Synthesis and Characterization of Copper(II) Complexes with Unsymmetrical Quadridentate Schiff Bases derived from β-Diketone, Diamine, and *o*-Hydroxybenzaldehyde Ligands†

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Several copper(II) complexes with unsymmetrical quadridentate Schiff bases derived from β-diketone (acetylacetone, benzoylacetone), diamine (ethylenediamine, trimethylenediamine), and *o*-hydroxybenzaldehyde (salicylaldehyde, *o*-hydroxyacetophenone, 2-hydroxy-1-naphthalenecarbaldehyde) have been prepared and characterized. The physical properties (melting points, absorption maxima, absorption coefficients) of the unsymmetrical copper(II) complexes are intermediate between the corresponding symmetrical copper(II) complexes. One of the unsymmetrical complexes, trimethylene-*N*-(acetylacetoneiminato)-*N'*-salicylideneiminatocopper(II), has been subjected to a single-crystal *X*-ray analysis; the result verified the detailed structure in which the copper(II) atom assumes a distorted-tetrahedral co-ordination geometry, with a dihedral angle of 19.1° between two OCuN planes. The unsymmetrical copper(II) complexes react with ethyl isocyanate and with phenyl isocyanate to produce compounds substituted at the methine position of the β-diketonate moiety. The ligands were prepared by the reaction of the copper(II) complexes with gaseous hydrogen sulphide. The copper(II) complexes and the ligands have been characterized by elemental analyses, i.r., ^{1}H n.m.r., e.s.r., and electronic spectra.

The γ-position of six-membered conjugated chelate rings, such as those formed by di-iminate and acetylacetonate ligands, has been found to be a very reactive nucleophilic centre[1] since Collman *et al.*[2] discovered the quasi-aromatic character of tris(acetylacetonato)cobalt(III) and its derivatives. In these studies,[1,2] the metal complex possesses in most cases two or three chelate rings, *i.e.* two or three nucleophilic centres. Binuclear metal complexes containing metal centres in close proximity are of current interest[3] since the structural unit is thought to be involved in a variety of biological processes,[4] such as oxygen tranport and oxygen activation. Metal complexes containing a nucleophilic centre can be effective starting compounds for the preparation of binuclear complexes, because it is expected that such complexes react with two-centre electrophilic reagents to produce binuclear complexes selectively. From this viewpoint we are interested in metal complexes containing a nucleophilic centre.[5]

In this study, the unsymmetrical quadridentate Schiff-base copper(II) complexes with the general formula (**1**) have been prepared. The reaction procedure from (**1**) to the substituted complexes (**2**) and the ligands (**3**) are shown in Figure 1. The properties of the unsymmetrical complexes are compared with those of the corresponding symmetrical complexes (melting points, electronic and e.s.r. spectra). One of the unsymmetrical copper(II) complexes, trimethylene-*N*-(acetylacetoneiminato)-*N'*-salicylideneiminatocopper(II), [CuL^2], has been subjected to a single-crystal *X*-ray analysis. The electrophilic substitution reaction of the unsymmetrical copper(II) complexes with ethyl isocyanate and phenyl isocyanate has been employed to produce mononuclear copper(II) complexes substituted at the methine position. The ligands were prepared by a demetallation reaction with hydrogen sulphide and characterized by ^{1}H n.m.r. spectroscopy.

