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# SYNTHESIS, CHARACTERIZATION AND STRUCTURAL PROPERTIES OF SOME COPPER(II) TRANS-CINNAMATES AND RELATED COMPOUNDS

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Abstract—From the compounds  $Cu(Cin)_2$  (Cin = trans-cinnamic acid),  $Cu(Dmba)_22H_2O$ (Dmba = 3,4-dimethoxybenzoic acid) and  $Cu(Dmca)_2H_2O$  (Dmca = 3,4-dimethoxy-transcinnamic acid) were prepared three pyridine complexes. The species, [Cu(Cin)<sub>2</sub> (Py)<sub>2</sub>H<sub>2</sub>O·Py](Py = pyridine) (1), [Cu(Dmba)<sub>2</sub>(Py)<sub>2</sub>H<sub>2</sub>O](2) and [Cu(Dmca)<sub>2</sub>(Py)<sub>2</sub>] (3), were the subject of single crystal X-ray crystallographic studies. Compounds 1 and 2 are polymeric with the monomers, each of which contains one copper atom, being linked by hydrogen bonds. The copper atoms in the complexes 1 and 2 are five-coordinated with distorted square–pyramidal geometries. The basal planes of the square–pyramids consist of two oxygen atoms, from monodentate carboxylate groupings, and two nitrogen atoms, from pyridine ligands. The apices of the pyramids are occupied by water molecules. Compound 3 is monomeric with the copper atom occupying a six-coordinate pseudo-octahedral environment, being bonded to four oxygen atoms from two bidentate carboxylate moieties, and two nitrogen atoms, from the pyridine ligands.

The mass and infra-red spectra of the pyridine adducts and of the parent carboxylate complexes were measured and from a consideration of the evidence obtained, it is suggested that the parent complexes are dimeric in the solid state.

Trans-cinnamic acid occurs widely in nature and is likely to interact with metal ions. As part of a study investigating metal-cinnamate complexes, a number of copper(II) complexes have been prepared and characterized. The nature of the interaction between metal ions and the carboxylate group is well understood.<sup>1,2</sup> However, there are only a few reports of cinnamate complexes in the literature, but none of these contain trans-cinnamates. There have been several structural studies of copper(II) complexes of hydrocinnamic acid. Thus the copper(II) complex of 3,4-dimethoxyhydrocinnamic  $Cu[(CH_3O)_2C_6H_3CH_2CH_2CO_2]_2 \cdot CH_3OH^3,$ acid. has been shown to be dimeric, with four bridging carboxylate groups. Likewise, the complex  $[Cu_2(C_6H_5CH_2CH_2CO_2)_2(Phen)_2(H_2O)_2]^{2+}$ (Phen = 1,10-phenanthroline) is also dimeric but with

two bridging carboxylate groups.<sup>4</sup> The tin(IV) complex,  $SnCl_4(C_6H_5CHCHCO_2CH_2CH_3)_2$ , contains the ethyl ester of *cis*-cinnamic acid.<sup>5</sup>

In this paper we report the synthesis and characterization of the copper(II) complexes of *trans*cinnamic acid (CinH), 3,4-dimethoxy-*trans*-cinnamic acid (DmcaH) and 3,4-dimethoxybenzoic acid (DmbaH), and of their pyridine adducts. The crystal and molecular structures of the three pyridine adducts are also reported.

### **EXPERIMENTAL**

Infrared spectra in the region 4000–220 cm<sup>-1</sup> were measured as KBr discs with a Perkin–Elmer 1720-X FT Spectrometer. The diffuse reflectance spectra of solid samples were measured from 50,000–5000 cm<sup>-1</sup> on a Beckman Acta MIV Spectrophotometer. Fast Atom Bombardment (FAB) mass spectra were determined by the SERC Mass

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Spectrometry Service, University College, Swansea. Elemental analyses (CHN) were carried out by Medac Ltd of Brunel University. Copper contents were determined by digesting a known amount of sample in a mixture of sulphuric acid (3 cm<sup>3</sup>), nitric acid  $(2 \text{ cm}^3)$  and perchloric acid  $(1 \text{ cm}^3)$ , and diluting to a known volume. The copper content of the resulting solution was determined with a Perkin-Elmer 1100B Atomic Absorption Spectrophotometer. Water content was determined by thermogravimetric methods with a Stanton Redcroft STA 780 Thermogravimetric Balance.

