Synthesis, Spectroscopic and X-Ray Structural Characterization of Ternary Complexes of Copper(II) and 2,5-Dimethoxycinnamic Acid with Phenanthrolines†

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The complexes [Cu(dmc)$_2$L] [Hdmc = 2,5-dimethoxycinnamic acid; L = 1,10-phenanthroline (phen), 4,7-dimethyl-1,10-phenanthroline (4,7-dmphen) or 2,9-dimethyl-1,10-phenanthroline (2,9-dmphen)] were synthesised and characterized by magnetic measurements, EPR and reflectance electronic spectroscopy. The crystal structure of [Cu(dmc)$_2$(2,9-dmphen)] has been determined by X-ray diffraction: it consists of discrete units [Cu(dmc)$_2$(2,9-dmphen)] in which a very asymmetric $CuN_2O_2O'_2$ chromophore is present with the two nitrogen atoms from 2,9-dmphen nearly symmetrically chelated [Cu–N 1.988(4) and 2.045(3) Å], two carboxylic oxygens of a bidentate dmc molecule [Cu–O 1.979(3) and 2.242(3) Å], and the oxygen atom of a monodentate carboxylic acid group of a second dmc molecule. Copper deviates from the 2,9-dmphen plane by 0.1811(7) Å and the carboxylic acid groups lie on planes roughly orthogonal [92.1(3)°]; the second carboxylic oxygen of the monodentate dmc molecule is involved in a long contact with the metal [Cu $\cdots$ O 2.959(4) Å].

It has been suggested that under certain conditions copper phenanthroline complexes play a role in the cleavage of DNA amd differences in the chemical arrangement can result in very striking differences in biopharmacological activity.[1] Binary copper–1,10-phenanthroline and –2,9-dimethyl-1,10-phenanthroline systems have been reported to possess very different biological characteristics despite being conformational homologues.[2–8] Interesting papers have been published on ternary complexes containing phenanthrolines and amino acids which are potential models for enzyme–metal ion substrate interactions and may be related to a transport form of copper in human serum.[9–11].

In the present study our attention has been focused on ternary complexes of the type [Cu(dmc)$_2$L] [L = 1,10-phenanthroline (phen), 4,7-dimethyl-1,10-phenanthroline (4,7-dmphen) or 2,9-dimethyl-1,10-phenanthroline (2,9-dmphen); Hdmc = 2,5-dimethoxycinnamic acid]. The compounds were characterized in the solid state by means of magnetic measurements, EPR, reflectance electronic spectroscopy and X-ray diffraction measurements for [Cu(dmc)$_2$(2,9-dmphen)]. The aim was to ascertain whether the structural variety of the above binary systems is preserved or even enlarged in these new ternary compounds and whether the presence of methyl substituents or their position on the aromatic ring is the dominant factor in determining the co-ordination behaviour of the ligands.

Cinnamic acids are widely distributed in higher plants both in the free form and as glucose esters and amides.[12] The biological activity of some of them has been demonstrated[13] and some of their copper(II) complexes inhibit the growth of different microbial strains.[14] The association of cinnamic acids with copper phenanthrolines may be a model for conjugated ('bound') auxins.[15,16]

Experimental

Analytical and Physical Measurements.—Elemental analyses were carried out on a Perkin-Elmer 240B instrument. Thermogravimetry was carried out under an air flow on a Perkin-Elmer TGS-2 instrument using a heating rate of 5 °C min^{-1} in the temperature range 25–850 °C. Magnetic susceptibilities were measured at room temperature by using a Bruker B-MB4 Faraday system with a Cahn 1000 electrobalance using Hg[Co(SCN)$_4$] as a calibrant, and correcting for diamagnetism with the appropriate Pascal constants. Reflectance electronic spectra were recorded on a Beckman-Acta MIV and a JASCO Uvidec 610 spectrophotometer. The EPR spectra of polycrystalline samples at 298 and 125 K were obtained in the X-band using a Bruker ER 220D-SRC spectrometer. The microwave frequency was calibrated against powder diphenylpicrylhydrazyl (dpph) (g = 2.0036).

