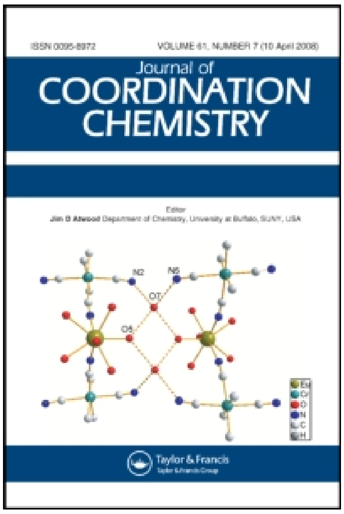

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4-Aminopyridine Adducts of Cu(II) 2-Chloro- and 2,6-Dichlorobenzoate

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4-AMINOPYRIDINE ADDUCTS OF Cu(II) 2-CHLORO- AND 2,6-DICHLOROBENZOATE

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Reaction products of Cu(II) 2-chlorobenzoate and 4-aminopyridine (**1**), and of Cu(II) 2,6-dichlorobenzoate and 4-aminopyridine (**2**) formulated as $CuL'_2(4\text{-apy})_2$ and $CuL''_2(4\text{-apy})_2$ ($L' = C_7H_4ClO_2^-$, $L'' = C_7H_3Cl_2O_2^-$, 4-apy = 4-aminopyridine), were prepared and characterized by structural and spectroscopic measurements, thermochemical properties and magnetic susceptibilities. Compound (**1**) crystallizes in the orthorhombic space group *Pbca*, $a = 8.875(2)$, $b = 13.236(4)$, $c = 21.603(3)$ Å, $V = 2537.7(10)$ Å^3, $Z = 4$, and the Compound (**2**) crystallizes in the monoclinic space group $P2_1/c$, $a = 11.516(2)$, $b = 8.749(2)$, $c = 13.469(3)$ Å, $\beta = 103.36(3)°$, $V = 1320.3(5)$ Å^3, $Z = 2$. Complexes (**1**) and (**2**) decomposes to gaseous products at 473 and 513 K, respectively.

Keywords: Copper; 2-Chlorobenzoic acid; 2,6-Dichlorobenzoic acid; Complexes; X-ray analysis; Thermal properties

INTRODUCTION

A general survey of the literature on complexes of Cu(II) with nitrogen donors reveals that a considerable amount of work has been carried out on the preparation and characterisation of addition complexes of Cu(II) carboxylates with nitrogen donors. During the course of this investigation some adducts of Cu(II) chlorobenzoate with 1,3-propanodiamine [1–3], and with pyridine [4] were noted. Carboxylates of divalent metals with various donor ligand give complexes of three different stoichiometries, 1 : 1, 1 : 2 and 1 : 4. In some cases a metal carboxylate may give adducts of two different stoichiometries with the same ligand under different experimental conditions [5,6].

Complexes of bridged bis(imidazole) and bis(benzimidazole) ligands of various bridging types with transition metals have been examined as potential models of the structure and mobility of biological metal binding sites in metalloproteins like haemerythrin, hemocyanin, tyrosinase or azurin [7–13]. One of these *N*-donor ligands

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is 4-aminopyridine. This work is a continuation of our study of the structure and properties of metal complexes with dichlorobenzoic acids and *N*-donor ligands and concerns the above amine, and copper salts of chlorobenzoic acids.

EXPERIMENTAL

2-Chloro- and 2,6-dichlorobenzoates of Cu(II) were obtained by a modified literature method [14,15]. Basic Cu(II) carbonate ($CuCO_3 \cdot Cu(OH)_2 \cdot H_2O$, 0.01 mol) was added to a hot solution of 2-chlorobenzoic acid (0.02 mol in 0.2 dm^3 of water) and the suspension was heated with stirring for about 4 h. The same procedure was applied in the reaction of the 2,6-dichlorobenzoate salt of Cu(II). After filtering the saturated solutions, the Cu(II) complexes were subjected to slow crystallization. The precipitates formed were filtered, washed with water and dried at 303 K to constant mass.

