Copper(II) Complexes with Anti-inflammatory Drugs as Ligands. Molecular and Crystal Structures of Bis(dimethyl sulphoxide)tetrakis(6-methoxy-α-methyl-2-naphthaleneacetato)dicopper(II) and Bis(dimethyl sulphoxide)tetrakis[1-methyl-5-(*p*-toluoyl)-1*H*-pyrrole-2-acetato]dicopper(II)†

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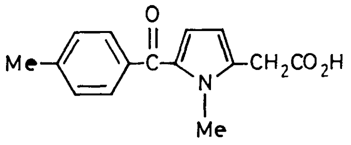
The copper complexes of tolmetin [1-methyl-5-(*p*-toluoyl)-1*H*-pyrrole-2-acetic acid (HL^1)], ibuprofen [α-methyl-4-(isopropylmethyl)benzeneacetic acid (HL^2)], and naproxen [6-methoxy-α-methyl-2-naphthaleneacetic acid (HL^3)], common anti-inflammatory drugs were prepared and characterized. The available evidence supports a dimeric structure for the dimethyl sulphoxide (dmso) adducts and monomeric for the pyridine analogues. The e.s.r. spectra of the powdered solids are consistent with spin $S = 1$ and g values for dimers, $g_{\parallel} = 2.38$ and $g_{\perp} = 2.07$. The crystal structures of $[Cu_2L^1_4(dmso)_2]$ and $[Cu_2L^3_4(dmso)_2]$ have been determined and refined by least-squares methods using three-dimensional Mo-K_α data. The complex $[Cu_2L^1_4(dmso)_2]$ crystallizes in space group $P\bar{1}$ in a cell of dimensions $a = 9.008(2)$, $b = 12.902(4)$, $c = 14.446(4)$ Å, $\alpha = 97.98(2)$, $\beta = 81.52(2)$, and $\gamma = 108.94(2)°$. The Cu $\cdots$ Cu separation was 2.662(1) Å. The complex $[Cu_2L^3_4(dmso)_2]$ crystallizes in space group $P2_1$ in a cell of dimensions $a = 17.166(2)$, $b = 10.518(2)$, $c = 18.184(3)$ Å, and $\beta = 118.69(1)°$. The Cu $\cdots$ Cu separation was 2.629 (1) Å.

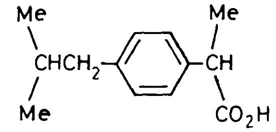
It is well known that copper(II) complexes of inactive ligands and active anti-inflammatory drugs are more active than the ligands themselves.[1] Ligands such as anthranilic acid and 3,4-di-isopropylsalicylic acid were found to be inactive. However, their copper complexes were found to be anti-inflammatory agents. Aspirin (2-acetyloxybenzoic acid) and D-penicillamine (3-mercapto-D-valine), active anti-inflammatory agents, were shown to be more effective as copper complexes than the parent drugs.[2a] The crystal structure of Cu^{II} with a lipophilic ligand such as indomethacin [1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indole-3-acetic acid] was studied[2b] in order to elucidate possible structure–function correlations. Besides, magnetic exchange interactions are believed to be important in a number of metalloprotein systems, including some copper-containing proteins.[3]

We have initiated studies on the co-ordination chemistry of sulphonylurea drugs with transition-metal and d^{10} metal ions in an attempt to examine their mode of binding and how they affect drug delivery.[4a,b]

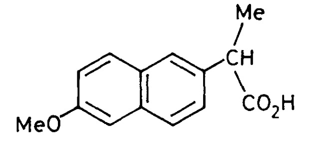
In this paper we report the preparation and characterization of mononuclear and binuclear copper(II) complexes with the anti-inflammatory drugs, 1-methyl-5-(*p*-toluoyl)-1*H*-pyrrole-2-acetic acid(tolmetin) (HL^1), α-methyl-4-(isopropylmethyl)-benzeneacetic acid(ibuprofen) (HL^2), and 6-methoxy-α-methyl-2-naphthaleneacetic acid(naproxen) (HL^3), as ligands. We also report the molecular and crystal structure of the binuclear compounds $[Cu_2L^3_4(dmso)_2]$ and $[Cu_2L^1_4(dmso)_2]$ (dmso = dimethyl sulphoxide).



HL^1



HL^2



HL^3

Results and Discussion

The synthesis of the binuclear and mononuclear complexes (Table 1) has been achieved *via* the reaction of $CuCl_2$ with the sodium salts of the ligands. All the dimeric complexes are green crystalline solids soluble in dimethylformamide (dmf), dmso, and partly soluble in CH_2Cl_2. Crystals of the $[Cu_2L^3_4(dmso)_2]$ and $[Cu_2L^1_4(dmso)_2]$ complexes, suitable for *X*-ray analysis were formed by slow evaporation of dmso–CH_2Cl_2 (3:1) solutions.

The mononuclear complexes are blue crystalline solids, soluble in dmf and CH_2Cl_2. All the complexes are non-electrolytes in dmf or CH_2Cl_2 solutions.

Description of Structures.—The crystal structure of $[Cu_2L^1_4(dmso)_4]$ is composed of centrosymmetric dimers. Four bidentate carboxylate anions form *syn-syn* bridges between isolated pairs of copper atoms separated by 2.662(1) Å. An ORTEP diagram of the complex appears in Figure 1, crystallographic details in Tables 2—4. The copper to carboxylate oxygen distances range from 1.961(3) to 1.973(2) Å.