### Synthesis of the complexes

The turquoise complex,  $Cu(Cin)_2$ , (Cin = transcinnamic acid), was prepared by adding a solution of copper(II) chloride dihydrate (0.85 g, 5 mmol) in ethanol (10 cm<sup>3</sup>) to a warm solution consisting of *trans*-cinnamic acid (1.48 g, 10 mmol), triethylamine (1.40 cm<sup>3</sup>, 10 mmol) and ethanol (30 cm<sup>3</sup>). Bulk samples of blue rod-shaped crystals of the pyridine adduct,  $Cu(Cin)_2(Py)_2H_2O \cdot Py$ , (2) were prepared by dissolving  $Cu(Cin)_2$  in a minimum volume of a mixture of hot ethanol and pyridine (2:1 v/v ratio). Single crystals of 1, which were suitable for X-ray diffraction work, were grown from a solution of  $Cu(Cin)_2$  in chloroform and pyridine (4:1 v/v ratio).

The emerald green complex,  $Cu(Dmba)_22H_2O$ , (Dmba = 3,4-dimethoxybenzoic acid) was prepared by adding a solution of copper(II) chloride dihydrate (0.85 g, 5 mmol) in water (5 cm<sup>3</sup>) to a warm solution consisting of 3,4-dimethoxybenzoic acid (1.82 g, 10 mmol), triethylamine (1.39 cm<sup>3</sup>, 10 mmol), water (20 cm<sup>3</sup>) and ethanol (5 cm<sup>3</sup>). Blue rod-shaped crystals of the pyridine adduct  $Cu(Dmba)_2(Py)_2H_2O$ , **2**, were prepared by dissolving Cu(Dmba)<sub>2</sub>2H<sub>2</sub>O in a hot mixture of ethanol and pyridine (2:1 v/v ratio). The crystals were found to be single and suitable for an X-ray diffraction study.

The green complex  $Cu(Dmca)_2H_2O$  (Dmca = 3.4-dimethoxy-trans-cinnamic acid), was prepared by adding a solution of copper(II) chloride dihydrate (0.17 g, 1 mmol) in ethanol  $(10 \text{ cm}^3)$  to a warm consisting of 3,4-dimethoxycinsolution namic acid (0.42 g, 2 mmol), triethylamine (0.28 cm<sup>3</sup>, 2 mmol) and ethanol (20 cm<sup>3</sup>). A bulk sample of the blue complex, Cu(Dmca)<sub>2</sub>(Py)<sub>2</sub>, 3, was prepared by dissolving Cu(Dmca)<sub>2</sub>H<sub>2</sub>O in a warm mixture of ethanol and pyridine (2:1 v/v ratio)while small diamond shaped crystals of Cu  $(Dmca)_2(Py)_2$ , which were suitable for X-ray diffraction studies, were grown from a solution of Cu(Dmca)<sub>2</sub>H<sub>2</sub>O in a mixture of dichloromethane, methanol and pyridine (2:1:1 v/v ratio).

The analytical data for the complexes are listed in Table 1.

# X-ray data collection, structure determination and refinement

Intensity data were collected with a Stoe Stadi2 diffractometer, using a graphite monochromator with Zr-filtered Mo- $K_{\alpha}$  radiation. A variable width scan,  $\omega$ , with a scan speed of  $0.0333^{\circ}$  s<sup>-1</sup>, applied to a width of  $1.5+0.5 \sin \mu/\tan \theta$ . Crystal data for 1, 2 and 3 are given in Table 2. In each case, the copper atom was located from a Patterson map, and the positions of all non-hydrogen atoms were determined from Fourier syntheses. The positions of the hydrogen atoms, bonded to the carbon atoms, were included in fixed positions estimated by assuming either tetrahedral or trigonal positions, as appropriate. Hydrogen atoms bonded in the