Materials.—2,5-Dimethoxycinnamic acid, the phenanthrolines (Aldrich) and the pure metal salt (Fluka) were used as received. The solvents and chemicals were of high purity. The binary complex [{Cu(dmc)$_2$}$_2$]·2H$_2$O was used as a starting material in the synthesis of the ternary complexes.

Preparation of the Binary Complex.—The complex [{Cu(dmc)$_2$}$_2$]·2H$_2$O was prepared by mixing a methanolic solution (27 cm^3) of copper(II) acetate hydrate (0.33 mmol, 66 mg) with a solution of 2,5-dimethoxycinnamic acid (0.66 mmol, 137 mg) in the same solvent (17 cm^3). Under magnetic stirring the solution yielded a green powdery precipitate (Found: C, 51.45; H, 5.10;

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Table 1 Experimental data for the crystallographic analysis

Formula	$C_{36}H_{34}CuN_2O_8$
M	686.2
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	18.213(1)
b/Å	8.649(1)
c/Å	20.728(2)
β/°	105.32(1)
U/Å^3	3149.1(5)
Z	4
D_c	1.447
D_m	1.49
Reflections for lattice parameters number	25
θ range/°	22.6–40.1
F(000)	1428
T/K	294
Crystal size/mm	0.13 × 0.36 × 0.55
μ/cm^{-1}	14.18
Scan speed/° min^{-1}	4–12
Scan width/°	1.2 + 0.35 tan θ
θ range/°	3–60
h,k,l ranges	−25 to 25, 0–12, 0–22
Standard reflection	521
Maximum intensity variation (%)	3
Scan mode	ω–2θ
No. of reflections measured	5234
No. of reflections used in the refinement	3752 [$I > 3\sigma(I)$]
No. of refined parameters	545
$R = \Sigma\|\Delta F\|/\Sigma\|F_o\|$	0.0415
$R' = [\Sigma w(\Delta F^2)/\Sigma w F_o{}^2]^{\frac{1}{2}}$	0.0443
k, g in $w = k/[\sigma^2(F_o) + gF_o{}^2]$	1,258, 8.77 × 10^{-4}
Maximum, minimum height in final ΔF map/e Å^{-3}	0.35, −0.22

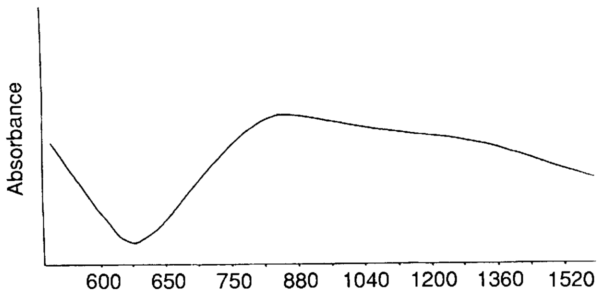

Fig. 1 Reflectance electronic spectrum of [Cu(dmc)$_2$(2,9-dmphen)]

Cu, 12.0; H_2O, 7.0. Calc. for $C_{22}H_{26}CuO_{10}$: C, 51.4; H, 5.05; Cu, 12.3; H_2O, 7.0%).

Preparation of the Ternary Complexes.—[Cu(dmc)$_2$(phen)]·H_2O. To a methanolic (11 cm^3) suspension of the binary complex [{Cu(dmc)$_2$}$_2$]·2H_2O (0.1 mmol, 100 mg) was added dropwise a solution of 1,10-phenanthroline (0.2 mmol, 40 mg) in the same solvent (9 cm^3) with stirring. To the resultant solution was added diethyl ether (100 cm^3) and after 1 d small blue-green crystals of the compound separated (Found: C, 60.3; H, 4.35; Cu, 9.0; N, 4.15; H_2O, 2.0. Calc. for $C_{34}H_{32}CuN_2O_9$: C, 60.4; H, 4.75; Cu, 9.4; N, 4.15; H_2O, 2.6%). Loss of the water molecule occurs in the range 40–70 °C, suggesting the non-involvement of this molecule in the co-ordination sphere of copper(II).