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Table 1. Analytical, physical, and magnetic data for the mono- and bi-nuclear copper(II) carboxylate complexes

Compound	M.p. (θ/°C)	Colour	Analysis (%) Cu	C	H	N	$\mu_{eff.}$
(**1**) $[CuL^1_2(py)_2]$	155	Blue	8.55 (8.65)	65.40 (65.40)	5.20 (5.15)	7.70 (7.65)	1.90
(**2**) $[CuL^3_2(py)_2]$	140	Blue	9.35 (9.30)	66.80 (68.40)	5.20 (5.30)	4.05 (4.10)	1.85
(**3**) $[CuL^2_2(py)_2]$	115	Blue	10.10 (10.05)	68.40 (68.30)	6.80 (6.95)	4.40 (4.40)	1.83
(**4**) $[Cu_2L^1_4(dmso)_2]$	195	Green	9.50 (9.70)	58.65 (58.75)	4.90 (5.20)	3.70 (4.30)	1.32
(**5**) $[Cu_2L^3_4(dmso)_2]$	165	Green	10.35 (10.60)	60.45 (60.00)	5.60 (5.55)		1.29
(**6**) $[Cu_2L^2_4(dmso)_2]$	220	Green	11.60 (11.50)	61.05 (60.90)	7.30 (7.25)		1.53

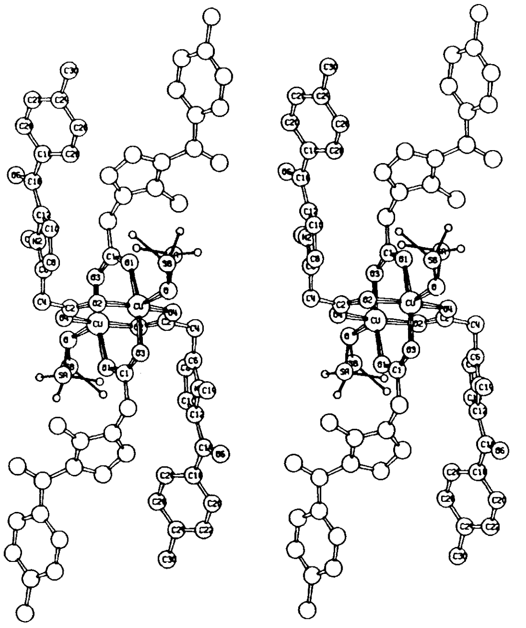

Figure 1. An ORTEP stereoview of $[Cu_2L^1_4(dmso)_2]$

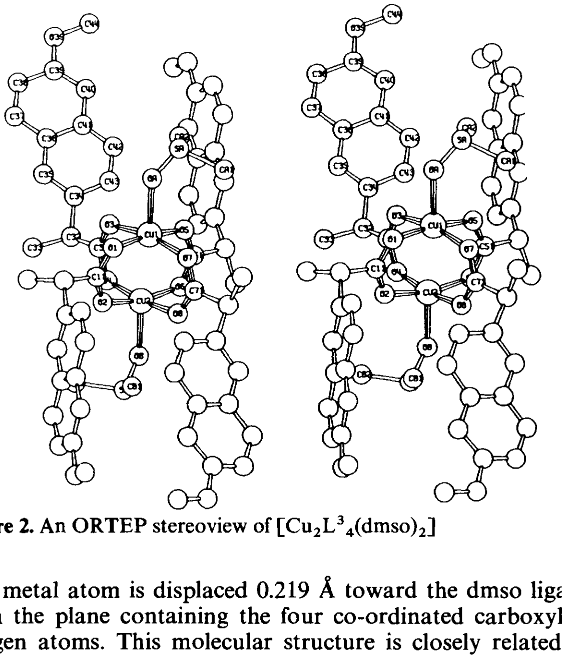

Figure 2. An ORTEP stereoview of $[Cu_2L^3_4(dmso)_2]$

The metal atom is displaced 0.219 Å toward the dmso ligand from the plane containing the four co-ordinated carboxylate oxygen atoms. This molecular structure is closely related to those of the carboxylate adducts $[Cu_2(O_2CR)_4L_2]$ [R = Me, $ClCH_2$, Et, $4\text{-}HOC_6H_4$, H, FCH_2, or Ph; L = pyridine (py), urea, dmso, quinoline, or methylpyridine].[5]

The sum of all interatomic distances in the CuO_5 chromophore (half the Cu ··· Cu distance, 1.331 Å, is included) is 11.33 Å, almost the same as the 11.34 Å average for a series of copper(II) binuclear carboxylate compounds.[6] The displacement of the copper atom from the basal plane (0.219 Å) is in the range 0.19—0.22 Å known for binuclear carboxylate complexes.[6] The eight oxygens of the four carboxylate groups create an oblique parallelepiped. The two unco-ordinated sulphur atoms of the dmso molecules are oriented towards O(1) and O(2) of the parallelepiped (Figure 1).

The crystal structure of $[Cu_2L^3_4(dmso)_2]$ shown in Figure 2 is very similar. The Cu ··· Cu distance of 2.629 (1) Å is shorter, apparently as a consequence of the bridging ligand since the terminal ligand (dmso) is the same in both structures. The correlation between the strength of the parent carboxylic acid and the Cu ··· Cu separation allows one to suggest that the tolmetin ligand is a better donor than naproxen. However, the available data are probably insufficient firmly to establish such a correlation. The copper to carboxylate oxygen distances range from 1.958 to 1.995 Å. The Cu to dmso oxygen distances are Cu(1)–O(A) 2.155 Å and Cu(2)–O(B) 2.123 Å. The metal atom is displaced 0.210 Å for Cu(1) and 0.196 Å for Cu(2) toward the dmso ligand from the planes containing the four co-ordinated carboxylate oxygen atoms. The bridging path length of 6.414 and 6.424 Å for $[Cu_2L^1_4(dmso)_2]$ and 6.461, 6.407, 6.463, and 6.413 Å for $[Cu_2L^3_4(dmso)_2]$ are within the range observed for most other copper(II) carboxylate dimers.[6] It is interesting that the principal structural change accompanying the longer metal–metal distance in $[Cu_2L^1_4(dmso)_2]$ is the movement of the Cu^{II} further out of its basal co-ordination plane. The sum of all interatomic distances in the $Cu(1)O_5$ chromophore is 11.37 Å and in the $Cu(2)O_5$ chromophore is 11.27 Å. It is noticeable that Cu ··· Cu distances (2.56—2.88 Å) of binuclear copper(II) carboxylates are the shortest among the oxo-bridged binuclear copper(II) compounds, 2.903—3.034 Å for dialkoxo-bridged compounds, 3.244—3.529 Å for di-(heterocyclic *N*-oxide)-bridged binuclear compounds, and 2.98—3.383 Å for binuclear Schiff-base compounds.[6] The $[Mn_3(\text{Schiff base})_2(O_2CMe)_4(MeOH)_2]$ complexes also possess bridging carboxylate ligands but the metal–metal distances are very long, about 3.50 Å.[7]