The final complexes were obtained by dissolving the Cu(II) complex of 2-chlorobenzoic acid (**1**) and 2,6-dichlorobenzoic acid (**2**) (0.01 mol) in 0.2 dm^3 of a 0.1 M solution of 4-aminopyridine in water. The solutions were subjected to slow crystallization. Crystals of (**1**) and (**2**), suitable for X-ray data collection, were deposited after three weeks. The products were filtered off, washed with water and dried at 303 K to constant mass.

Carbon, hydrogen and nitrogen contents were determined using a Perkin Elmer CAN 2000 instrument. Chlorine contents were measured by the Schöniger method and Cu(II) by AAS using an AAS-3 (Carl Zeiss-Jena) instrument. The experimental results are consistent with the calculated data [Cu 11.29 (11.3), C 51.17 (51.2), H 3.55 (3.5), Cl 13.32 (13.5), N 9.95 (10.0)% for (**1**) and Cu 10.06 (10.0), C 45.59 (45.7), H 2.85 (3.0), Cl 22.48 (22.4), N 8.86 (8)% for (**2**)].

IR spectra were recorded over the range 4000–400 cm^{-1} using a Perkin Elmer FT-IR 1725X spectrophotometer. Thermal stabilities of the Cu(II) complexes were determined using a Paulik-Paulik-Erdey Q 1500 D derivatograph with Derill converter; TG, DTG and DTA curves were recorded. Samples (100 mg) were heated in platinum crucibles to 1273 K in static air at a heating rate of 10 K min^{-1}. Magnetic susceptibilities were measured by the Faraday method at 295 K on a magnetic balance (Scherwood Scientific MSB MK1). $Hg[Co(NCS)_4]$ was used as reference.

X-Ray Structure Determination

X-ray measurements for Compounds (**1**) and (**2**) were made on a Kuma KM4 κ-axis four-circle diffractometer with a graphite monochromator using CuKα or MoKα radiation. The data were corrected for Lorentz and polarization effects. No absorption correction was applied. Data reduction and analysis were carried out with Kuma Diffraction (Wrocław) programs.

Crystallographic data and refinement details are given in Table I. The structures were solved by direct methods with SHELXS97 [16], and refined by full-matrix least-square methods on all F^2 data using the SHEXL97 [17] program. Nonhydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were fixed from the geometry of the molecules. During refinement they were treated as rigid groups with fixed interatomic distances. The final refinement resulted in $R_1 = 0.0463$ for Compound (**1**) and $R_1 = 0.0355$ for Compound (**2**). Final fraction atomic coordinates

TABLE I Crystal data and refinement details for compounds (**1**) and (**2**)

	(*1*)	(*2*)
Empirical formula	$C_{24}H_{20}Cl_2CuN_4O_4$	$C_{24}H_{18}Cl_4CuN_4O_4$
Temperature (K)	293(2)	297(2)
Molecular weight	562.88	631.76
Wavelength (Å)	1.54180	0.71069
Crystal system	orthorhombic	monoclinic
Space group	*Pbca*	$P2_1/c$
a (Å)	8.875(2)	11.516(2)
b (Å)	13.236(4)	8.749(2)
c (Å)	21.603(3)	13.469(3)
β (°)	–	103.36(3)
V (Å^3)	2537.7(10)	1320.3(5)
Z	4	2
$F(000)$	1148	638
D_m flotation (mg / m^3)	1.48	1.58
D_c (mg / m^3)	1.473	1.589
Crystal size (mm)	0.15 × 0.18 × 0.20	0.15 × 0.15 ×0.30
Diffractometer	Kuma KM4	Kuma KM4
2θ limit (°)	8–160	4–56
Ranges *h*	0 to 10	0 to 12
k	0 to 16	0 to 19
l	0 to 27	−14 to 14
Reflections (unique)	1559	1637
Data $[I > 2\sigma(I)]$/parameters	1559/161	1180/169
GOF on F^2	1.045	1.164
R_1, wR_2 $[I > 2\sigma(I)]$	0.0463, 0.1269	0.0355, 0.0978
$\Delta^-\rho$ / e Å^{-3}	0.581 and −0.369	0.296 and −0.428

for nonhydrogen atoms and equivalent isotropic thermal parameters are presented in Table II. Bondlengths and bondangles are listed in Table III.