Compound	%C	%H	%N	%Cu	%H <sub>2</sub> O	$v(CO_2)_{asym}/cm^{-1}$	$v(CO_2)_{sym}/cm^{-1}$
Cu(Cin) <sub>2</sub>	59.9	3.9	0	17.4	0	1564	1401
	(60.4)	(4.0)	(0)	(17.8)	(0)		
$Cu(Cin)_2(Py)_2H_2O \cdot Py(1)$	64.4	4.9	6.7	10.2	not	1577	1382
	(64.6)	(5.1)	(6.9)	(10.4)	determined		
Cu(Dmca) <sub>2</sub> H <sub>2</sub> O	53.4	4.7	0	13.0	2.8	1561	1396
	(53.3)	(4.9)	(0)	(12.4)	(3.6)		
$Cu(Dmca)_2(Py)_2(3)$	60.8	5.3	4.5	10.1	0	1558	1385
	(60.4)	(5.1)	(4.7)	(10.0)	(0)		
Cu(Dmba) <sub>2</sub> 2H <sub>2</sub> O	47.1	5.1	0	13.3	7.2	1575	1388
	(46.8)	(4.8)	(0)	(13.8)	(7.8)		
$Cu(Dmba)_2(Py)_2H_2O(2)$	55.9	5.2	4.6	10.5	not	1555	1367
	(55.8)	(5.0)	(4.7)	(10.6)	determined		

Table 1. Analytical data (calculated values in parentheses) and positions of  $\nu(CO_2)_{asym}$  and  $\nu(CO_2)_{sym}$ 

	1	2	3
Formula	$CuN_{3}O_{5}C_{33}H_{31}$	$CuN_2O_9C_{28}H_{30}$	$CuN_2O_8C_{32}H_{32}$
M <sub>r</sub>	612.8	601.7	635.8
Class	Orthorhombic	Orthorhombic	Orthorhombic
Space group	P22 <sub>1</sub> 2 <sub>1</sub>	$P2_{1}2_{1}2_{1}$	Fd2d
a(Å)	5.882(6)	6.04(1)	9.10(1)
$b(\mathbf{A})$	10.829(12)	9.37(1)	14.91(1)
c(Å)	23.364(22)	22.61(2)	45.35(4)
$V(Å^3)$	1488.2	2645.5	6152.9
$D_{\rm m}(\rm g~cm^{-3})$	1.36	1.42	1.39
$D_{\rm c}(\rm g~cm^{-3})$	1.41	1.51	1.37
Z	2	4	8
$\mu$ (Mo- $K_{\alpha}$ ) cm <sup>-1</sup>	8.11	9.21	7.94
$2\theta \max$	50	50	50
No. of reflections measured	1543	2495	1506
used in final refinement	965	1033	653
criterion for observed	$I > 2\sigma(I)$	$I > 3\sigma(I)$	$I > 2\sigma(I)$
Final R value	0.082	0.079	0.076
R <sub>w</sub>	0.093	0.085	0.085

Table 2. Crystal data for compounds 1, 2 and 3

water molecules could not be located. It was not possible to identify the nitrogen atom in the solvent pyridine molecule in 1 and so all atoms were refined as carbon. Hydrogen atoms were not included in this solvent molecule. Calculations were carried out using the Shelx-76<sup>6</sup> system of programmes, together with some of our own programs on the Amdahl 5870 computer at The University of Reading. All three structures were refined by full matrix leastsquares until convergence was obtained. For 1 all non-hydrogen atoms were refined anisotropically. For 2 and 3 only the copper atoms were refined anisotropically and all other non-hydrogen atoms were refined isotropically. The weighting schemes were chosen to give equivalent values of  $w\Delta^2$  over ranges of  $F_0$  and  $\sin \theta / \lambda$ , where  $\sigma(F)$  was taken from counting statistics. Final  $R(R_w)$  values were 0.082, (0.093), 0.079, (0.085) and 0.076, (0.085) for 1, 2 and 3, respectively. In the final cycles of refinement, no shift/error ratio was greater than  $0.1\sigma$ . In the final difference Fourier maps, maximum and minimum peaks were 0.46, -0.55; 0.73, -0.81, 0.62, $-0.67 \text{ e/A}^3$  for 1, 2 and 3, respectively.

The dimensions in the metal coordination spheres for 1, 2 and 3 are given in Table 3. Details of the hydrogen bonds formed in 1 and 2 are given in Table 4. Supplementary Publication Material includes the final positional parameters for 1, 2 and 3, remaining dimensions not given in Table 3, anisotropic thermal parameters, hydrogen atom positions and structure factor tables.

