Copper and Related Metal Complexes with *NN'*-(1,7,7-Trimethylbicyclo[2.2.1]heptane-2,3-diylidene)dianiline Ligands

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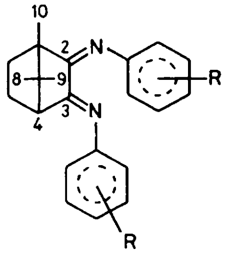
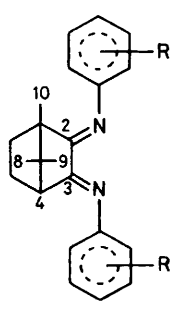
Reactions of the title ligands [L^1 (R = H), L^2 (R = *p*-Me), or L^3 (R = *o*-Me in the aniline ring)] with the appropriate bivalent metal salts yield the following complexes: [MCl_2L] (M = Cu, L = L^1, L^2, or L^3; M = Zn or Pd, L = L^2 or L^3), [$CuBr_2L^2$], and [$M(BF_4)_2L_2$] (M = Cu, L = L^1, L^2, or L^3; M = Ni or Zn, L = L^1 or L^3). The complexes have been characterised by a variety of physicochemical techniques, and structures are proposed; [$CuCl_2L$], pseudo-tetrahedral and [$Cu(BF_4)_2L_2$], distorted tetragonal. Co-ordination of the [BF_4]$^-$ ion is strongest for the L^3 ligand complexes. Analogous copper(I) complexes have been synthesised and formulated as [CuL_2][$CuCl_2$] (L = L^1, L^2, or L^3), as well as a related complex [$CuL^4{}_2$] of a thiaether ligand L^4.

CURRENTLY considerable attention is being focused on copper complexes in an attempt to gain further insight into the structural and mechanistic features of copper-containing proteins.[1] It has been suggested [2] that a highly constrained site is generated for metal ions at the active centre of some metalloproteins, and for this reason there is interest in ligand systems which will force the copper away from the more usual planar or elongated octahedral co-ordination environments. The condensation of 1,7,7-trimethylbicyclo[2.2.1]heptane-2,3-dione (camphorquinone) with anilines affords the di-imine ligands L^1—L^3 which differ from more conventional di-imines in that the presence of the rigid bicyclic ring system means that the nitrogen-donor atoms, as well as having little flexibility in their relative positions, would be expected to generate a moderately wide ligand bite angle for co-ordination. For the free ligands four stereoisomers are theoretically possible; however, Dvolaitzky [3] has shown by ^{1}H n.m.r. studies that in fact only two isomers are found in the case of L^1. These have been assigned to the *syn,anti* and *anti,anti* structures depicted above, and it is the latter which predominates in $CHCl_3$ solution at room temperature. We find a similar behaviour for L^2, but when the methyl groups are in the *ortho* position, as in L^3, it is the *syn,anti* form that is favoured. Molecular models show that the interaction of the *o*-methyl group (on the aniline attached to C^2) with the camphor skeleton, especially the 10-methyl group, is minimised in this form. However, the more sterically 'strained' *anti,anti* structure must be adopted for co-ordination of L^3 to a metal ion to occur.



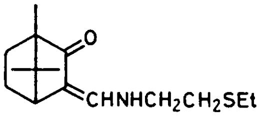
syn, anti (2*Z*, 3*E*)



anti, anti (2*E*, 3*E*)

L^1 R = H
L^2 R = *p*-Me
L^3 R = *o*-Me

Apart from a brief mention [3,4] of one zinc complex, *i.e.* [$ZnCl_2L^1$], the interaction of the di-imines L^1—L^3 with metal ions has not been previously investigated. Therefore in this paper we report the synthesis and characterisation of a series of copper and related metal-ion complexes with these ligands. In the case of the halogeno-complexes [$CuCl_2L$], spectroscopic evidence suggests that a pseudo-tetrahedral geometry is generated around the copper; however, in the bis(ligand) complexes [$Cu(BF_4)_2L_2$] the distortion is such that as the ligand becomes more sterically hindered (*i.e.* when the methyl group is *ortho* as in L^3) co-ordination of the weakly co-ordinating tetrafluoroborate anion is enhanced. This effect is accentuated in the analogous nickel and zinc complexes, which have been investigated to gain further information on the co-ordination characteristics of this ligand type. Copper(I) complexes with the ligands L^1—L^3 are also reported. Condensation of $H_2NCH_2CH_2SEt$ with 3-hydroxymethylenecamphor affords HL^4 which has potential oxygen and sulphur, as well as nitrogen, donor atoms. This ligand, in its deprotonated form, yields the copper(II) complex [$CuL^4{}_2$], which has been included as another type of complex in which the ligand has the camphor skeleton.