RESULTS AND DISCUSSION

The complexes $CuL'_2(4\text{-apy})_2$ (**1**) and $CuL''_2(4\text{-apy})_2$ (**2**) ($L' = C_7H_4ClO_2^-$, $L'' = C_7H_3Cl_2O_2^-$, 4-apy = 4-aminopyridine) were prepared as violet crystalline solids. Characteristic IR data for (**1**), (**2**) and 4-aminopyridine are listed in Table IV. In the IR spectra of the complexes there are sharp bands at 3400, 3336 and 3224 cm^{-1} for (**1**) and 3400, 3320 and 3316 cm^{-1} for (**2**), characteristic of asymmetric and symmetric N–H vibrations and sharp bands at 1664 cm^{-1} for (**1**) and 1652 cm^{-1} for (**2**) for deformation vibrations of this group. The bands slightly shifted to higher frequencies compared to those for free 4-aminopyridine and this suggests that N–H groups of 4-aminopyridine do not coordinate to copper.

In the IR spectra of free 2-chlorobenzoic acid [14] and 2,6-dichlorobenzoic acid [15], there are sharp COOH group bands at 1688 and 1716 cm^{-1}, respectively. In the IR spectra of the complexes these bands disappear and ν_{as}(OCO) and are observed ν_s(OCO) bands at 1576 and 1392 cm^{-1} for (**1**) and 1560 and1376 cm^{-1} for (**2**) are observed. The splitting of 184 cm^{-1} for (**1**) and (**2**) suggests that the carboxylate groups in (**1**) and (**2**) act as bidentate chelates [18–20]. These results were confirmed by determination of the crystallographic and molecular structures of the complexes. In the IR spectra of the complexes bands at 656 cm^{-1} for (**1**) and 624 cm^{-1} for (**2**) can be assigned to stretching of the Cu–N bond.

TABLE II Atomic coordinates and equivalent isotropic displacement parameters for compounds (**1**) and (**2**). U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x/a	y/b	z/c	U_{eq}
(*1*)				
Cu	0.0000	0.0000	0.5000	0.0391(2)
Cl	0.3712(2)	0.1520(1)	0.3716(1)	0.0845(5)
O(1)	0.0585(3)	0.0466(2)	0.4151(1)	0.0424(5)
O(2)	0.1803(3)	−0.0972(2)	0.0474(1)	0.0514(6)
N(1)	0.1722(3)	0.0760(2)	0.5351(1)	0.0419(7)
N(2)	0.5484(4)	0.2298(2)	0.5990(2)	0.0617(10)
C(1)	0.2100(5)	−0.0098(3)	0.3327(2)	0.0541(10)
C(2)	0.3050(5)	0.0693(3)	0.3154(2)	0.0651(12)
C(3)	0.3532(7)	0.0790(6)	0.2543(3)	0.104(2)
C(4)	0.3075(11)	0.0142(8)	0.2116(3)	0.139(4)
C(5)	0.2169(10)	−0.0659(7)	0.2268(3)	0.125(3)
C(6)	0.1696(7)	−0.0784(5)	0.2874(2)	0.086(2)
C(7)	0.1481(4)	−0.0223(2)	0.3961(2)	0.0419(8)
C(8)	0.1658(5)	0.1746(3)	0.5490(2)	0.0520(9)
C(9)	0.2847(5)	0.2285(3)	0.5702(2)	0.0537(10)
C(10)	0.4250(5)	0.1815(3)	0.5784(2)	0.0441(8)
C(11)	0.4307(5)	0.0783(3)	0.5644(2)	0.0480(8)
C(12)	0.3044(5)	0.0307(3)	0.5434(2)	0.0458(8)
(**2**)				
Cu	0.5000	0.0000	0.0000	0.0383(3)
Cl(1)	0.1004(2)	-0.0451(3)	−0.1963(1)	0.0894(7)
Cl(2)	0.2464(2)	0.3692(2)	0.1019(1)	0.0695(6)
O(1)	0.3391(3)	0.0341(4)	0.0282(3)	0.0391(9)
O(2)	0.3405(4)	0.1728(4)	−0.1083(3)	0.0472(10)
N(1)	0.5637(4)	0.1766(5)	0.0849(3)	0.0391(11)
N(2)	0.6848(5)	0.5647(6)	0.2534(3)	0.0528(14)
C(1)	0.1613(6)	0.1641(6)	−0.0468(4)	0.0460(15)
C(2)	0.0701(7)	0.0919(8)	−0.1135(5)	0.064(2)
C(3)	−0.0488(7)	0.1252(11)	−0.1135(7)	0.089(3)
C(4)	−0.0724(8)	0.2307(12)	−0.0454(9)	0.101(3)
C(5)	0.0178(9)	0.3047(9)	0.0204(7)	0.087(3)
C(6)	0.1342(6)	0.2724(7)	0.0188(5)	0.055(2)
C(7)	0.2908(5)	0.1226(6)	−0.0440(4)	0.0382(13)
C(8)	0.5911(6)	0.3048(7)	0.0427(4)	0.055(2)
C(9)	0.6312(6)	0.4331(7)	0.0944(4)	0.054(2)
C(10)	0.6470(5)	0.4388(6)	0.1998(4)	0.0388(13)
C(11)	0.6181(6)	0.3043(7)	0.2444(4)	0.50(2)
C(12)	0.5799(6)	0.1805(7)	0.1864(4)	0.051(2)