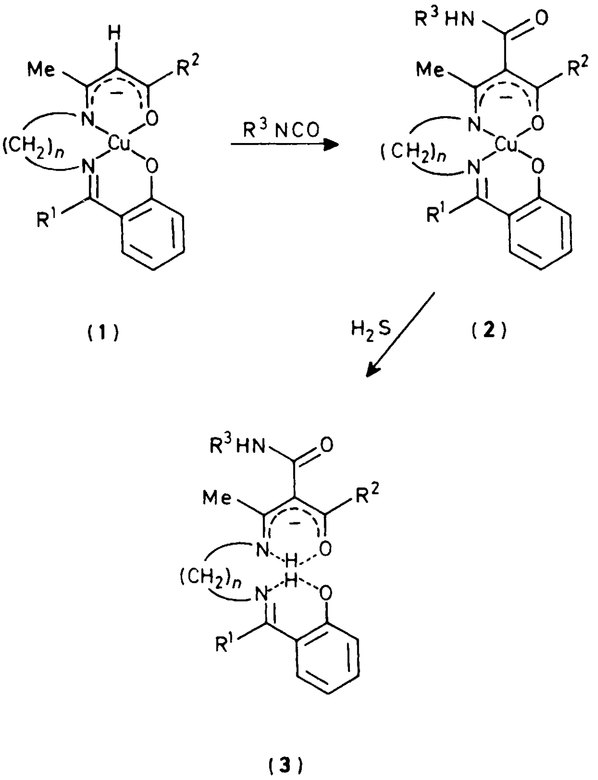

Figure 1. The reactions of unsymmetrical quadridentate Schiff-base copper(II) complexes (**1**) with isocyanates to give substituted copper(II) complexes (**2**), and demetallation to give the ligands (**3**). R^1 = H or Me, R^2 = Me or Ph, R^3 = Et or Ph, n = 2 or 3

Experimental

Unsymmetrical Copper(II) *Complexes.*—The unsymmetrical quadridentate Schiff-base copper(II) complexes [CuL] (L = L^1, L^2, L^7, L^8, or L^{11}) studied in this work were prepared

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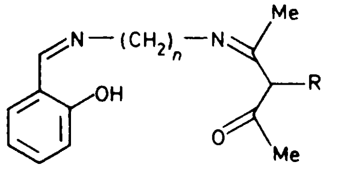
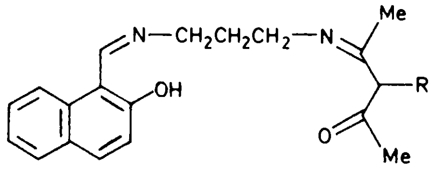
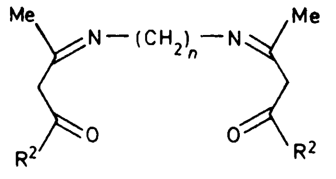
† *Supplementary data available* (No. SUP 56077, 19 pp.): H-atom co-ordinates, structure factors, thermal parameters, ^{1}H n.m.r. data. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii–xix.



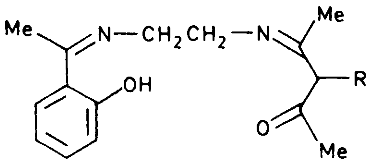
	n	R
H_2L^1	2	H
H_2L^2	3	H
H_2L^3	2	CONHEt
H_2L^4	3	CONHEt
H_2L^5	2	CONHPh
H_2L^6	3	CONHPh



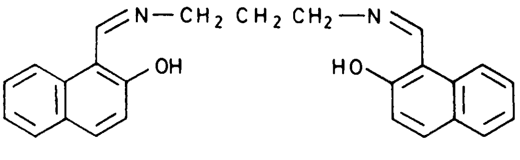
	R
H_2L^8	H
H_2L^9	CONHEt
H_2L^{10}	CONHPh



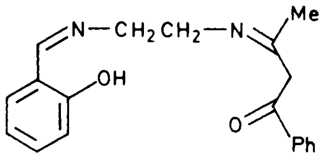
	n	R^2
H_2L^{15}	2	Me
H_2L^{16}	3	Me
H_2L^{17}	2	Ph



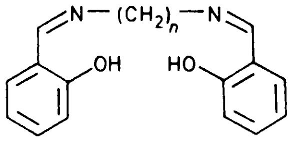
	R
H_2L^{11}	H
H_2L^{12}	CONHPh



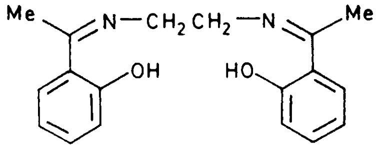
H_2L^{18}



H_2L^7



	n
H_2L^{13}	2
H_2L^{14}	3



H_2L^{19}

by the method of Kusuka *et al.*[6] For comparison, corresponding symmetrical copper(II) complexes [CuL] (L = L^{13}—L^{19}) were prepared according to the literature.[7]