HL^4

RESULTS AND DISCUSSION

Copper(II) *Halide and Related Complexes*.—The complexes [MCl_2L] (M = Cu, L = L^1, L^2, or L^3; M = Zn or Pd, L = L^2 or L^3) and [$CuBr_2L^2$] were prepared by the reaction of the ligands with the appropriate metal salt in acetone or ethanol except in the case of the palladium complexes where [$PdCl_2(NCPh)_2$] in toluene was used.

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TABLE 1

Colours, analytical, conductivity, and i.r. spectral data for the complexes

Complex	Colour	Analysis[a] (%) C	H	N	Λ[b] S cm^2 mol^{-1}	ν(M–Cl)[c] cm^{-1}
$[CuCl_2L^1]$	Yellow-brown	58.5 (58.6)	5.4 (5.4)	5.8 (6.2)	8	308 (sh), 295, 284 (sh)
$[CuCl_2L^1]\cdot EtOH$	Yellow-brown	57.9 (58.0)	5.8 (6.1)	5.6 (5.6)		306 (sh), 296, 284 (sh)
$[CuCl_2L^2]$	Yellow-brown	60.2 (60.2)	5.9 (5.9)	5.9 (5.85)	8	306, 284
$[CuCl_2L^3]$	Olive-green	60.2 (60.2)	6.05 (5.9)	5.7 (5.85)	1	328 (sh), 315, 305
$[CuBr_2L^2]$	Brown	50.95 (50.8)	5.0 (5.0)	4.9 (4.9)	8	*d*
$[ZnCl_2L^2]$	Yellow	59.9 (59.95)	5.8 (5.9)	5.8 (5.8)		344, 317
$[ZnCl_2L^2]\cdot Me_2CO$	Yellow	60.05 (60.2)	5.9 (6.4)	5.8 (5.2)		345, 317
$[ZnCl_2L^3]$	Yellow	59.9 (59.95)	5.9 (5.9)	5.6 (5.8)		348, 308
$[PdCl_2L^2]\cdot 0.5H_2O$	Yellow	54.1 (54.3)	5.3 (5.5)	5.2 (5.3)		338
$[PdCl_2L^3]$	Yellow	54.7 (55.2)	5.7 (5.4)	5.1 (5.4)		340, 325 (sh)
$[Cu(BF_4)_2L^1{}_2]$	Brown	60.8 (60.7)	5.5 (5.6)	6.4 (6.4)	24	
$[Cu(BF_4)_2L^2{}_2]$	Brown	62.1 (62.25)	6.5 (6.1)	6.0 (6.05)	24	
$[Cu(BF_4)_2L^3{}_2]$	Brown	62.2 (62.25)	6.4 (6.1)	6.0 (6.05)	23	
$[Zn(BF_4)_2L^1{}_2]$	Yellow	60.0 (60.6)	5.8 (5.55)	6.2 (6.4)	30	
$[Zn(BF_4)_2L^3{}_2]$	Yellow	61.5 (62.1)	6.3 (6.1)	5.9 (6.0)	11	
$[Ni(BF_4)_2L^1{}_2]$	Orange	61.1 (61.1)	5.9 (5.6)	6.3 (6.5)	26	
$[Ni(BF_4)_2L^3{}_2]$	Orange	62.4 (62.6)	6.4 (6.1)	6.0 (6.1)	16	
$[CuL^1{}_2][CuCl_2]$	Dark maroon	63.6 (63.6)	5.8 (5.8)	6.45 (6.75)	24	405
$[CuL^2{}_2][CuCl_2]$	Dark maroon	64.8 (65.0)	6.4 (6.4)	5.9 (6.3)	25	*d*
$[CuL^3{}_2][CuCl_2]\cdot Me_2CO$	Dark green	63.95 (64.65)	6.5 (6.8)	5.6 (5.65)	21	402
$[CuL^4{}_2]$	Brown	60.8 (60.4)	8.1 (8.1)	4.7 (4.7)		

[a] Calculated values are given in parentheses. [b] For 10^{-3} mol dm^{-3} nitrobenzene solutions. [c] As Nujol mulls; sh = shoulder. [d] Below 250 cm^{-1}.