[Cu(dmc)$_2$(4,7-dmphen)]. To a methanolic (15 cm^3) suspension of the binary complex [{Cu(dmc)$_2$}$_2$]·2H_2O (0.12 mmol, 128 mg) was added dropwise a solution of 4,7-dimethyl-1,10-phenanthroline (0.24 mmol, 50 mg) in the same solvent (6 cm^3). To the resultant solution was added diethyl ether (100 cm^3) and after 1 d small blue crystals separated (Found: C, 62.5; H, 4.80; Cu, 9.0; N, 4.15. Calc. for $C_{36}H_{34}CuN_2O_8$: C, 63.05; H, 4.95; Cu, 9.25; N, 4.10%).

[Cu(dmc)$_2$(2,9-dmphen)]. To a methanolic (15 cm^3) suspension of the binary complex [{Cu(dmc)$_2$}$_2$]·2H_2O (0.24 mmol, 240 mg) was added dropwise a methanolic solution (6 cm^3) of 2,9-dimethyl-1,10-phenanthroline (0.96 mmol; 200 mg) with slow magnetic stirring at 60 °C. The resultant solution was allowed to stand at room temperature and after 1 d gave yellow crystals of the compound suitable for X-ray structural analysis (Found: C, 63.3; H, 5.05; Cu, 10.0; N, 4.20. Calc. for $C_{36}H_{34}CuN_2O_8$: C, 63.05; H, 4.95; Cu, 9.25; N, 4.10%).

Crystallography. The crystal of [Cu(dmc)$_2$(2,9-dmphen)] was mounted in a random orientation on a Siemens AED single-crystal automated diffractometer: the resulting crystal data and details concerning data collection and refinements are in Table 1. The structure was solved by Patterson and Fourier methods and refined by full-matrix least squares with anisotropic thermal parameters for the non-hydrogen atoms; these were located from a ΔF map and introduced in the last refinement cycle. No absorption correction was applied. The final atomic coordinates are given in Table 2. Atomic scattering factors were taken from ref. 17. The calculations were performed on a GOULD 33/77 computer with SHELX,[18] ORTEP[19] and PARST[20] programs.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

EPR and Electronic Measurements.—All the ternary complexes show a 'normal' room-temperature magnetic moment (μ_{eff} = 1.8–1.9), characteristic of magnetically dilute copper(II) compounds.

The EPR spectra of polycrystalline samples of [Cu(dmc)$_2$(phen)]·H_2O and of [Cu(dmc)$_2$(4,7-dmphen)] are of axial type ($g_{\parallel}$ = 2.276, $g_{\perp}$ = 2.06) with $g_{\parallel} > g_{\perp} >$ 2.040 suggesting for both compounds a $d_{x^2-y^2}$ (or d_{xy}) ground state, characteristic of a square-planar, square-based pyramidal, or octahedral stereochemistry.[21] The reflectance electronic spectra in the range λ_{max} = 650–700 nm are consistent with a distorted-tetragonal environment involving nitrogen donors. In conclusion the EPR and reflectance electronic spectra indicate an essentially identical structure and the same donor set N_2O_2 for both compounds.

On the contrary, the EPR spectrum of a polycrystalline powder of [Cu(dmc)$_2$(2,9-dmphen)] is clearly of the rhombic type with g_1 = 2.29, g_2 = 2.181, g_3 = 2.034, suggesting a pronounced distortion from square symmetry. In this case, the lowest g value lies between the values obtainable in rhombic spectra for distorted square-based pyramidal or for distorted trigonal-bipyramidal stereochemistry.[22] The EPR spectrum is slightly dependent on temperature with some differences in the g values: g_1 = 2.31, g_2 = 2.17, g_3 = 2.02 at 125 K. Although difficult to interpret in detail, this can presumably be attributed to packing effects in the solid compound or possibly to some non-rigid property of five-co-ordinate structures having the d^9 configuration.[23–25] The reflectance electronic spectrum of the powdered compound (Fig. 1) is consistent with five-co-ordination of the metal ion and with a distorted square-pyramidal structure, in that there is doublet band, even if only partially resolved, at λ_{max} = 840 and 1280 nm with a similar splitting to those reported for copper(II) complexes having the same structure.[26]