E.S.R. Spectra.—Mononuclear copper(II) *carboxylate complexes in frozen solutions* (77 K). The rapidly frozen samples exhibit spectra as shown in Figure 3(*a*). The values of their spin-Hamiltonian parameters (Table 5) are not influenced by the ligands in a noticeable way. The glass spectra obtained are axial.

Table 2. Summary of crystal and intensity data

Compound	$[Cu_2L^3_4(dmso)_2]$	$[Cu_2L^1_4(dmso)_2]$
Formula	$C_{60}H_{64}O_{14}Cu_2S_2$	$C_{64}H_{68}N_4O_{14}Cu_2S_2$
M	1 200.37	1 308.47
a/Å	17.166(2)	9.008(2)
b/Å	10.518(2)	12.902(4)
c/Å	18.184(3)	14.446(4)
α/°		97.98(2)
β/°	118.69(1)	81.52(2)
γ/°		108.94(2)
U/Å^3	2 880.2(8)	1 563.1(8)
Z	2	1
D_c/Mg m^{-3}	1.384	1.390
D_m/Mg m^{-3}	1.350	1.370
Space group	$P2_1$	$P\bar{1}$
μ-cm^{-1}	8.63	8.00
Scan speed/°min^{-1}	2.0—18.0	2.0—20.0
2θ limit/°	49.0	50.0
Data collected, unique; R_{int}	5 301; 5 123; 0.0113	5 828; 5 552; 0 0085
Data used, $[F_o > 6.0\sigma(F_o)]$	5 119	4 504
h,k,l range	−20 to 20, −12 to 0, 0—21	−10 to 10, 0—15, −17 to 17
F(000)	1 252	682
No. of refined parameters	746	514
$[\Delta/\sigma]_{max.}$	0.181	0.554
$(\Delta\rho)_{max.}$, $(\Delta\rho)_{min.}$/e Å^{-3}	0.99, −0.70	0.36, −0.37
S[b]	1.70	1.81
R[c] (obs., all data)	0.0446, 0.0459	0.0430, 0.0569
R'[d] (obs., all data)	0.0443, 0.0460	0.0455, 0.0956

[a] Details in common: scan range, $1.6 + (\alpha_1 - \alpha_2)°$; background counting, 0.5 of scan time. [b] $S = [\Sigma w(\Delta F)^2/(N - P)]^{\frac{1}{2}}$, where P = number of parameters and N = number of observed reflections. [c] $R = \Sigma(\Delta F)/\Sigma F_o$. [d] $R' = [\Sigma w(\Delta F)^2/\Sigma w(F_o)^2]^{\frac{1}{2}}$.

They can be described by the spin Hamiltonian (1). The spectra

$$\mathscr{H} = g_{\parallel}\mu S_z H_z + g_{\perp}\mu(S_x H_x + S_y H_y) + A_{\parallel} S_z I_z + A_{\perp}(S_x I_x + S_y I_y) \quad (1)$$

consist of well resolved superhyperfine splitting lines with a splitting of *ca.* 14×10^{-4} cm^{-1} characteristic of in-plane bonded nitrogen atoms. The experimental g and A parameters (Table 5) are typical of octahedral copper(II) complexes with $d_{x^2-y^2}$ ground states.[8] The observed features may be explained if we assume that two types of complexes are possible, shown schematically in Figure 4.

The apical position of the two pyridine molecules in complex (I) is supported by the lack of superhyperfine splitting. The basal position of the two pyridine molecules in complex (II) is consistent with the observed spectra. The g values of the complexes are consistent with those reported for complexes of similar structure.[9]

The e.s.r. signals of the binuclear copper(II) carboxylate complexes could not be observed in the region of the spectrum investigated even after freezing (77 K). The binuclear copper(II) ions are strongly antiferromagnetically coupled,[10] with a singlet–triplet splitting of the order of $2J > -300$ cm^{-1}. At 77 K the excited magnetic triplet state is practically depopulated and the e.s.r. spectrum is not detected. At 100 K the e.s.r. spectra of the studied complexes, in dmf solution, show the features of the binuclear and mononuclear complexes. We can assume that there is an equilibrium (2).

$$2[Cu(O_2CR)_2(dmso)_2] \rightleftharpoons [Cu_2(O_2CR)_4(dmso)_2] + 2\,dmso \quad (2)$$

The most interesting aspect of these spectra is that the e.s.r. signal of mononuclear complex [Figure 3(*b*)] consists of two features corresponding to the two types of complex (Figure 4). One feature is consistent with basal position of the two dmso ligands (structure (II)] with $g_{\parallel} = 2.279$—2.287 and $A_{\parallel} =$ 165—179 cm^{-1} (Table 5). This is also supported by the g values which are lower than those for dmso in the apical positions [structure (I)].

This is rather surprising as the mononuclear complexes of the pyridine analogue show e.s.r. spectra corresponding to structure (II).