TABLE 2

Electronic-spectral data for the complexes

Complex	Absorption maxima (cm^{-1})[a]	State
$[CuCl_2L^1]$	11 630 (121), 8 500 (sh) (55)	*b*
	11 980, 8 300 (sh)	*c*
$[CuCl_2L^1]\cdot EtOH$	11 630 (113), 8 500 (sh) (55)	*d*
	11 900, 8 200 (sh)	*c*
$[CuCl_2L^2]$	11 760 (125), 8 500 (sh) (61)	*b*
	12 200, 8 900 (sh)	*c*
$[CuCl_2L^3]$	12 660 (113), 9 000 (sh) (59)	*b*
	12 350, 9 900 (sh)	*c*
$[CuBr_2L^2]$	18 020 (sh) (990), 15 500 (sh) (324), 11 660 (203), 7 700 (sh) (93)	*b*
	18 200 (sh), 12 580, 8 900 (sh)	*c*
$[Cu(BF_4)_2L^1{}_2]$	22 120 (5 120), 14 600 (220)	*b*
	20 370, 14 220	*c*
$[Cu(BF_4)_2L^2{}_2]$	20 790 (5 660), 14 970 (314)	*b*
	19 800, 14 080	*c*
$[Cu(BF_4)_2L^3{}_2]$	21 370 (4 955), 15 620 (sh) (232)	*b*
	21 100, 14 640	*c*
$[Ni(BF_4)_2L^1{}_2]$	21 300 (sh) (230), 15 900 (sh) (15), 9 170 (19)	*b*
	21 300 (sh), 14 700 (sh), 11 300 (sh), 9 400	*c*
$[Ni(BF_4)_2L^3{}_2]$	21 700 (sh) (96), 14 810 (14), 11 050 (11)	*b*
	21 700 (sh), 14 600 (sh), 12 320	*c*
$[CuL^1{}_2][CuCl_2]$	19 840 (4 920)	*e*
$[CuL^2{}_2][CuCl_2]$	19 530 (4 460)	*e*
$[CuL^3{}_2][CuCl_2]\cdot Me_2CO$	21 930 (3 580)	*e*
$[CuL^4{}_2]$	21 280 (920), 12 050 (sh) (50)	*f*

[a] Absorption coefficients (ε/dm^3 mol^{-1} cm^{-1}) are given in parentheses. [b] Dichloromethane solution. [c] Solid. [d] Ethanol solution. [e] Methanol solution. [f] n-Hexane solution.

Analytical data and colours of the complexes are given in Table 1. In some cases, *e.g.* $[CuCl_2L^1]$ and $[ZnCl_2L^2]$, i.r. and analytical data showed the complexes to contain a solvent molecule which could be removed by heating *in vacuo*. The spectral properties [*d–d* and ν(Cu–Cl) bands] of $[CuCl_2L^1]$ and $[CuCl_2L^1]\cdot EtOH$, for example, are virtually identical (Tables 1 and 2) thus indicating that the solvent molecule simply occupies a void in the crystal lattice. The complexes $[CuCl_2L]$ (L = L^1, L^2, or L^3) are essentially non-electrolytes in nitrobenzene (Table 1) and exhibit spectral properties consistent with a distorted-tetrahedral arrangement of ligands about Cu^{II}. In particular, the spectra are similar to those reported[5] for dichloro[(—)-β-isosparteine]copper(II) which also is a $CuCl_2N_2$ system and whose structure has been confirmed by a single-crystal *X*-ray analysis to be distorted tetrahedral.[6] For instance, the electronic spectra (Table 2) show broad unsymmetrical *d-d* absorption bands with maxima at *ca.* 12 000 cm^{-1} ($\varepsilon \approx$ 120 dm^3 mol^{-1} cm^{-1}) tailing into the near i.r. with a shoulder distinguishable near 9 000 cm^{-1}. The complex $[CuCl_2\{(-)\text{-}\beta\text{-isosparteine}\}]$ exhibits a similar maximum at 12 120 cm^{-1} (ε 100 dm^3 mol^{-1} cm^{-1}) as do other copper(II) complexes for which a distorted-tetrahedral stereochemistry has been assigned.[7-11] The solid-state reflectance spectra for the $[CuCl_2L]$ (L = L^1, L^2, or L^3) complexes are not markedly different from those in solution, thus implying similar structures in both states. In the i.r. (Table 1), bands assignable to essentially Cu–Cl stretching frequencies appear in the 300 cm^{-1} region, slightly higher than observed[5] for $[CuCl_2\{(-)\text{-}\beta\text{-isosparteine}\}]$ [ν(Cu–Cl) at 282 and 275 cm^{-1}] but still in the range expected for terminal Cu^{II}–Cl bonds.