Description of the Structure of [Cu(dmc)$_2$(2,9-dmphen)].—The unit cell comprises four discrete monomeric units of [Cu(dmc)$_2$(2,9-dmphen)] (Fig. 2). The copper co-ordination geometry cannot be described in terms of a regular polyhedron, but as a very distorted square pyramid or trigonal bipyramid. In the first case the base is formed by atoms N(1), N(2) from a 2,9-dmphen molecule and O(5) and O(6) from one carboxylic group of a dmc ligand; the apex is occupied by the carboxylic oxygen O(1) of a second dmc molecule. In the second case the

Table 2 Atomic coordinates with their estimated standard deviations (e.s.d.s) in parentheses for [Cu(dmc)$_2$(2,9-dmphen)]

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Cu	0.146 56(3)	0.146 24(7)	0.423 03(3)	C(14)	0.386 6(2)	−0.115 7(5)	0.494 4(2)
O(1)	0.197 6(2)	0.306 6(4)	0.379 6(2)	C(15)	0.457 0(2)	−0.201 4(5)	0.497 8(2)
O(2)	0.094 1(2)	0.449 6(5)	0.362 0(2)	C(16)	0.517 5(2)	−0.192 1(5)	0.554 9(2)
O(3)	0.334 3(2)	0.417 7(4)	0.215 5(2)	C(17)	0.567 1(3)	−0.083 4(8)	0.663 3(2)
O(4)	0.279 8(2)	1.044 8(4)	0.211 9(2)	C(18)	0.585 6(2)	−0.266 4(6)	0.556 9(2)
O(5)	0.200 3(2)	−0.028 8(4)	0.394 2(2)	C(19)	0.593 6(2)	−0.351 3(6)	0.502 9(2)
O(6)	0.253 6(2)	0.059 5(4)	0.494 2(2)	C(20)	0.533 5(3)	−0.361 8(5)	0.445 6(2)
O(7)	0.504 8(2)	−0.109 6(4)	0.607 4(2)	C(21)	0.486 8(3)	−0.463 3(7)	0.335 8(3)
O(8)	0.547 6(2)	−0.447 5(4)	0.394 6(2)	C(22)	0.466 0(2)	−0.286 9(5)	0.442 9(2)
N(1)	0.105 1(2)	0.261 5(4)	0.488 6(2)	C(23)	0.221 7(3)	0.404 3(7)	0.539 3(3)
N(2)	0.036 2(2)	0.073 9(5)	0.389 4(2)	C(24)	0.141 0(3)	0.361 4(5)	0.535 8(2)
C(1)	0.159 4(2)	0.426 3(6)	0.358 2(2)	C(25)	0.104 1(3)	0.425 6(6)	0.581 3(2)
C(2)	0.194 6(3)	0.547 5(5)	0.324 1(2)	C(26)	0.030 0(3)	0.390 2(6)	0.576 5(3)
C(3)	0.254 0(2)	0.524 1(5)	0.300 8(2)	C(27)	−0.009 4(3)	0.289 8(6)	0.526 5(2)
C(4)	0.282 9(2)	0.631 0(5)	0.258 1(2)	C(28)	−0.088 1(3)	0.250 1(7)	0.515 6(3)
C(5)	0.323 4(2)	0.574 3(5)	0.214 6(2)	C(29)	−0.123 7(3)	0.159 1(7)	0.464 5(3)
C(6)	0.369 1(3)	0.354 2(6)	0.166 9(3)	C(30)	−0.083 6(3)	0.095 5(6)	0.419 4(3)
C(7)	0.349 1(3)	0.674 6(5)	0.172 3(2)	C(31)	−0.116 9(3)	−0.003 0(7)	0.364 9(2)
C(8)	0.334 1(3)	0.830 1(6)	0.173 2(2)	C(32)	−0.074 9(3)	−0.055 0(7)	0.325 3(3)
C(9)	0.292 6(2)	0.887 5(5)	0.215 5(2)	C(33)	0.003 0(3)	−0.017 1(6)	0.336 9(3)
C(10)	0.232 3(3)	1.106 7(6)	0.249 2(3)	C(34)	0.047 5(3)	−0.073 3(10)	0.291 0(3)
C(11)	0.267 1(2)	0.789 9(5)	0.258 0(2)	C(35)	−0.006 8(2)	0.128 7(5)	0.428 9(2)
C(12)	0.255 8(2)	−0.028 9(5)	0.447 0(2)	C(36)	0.030 6(2)	0.228 9(5)	0.482 9(2)
C(13)	0.320 7(2)	−0.131 3(5)	0.449 0(2)				