Substituted Copper(II) *Complexes*.—The copper(II) complexes of the substituted ligands, [CuL] (L = L^3—L^6, L^9, L^{10}, or L^{12}) were prepared by the reaction of the unsubstituted copper(II) complexes with the appropriate isocyanate (Figure 1).[8]

[CuL^5]. To a solution of [CuL^2] (2 g) in dichloromethane (50 cm^3) was added a small excess of phenyl isocyanate. The mixture was refluxed for 3 h, during which time pale violet needle crystals were precipitated. They were collected, washed with dichloromethane and diethyl ether, and dried *in vacuo*. The other substituted copper(II) complexes were prepared similarly.

Ligands.—The demetallation reaction of the copper(II) complexes with hydrogen sulphide gave the corresponding ligands. The reaction procedure is exemplified by H_2L^{11}. Gaseous hydrogen sulphide was passed through a suspension of [CuL^{11}] in chloroform (50 cm^3) for 30 min at room temperature, during which time the colour changed from purple to chocolate brown. The brown suspension was filtered and washed with chloroform. The filtrate was evaporated and diethyl ether (50 cm^3) was added to precipitate pale yellow crystals. They were collected and recrystallized from n-hexane–chloroform (*ca.* 1 : 2).

Physical Measurements.—Melting points were measured on a Yanagimoto micromelting-point apparatus and are uncorrected. Elemental analyses were performed by Mr. Shinichi Miyazaki at the Technical Service Centre of Kumamoto University. Visible and u.v. spectra in chloroform solution were recorded with a Hitachi spectrophotometer model 323; i.r. spectra were recorded as KBr discs with a Shimadzu spectrophotometer model IR-410. The 100-MHz ^1H n.m.r. spectra were recorded on a JEOL MH 100 spectrometer; $CDCl_3$ was used as solvent and chemical shifts are relative to $SiMe_4$. E.s.r. spectra (*X*-band) were recorded on a JEOL JES-FEAX spectrometer using Mn^{2+} doped in MgO as reference.

X-*Ray Diffraction Analysis of* [CuL^2].—Green-black rhombic crystals were obtained by slow evaporation from a chloroform solution at room temperature. A crystal with approximate dimensions 0.5 × 0.5 × 0.6 mm was cut out from a large crystal and used for the *X*-ray diffraction study. Diffraction data were obtained on a Rigaku AFC-5 four-circle diffractometer at the Institute for Molecular Science, using graphite-monochromated Mo-K_α radiation (λ = 0.710 73 Å) at ambient temperature. Lattice parameters and their standard deviations were obtained from a least-squares fit to 30 2θ values in the range $20 < 2\theta < 30°$.

Crystal data. $C_{15}H_{18}CuN_2O_2$, M = 321.86, monoclinic, a = 18.357(4), b = 9.251(1), c = 8.743(1) Å, β = 103.58(1)°, U = 1 443.4(5) $Å^3$, D_m = 1.48 g cm^{-3}, Z = 2, D_c = 1.481 g cm^{-3}, $F(000)$ = 668, μ(Mo-K_α) = 10.24 cm^{-1}, space group $P2_1/n$.

For the intensity data collection, the θ—2θ scan mode was used at a scan rate of 3° min^{-1}. Three standard reflections were monitored every 100 reflections and their intensities showed good stability (less than 3% change). A total of 2 884 reflections were collected in the range $1.5 \leqslant 2\theta \leqslant 50°$, of which 2 034

Table 1. Atomic co-ordinates (× 10^4) for [CuL^2]