## **RESULTS AND DISCUSSION**

### Description of structures

The three structures all contain monomeric copper complexes. The complex [Cu(Cin)<sub>2</sub>  $(Py)_2H_2O \cdot Py$ ] 1, (Fig. 1), has a two-fold-axis of symmetry along the Cu-O<sub>water</sub> bond [O(100)]. The two cinnamic acid ligands are related by symmetry, as are the two coordinated pyridine ligands. The remaining pyridine molecule is not coordinated, and surrounds a two-fold axis. The copper atom is in a five-coordinate environment, and has a distorted square-pyramidal geometry. The basal plane consists of two trans oxygen atoms, O(1) and the symmetry related  $O(1^*)$ , from the carboxylate groups, [Cu-O 1.894(14) Å] and two trans nitrogen atoms N(41) and the symmetry related  $N(41^*)$  from the pyridine ligands [Cu-N 2.074(17) Å]. The apex of the pyramid is occupied by the oxygen atom O(100)which is from the water molecule [Cu-O 2.243(16) Å]. Two of the five independent angles subtended at the metal centre deviate from the values found in а regular square based pyramid N(41)—Cu—O(100) 95.8(6)° and N(41)—Cu— N(41\*) 168.3(8)°.

The metal atom in the complex  $Cu(Dmba)_2$ (Py)<sub>2</sub>H<sub>2</sub>O, **2**, (Fig. 2), like the metal centre in **1**, is five coordinate with a coordination sphere of distorted square-pyramidal geometry. The complex is similar to **1** although it contains no cry-

Dista	nces (Å), angles (°)	
In 1	<b>a a</b> (1)	
	Cu - O(1)	1.894(14)
	CuN(41)	2.074(17)
	Cu—O(100)	2.243(16)
	O(1)— $Cu$ — $N(41)$	90.9(5)
	O(1)—Cu—O(100)	89.8(5)
	N(41)—Cu—O(100)	95.8(6)
	N(41)— $Cu$ — $N(41*)$	168.3(8)
	O(1)—Cu—O(1*)	179.6(8)
In 2		
	Cu—O(1)	1.948(18)
	Cu—O(21)	1.896(16)
	Cu-N(41)	1.952(22)
	Cu—N(51)	2.008(23)
	Cu-O(100)	2.494(17)
	O(1)CuO(21)	166.5(8)
	N(41)—Cu—N(51)	176.1(9)
	O(1)—Cu—N(41)	90.4(9)
	O(21)—Cu—N(41)	90.4(9)
	O(1)-Cu-N(51)	88.0(10)
	O(21)—Cu—N(51)	90.3(9)
	O(1)-Cu-O(100)	96.7(6)
	O(21)-Cu-O(100)	96.7(8)
	N(41)-Cu-O(100)	92.0(7)
	N(51)—Cu—O(100)	91.7(7)
In 3		
	Cu—O(1)	1.967(12)
	Cu—O(2)	2.583(13)
	Cu—N(41)	2.057(36)
	Cu—N(51)	1.951(40)
	O(1)CuO(2)	56.08(45)
	O(1)-Cu-N(41)	91.72(47)
	O(1)-Cu-N(51)	88.28(47)
	O(2)—Cu—N(41)	88.84(42)
	O(2)-Cu-N(51)	91.16(42)
	O(1)—Cu—O(1')	176.5(67)
	O(2)—Cu—O(2')	177.7(61)
	N(41)—Cu—N(51)	180.00†

Table 3. Dimensions in the metal coordination spheres in 1, 2 and 3

\* Symmetry element  $\frac{1}{2}$  - x, y,  $\frac{1}{2}$  - z.

† Parameter fixed.

stallographic symmetry. The basal plane consists of two *trans* oxygen atoms, [Cu—O(1) 1.948(18) Å and Cu—O(21) 1.896(16) Å], from the carboxylate groups, and two *trans* nitrogen atoms, [Cu—N(41) 1.952(22) Å and Cu—N(51) 2.008(23) Å], from the pyridine ligands. In 2 the basal metal-ligand bond lengths are of equivalent length while in 1 there is a significant difference in length between the two independent bonds. As in 1, the apex of the pyramid is occupied by the oxygen atom O(100) from the water molecule. However, the copper–oxygen dis-