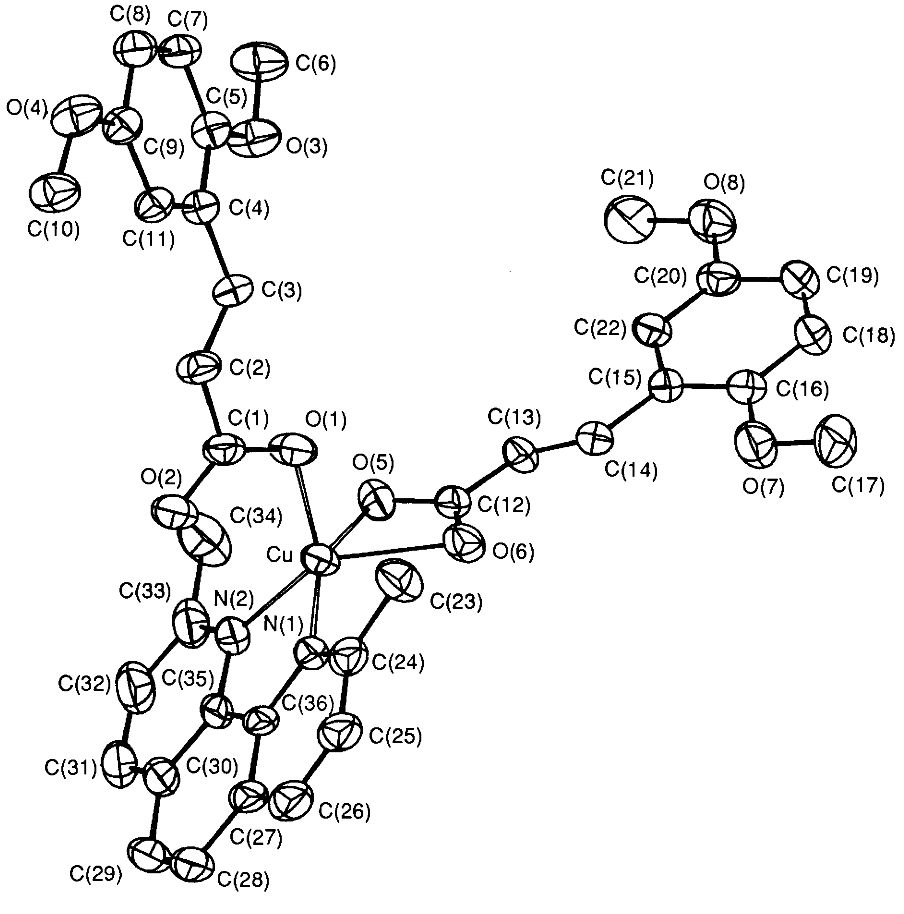

Fig. 2 Perspective view of [Cu(dmc)$_2$(2,9-dmphen)]

apices are O(6) and N(2) and the equatorial plane contains atoms N(1), O(1) and O(5).

The two dmc molecules show different behaviours being co-ordinated *via* carboxylate groups which are mono- or bidentate. The bidentate C(12)O(5)O(6) group is asymmetrically chelated with Cu–O(5) 1.979(3) and Cu–O(6) 2.242(3) Å, while the C(1)O(1)O(2) of the other molecule is monodentate with Cu–O(1) 2.010(3) Å; the second carboxylic oxygen O(2) forms a long contact with the metal Cu···O(2) 2.959(4) Å. Both modes are found in the literature, but asymmetric bidentate carboxylate groups are less common: similar situations were found, for example, in (*o*-phthalato)bis(pyridine)copper(II)[27] with Cu–O 1.954(5), 2.285(4) and 1.967(5), 2.316(4) Å, O–Cu–O 61.4(2) and 60.6(2)° and in μ-carbonato-bis[*N*,*N*,-