Atom	*x*	*y*	*z*
Cu	189.8(2)	325.5(5)	2 468.0(5)
O(1)	832(1)	−1 206(3)	3 457(3)
O(2)	1 122(1)	1 311(3)	2 654(3)
N(1)	−720(2)	−544(3)	2 890(4)
N(2)	−302(1)	1 616(3)	732(3)
C(1)	1 254(3)	−3 420(5)	4 592(6)
C(2)	636(2)	−2 353(4)	4 048(5)
C(3)	−75(2)	−2 632(5)	4 204(5)
C(4)	−721(2)	−1 784(5)	3 623(4)
C(5)	−1 445(2)	−2 427(6)	3 863(5)
C(6)	−1 464(2)	146(5)	2 374(6)
C(7)	−1 469(2)	1 540(5)	1 529(5)
C(8)	−1 117(2)	1 478(5)	122(4)
C(9)	23(2)	2 607(4)	119(4)
C(10)	795(2)	3 022(4)	565(4)
C(11)	1 042(2)	4 128(5)	−291(4)
C(12)	1 771(2)	4 595(4)	78(6)
C(13)	2 273(2)	3 952(5)	1 331(5)
C(14)	2 042(2)	2 868(4)	2 175(5)
C(15)	1 305(2)	2 358(4)	1 826(4)

Table 2. Elemental analytical data and melting points

	Analysis[a] (%)			
Complex	C	H	N	M.p. (°C)
[CuL^7]	61.6 (61.7)	5.00 (4.90)	7.55 (7.55)	253—256
[CuL^2]	55.7 (56.0)	5.55 (5.65)	8.40 (8.70)	143—145
[CuL^8]	61.4 (61.35)	5.50 (5.40)	7.55 (7.55)	176—178
[CuL^3]	53.9 (53.65)	5.60 (5.70)	11.1 (11.1)	208—210
[CuL^4]	54.45 (55.0)	6.10 (5.90)	10.9 (10.7)	187—190
[CuL^9]	55.2 (55.65)	5.35 (5.40)	8.45 (8.65)	227—231
[CuL^5]	59.05 (59.1)	4.90 (4.95)	9.85 (9.85)	239—241
[CuL^{12}]	59.75 (59.9)	5.30 (5.25)	9.50 (9.55)	260 (decomp.)
[CuL^6]	59.9 (59.9)	5.20 (5.25)	9.50 (9.55)	226—227
[CuL^{10}][b]	59.7 (59.65)	4.70 (4.90)	7.95 (7.90)	165—167
H_2L^{11}	69.3 (69.2)	7.75 (7.75)	10.65 (10.75)	130—132
H_2L^3	63.9 (64.35)	7.40 (7.30)	13.1 (13.25)	152—153
H_2L^5	67.8 (67.35)	6.00 (6.45)	11.2 (11.2)	127—129
H_2L^{12}	69.15 (69.65)	6.70 (6.65)	11.05 (11.05)	175—177
H_2L^6	69.6 (69.65)	6.75 (6.65)	11.05 (11.05)	124—127

[a] Calculated values are in parentheses. [b] With $0.5CH_2Cl_2$ solvate.

independent reflections with $|F_o| > 3\sigma|F_o|$ were used for the structure determination. The intensity data were corrected for Lorentz-polarization effects, but not for absorption.

Solution and refinement of the structure. All the calculations were carried out on the Hitac M-2001 computer at the Computer Centre of the Institute for Molecular Science with the Universal Crystallographic Computation Program System UNICS III.[9] Atomic scattering factors for non-hydrogen atoms were taken from ref. 10 and those for hydrogen atoms from Stewart *et al.*[11] The effects of anomalous dispersion for non-hydrogen atoms were corrected for in the structure factor calculations.

The structure was solved by the heavy-atom method and refined by block-diagonal least-squares methods. Reliability factors are defined as $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$, where the weights (*w*) were taken as $w = [\sigma(F_o) + 0.015|F_o|^2]^{-1}$. The position of the copper atom was determined from three-dimensional Patterson functions, and successive Fourier syntheses located all the non-hydrogen atoms. Anisotropic thermal parameters were introduced for all the non-hydrogen atoms. Further difference-Fourier syntheses located all the hydrogen atoms and their positional and isotropic thermal parameters were refined. The final indices *R* and *R′* were 0.0337 and 0.0559 respectively. A final difference-Fourier map was featureless. Final positional parameters with their estimated standard deviations are given in Table 1.