Table 4. Hydrogen bonds in 1 and 2

In (1)	O(100)···O(2)	2.68(2)	(1 + x, y, z)
In (2)	O(100)···O(22)	2.75(2)	(x,y,z)
	O(100)···O(2)	2.67(2)	(1 + x, y, z)

tance is much longer in [2 (Cu-O(100) 2.494(17) Å] than in 1 [Cu-O(100) 2.243(16) Å] and this could be attributed to differences between the hydrogen bond patterns in the two structures (see later). Of the ten angles subtended at the metal centre in 2 three differ from the angles of a regular square-based pyramid. The trans angle O(1)—Cu—O(21) is less than  $180^{\circ}$  [166.5(8)°] with the related O(100)—Cu—O(1)and O(100)—Cu—O(21) angles exceeding  $90^{\circ}$  being 96.7(6)° and 96.7(8)°, respectively. Interestingly, while in 2 it is the angles involving the basal oxygen atoms that deviate from the regular values [the angles O(1)—Cu—O(21), O(100)—Cu—O(1) and O(100)—Cu—O(21)] it is the angles formed by the basal nitrogen atoms in 1 (N(41)-Cu-O(100) and N(41)—Cu—N(41\*)] that show the deviation.

The complex,  $Cu(Dmca)_2(Py)_2$ , (3), (Fig. 3), has a two fold axis of symmetry, upon which the N(41)—Cu—N(51) moiety lies. The two pyridine ligands are bisected by this axis and the two Dmca ligands are related by the symmetry axis. The copper atom has a six-coordinate distorted octahedral environment, being bound to four oxygen atoms, O(1) [Cu-O 1.967(12) Å] and O(2) (Cu-O 2.583(13) Å], and the symmetry related O(1)' and O(2)' from the carboxylate groups, and two nitrogen atoms, N(41) [Cu-N 2.057(36) Å] and N(51) [Cu—N 1.951(40) Å], from the pyridine ligands. In the absence of the water molecule, that is present in both 1 and 2, in 3 both oxygen atoms of the carboxylate groups are bonded to the metal to form four membered chelate rings [Cu-O(1)-C(3) -O(2) and the symmetry related ring]. It is interesting to note that of the angles subtended at the metal centre only the carboxylate "bite" angle, that is part of the four membered chelate ring, deviates significantly from the value seen in a regular octahedron  $[O(1)-Cu-O(2) 56.1(4)^{\circ}]$ . Furthermore the two Cu-O distances in the chelate ring differ significantly [Cu-O(1) 1.967 (12) Å] and [Cu-O(2) 2.583(13) Å]. It is noteworthy that the O(1)—C(3)—O(2) angle  $[119(2)^{\circ}]$ of the carboxyl group is equivalent to the carboxyl group angle found in 1  $[O(1)-C(3)-O(2) 122(2)^{\circ}]$ but smaller than those in 2 [O(1)-C(3)-O(2)] $126(3)^{\circ}$  and O(21)—C(23)—O(22) 127(3)°]. In both 1 and 2 the carboxyl groups are monodentate but



Fig. 1. The structure of 1 in the c projection. Hydrogen atoms are omitted for clarity. Hydrogen bonds are shown as unshaded lines.

are involved in complex hydrogen bonding interactions that may account for the difference in their O--C--O angles (see later).

Intermolecular hydrogen bonding is exhibited by both 1 and 2, and the relative dimensions are listed in Table 4. In 1, the oxygen atoms from the carboxylate groups, that are not bonded to copper  $[O(2) \text{ and } O(2^*)]$ , both lie below the basal plane on the opposite side to the water molecule (Fig. 1). They take part in two intermolecular hydrogen



Fig. 2. The structure of 2 in the c projection. Hydrogen bonds are shown as unshaded lines.



Fig. 3. The structure of 3.

bonds, one from each atom, to the hydrogen atoms bound to the oxygen atom O(100) in another  $Cu(Cin)_2(Py)_2H_2O$  unit thus forming a giant chelate ring. The copper benzoate complexes  $[Cu(C_6H_5)]$  $(COO)_{2}(Py)_{2}(H_{2}O)^{7}$ and  $[Cu(C_6H_5COO)_2(\beta (C_6H_7N)_2(H_2O)^8$  exhibit similar features. This type of hydrogen bonding arrangement can be contrasted with that found in 2, where the two uncoordinated oxygen atoms from the carboxylate groups, lie on opposite sides of the basal plane (Fig. 2). The oxygen atom, O(2), lies on the same side as the water molecule while O(22) lies on the opposite side. O(2) thus forms an intramolecular hydrogen bond to O(100) while O(22) forms an intermolecular hydrogen bond to O(100) in the adjacent molecule. It seems likely that the greater Cu-Owater bond length in 2 compared to that in 1 is due to the formation of the intramolecular hydrogen bond. The difference in the size of the O-C-O angle in 1  $[O(1)-C(3)-O(2) 122(2)^{\circ}]$  compared to those in 2  $[O(1)-C(3)-O(2) \ 126(3)^{\circ}$  and O(21)-C(23)---O(22) 127(3)°] can be attributed to the different hydrogen bonding patterns in 1 and 2. It is clear from Fig. 1 that  $[Cu(Cin)_2(Py)_2H_2O \cdot Py]$  1, is comprised of chains of Cu(Cin)<sub>2</sub>(Py)<sub>2</sub>H<sub>2</sub>O units, with two hydrogen bonds linking each pair of units, while from Fig. 2 it is apparent that the complex  $[Cu(Dmba)_2(Py)_2H_2O]$  2, is composed similarly of chains but which have only one hydrogen bond linking each pair of molecules. A similar pattern of hydrogen bonding to that in **2** is seen in the benzoate complex,  $\{Cu(C_6H_5COO)_2[\gamma-(C_6H_7N)]_2\}$ .<sup>9</sup>