It has only recently become apparent that for four-co-ordinate copper(II) complexes the e.s.r. parameters, in particular those of the parallel region, can serve to give an indication of the copper co-ordination environment. Essentially, for a related series of complexes, distortion from square planar towards tetrahedral, causes $g_{\parallel}$ to increase as $A_{\parallel}$ decreases from *ca.* 200 × 10^{-4} to *ca.* 100 × 10^{-4} cm^{-1} or even less.[12-17] Covalency can cause a further decrease in $A_{\parallel}$, as well as in $g_{\parallel}$,[12] reflecting the sensitivity of the parameters to the bonding characteristic of the metal–ligand linkage. In the present study the e.s.r. spectra of the $[CuCl_2L]$ (L = L^1, L^2, or L^3) complexes in frozen EtOH solution (77 K) (Table 3) are axial in nature, and exhibit well resolved parallel regions. In addition no signals were observed in the $g = 4$ region, suggesting the complexes are mononuclear.[18] The parameters ($g_{\parallel} \approx 2.3$, $A_{\parallel} \approx 120 \times 10^{-4}$ cm^{-1}, and $g_{\perp} \approx 2.1$) point to a distorted-tetrahedral $CuCl_2N_2$ centre. Although the e.s.r. parameters for [$CuCl_2${(—)-β-isosparteine}] itself have not been reported, those of the related (—)-sparteine complex, which appears to have essentially the same structure, have.[7] For this latter complex the g values ($g_{\parallel}$ 2.299 and $g_{\perp}$ 2.075) are similar to those observed for the [$CuCl_2L$] (L = L^1, L^2, or L^3) complexes but $A_{\parallel}$ at 85×10^{-4} cm^{-1} is lower; however, the spectrum was recorded on the complex doped into a [$ZnCl_2${(—)-β-isosparteine}] host lattice which itself may enforce a more regular tetrahedral geometry on to the $CuCl_2N_2$ centre. Another example of a $CuCl_2N_2$ distorted-tetrahedral co-ordination environment is given by [$CuCl_2$(phen)] (phen = 1,10-phenanthroline) doped into a zinc host lattice,[19] and which exhibits $A_{\parallel} = 123 \times 10^{-4}$ cm^{-1} similar to the values reported in this study.

TABLE 3

E.s.r. data for the copper(II) complexes

Complex	$g_{\parallel}$	$10^4 A_{\parallel}$/cm^{-1}	$g_{\perp}$	State [a]
[$CuCl_2L^1$]	2.303	127	2.085	*b*
[$CuCl_2L^2$]	2 300	125	2.081	*b*
[$CuCl_2L^3$]	2.308	117	2.109	*b*
[$CuBr_2L^2$]	2.334	123	2.086	*b*
	2.274	150	2.013	
[$Cu(BF_4)_2L^1_2$]	2.299	139	2.073	*c*
[$Cu(BF_4)_2L^2_2$]	2.304	138	2.076	*c*
[$Cu(BF_4)_2L^3_2$]	2.262	144	2.077	*c*
[CuL^4_2]	2.233(g_1)	142	2.058(g_2) 2.010(g_3)	*d*

[a] At 77 K. [b] Ethanol solution. [c] Dichloromethane solution. [d] n-Hexane solution.

The reflectance spectrum of the bromo-complex [$CuBr_2L^2$] shows, in addition to the *d–d* band at 12 580 cm^{-1}, a band at 18 020 cm^{-1}, not seen in the analogous chloro-complexes, which is assignable to a Br→Cu charge-transfer transition. In solution, however, another band at 15 500 cm^{-1} (ε 324 dm^3 mol^{-1} cm^{-1}), indicative of a square-planar or tetragonal copper(II) centre,[20] appears. Support for the presence of this additional species comes from the e.s.r. spectrum which shows the presence of two copper centres, one with parameters similar to those observed for the chloro-complex analogues, and another with $A_{\parallel} = 150 \times 10^{-4}$ cm^{-1} (Table 3). Interaction of the larger bromine atom with the 9-methyl group on the di-imine ligand could be envisaged to cause the distorted-tetrahedral structure to be less favoured. The coexistence of two distinct chromophores, one tetrahedral and the other tetragonal, has been postulated previously for the complex dibromobis(dehydrodithizone)copper(II).[21]

The ^{1}H n.m.r. spectra of the diamagnetic [$ZnCl_2L$] and [$PdCl_2L$] (L = L^2 or L^3) complexes are listed in Table 5 and resemble those of the *anti,anti* form of the free ligands. On going from the *syn,anti* to the *anti,anti* isomer, the 10-methyl protons move upfield (*ca.* 0.5—0.6 p.p.m.) as they suffer a shielding effect from the phenyl π-electron cloud. In the palladium complexes, but not in those of zinc (which are presumably tetrahedral), the 10-methyl protons show a further upfield shift (*ca.* 0.2 p.p.m.) on co-ordination which can be envisaged to arise from an anisotropic ring-current effect as the phenyl ring is forced to face the 10-methyl group in order to minimise the phenyl–chlorine interaction which would occur in a square-planar complex. In the free ligand, L^3, it is clear from the observation of a number of resonances assignable to the protons of the *o*-methyl groups, that in addition to the two main isomers (the *syn,anti* and *anti,anti*) further forms of the ligand can occur, resulting from restricted rotation of the phenyl rings about the C–N bonds. On increasing the temperature from 22 to 60 °C the resonances show a reversible coalescence. However, for the [$PdCl_2L^3$] complex a similar temperature increase causes no alteration in the spectrum indicating rotation of the phenyl rings has been prevented, because, as shown by a molecular model with square-planar geometry, the *o*-methyl group interacts with co-ordinated chlorine atoms.

