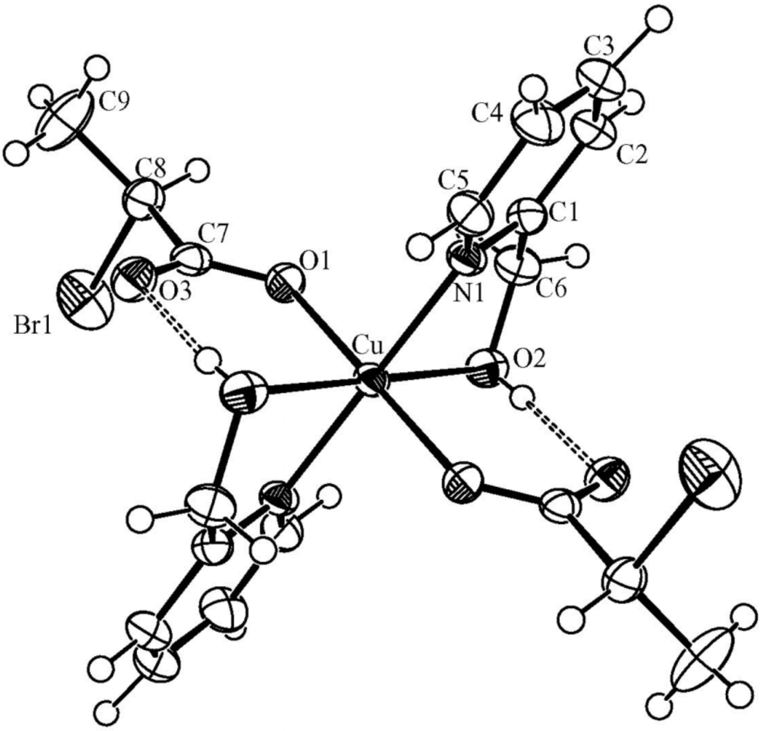

FIGURE 5 Perspective view of the complex $[Cu(CH_3CHBrCO_2)_2(2\text{-pyme})_2]$ (**2**), with atom numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

TABLE V Selected bond lengths (Å) and angles (°) for complexes $CuX_2(2\text{-pyme})_2$ (X = mefenamate, clofibriate, salicylate and 2-bromopropionate)

	Mefenamate *Ref.* [101]	*Clofibriate* *Ref.* [98]	*Salicylate* *Ref.* [100]	*2-Bromopropionate*
$Cu–O_{eq}$	1.966(2)	1.997(2)	1.981(1)	2.003(2)
$Cu–N_{eq}$	1.990(3)	1.978(2)	1.981(1)	1.984(2)
$Cu–O_{ax}$	2.415(3)	2.388(2)	2.331(2)	2.404(2)
$N_{eq}–Cu–O_{ax}$	75.82(1)	76.83(7)	77.62(7)	76.97(7)
$N_{eq}–Cu–O_{ax}$	96.26(9)	94.19(6)	95.13(5)	96.13(7)

square-planar arrangement to the nitrogen atoms of two 2-pyridylmethanols and one oxygen atom from each of two carboxylates. The remaining axial positions are occupied by methanol oxygen atoms of two 2-pyridylmethanol ligands. This type of molecular structure can be proposed for all copper(II) complexes with 2-pyridylmethanol and larger aliphatic or aromatic carboxylates.

The value of the T parameter for $CuX_2(2\text{-pyme})_2$, indicating the degree of tetragonal distortion about the copper(II) centers, decreases in the order: X = salicylate 0.850 [100] > clofibriate 0.832 [98] > 2-bromopropionate 0.829 > mefenamate 0.819 [101].

The crystal structure of **2** consists of 2D sheets (Fig. 6). The layers are situated in the *ab* plane and arise from weak hydrogen bonds [$C3–H3\cdots O3^{e}$ and $C3–H3\cdots O3^{f}$]

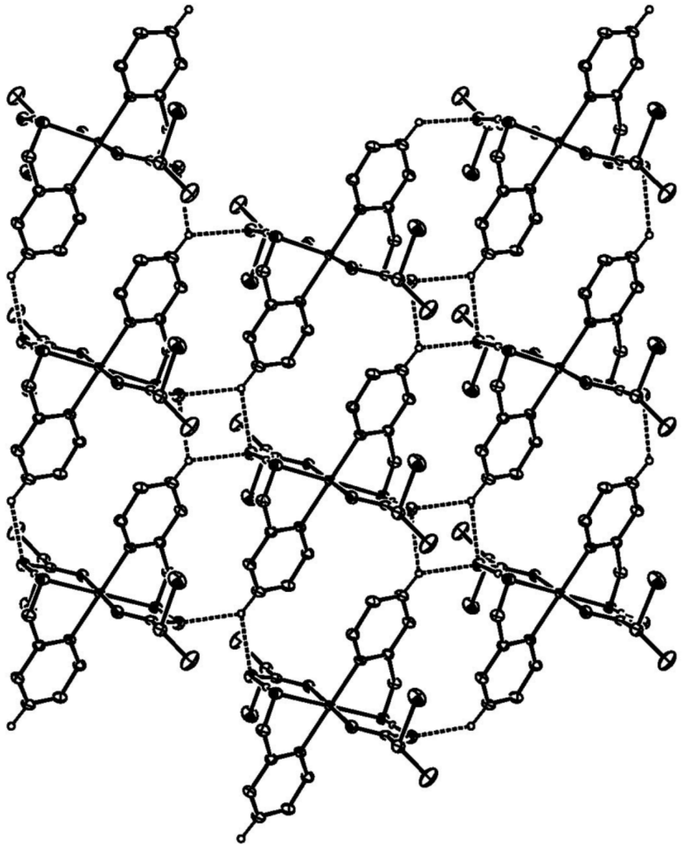

FIGURE 6 The 2D layer of molecules of [Cu($CH_3CHBrCO_2$)$_2$(2-pyme)$_2$] (**2**) in plane *ab*. Hydrogen atoms are omitted for clarity.

(Table III). As can be seen in Fig. 6, the oxygen atom of the methanol group of 2-pyridylmethanol is a very good "acceptor" of hydrogen bonds.

CONCLUSION

Two coordination compounds formed by copper(II) with 2,2-dichloropropionate and methyl-3-pyridylcarbamate and with 2-bromopropionate and 2-pyridylmethanol have been prepared and characterized. The crystal structures of **1** and **2** consist of 2D sheets. The layers consist of mononuclear molecules linked by weak and strong hydrogen bonds. We propose that the methyl-3-pyridylcarbamate can be used for the construction of supramolecular systems.

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Supplementary Data

Crystallographic data (excluding structure factors) for the structures in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 217448 (**1**) and 217449 (**2**). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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