Results and Discussion

Syntheses.—The new unsymmetrical copper(II) complexes have been prepared according to the general procedure of Kusuka *et al.*,[6] which was applied for the syntheses of [CuL^1] and [CuL^{11}]. As the unsymmetrical copper(II) complexes exhibit solubility properties intermediate between the corresponding symmetrical complexes, the unsymmetrical complexes are obtained by column chromatography or recrystallization. The complexes containing a saturated six-membered chelate ring such as [CuL^2] and [CuL^8] ($\overline{NCH_2CH_2CH_2NCu}$ chelated complexes) are much more soluble in organic solvents than those containing the five-membered chelate ring such as [CuL^1], [CuL^{11}], and [CuL^7] ($\overline{NCH_2CH_2NCu}$ chelated complexes), and the differences in solubility among the unsymmetrical and symmetrical $\overline{NCH_2CH_2CH_2NCu}$ chelated complexes are smaller than those of the $\overline{NCH_2CH_2NCu}$ chelated complexes. The unsymmetrical copper(II) complexes react with ethyl isocyanate and phenyl isocyanate in dichloromethane or benzene, even at ambient temperature, to produce the complexes substituted at the methine position of the β-diketonate residue, almost quantitatively. The substituted complexes are less soluble in dichloromethane or benzene than the unsubstituted complexes, so that the reaction products with the isocyanates are easily precipitated; those of ethyl isocyanate are much more soluble than those of phenyl isocyanate. The ligands were obtained by the demetallation reaction of the copper(II) complexes with gaseous hydrogen sulphide.

The elemental analytical data and melting points of the unsymmetrical copper(II) complexes, along with those of the reaction products with isocyanates, and the ligands are given in Table 2. The melting points of the unsymmetrical complexes are intermediate between those of the corresponding symmetrical complexes: *e.g.* > 290, 143, and 94 °C for [CuL^{14}], [CuL^2], and [CuL^{16}] respectively. The products of the reactions with isocyanates possess new i.r. absorptions at *ca.* 1 650 and 3 250br cm^{-1}. The bands are assignable to ν(C=O) and ν(NH) of the substituent carbamoyl group ($-CONHR^3$), based on the study of the analogous reaction products derived from [CuL^{15}] and isocyanates.[8]

*Hydrogen-*1 *N.M.R. Spectra.*—The results with their assignments are given in SUP 56077. The chemical shifts and coupling constants are consistent with the structures and appear in the anticipated regions. The spectra in general consist of five distinct regions: methyl, methylene, methine, aromatic, and imine proton resonances from the high-field region. The methine proton resonance of H_2L^1, H_2L^2, H_2L^{11}, and H_2L^8 appeared at 5.0 p.p.m. as a singlet signal. The methine proton resonance in the spectra of the unsubstituted ligands is absent in those of the substituted ligands, being indicative of the introduction of the $CONHR^3$ substituent. The signal at 8.5 p.p.m. is assigned to the imine proton resonance, since it is not observed for H_2L^{11} (Figure 1, R^1 = Me).

Crystal Structure of [CuL^2].—Figure 2 shows a perspective view of [CuL^2] with the atom numbering scheme. The *X*-ray structure analysis verified the formation of the unsymmetrical