Table 3 Selected bond distances (Å) and angles (°) with e.s.d.s in parentheses

Cu–O(1)	2.010(3)	Cu–N(1)	1.988(4)
Cu–O(5)	1.979(3)	Cu–N(2)	2.045(3)
Cu–O(6)	2.242(3)		
O(1)–Cu–N(1)	105.3(1)	O(5)–Cu–N(1)	153.8(4)
O(1)–Cu–N(2)	126.0(1)	O(5)–Cu–N(2)	100.5(1)
O(1)–Cu–O(5)	93.9(1)	O(6)–Cu–N(1)	98.0(1)
O(1)–Cu–O(6)	95.8(1)	O(6)–Cu–N(2)	136.7(1)
O(5)–Cu–O(6)	61.9(1)	N(1)–Cu–N(2)	82.5(1)

N'N'',*N''*-pentaethyldiethylenetriamine)copper(II)] diperchlorate,[28] Cu–O 1.946(5), 2.305(6) and 1.954(5), 2.346(5) Å, O–Cu–O 61.2(2) and 61.1(2)°. The 2,9-dimethylphenanthroline molecule is planar and the copper deviates from this plane by 0.1811(7) Å; the ligand is nearly symmetrically chelated and the values Cu–N 1.988(4) and 2.045(3) Å and N(1)–Cu–N(2) 82.5(1)° fully agree with those usually found, *e.g.* 1.994(3) and 2.020(3) Å and N–Cu–N 82.0(1)° in (L-aspartato)aqua(1,10-phenanthroline)copper(II) tetrahydrate.[29] The two carboxylic groups lie on planes roughly orthogonal [92.1(3)°] and form with those of 2,9-dimethylphenanthroline the dihedral angles 78.2(3) and 43.0(3)° for C(1)O(1)O(2) and C(12)O(5)O(6) respectively. The molecular packing involves several contacts among carbon and oxygen atoms, some of which could be interpreted as weak hydrogen bonds: C(23) ··· O(6) 3.224(7) Å, C(23)–H(25) ··· O(6) 144(2)°; C(7) ··· O(7^{I}) 3.490(6) Å, C(7)–H(6) ··· O(7^{I}) 148(2)° (I $x, \frac{1}{2} - y, z - \frac{1}{2}$); C(8) ··· O($8^{II}$) 3.452(6) Å, C(8)–H(7) ··· O(8^{II}) 161(3)° (II $1 - x, \frac{3}{2} + y, \frac{1}{2} - z$); C(26) ··· O($2^{III}$) 3.189(7) Å, C(26)–H(27) ··· O(2^{III}) 158(3)° (III $-x, 1 - y, 1 - z$).

Conclusion

The spectroscopic results for the solid compounds show a clear distinction between the tetragonal environment in both [Cu(dmc)$_2$(phen)] and [Cu(dmc)$_2$(4,7-dmphen)] and the strong distortion from square-planar symmetry for [Cu(dmc)$_2$(2,9-dmphen)]. However, it has been very difficult to distinguish clearly in five-co-ordination between the possible square-based pyramidal and trigonal-bipyramidal stereochemistries in the third compound.

The striking differences found in the spectroscopic, supported by the X-ray diffraction measurements for [Cu(dmc)$_2$(2,9-dmphen)], substantiate that the steric hindrance caused by the presence of methyl groups in the 2,9 positions on the aromatic ring close to the co-ordination sites plays a fundamental role in the co-ordination behaviour of the ligands. Methyl groups in the 4,7 positions have no affect on the co-ordination when compared with the complex with unsubstituted phenanthroline.

The differences in the complexes with these phenanthroline ligands had been demonstrated previously in solution by ESR measurements[1] and by electrochemical studies on binary complexes of copper(II) phenanthrolines, as well as on ternary complexes of copper(II) with the same phenanthrolines and 2,5-dimethoxycinnamic acid ligands.[30]

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Received 4*th December* 1990; *Paper* 0/05453D