Bis(2-chlorobenzoato-*O*)bis(4-aminopyridine-*N*)copper(II) (**1**) crystallizes in the orthorhombic space group *Pbca*. The structure is illustrated in Fig. 1 with the numbering of the atoms. Table V lists hydrogen bond parameters. The copper(II) ion is coordinated two 4-aminopyridine and two 2-chlorobenzoate ligands forming a centrosymmetric monomer. The 4-aminopyridine ligand coordinates through the nitrogen atom of the aromatic ring with Cu–N 1.980(3) Å. The aromatic ring of 2-chlorobenzoate is nearly perpendicular to the pyridine ring with a dihedral angle of 83.8(2)°. The angle between the carboxylic acid group and the benzene ring of 2-chlorobenzoate is 64.9(2)°, which makes possible the strong coordination of only one of the oxygen atoms with copper(II), Cu–O1 2.003(2)Å. The second oxygen atom (O2) of carboxylate group is far from metal ion, 2.585 Å, and is considered to be weakly bonded.

TABLE III Selected bond distances (Å) and angles (°) for the complexes

	(*1*)	(*2*)
Cu–N(1)i	1.980(3)	1.961(4)
Cu–N(1)	1.980(3)	1.961(4)
Cu–O(1)i	2.003(2)	1.998(4)
Cu–O(1)	2.003(2)	1.998(4)
Cu–O(2)i	2.585(2)	2.560(4)
Cu–O(2)	2.585(2)	2.560(4)
O(1)–C(7)	1.277(4)	1.268(6)
O(2)–C(7)	1.233(4)	1.225(6)
C(1)–C(7)	1.485(5)	1.526(8)
N(1)i–Cu–N(1)	180.0	180.0
N(1)i–Cu–O(1)i	89.70(11)	90.6(2)
N(1)–Cu–O(1)i	90.30(11)	89.4(2)
N(1)i–Cu–O(1)	90.30(11)	89.4(2)
N(1)–Cu–O(1)	89.70(11)	90.6(2)
O(1)i–Cu–O(1)	180.0	180.0
C(7)–O(1)–Cu	103.6(2)	102.0(3)
O(2)–C(7)–O(1)	122.9(3)	124.6(5)
O(2)–C(7)–C(1)	120.5(3)	120.7(5)
O(1)–C(7)–C(1)	116.6(3)	114.7(5)

Symmetry transformations used to generate equivalent atoms: for (**1**) $-x$, $-y$, $-z+1$; for (**2**) $-x+1$, $-y$, $-z$.