Copper(II) *Tetrafluoroborate and Related Complexes.*—The complexes [$M(BF_4)_2L_2$] (M = Cu, L = L^1, L^2, or L^3; M = Ni or Zn, L = L^1 or L^3) were prepared by the interaction of the ligands with the metal tetrafluoroborate salts in acetone or ethanol. Conductivity data for the complexes in nitrobenzene point to co-ordination of the [BF_4]$^-$ anion. The molar conductivity values (Λ 10—30 S cm^2 mol^{-1}) (Table 1) fall well below the range expected[22] for 2 : 1 electrolytes (Λ 50—60 S cm^2 mol^{-1}) and for the [$M(BF_4)_2L^3_2$] (M = Ni or Zn) complexes below the 1 : 1 electrolyte range (Λ 20—30 S cm^2 mol^{-1}).

Infrared data give further information on [BF_4]$^-$ anion co-ordination. For the unsubstituted L^1 ligand complexes the ν_3 band of the [BF_4]$^-$ anion is broad with shoulders, and centred at *ca.* 1 055 cm^{-1} (Table 4). The band resembles that exhibited by such complexes as [$Cu(BF_4)_2L_2$] (L = ethylenediamine[23] or 2,5-dithiahexane[24]) where the [BF_4]$^-$ ion has been shown by single-crystal *X*-ray analyses to be semi-co-ordinated.[25,26] While the [BF_4]$^-$ ν_1 and ν_4 bands would be expected to be observed at *ca.* 760 and at *ca.* 520 cm^{-1} respectively,[23] the presence of di-imine ligand absorptions prevents this. For the [$Cu(BF_4)_2L^3_2$] complex the ν_1 [BF_4]$^-$ anion absorption shows an increased splitting. These frequencies may be compared to those reported[27] for [$Cu(BF_4)(PPh_3)_3$] (1 128, 1 088, 1 018, and 970 cm^{-1})

TABLE 4

Infrared data (cm^{-1}) for the [BF_4]$^-$ complexes

Complex	ν(B–F) *
[$Cu(BF_4)_2L^1_2$]	1 095 (sh), 1 057s, br
[$Cu(BF_4)_2L^2_2$]	1 105 (sh), 1 090s, 1 000 (sh)
[$Cu(BF_4)_2L^3_2$]	1 108 (sh), 1 083s, 1 039m, 980s
[$Ni(BF_4)_2L^1_2$]	1 080 (sh), 1 055s, br
[$Ni(BF_4)_2L^3_2$]	1 154m, 1 115s, 953m, 921s
[$Zn(BF_4)_2L^1_2$]	1 090 (sh), 1 055s, 1 005 (sh)
[$Zn(BF_4)_2L^3_2$]	1 151m, 1 108s, 975 (sh), 934s

* As Nujol mulls; sh = shoulder, s = strong, m = medium, br = broad.

where the length of the Cu–F bond indicates $[BF_4]^-$ co-ordination, albeit weak. In the case of the complexes $[M(BF_4)_2L^3{}_2]$ (M = Ni or Zn) the ν_1 $[BF_4]^-$ absorption is clearly resolved into two components (each isotopically split [28]), indicating that co-ordination of the anion is strong.