The metal centres in 1 and 2 are truly five coordinate and there are no interactions between the copper atom and the oxygen atom [O(100)], from the water molecule in a neighbouring unit, in either 1 or 2. This is shown by the intermolecular Cu—O(100) distances, which are 3.64(2) Å and 3.61(2) Å in 1 and 2, respectively. These structures can be contrasted with the structure adopted by the complex [Cu(TsglyH)<sub>2</sub>(4-Mepy)<sub>2</sub>(H<sub>2</sub>O)](TsglyH = N-tosylglycinate, 4-Mepy = 4-methylpyridine), in which square planar  $CuO_2N_2$  moieties, formed by Cu(TsglyH)<sub>2</sub>(4-Mepy)<sub>2</sub>, are linked by bridging H<sub>2</sub>O molecules, to yield polymeric chains containing six coordinate metal centres with Cu—O<sub>water</sub> bond distances of 2.755(1) Å.<sup>10</sup>

### Spectroscopic studies

Having determined the structures of 1, 2 and 3 it is helpful to compare their mass and infra-red spectra with those of the parent carboxylate compounds from which the pyridine adducts were prepared.

The mass spectra of four of the six complexes studied were measured, namely those of

 $[Cu(Dmba)_2(H_2O)_2]$ ,  $[Cu(Dmca)_2(H_2O)]$ , 2 and 3. The m/z ratios of the dominant peaks in the mass spectrum of [Cu(Dmba)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] were as follows with relative intensity and the assignments being given in parentheses 851 (15) [Cu<sub>2</sub>(Dmba)<sub>4</sub>], 668 (28) [Cu<sub>2</sub>(Dmba)<sub>3</sub>], 489 (55) [Cu<sub>2</sub>(Dmba)<sub>2</sub>], 424 (18) [Cu(Dmba)<sub>2</sub>], 165 (100) [(CH<sub>3</sub>O)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>CO]. For  $[Cu(Dmca)_2(H_2O)]$  the related data are 957 (15)  $[Cu_2(Dmca)_4]$ , 748 (12)  $[Cu_2(Dmca)_3]$ , 542 (77) [Cu<sub>2</sub>(Dmca)<sub>2</sub>], 497 (15) [?], 477 (33) [Cu(Dmca)<sub>2</sub>], 362 (42) [?], 333 (27) [?], 208 (100) [Dmca]. From a consideration of these data it would be tempting to state that unequivocal evidence was obtained for  $[Cu(Dmba)_2(H_2O)_2]$  $[Cu(Dmca)_2(H_2O)]$ being dimeric in the solid state. However, the mass spectra of 2 and 3, that were clearly shown to be monomeric in the solid state, contained peaks that were also assignable to Cu<sub>2</sub>(Dmba)<sub>4</sub> and Cu<sub>2</sub>(Dmca)<sub>4</sub>. Indeed the whole mass spectra of the two pyridine complexes, except for the low mass features ascribable to pyridine, were very similar to those of the appropriate parent compound. However, the spectra of pyridine complexes were obtained from solutions of the compounds in dimethylsulphoxide and it is probable that on dissolution the compounds dimerise with loss of pyridine.