TABLE IV Characteristic IR data for (**1**), (**2**) and 4-aminopyridine

(*1*)	(*2*)	*4-Aminopyridine*	*Assignment*
3400	3400	3432	ν_{as}(N–H)
3336, 3224	3320, 3216	3326, 3316	ν_{s}(N–H)
1652	1664	1648	
1576	1560		$\nu_{\mathrm{as}}(\mathrm{OCO}^-)$
1520	1520	1504	ν(N–H)
1432	1432	1432	ν(C···C)
1392	1376		$\nu_{\mathrm{s}}(\mathrm{OCO}^-)$
1336	1336	1336	ν(C–N)
1296	1296	1272	ν(C···C)
1208, 1028	1208, 1032	1216, 982	ν(C–N)
824	824	824	ν(C–H)
752	776		ν(C–Cl)
720	760, 736, 704		ν(C···C)
656	624		ν(Cu–N)
528	528	536	ν(C···C)
456, 428	492, 448	440	ν(C–H)

The sum of Cu–O1 and Cu–O2, 2.294 Å, is near to that in Cu(phen)$_2$·(CH$_3$COO)BF$_4$·2H$_2$O, [22], where the carboxylate group has chelating, symmetric character. The symmetry of the carboxylic group is dictated by the fact that copper(II) ion and the carboxylic acid lie on a two-fold axis. Angles and distances in the aromatic rings of the ligands are normal [21]. The angle O1–C7–O2 is 122.9(3)°, typical of monodentate coordination [23].

The related compound bis(2,6-dichlorobenzoato-*O*)bis(4-aminopyridine-*N*)copper(II) (**2**) crystallizes in the monoclinic space group $P2_1/c$. The structure is illustrated in Fig. 2 with the numbering of the atoms. Copper(II) a coordinates two 4-aminopyridine and two 2,6-dichlorobenzoate ligands forming a centrosymmetric

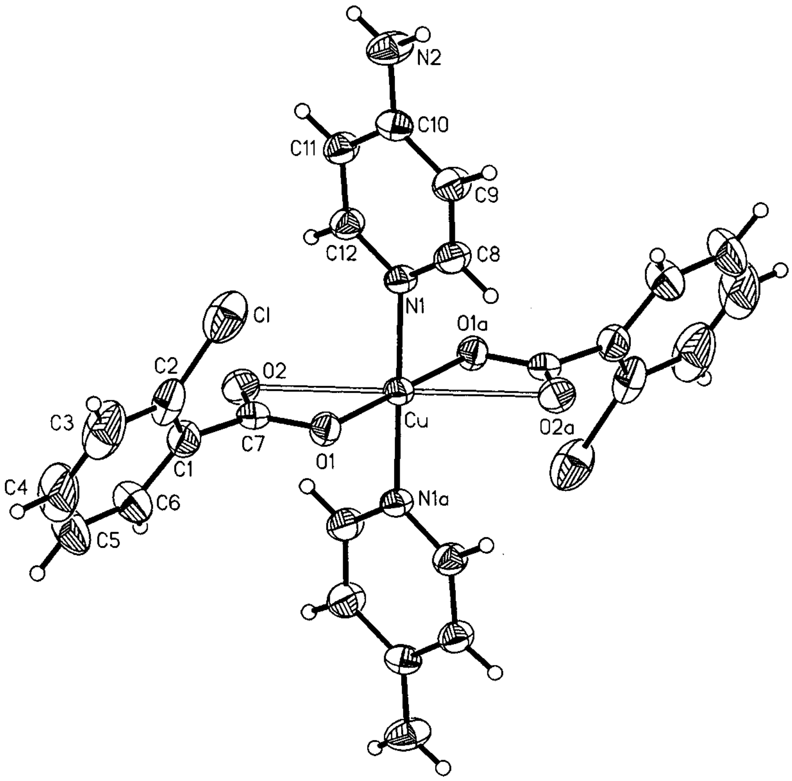

FIGURE 1 Molecular structure of $Cu(C_6H_4ClCOO)_2 \cdot 2(4\text{-apy})$ (**1**).