Binuclear copper(II) *carboxylate complexes in the solid state.* The e.s.r. spectra of the binuclear complexes were recorded at room temperature, no signal being detected at 77 K. The shape and line positions of the powder spectra [Figure 3(*c*)] were not substantially influenced by the ligands. The spectra can be described with the axial spin Hamiltonian (3). When D is larger

$$\mathscr{H} = g_{\parallel}\mu_B S_z H_z + g_{\perp}\mu_B(S_x H_x + S_y H_y) + D(S_z^2 - 2H) \quad (3)$$

than $h\nu$, as is usually the case for compounds containing copper dimers, the powder spectrum will consist of only four lines. If, in addition, $E = 0$ then expressions (4)—(6) are obtained and

$$H_{\perp 2}^2 = (g_e/g_{\perp})^2[H_o(H_o + D)] \quad (4)$$

$$H_{z1} = -(g_e/g_{\parallel})(H_o - D) \quad (5)$$

$$H_{z2} = (g_e/g_{\parallel})(H_o + D) \quad (6)$$

we note that only three lines occur. For our solid binuclear complexes the positions of the lines lead to the spin-Hamiltonian parameters $g_{\parallel} = 2.28$—2.35, $g_{\perp} = 2.07$—2.08, and $D = 0.380$—0.395 cm^{-1}. These values are in good agreement with those reported for binuclear copper(II) carboxylate complexes.[9]

Magnetic Measurements.—The mononuclear copper(II) complexes, with a d^9 electronic configuration, are considered to have magnetic moments close to the spin-only value, 1.73 at room temperature. Actually, the observed values (Table 1) are 1.83—1.90. These values suggest strong covalent bonds.[11,12]

The binuclear copper(II) compounds show subnormal

Table 3. Fractional atomic co-ordinates (× 10^4)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
(*a*) $[Cu_2L^1_4(dmso)_2]$							
Cu	−185.6(5)	−139.6(3)	4 089.0(3)	C(4)	−1 131(4)	2 816(3)	5 283(3)
O(1)	2 060(3)	756(2)	3 992(2)	C(6)	−204(4)	3 542(3)	4 551(3)
O(3)	2 364(3)	987(2)	5 514(2)	C(8)	−669(4)	3 775(3)	3 766(3)
C(1)	2 856(4)	1 116(3)	4 671(2)	C(10)	633(4)	4 472(3)	3 294(3)
C(3)	4 578(4)	1 772(3)	4 468(3)	C(12)	1 912(4)	4 671(3)	3 788(3)
C(5)	5 135(4)	2 049(3)	3 487(3)	N(2)	1 367(3)	4 087(2)	4 568(2)
C(7)	5 360(4)	3 011(3)	3 113(3)	C(14)	2 291(4)	4 006(3)	5 286(3)
C(9)	5 990(4)	2 906(3)	2 192(3)	C(16)	3 482(4)	5 464(3)	3 663(3)
C(11)	6 130(4)	1 868(3)	1 992(3)	O(6)	4 295(3)	5 796(2)	4 314(2)
N(1)	5 583(3)	1 347(2)	2 804(2)	C(18)	4 095(4)	5 922(3)	2 737(3)
C(13)	5 565(6)	234(3)	2 943(3)	C(20)	5 207(5)	6 960(3)	2 729(3)
C(15)	6 643(5)	1 344(4)	1 096(3)	C(22)	5 858(5)	7 419(3)	1 905(4)
O(5)	6 279(4)	343(3)	910(2)	C(24)	5 443(5)	6 881(4)	1 054(3)
C(17)	7 673(5)	2 073(4)	378(3)	C(26)	4 340(6)	5 842(4)	1 054(3)
C(19)	7 455(6)	1 799(3)	−563(4)	C(28)	3 692(5)	5 368(4)	1 876(3)
C(21)	8 500(7)	2 402(6)	−1 228(4)	C(30)	6 177(6)	7 305(4)	152(4)
C(23)	9 780(6)	3 257(3)	−1 024(4)	O	−438(3)	−254(2)	2 631(2)
C(25)	9 967(5)	3 542(4)	−95(4)	S(A)	930(3)	328(2)	1 989(2)
C(27)	8 933(5)	2 967(4)	602(3)	C(A1)	540(10)	1 649(4)	2 216(7)
C(29)	10 947(7)	3 872(6)	−1 777(4)	C(A2)	156(9)	107(7)	854(3)
O(2)	−766(3)	1 217(2)	4 412(2)	S(B)	77(4)	523(2)	1 896(2)
O(4)	−463(3)	1 433(2)	5 936(2)	C(B1)	1 315(9)	1 901(4)	2 282(7)
C(2)	−756(4)	1 735(3)	5 208(3)	C(B2)	2 129(6)	527(8)	1 706(7)
(*b*) $[Cu_2L^3_4(dmso)_2]$							
Cu(1)	6 824.4(4)	1 140.0(0)	5 211.0(4)	C(41)	3 127(4)	8(6)	1 644(4)
Cu(2)	8 134.3(4)	902.1(8)	4 858.7(4)	C(42)	3 782(4)	938(7)	2 043(4)
O(1)	7 302(2)	−396(4)	5 889(2)	C(43)	4 654(4)	647(6)	2 449(4)
O(2)	8 365(3)	−686(4)	3 532(3)	C(44)	402(4)	756(9)	86(5)
O(A)	5 753(3)	1 190(5)	5 512(3)	O(39)	719(3)	−494(5)	284(3)
O(B)	9 245(3)	809(6)	4 645(3)	O(5)	6 504(2)	2 651(4)	4 485(2)
S(A)	5 119(1)	2 215(2)	5 472(1)	O(6)	7 644(3)	2 321(4)	4 234(3)
C(A1)	5 732(3)	3 633(7)	5 812(5)	C(51)	6 962(3)	3 056(5)	4 171(3)
C(A2)	4 475(4)	2 396(8)	4 395(5)	C(52)	6 675(3)	4 307(5)	3 677(4)
S(B)	10 115(2)	124(3)	5 051(2)	C(53)	7 350(4)	4 768(6)	3 429(4)
C(B1)	10 448(5)	70(10)	6 160(5)	C(54)	5 738(3)	4 214(5)	2 955(3)
C(B2)	9 820(10)	−1 450(10)	4 764(9)	C(55)	5 023(3)	4 539(5)	3 074(3)
C(11)	7 930(3)	−1 015(6)	5 887(3)	C(56)	4 132(3)	4 468(5)	2 423(3)
C(12)	8 131(4)	−2 311(6)	6 332(4)	C(57)	3 402(3)	4 723(6)	2 566(3)
C(13)	7 813(4)	−3 351(6)	5 662(5)	C(58)	2 556(4)	4 599(6)	1 921(4)
C(14)	9 117(4)	−2 449(3)	6 983(3)	C(59)	2 398(4)	4 277(6)	1 127(4)
C(15)	9 765(4)	−2 748(6)	6 777(4)	C(60)	3 081(4)	4 035(6)	957(3)
C(16)	10 678(4)	−2 802(6)	7 395(3)	C(61)	3 968(4)	4 115(6)	1 611(3)
C(17)	11 347(4)	−3 064(7)	7 182(4)	C(62)	4 708(4)	3 814(6)	1 500(3)
C(18)	12 221(4)	−3 097(6)	7 781(4)	C(63)	5 556(4)	3 864(6)	2 146(4)
C(19)	12 466(4)	−2 903(6)	8 621(4)	C(64)	1 296(4)	3 968(9)	−301(4)
C(20)	11 842(4)	−2 678(6)	8 851(4)	O(59)	1 513(3)	4 204(5)	542(3)
C(21)	10 923(4)	−2 599(6)	8 239(3)	O(7)	7 702(3)	2 192(5)	6 148(2)
C(22)	10 249(4)	−2 312(7)	8 448(4)	O(8)	8 812(3)	1 883(5)	5 858(3)
C(23)	9 380(4)	−2 225(6)	7 840(4)	C(71)	8 476(4)	2 372(6)	6 274(3)
C(24)	13 648(4)	−2 970(10)	10 015(4)	C(72)	9 095(4)	3 257(7)	6 990(4)
O(19)	13 367(3)	−2 990(6)	9 154(3)	C(73)	8 708(3)	3 644(9)	7 563(5)
O(3)	6 200(2)	55(4)	4 195(2)	C(74)	10 028(4)	2 693(6)	7 478(3)
O(4)	7 296(2)	16(5)	3 871(2)	C(75)	10 759(4)	3 344(6)	7 617(4)
C(31)	6 515(4)	−200(5)	3 725(3)	C(76)	11 632(4)	2 844(7)	8 096(4)
C(32)	5 949(4)	−909(6)	2 901(4)	C(77)	12 391(3)	3 542(8)	8 271(5)
C(33)	6 202(5)	−2 291(7)	3 040(5)	C(78)	13 219(5)	3 067(8)	8 770(5)
C(34)	4 965(4)	−623(6)	2 519(4)	C(79)	13 324(4)	1 898(8)	9 132(5)
C(35)	4 334(4)	−1 560(6)	2 169(3)	C(80)	12 609(4)	1 151(8)	8 971(4)
C(36)	3 418(4)	−1 274(6)	1 730(3)	C(81)	11 728(4)	1 636(6)	8 448(4)
C(37)	2 754(4)	−2 245(6)	1 343(4)	C(82)	10 965(4)	948(7)	8 293(4)
C(38)	1 886(4)	−1 944(7)	890(4)	C(83)	10 143(4)	1 469(6)	7 826(4)
C(39)	1 616(4)	−660(7)	781(4)	C(84)	14 360(6)	380(10)	10 082(6)
C(40)	2 212(4)	284(6)	1 153(4)	O(79)	14 199(3)	1 566(6)	9 650(4)