Electronic spectra of the copper(II) complexes (Table 2) show a band near 20 000 cm^{-1} (ε *ca.* 5 000 dm^3 mol^{-1} cm^{-1}) which, on the basis of its intensity, must be charge transfer in nature. Absorption maxima are not seen in this region for either the free ligands or the copper chloride complexes. The bands are tentatively assigned to a transition of the ligand-to-metal type although its energy is lower than seen for copper(II) complexes of other di-imine ligands such as 2,2′-bipyridyl.[29,30] An additional band is found at *ca.* 14 000—15 000 cm^{-1} (assignable to a *d–d* transition), a lower value than expected for a CuN_4 tetragonal complex. Amine complexes, such as $[Cu(BF_4)_2L_2]$ (L = ethylenediamine), exhibit absorption maxima in the 19 000 cm^{-1} region.[31] As the nitrogen donor atoms twist out of the plane, to give in the extreme case a distorted-tetrahedral CuN_4 chromophore, as found in $[CuL_2][ClO_4]_2$ (L = 2,2′-bipyridylamine) the maxima shift to longer wavelengths.[32] In this latter case the $[ClO_4]^-$ anion is clearly anionic in nature.[33] The complex $[Cu(ClO_4)_2L_2]$ (L = 2,2′-bipyridyl) illustrates the intermediate case, and although the CuN_4 core can be described as flattened tetrahedral the $[ClO_4]^-$ anion can still be regarded as being weakly co-ordinated.[34] The spectrum shows a *d–d* band at 15 100 cm^{-1},[29,30] similar to the values exhibited by the di-imine ligand complexes in the present work. Moreover, the e.s.r. spectra of the $[Cu(BF_4)_2L_2]$ (L = L^1, L^2, or L^3) complexes reveal $A_{\parallel}$ values of *ca.* 140×10^{-4} cm^{-1}, lower than reported (180×10^{-4}—200×10^{-4} cm^{-1}) for complexes with a more regular tetragonal co-ordination.[35] The electronic spectra of the complexes $[Ni(BF_4)_2L_2]$ (L = L^1 or L^3) also point to distorted [36] rather than regular octahedral co-ordination.

TABLE 5

Hydrogen-1 n.m.r. spectra data (p.p.m.) [a]

Compound	10-Me anti,anti	10-Me syn,anti	8- and 9-Me anti,anti	8- and 9-Me syn,anti	H^4	Me(aryl)
L^1	0.62	1.19	0.82, 1.01	0.94, 1.01	2.64 [b]	
L^2	0.63	1.16	0.83, 0.99	0.94, 0.99	2.67 [b]	2.24, 2.32, 2.34
L^3	0.58	1.22	0.81, 0.99	0.95, 0.99	2.56 [b]	1.75, 1.88, 2.08, 2.15
$[ZnCl_2L^2]$	0.78		0.92, 0.99		3.08 [c]	2.36
$[ZnCl_2L^3]$	0.62		0.93, 1.08		2.64 [c]	2.34
$[PdCl_2L^2]$	0.46		0.84, 0.99		2.56 [d]	2.34
$[PdCl_2L^3]$	0.46, 0.43		0.84, 0.88 1.02, 1.17			2.50 [e]
$[Zn(BF_4)_2L^1{}_2]$	0.40 [f]		0.82, 0.99 [f]		2.52 [d]	
$[Zn(BF_4)_2L^3{}_2]$	0.23 [f]		0.79, 1.00 [f]			1.95 [e]

[a] In $CDCl_3$; $SiMe_4$ internal standard. H^5 and H^6 give a complex multiplet at *ca.* 1.5—2.0 p.p.m. [b] Multiplet. [c] Doublet. [d] Broad singlet. [e] Complex multiplet, includes H^4–H^6. [f] Broad.

With the bis(ligand) complexes the possibility of two isomers (the 10-methyl groups being either *cis* or *trans*) arises; however, their separation would be expected to be difficult. The ^1H n.m.r. spectra of the zinc complexes (Table 5) do not show the 8-, 9-, and 10-methyl resonances to be singlets of equal peak height, as expected for one isomer if their rotation is not restricted, but instead a broadening for two of the resonances is apparent.

On the basis of the available evidence it appears that $[Cu(BF_4)_2L_2]$ (L = L^1, L^2, or L^3) are essentially distorted tetragonal in nature. To reduce the interligand interactions which would occur with a strictly square-planar CuN_4 core the nitrogen-donor atoms are required to twist out the copper plane. Since methyl substitution into the aromatic ring is unlikely to cause a significant change in the basicity or π-bonding capacity of the di-imine ligands, the accentuated $[BF_4]^-$ co-ordination must result from steric factors. It can be noted that the 10-methyl resonance in the $[Zn(BF_4)_2L^3{}_2]$ complex is highly shielded (Table 5) again suggesting that the aromatic rings are being forced to face the camphor skeleton. Molecular models show that the introduction of the *o*-methyl groups would cause greater interligand interactions which would be relieved by a lengthening of the Cu–N bonds. In order to maintain electroneutrality a concomitant shortening of the Cu–F bond is required. For the nickel and zinc complexes, where the Jahn–Teller effect does not operate, the metal–tetrafluoroborate interaction is enhanced. An analogous situation could be envisaged to occur in metalloproteins where a very slight change in co-ordination environment could enhance the metal–substrate interaction, thus facilitating catalytic behaviour.