From studies of the IR spectra of carboxylate complexes, it has been suggested that the difference in wave number between the positions of  $v(CO_2)_{asym}$ and  $v(CO_2)_{sym}$  (commonly denoted  $\Delta$ ) can be used as secondary evidence for assigning structure to compounds.<sup>11</sup> Thus, for example,  $\Delta > 200$  cm<sup>-1</sup> is said, for ethanoates, to be indicative of the presence of monodentate carboxylate groups. However, it was found that  $\Delta$  for some monodentate ethanoates was lower than 200 cm<sup>-1</sup>, and in these cases X-ray diffraction studies showed that the uncoordinated oxygen atom of the carboxyl group was involved in hydrogen bonding. In summary, although there is some overlap between the groups, in general  $\Delta$ values are said to form a series with  $\Delta_{unidentate}$  >  $\Delta_{\text{ionic}} > \Delta_{\text{bridging}} > \Delta_{\text{chelating}}$ . Values for  $\nu(\text{CO}_2)_{\text{asym}}$  and  $v(CO_2)_{sym}$  for 1, 2, 3 and their parent compounds are listed in Table 1. Compounds 1 and 2 contain monodentate carboxylate groupings, in which the oxygen atom not coordinated to copper participates in hydrogen bonding, and have relatively high  $\Delta$ values  $[195 \text{ cm}^{-1} \mathbf{1} \ 188 \text{ cm}^{-1} \mathbf{2}]$ . Compound 3 contains very unsymmetrical chelating carboxyl groups and exhibits a  $\Delta$  of 173 cm<sup>-1</sup> which is significantly lower than for 1 and 2. The parent compounds of pyridine complexes, namely, the  $Cu(Cin)_2$ ,  $[Cu(Dmca)_2(H_2O)]$  and  $[Cu(Dmba)_2(H_2O)_2]$  have  $\Delta$ 

values of 163, 165, and 187 cm<sup>-1</sup>, respectively and the values are within the range expected for chelating and/or bridging carboxyl groups.

It is clear that the mass and IR spectra of the parent carboxylate complexes do not provide definitive evidence for structure. However, we believe that it is likely that the parent carboxylates are dimeric in the solid state. Facilities for the measurement of magnetic properties over a temperature range, that could have provided useful data, were not available to us and the diffuse reflectance spectra of all six complexes were broad. The spectra of the green complexes Cu(Cin)<sub>2</sub>,  $[Cu(Dmca)_2(H_2O)]$  and  $[Cu(Dmba)_2(H_2O)_2]$  each contain one broad band at approximately 14,500  $cm^{-1}$ . It is not possible to assign these bands but the electronic spectrum of the dimeric green hydrocinnamate  $[Cu((CH_3O)_2C_6H_3CH_2CH_2CO_2)_2]$  $(CH_3OH)$ <sup>3</sup> also contains one band in this region, at about 14,700 cm<sup>-1</sup>. The difficulty in using diffuse reflectance spectra as a structural tool is illustrated by the results obtained for the pyridine compounds. The spectra of the five-coordinate compounds 1, and 2 contain one band at approximately 15,500  $cm^{-1}$  as does the spectrum of the six-coordinate compound 3.

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#### REFERENCES

- 1. C. Oldham, Prog. Inorg. Chem. 1968, 10, 223.
- 2. J. Catterick and P. Thornton, Adv. Inorg. Chem. Radiochem. 1977, 20, 291.
- L. P. Battaglia, A. B. Corradi and M. A. Zorrodu, J. Cryst. Spectrosc. 1990, 20, 161.
- 4. E. Dubler, U. K. Haring, K. H. Scheller, P. Baltzer and H. Sigel, *Inorg. Chem.* 1984, 23, 3785.
- J. C. Huffman, L. N. Lewis and K. G. Caulton, *Inorg.* Chem. 1980, 19, 2755.
- 6. G. M. Sheldrick, "SHELX-76", Program for Crystal Structure Determination, University of Cambridge, England (1976).
- F. N. Musaev, K. S. Mamedov, E. M. Movsumov and I. R. Amiraslanov, *Koord. Khim.* 1979, 5, 119.
- M-M. Borel, F. Busnot and A. Leclaire, Z. Anorg. Allg. Chem. 1979, 449, 177.
- M-M. Borel, L. Boniak, F. Busnot and A. Leclaire, *Rev. Chim. Min.* 1978, 15, 397.
- L. P. Battaglia, A. B. Corradi and L. Menabue, *Inorg. Chem.* 1983, 22, 3251.
- 11. G. B. Deacon and R. J. Phillips, Coord. Chem. Rev. 1980, 33, 227.