magnetic moments at room temperature. 1.29—1.53, due to copper–copper magnetic exchange. These values are consistent with those reported in the literature.[13]

Electronic Absorption Spectra.—The ultraviolet and visible spectra of many dimeric copper(II) carboxylate complexes have been measured in the solid state and in solution.[14] It has been

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

(*a*) $[Cu_2L^3{}_4(dmso)_2]$

Cu(1)–O(A)	2.155(5)	Cu(2)–O(B)	2.123(5)
Cu(1)–O(1)	1.958(4)	Cu(2)–O(2)	1.995(4)
Cu(1)–O(3)	1.991(4)	Cu(2)–O(4)	1.919(4)
Cu(1)–O(5)	1.968(4)	Cu(2)–O(6)	1.995(4)
Cu(1)–O(7)	1.983(4)	Cu(2)–O(8)	1.921(4)
O(1)–C(11)	1.260(8)	O(2)–C(11)	1.248(9)
O(3)–C(31)	1.241(8)	O(4)–C(31)	1.256(7)
O(5)–C(51)	1.247(8)	O(6)–C(51)	1.253(7)
O(7)–C(71)	1.248(8)	O(8)–C(71)	1.261(9)
O(1)–Cu(1)–O(A)	90.6(2)	O(2)–Cu(2)–O(B)	98.2(2)
O(1)–Cu(1)–O(3)	89.3(2)	O(2)–Cu(2)–O(4)	90.4(2)
O(1)–Cu(1)–O(5)	170.6(2)	O(2)–Cu(2)–O(6)	165.7(2)
O(1)–Cu(1)–O(7)	90.2(2)	O(2)–Cu(2)–O(8)	91.0(2)
O(3)–Cu(1)–O(A)	90.0(2)	O(4)–Cu(2)–O(B)	98.1(2)
O(3)–Cu(1)–O(5)	89.3(2)	O(4)–Cu(2)–O(6)	87.7(2)
O(3)–Cu(1)–O(7)	164.9(2)	O(4)–Cu(2)–O(8)	171.0(2)
O(5)–Cu(1)–O(A)	98.8(2)	O(6)–Cu(2)–O(B)	96.1(2)
O(5)–Cu(1)–O(7)	88.7(2)	O(6)–Cu(2)–O(8)	88.8(2)
O(7)–Cu(1)–O(A)	99.1(2)	O(8)–Cu(2)–O(B)	90.5(2)
O(1)–C(11)–O(2)	125.7(5)	O(5)–C(51)–O(6)	124.8(5)
O(3)–C(31)–O(4)	126.2(5)	O(7)–C(71)–O(8)	125.4(5)
Cu(1)–O(1)–C(11)	121.7(4)	Cu(2)–O(2)–C(11)	123.9(4)
Cu(1)–O(3)–C(31)	122.9(3)	Cu(2)–O(4)–C(41)	122.0(4)
Cu(1)–O(5)–C(51)	123.3(3)	Cu(2)–O(6)–C(51)	123.8(4)
Cu(1)–O(7)–C(71)	123.1(4)	Cu(2)–O(8)–C(71)	122.9(3)