TABLE V Hydrogen bond parameters for (**1**) and (**2**) [(Å) and (°)]

D–H···A	*D–H*	*H···A*	*D···A*	*Angle*
(*1*)				
N(2)–H(7) ··O(2)i	0.86	2.23	3.033(5)	155
N(2)–H(8) ··O(1)ii	0.86	2.18	2.977(5)	154
(*2*)				
N(2)–H(2) ··O(2)i	0.86	2.19	2.985(7)	155
N(2)–H(2) ··O(1)ii	0.86	2.20	3.028(7)	162

Symmetry codes: for (**1**) (i)$1-x$, $-y$, $1-z$; (ii) $0.5+x$, $0.5-y$, $1-z$; for (**2**) (i)$1-x$, $1-y$, z; (ii) $1-x$, $0.5+y$, $0.5-z$.

monomer. Coordinating nitrogen and oxygen atoms form a square plane around the copper(II) ion with Cu–N 1.961(4) and Cu–O1 1.998(4) Å. The aromatic rings are almost perpendicular to one another; the dihedral angle is 80.69(22)°. The carboxylate group is also twisted with respect to the benzene ring plane, the angle between both planes being 78.33(16)°. The second oxygen atom O2 of the carboxylate group coordinates in the same way as in (**1**) forming a semicoordinate bond. The bond distance in this case is 2.560(4) Å. The monomers in both structures are connected by a hydrogen bonding network, which involves the amino groups and oxygen atoms of carboxylic groups (Table V).

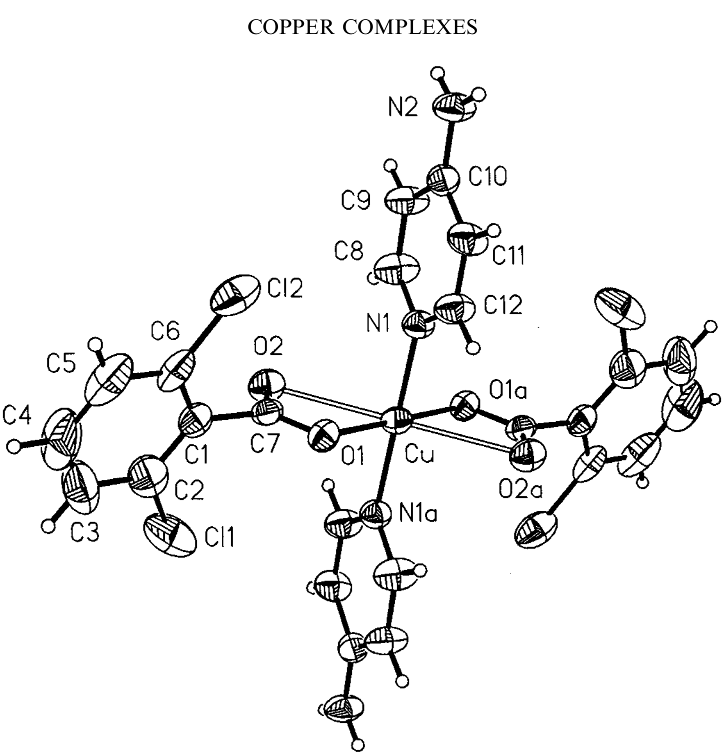

FIGURE 2 Molecular structure of $Cu(C_6H_3Cl_2COO)_2 \cdot 2(4\text{-apy})$ (**2**).

Complexes (**1**) and (**2**) are stable in air at room temperature. With a heating rate of 10 K/min, the complexes are stable to 473 and 513 K, respectively, and then decompose to yield gaseous products (similar to Co(II) complexes with 2,3- [24], 2,4- [25], 2,5- [26], 2,6- [27], 3,4- [28] and 3,5- [23] dichlorobenzoic acids). The magnetic susceptibilities for (**1**) and (**2**) 295 K were for diamagnetic susceptibilities of ligands and calculated using the formula $\mu_{\text{eff}} = 2.84(X_M T)^{1/2}$. Magnetic moments for (**1**) and (**2**) are 1.57 and 1.64 BM, respectively, near to the theoretical spin-only value typical of Cu(II) complexes.

Supplementary Material

Full lists of crystallographic data are available from the authors on request.

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