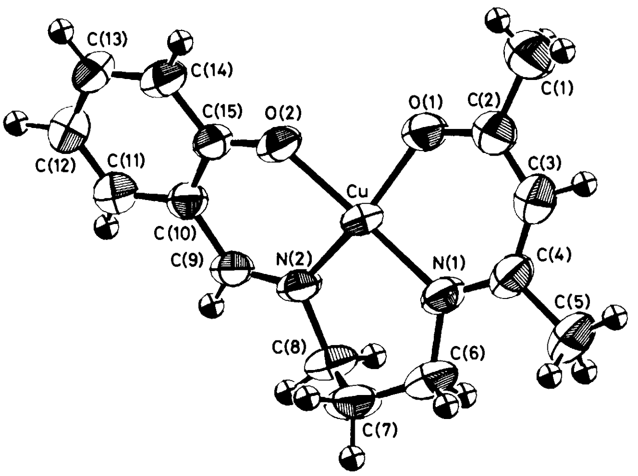


Figure 2. Perspective drawing of [CuL^2] showing the atom numbering scheme

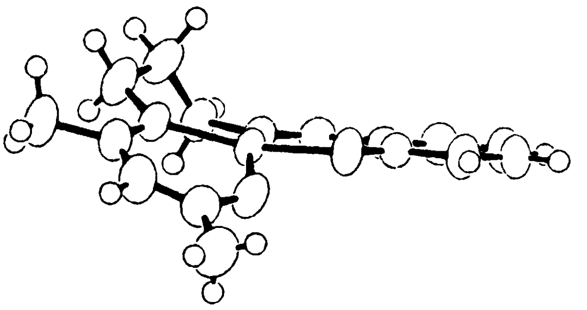


Figure 3. An edge-on view from the salicyladehyde moiety of [CuL^2]; the dihedral angle between the planes O(1)CuN(1) and O(2)CuN(2) is 19.1°

quadridentate Schiff-base copper(II) complex formed from acetylacetone, trimethylenediamine, and salicylaldehyde moieties. Figure 3 shows an edge-on view from the salicylaldehyde moiety, showing apparently a tetrahedral distortion from square-planar co-ordination geometry. The dihedral angle between the planes of O(1)CuN(1) and O(2)CuN(2) is 19.1°. Table 3 lists relevant bond distances and angles with their estimated standard deviations. The saturated six-membered chelate ring adopts a boat conformation, where the atoms Cu and C(7) deviate by 0.11 and 0.70 Å from the mean plane passing through the atoms N(1), N(2), C(8), and C(9). The geometries around the imine nitrogens N(1) and N(2) are perfectly planar. The six-membered chelate ring comprising the Cu atom and the acetylacetone residue is planar (maximum deviation of component atoms 0.02 Å), and the bond distances of C–C, C–N, and C–O of the chelate ring are intermediate between their single- and double-bond distances, indicating that the chelate ring is a π-electron conjugated system and giving evidence for aromatic character of the chelate ring. The bond distance Cu–N(1) is somewhat shorter than Cu–N(2), while the bond distances Cu–O(1) and Cu–O(2) are equal. Based on the Cu–N and Cu–O bond distances, it seem that [CuL^{16}] provides somewhat greater ligand-field strength than does [CuL^{14}]. The C–N bond distance of the acetylacetone moiety is somewhat longer than that of the salicylaldehyde moiety, while the C–O bond distance of the acetylacetone moiety is somewhat shorter than that of the salicylaldehyde moiety.

Table 3. Bond distances (Å) and angles (°) for [CuL^2] with estimated standard deviations in parentheses

(*a*) Distances

Cu–O(1)	1.914(3)	C(3)–C(4)	1.413(6)
Cu–O(2)	1.912(3)	C(4)–C(5)	1.516(7)
Cu–N(1)	1.965(3)	C(6)–C(7)	1.484(7)
Cu–N(2)	1.975(3)	C(7)–C(8)	1.519(7)
O(1)–C(2)	1.268(5)	C(9)–C(10)	1.430(5)
O(2)–C(15)	1.299(4)	C(10)–C(11)	1.404(5)
N(1)–C(4)	1.315(5)	C(10)–C(15)	1.409(5)
N(1)–C(6)	1.479(6)	C(11)–C(12)	1.371(6)
N(2)–C(8)	1.472(5)	C(12)–C(13)	1.389(6)
N(2)–C(9)	1.279(5)	C(13)–C(14)	1.370(6)
C(1)–C(2)	1.494(7)	C(14)–C(15)	1.398(5)
C(2)–C(3)	1.369(6)		