Copper(I) *Complexes.*—The reaction of copper(I) chloride with the ligands in acetone yielded intensely coloured 1 : 1 complexes CuCl(L) (L = L^1, L^2, or L^3) (Table 1). Their electronic spectra (Table 2) show maxima at *ca.* 20 000 cm^{-1} which can be assigned as a metal-to-ligand charge-transfer transition occurring in the $[CuL_2]^+$ (L = L^1 L^2, or L^3) chromophore. Zinc-dust reduction of methanol solutions of the copper(II) complexes $[Cu(BF_4)_2L_2]$ (L = L^1, L^2, or L^3) produced identical spectra. Such charge-transfer bands are typical of a variety of bis(di-imine)copper(I) complexes containing a CuN_4 centre.[37] In nitrobenzene solution the complexes showed an appreciable conductivity, and if the molar conductivities are calculated on the basis of the formulation $[CuL_2][CuCl_2]$ (L = L^1, L^2, or L^3) the values fall in the range expected for 1 : 1 electrolytes (Table 1).

Moreover, the i.r. spectra (Table 1) of the L^1 and L^3 complexes show an intense band near 400 cm^{-1} assignable to ν(Cu–Cl) and pointing to the presence of the linear $[CuCl_2]^-$ anion.[38] The absence of the band for the L^2 complex suggests that in the solid state the anion is probably involved in a polymeric structure. It appears therefore that these copper(I) complexes contain the $[CuL_2]^+$ cation and are not monomeric three-coordinate complexes as had been postulated previously [39] for some other di-imine complexes.

The Complex $[CuL^4{}_2]$.—Typical of the condensation reactions of primary amines with 3-hydroxymethylenecamphor,[40] the reaction of $H_2NCH_2CH_2SEt$ affords the compound HL^4. The copper(II) complex $[CuL^4{}_2]$, which was prepared in Bu^{t}OH with K(OBu^t) as base, was unusually soluble in common solvents, including hydrocarbons, and could be recrystallised from pentane, suggesting that the protection of the polar donor atoms and central copper ion by the rest of the ligand is considerable. That deprotonation of the NH hydrogen had occurred is shown by the absence of an N–H stretching frequency (observed at 3 210 and 3 140 cm^{-1} in HL^4) in the i.r. spectrum. A band at 1 681 cm^{-1} in the free ligand moves to 1 675 cm^{-1} in the complex $[CuL^4{}_2]$, and is assignable to essentially a ν(C=O) frequency, thus implying that at least one of the potential oxygen-donor atoms is only weakly co-ordinated, if at all. In the related complex $[CuL_2]$ (L = 3-hydroxymethylenecamphorate) the analogous frequency is decreased by *ca.* 80 cm^{-1} on co-ordination [41] in line with strong carbonyl-oxygen co-ordination. Evidence for sulphur co-ordination comes from the electronic spectrum where a band at 21 280 cm^{-1} (ε 920 dm^3 mol^{-1} cm^{-1}) can be assigned to a S→Cu charge-transfer transition as in other thiaether–copper(II) complexes.[24,42] A shoulder at 12 050 cm^{-1} (ε 50 dm^3 mol^{-1} cm^{-1}) must be a component of a ligand-field transition. In the e.s.r. spectrum, the observation of a three-*g* value spectrum with $g_{\parallel}$ (g_1) > $g_{\perp}$ (g_2 and g_3) is consistent with a distorted-tetragonal (*i.e.* $CuN_2S_2O_2$), possibly approaching square-pyramidal (*i.e.* CuN_2S_2O), co-ordination around the copper(II) ion.[30,43]

EXPERIMENTAL

Infrared spectra were recorded using a Hitachi–Perkin-Elmer 225 spectrophotometer (250—4 000 cm^{-1}) and electronic spectra on Hitachi EPS-4T and Shimadzu MPS 5000 spectrophotometers. N.m.r. spectra were obtained on JEOL JNM-C60 HL and JEOL MH-100 spectrometers and e.s.r. spectra on a JEOL JES-ME-2X spectrometer. All the solvents were purified according to established procedures. The metal tetrafluoroborate salts were prepared from the reactions of the appropriate metal carbonates with tetrafluoroboric acid (40%), and $[NEt_4]_2[CuBr_4]$ from copper(II) bromide and tetraethylammonium bromide.[44]

Synthesis of Ligands L^1—L^3.—*NN'*-(1,7,7-Trimethylbicyclo[2.2.1]heptane-2,3-diylidene)dianiline (L^1) was synthesised following the method of Dvolaitzky;[4] m.p. 113 °C (lit.,[4] 107 °C). The di(*p*-methylaniline) derivative L^2 was similarly prepared using *p*-toluidine and recrystallised from n-hexane–ethanol; m.p. 166—168 °C (Found: C, 83.6; H, 8.1; N, 8.1. $C_{24}H_{28}N_2$ requires C, 83.7; H, 8.2; N, 8.1%). For the di(*o*-methylaniline) derivative L^3 it was necessary to remove the excess of *o*-toluidine from the crude product by distillation *in vacuo* (0.01 mmHg * 120 °C). Recrystallisation was achieved using n-pentane cooled in a bath of solid CO_2 and acetone; m.p. 86—88 °C (Found: C, 83.5; H, 8.3; N, 8.0. $C_{24}H_{28}N_2$ requires C, 83.7; H, 8.2; N, 8.1%).