(*b*) $[Cu_2L^1{}_4(dmso)_2]$

Cu–O	2.131(1)	Cu–O(2)	1.961(3)
Cu–O(1)	1.973(2)	Cu–O(4)	1.958(2)
Cu–O(3)	1.956(2)	Cu–O(6)	1.247(5)
O(1)–C(1)	1.248(4)	Cu–O(8)	1.248(5)
O(3)–C(1)	1.247(4)		
O–Cu–O(1)	96.0(1)	O–Cu–O(2)	94.8(1)
O–Cu–O(3)	96.8(1)	O–Cu–O(4)	98.0(1)
O(1)–Cu–O(2)	89.2(1)	O(2)–Cu–O(3)	89.1(1)
O(1)–Cu–O(3)	167.2(1)	O(2)–Cu–O(4)	167.2(2)
O(1)–Cu–O(4)	88.9(1)	O(3)–Cu–O(4)	90.0(1)
Cu–O(1)–C(1)	124.8(2)	Cu–O(2)–C(2)	124.9(3)
Cu–O(3)–C(1)	122.1(2)	Cu–O(4)–C(2)	121.6(2)
O(1)–C(1)–O(3)	125.9(3)	O(2)–C(2)–O(4)	126.2(3)

shown that these complexes have an extra band (compared to the mononuclear complexes) at about 375 nm both in solution and in the crystalline phase. This band has not been observed for the present $[Cu_2L^1{}_4(dmso)_2]$. Three bands, at about 700 (band I), 375 (II), and 300 nm (III), are present when a dimeric structure exists (Table 6). The band at 700 nm was assigned to the normal metal–ligand interaction[15,16] with *d–d* transitions of the copper ions. The origin of band II is controversial. It has been attributed to a transition between Cu–Cu molecular orbitals or various types of *d–d* transitions[15] or considered to be characteristic of the bridging system rather than the Cu–Cu linkage.[17] Similar assignments have been made for silver dimers.[18] Band III has been assigned to a carboxy–copper(II) charge-transfer absorption since no significant solvent effect on this band was observed.[19]

For $[Cu_2L^1{}_4(dmso)_4]$, the band III (312 nm) has very high value of ε (about 80 000 dm^3 mol^{-1} cm^{-1}) and probably the tail of this band covers band II.

Experimental

Preparation of the Ligands.—The sodium salts of the ligands were prepared by reaction of the protonated ligand with sodium in diethyl ether. The white solids were recrystallized from methanol and dried in the air.

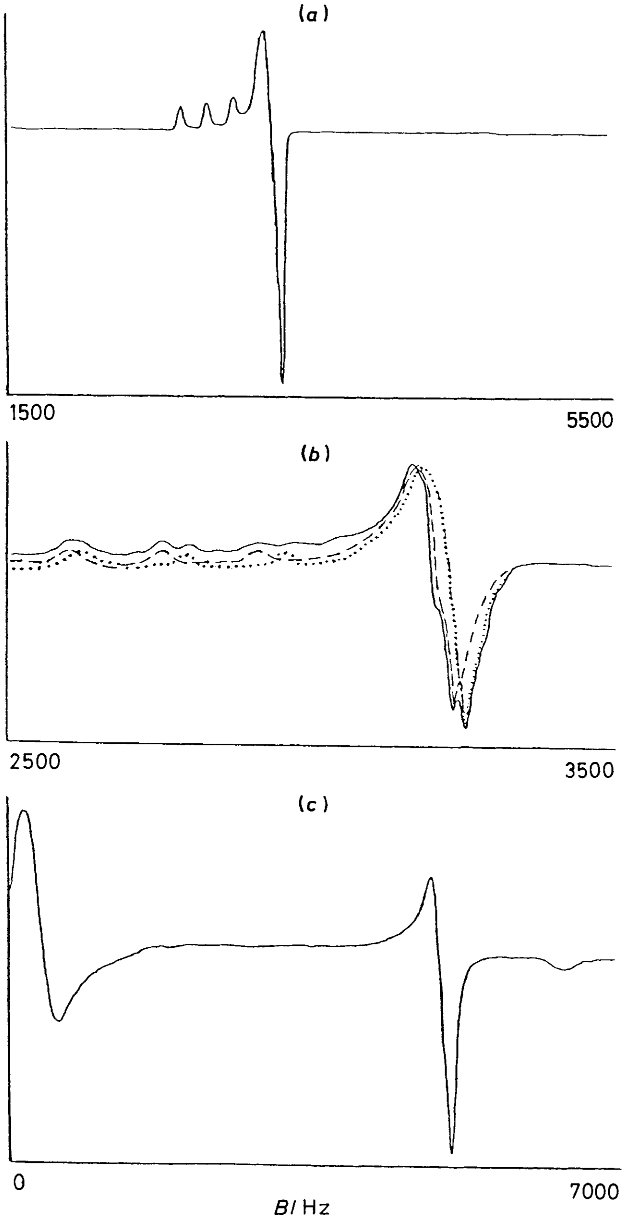

Figure 3. *X*-Band e.s.r. spectra of (*a*) $[CuL^3{}_2(py)_2]$ at 77 K in a CH_2Cl_2–dmf glass, (*b*) the mononuclear form of $[Cu_2L^3{}_4(dmso)_2]$ at 100 K in a dmf glass. The stick diagram shows the feature (– – –) for the structure of type (**I**) and that (. . . .) for the structure of type (**II**) of the complex. (*c*) $[Cu_2L^3{}_4(dmso)_2]$ at room temperature in the solid state