(*b*) Angles

O(1)–Cu–O(2)	82.5(1)	N(1)–C(4)–C(3)	124.2(3)
O(1)–Cu–N(1)	94.1(1)	N(1)–C(4)–C(5)	120.8(3)
O(2)–Cu–N(2)	90.9(1)	C(3)–C(4)–C(5)	114.9(3)
N(1)–Cu–N(2)	97.8(1)	N(1)–C(6)–C(7)	115.0(4)
N(2)–Cu–O(6)	156.4(1)	C(6)–C(7)–C(8)	114.6(4)
N(1)–Cu–O(2)	164.2(1)	N(2)–C(8)–C(7)	107.0(3)
Cu–O(1)–C(2)	126.8(2)	N(2)–C(9)–C(10)	127.4(3)
Cu–O(2)–C(15)	130.6(2)	C(9)–C(10)–C(11)	118.2(3)
Cu–N(1)–C(4)	123.1(2)	C(9)–C(10)–C(15)	122.0(3)
Cu–N(1)–C(6)	122.0(2)	C(11)–C(10)–C(15)	119.7(3)
Cu–N(1)–C(6)	114.7(3)	C(10)–C(11)–C(12)	121.5(3)
Cu–N(2)–C(8)	117.9(2)	C(11)–C(12)–C(13)	118.7(4)
Cu–N(2)–C(9)	125.5(2)	C(12)–C(13)–C(14)	120.4(4)
C(8)–N(2)–C(9)	116.4(3)	C(13)–C(14)–C(15)	122.3(3)
O(1)–C(2)–C(1)	114.6(3)	O(2)–C(15)–C(10)	123.3(3)
O(1)–C(2)–C(3)	124.4(3)	O(2)–C(15)–C(14)	119.5(3)
C(1)–C(2)–C(3)	120.9(4)	C(10)–C(15)–C(14)	117.0(3)
C(2)–C(3)–C(4)	126.8(4)		

Table 4. Electronic spectroscopic data in chloroform

Complex	10^{-3} $\tilde{\nu}$/cm^{-1} (10^{-3} ε/dm^3 mol^{-1} cm^{-1})	
	d–d	Other
[CuL^{13}]	17.6 (400)	25.6 (7.6), 28.6 (5.6)
[CuL^{19}]	18.0 (330)	27.3 (9.8)
[CuL^{1}]	18.0 (250)	25.7 (3.5)
[CuL^{11}]	18.1 (260)	26.6 (4.4)
[CuL^{7}]	17.9 (320)	25.6 (7.4), 28.7 (21.4)
[CuL^{15}]	18.3 (180)	26.8 (0.6)
[CuL^{17}]	18.2 (250)	29.2 (26.9)
[CuL^{14}]	16.5 (230)	27.0 (10.5)
[CuL^{18}]	16.9 (240)	25.0 (12.6), 26.0 (14.5)
[CuL^{2}]	16.6 (180)	26.3 (5.0)
[CuL^{8}]	16.8 (190)	24.9 (7.2), 25.6 (6.7)
[CuL^{16}]	16.7 (130)	26.5 (0.9)
[CuL^{4}]	16.4 (140)	26.5 (4.8)
[CuL^{9}]	17.0 (180)	25.0 (6.7), 25.8 (6.3)
[CuL^{6}]	16.6 (160)	26.4 (4.8)
[CuL^{10}]	16.9 (190)	25.0 (7.2), 25.8 (6.8)

Electronic Spectra.—Visible and u.v. spectra were obtained on 10^{-3}—10^{-4} mol dm^{-3} solutions in chloroform. The absorption maxima and absorption coefficients of the new complexes, along with those of the corresponding symmetrical complexes, for comparison, are given in Table 4. The electronic spectra of the unsymmetrical complexes are intermediate both in absorption maxima and absorption coefficients between