Synthesis of the Ligand HL^4.—The room-temperature reaction of $H_2NCH_2CH_2SEt$ and 3-hydroxymethylenecamphor (prepared according to literature methods [41,45]) in methanol gave 3-[(2-ethylthioethyl)aminomethylene]-1,7,7-trimethylbicyclo[2.2.1]heptan-2-one. Recrystallisation was achieved using methyl chloride–n-hexane; m.p. 82—83 °C (Found: C, 67.3; H, 9.4; N, 5.25; S, 12.0. $C_{15}H_{25}NOS$ requires C, 67.4; H, 9.4; N, 5.2; S, 12.0%).

Preparation of the Complexes.—$[MCl_2L]$ (M = Cu, L = L^1, L^2, *or* L^3; M = Zn, L = L^2 *or* L^3) *and* $[CuBr_2L^2]$. These were prepared by similar methods of which the following is typical. To copper(II) chloride dihydrate (0.341 g, 2.0 mmol), dissolved in acetone (10 cm^3) containing triethylorthoformate (0.5 cm^3) as dehydrating agent, was added L^3 (0.689 g, 2.0 mmol) dissolved in the minimum volume of acetone. The resulting dark yellow solution was heated to 60 °C for 5 min, then reduced in volume, and sufficient diethyl ether added to induce crystallisation. The yellow-brown product $[CuCl_2L^3]$ was filtered off, washed with diethyl ether, and dried *in vacuo*, yield 0.758 g (79%). In the case of $[CuCl_2L^1]$ and $[CuBr_2L^2]$ ethanol was used as solvent. Where the i.r. spectrum indicated the presence of solvent of crystallisation the complexes were heated *in vacuo* (100 °C) to achieve its removal.

$[PdCl_2L]$ (L = L^2 *or* L^3). To $[PdCl_2(NCPh)_2]$ (0.383 g, 1.0 mmol) dissolved in toluene (23 cm^3) was added the ligand (0.345 g, 1.0 mmol) dissolved in the same solvent (10 cm^3). After stirring for 1 h the yellow precipitate was filtered off, washed with toluene, recrystallised from dichloromethane–n-hexane, and dried *in vacuo*, yields 70—80%.

$[M(BF_4)_2L_2]$ (M = Cu, L = L^1, L^2, *or* L^3; M = Ni *or* Zn, L^1 *or* L^3). These complexes were prepared from the appropriate metal tetrafluoroborate (1 mmol) and the ligand (2 mmol) in a manner similar to that described above for the analogous metal halide complexes, yields 55—80%.

$[CuL_2][CuCl_2]$ (L = L^1, L^2, *or* L^3). To a suspension of copper(I) chloride (0.099 g, 1.0 mmol) in acetone (10 cm^3) under dinitrogen was added the ligand (1.0 mmol) dissolved in the same solvent (10 cm^3). After stirring at 50 °C for 30 min the resulting intensely coloured solution was stirred at room temperature for another 5 h, and then its volume was reduced to 5 cm^3. Diethyl ether (*ca.* 50 cm^3) was added and the solution left at 0 °C to allow the product to crystallise. After filtering off and washing with diethyl ether the crystals were dried *in vacuo*, yields *ca.* 60%. The copper(I) complexes are moderately stable in air in the solid state but decompose slowly in solution.

Bis{3-[(2-*ethylthioethyl*)*aminomethylene*]-1,7,7-*trimethylbicyclo*[2.2.1]*heptan*-2-*onato*}*copper*(II), $[CuL^4{}_2]$. Under dinitrogen, potassium (0.39 g, 10.0 mmol) was added to dry Bu^{t}OH (30 cm^3) at 80 °C and to the resulting solution, cooled to 60 °C, was added 3-hydroxymethylenecamphor (2.67 g, 10.0 mmol) followed by $[NEt_4]_2[CuBr_4]$ (3.61 g, 5.6 mmol). After stirring at room temperature for 3 h the solvent was removed *in vacuo* and the dark brown residue extracted into the minimum volume of n-hexane. The n-

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* Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa.

hexane solution was filtered and allowed to stand overnight at −78 °C. The resulting brown solid was washed with n-pentane at −78 °C and recrystallised from the same solvent; m.p. 64—67 °C, yield 1.73 g (58%).

A. M. B. thanks the Ministry of Education, Japan, for the award of a fellowship.

[8/758 *Received, 24th April,* 1978]

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