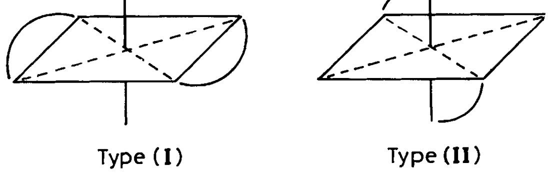

Figure 4. Proposed structures for the mononuclear copper(II) complexes

Preparation of the Binuclear Complexes.—The sodium salt of the ligands (4 mmol) was dissolved in MeOH (15 cm^3). With

Table 5. Spin-Hamiltonian parameters of mononuclear and binuclear copper(II) carboxylate complexes

Compound	$g_{\parallel}$	$g_{\perp}$	$10^4 A_{\parallel}/\text{cm}^{-1}$	$10^4 A_{\perp}/\text{cm}^{-1}$	D/cm^{-1}
Frozen solutions (77 K)					
(1)	2.290	2.050	175	13.6	—
(2)	2.301	2.057	176	13.5	—
(3)	2.295	2.049	176	14.3	—
Frozen solutions (100 K)					
Type (II) of (4)	2.287	2.058	169	—	—
Type (I) of (4)	2.327	2.069	147	—	—
Type (II) of (5)	2.279	2.060	178	—	—
Type (I) of (5)	2.327	2.069	160	—	—
Type (II) of (6)	2.287	2.060	179	—	—
Type (I) of (6)	2.319	2.070	152	—	—
Solid state (298 K)					
(4)	2.285	2.072	—	—	0.383
(5)	2.350	2.072	—	—	0.392
(6)	2.320	2.070	—	—	0.390

Table 6. Spectral data for mono- and bi-nuclear copper(II) carboxylate complexes

	I.r. (cm^{-1})		U.v.–visible
Compound	$\nu_{asym}(CO_2^-)$	$\nu_{sym}(CO_2^-)$	λ/nm ($\varepsilon/\text{dm}^3\ \text{mol}^{-1}\ \text{cm}^{-1}$)
$(CuL^1_2(py)_2]$	1 613vs	1 392s	650 (378), 312 (85 000)
$[CuL^3_2(py)_2]$	1 605vs	1 390s	650 (144), 330 (43 000), 320 (25 000), 308 (20 000)
$[CuL^2_2(py)_2]$	1 590vs	1 405s	670 (180), 310 (sh) (7 500)
$[Cu_2L^1_4(dmso)_2]$	1 613vs	1 392s	720 (389), 312 (77 000)
$[Cu_2L^3_4(dmso)_2]$	1 615vs	1 403s	700 (405), 365 (sh) (1 533), 330 (9 300), 315 (8 900), 282 (sh) (16 400), 270 (27 100)
$[Cu_2L^2_4(dmso)_2]$	1 585vs	1 410s	700 (178), 385 (sh) (225), 310 (sh) (8 000)

stirring, $CuCl_2$ (2 mmol) in dmso (20 cm^3) was added dropwise, generating a green solution. This solution was refluxed for 1 h after which time the mixture was allowed to reach room temperature and CH_2Cl_2 (20 cm^3) was added. A white solid which was deposited was removed by filtration. Slow evaporation of the solution gave green crystals which were collected by filtration and dried in the air.

Preparation of the Mononuclear Complexes. The sodium salt of the ligands (4 mmol) and $CuCl_2$ (2 mmol) were mixed in dmso (30 cm^3). After 1 h of reflux the reaction mixture was filtered and cooled to room temperature and pyridine (3 cm^3) was added. Blue crystals were deposited upon standing overnight.

The analytic data for the new compounds, melting points, and magnetic moments are given in Table 1.

Physical Measurements.—U.v.–visible spectra were recorded on a Perkin-Elmer–Hitachi dual-beam spectrophotometer, i.r. spectra (200—4 000 cm^{-1}) on a Perkin-Elmer 467 spectrometer with samples prepared as KBr pellets. Solution and solid-state e.s.r. spectra were recorded on a Brucker ER200E-SRC spectrometer equipped with a Varian variable-temperature controller. Diphenylpicrylhydrazyl was used as an external standard. Room temperature magnetic measurements were carried out by the Faraday method using mercury tetrathiocyanatocobaltate(II) as a calibrant. Electric conductance measurements were carried out with a WTW model LF530 conductivity outfit and a type c cell, which had a cell constant of 0.096. This represents a mean value calibrated at 25 °C with potassium chloride.

X-Ray Crystallography.—Complete crystal data and parameters for data collection are reported in Table 2. The space groups were determined by preliminary Weissenberg and precession photographs. Unit-cell dimensions were derived from a least-squares refinement of the setting angles of 15 automatically centred reflections in the range of $20 < 2\theta < 22°$ on a Syntex $P2_1$ diffractometer with niobium-filtered Mo-K_α radiation. Three standard reflections measured every 67 reflections showed $<3.0\%$ intensity fluctuations. Lorentz polarization but no absorption correction was applied. Scattering factors were taken from ref. 20.

Solution and refinement of the structures. The structures were solved by direct methods using the programs SHELX 86[21] for $[Cu_2L^3_4(dmso)_2]$ and SHELX 76[22] for $[CuL^1_4(dmso)_2]$. The refinement was carried out by blocked full-matrix least squares, in which w^2 was minimized using SHELX 76. Attempts to refine the structure of $[Cu_2L^1_4(dmso)_2]$ in space group $P1$ were unsuccessful leading to negative U values and very poor bond distances. The refinement proceeded in $P\bar{1}$. Unit weights were used since they gave a satisfactory analysis of variance.[22] The difference map for $[Cu_2L^1_4(dmso)_2]$ showed two positions for dimethyl sulphoxide, A and B. The site occupancies for these two positions were refined, keeping the sum of the two constant at 1. They refined to 0.465(1) for position A. The O–S and S–C distances were constrained to 1.48(1) and 1.83(1) Å. All the hydrogens of $[Cu_2L^3_4(dmso)_2]$ and the methyl hydrogens of $[Cu_2L^1_4(dmso)_2]$ were calculated as riding on carbon atoms at 0.96 Å. The non-hydrogen atoms were refined using anisotropic and the H atoms using isotropic thermal parameters.

The fractional atomic co-ordinates of the non-hydrogen atoms are listed in Table 3, bond lengths and angles of the co-ordination sphere in Table 4. ORTEP[23] stereoviews of $[Cu_2L^1_4(dmso)_2]$ and $[Cu_2L^3_4(dmso)_2]$ are given in Figures 1 and 2, respectively.

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

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References

1 J. R. J. Sorenson, in 'Metal Ions in Biological Systems,' vol. 14, ed. H. Sigel, Marcel Dekker, New York, 1982, p. 77.
2 (*a*) J. R. J. Sorenson, V. Kishore, A. Pezeshk, L. W. Oberley, S. W. C. Leuthauser, and T. D. Oberley, *Inorg. Chim. Acta*, 1984, **91**, 285; (*b*) V. Weser, K-H. Sellinger, E. Lengfelder, W. Werner, and J. Strahle, *Biochim. Biophys. Acta*, 1980, **631**, 232.
3 G. N. La Mar, G. R. Eaton, R. H. Holm, and F. A. Walker, *J. Am. Chem. Soc.*, 1973, **95**, 63 and refs. therein.
4 (*a*) D. P. Kessissoglou, G. E. Manoussakis, A. G. Hatzidimitriou, and M. G. Kanatzidis, *Inorg. Chem.*, 1987, **26**, 1395. (*b*) A. G. Hatzidimitriou, G. E. Manoussakis, D. P. Kessissoglou, P. N. Kourounakis, and G. Economidis, *J. Inorg. Biochem.*, in the press.
5 G. A. Barclay and C. H. L. Kennard, *J. Chem. Soc.*, 1961, 5244; E. Kokot and R. L. Martin, *Inorg. Chem.*, 1964, **3**, 1306; M. M. Borel and A. Leclaire, *Acta Crystallogr., Sect. B*, 1976, **32**, 1273; I. Bkouche-Waksman, C. Bois, G. A. Poporitch, and P. L. Haridon, *Bull. Soc. Chim. Fr.*, 1980, 69; V. I. Ivanov, Yu. A. Simonov, A. V. Ablov, and

L. N. Milkova, *Krystallografiya*, 1974, **19**, 1286; A. Bencini, D. Gatteschi, and C. Mealli, *Cryst. Struct. Commun.*, 1979, **8**, 305; F. Pavelcik and F. Hanic, *J. Cryst. Mol. Struct.*, 1978, **8**, 59.

6 M. Melnik, *Coord. Chem. Rev.*, 1982, **42**, 263.

7 Xh. Li, D. P. Kessissoglou, M. L. Kirk, C. Bender, and V. L. Pecoraro, *Inorg. Chem.*, 1988, **27**, 1; D. P. Kessissoglou, M. L. Kirk, C. A. Bender, M. S. Lah, and V. L. Pecoraro, *J. Chem. Soc., Chem. Commun.*, 1989, 84.

8 B. J. Hathaway and D. E. Billing, *Coord. Chem. Rev.*, 1970, **5**, 143; B. J. Hathaway, *Struct. Bonding* (*Berlin*), 1984, **57**, 55.

9 I. Bertini, D. Gatteschi, and A. Scozzafara, *Coord. Chem. Rev.*, 1979, **29**, 67.

10 R. J. Doedens, *Prog. Inorg. Chem.*, 1976, **21**, 209.

11 A. E. Martel and M. Calvin, 'Chemistry of the Metal Chelate Compounds,' Prentice-Hall, New York, 1952, p. 6.

12 P. W. Selwood, 'Magnetochemistry,' Interscience, New York, 1956, p. 235.

13 L. S. Forster and R. L. Martin, *J. Chem. Soc.*, 1956, 3837; I. G. Ross, *Trans. Faraday Soc.*, 1959, **55**, 1057; J. G. Ross and D. J. Royer, *Inorg. Chem.*, 1965, **4**, 1830; E. A. Bondreaux, *ibid.*, 1964, **3**, 506.

14 M. Kato, H. B. Jonassen, and J. C. Fanning, *Chem. Rev.*, 1964, **64**, 99.

15 L. S. Forster and C. J. Ballhausen, *Acta Chem. Scand.*, 1962, **16**, 1385.

16 R. Tsuchida and S. Yamada, *Nature* (*London*), 1955, **176**, 1171; S. Yamada, H. Nakamura, and R. Tsuchida, *Bull. Chem Soc. Jpn.*, 1957, **30**, 953.

17 L. Dubicki and R. L. Martin, *Inorg. Chem.*, 1966, **5**, 2203.

18 D. Mentzafos, H. A. Tazmir-Riahi, and A. Terzis, *Acta Crystallogr., Sect. C*, 1988, **44**, 784.

19 D. P. Graddon, *J. Inorg. Nucl. Chem.*, 1961, **17**, 222.

20 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.

21 G. M. Sheldrick, SHELX 86. Universitaet Gottingen, 1986.

22 G. M. Sheldrick, SHELX 76. Program for Crystal Structure determination, University of Cambridge, 1976.

23 C. K. Johnson, ORTEP II, Report ORNL-5138, Oak Ridge National Laboratory, Tennessee, 1976.

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