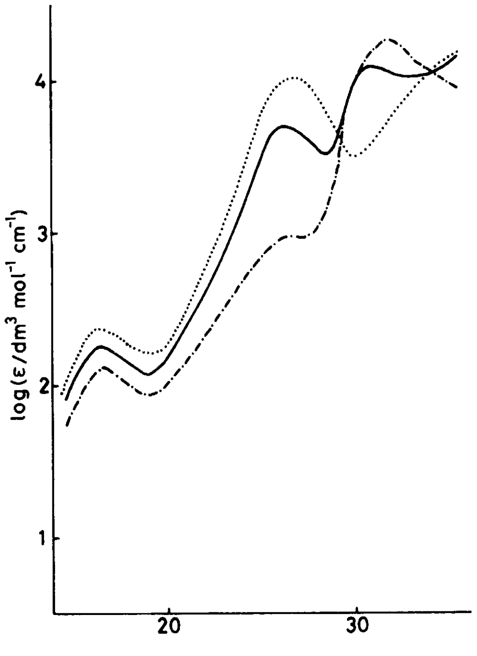


Figure 4. Electronic spectra of [CuL^{14}] (····), [CuL^2] (——), and [CuL^{16}] (— · —) in chloroform solution

those of the corresponding symmetrical complexes over the range 15 000—30 000 cm^{-1}. These results are consistent with those obtained previously for [CuL^1], [CuL^{13}], and [CuL^{15}].[6] As a typical example, the electronic spectra of [CuL^2], [CuL^{14}], and [CuL^{16}] are shown in Figure 4. The spectra consist of a band in the visible region assignable to the *d–d* transition with an absorption coefficient of the order of *ca.* 200 dm^3 mol^{-1} cm^{-1} and several peaks in the u.v. region assignable to the charge-transfer bands. The *d–d* transition shifts to lower energy in the order [CuL^{16}] > [CuL^2] > [CuL^{14}] or [CuL^{17}] > [CuL^7] > [CuL^{13}], being consistent with the series involving [CuL^1] and [CuL^{11}].[6] For the series involving [CuL^8], the *d–d* transition shifts to higher energy and the absorption coefficient increases in the order [CuL^{16}] < [CuL^8] < [CuL^{18}]. In all the cases, the average ligand-field strength rule is preserved.

Based on the *d–d* band maxima and absorption coefficients, the complexes can be classified into two groups, that is, the $\overline{NCH_2CH_2CH_2NCu}$ and $\overline{NCH_2CH_2NCu}$ chelated complexes. The complexes of the former type [CuL^2] and [CuL^8] exhibit a smaller wavenumber and larger absorption coefficient for the *d–d* transition than the complexes [CuL^1], [CuL^{11}], and [CuL^7] having five-membered chelate rings. Red shift and intensity enchancement of the *d–d* transition are recognised indicators of the transformation from square planar to tetrahedral stereochemistry.[12] Therefore, it is considered that the six-membered ring chelated complexes assume a distorted tetrahedral co-ordination geometry, as confirmed by the *X*-ray analysis of [CuL^2].

Electronic spectra of some of the complexes substituted at the methine position, especially those of the reaction products of the five-membered ring chelated complexes with phenyl isocyanate, were not measured due to the poor solubility in chloroform. The spectra of the substituted complexes resemble those of the corresponding unsubstituted complexes, and the substitution effects are not observed in the electronic spectra.

Table 5. E.s.r. parameters* in *NN*-dimethylformamide

Complex	g_0	$g_\parallel$	$g_\perp$	A_0	$A_\parallel$	$A_\perp$
[CuL^1]	2.115	2.179	2.083	91	219	27
[CuL^{11}]	2.110	2.193	2.069	87	202	30
[CuL^7]	2.108	2.192	2.066	87	202	30
[CuL^{12}]	2.106	2.190	2.064	90	205	33
[CuL^2]	2.122	2.216	2.075	77	191	20
[CuL^8]	2.121	2.220	2.072	79	181	29
[CuL^4]	2.122	2.216	2.075	78	186	23
[CuL^9]	2.125	2.253	2.061	80	179	30
[CuL^6]	2.127	2.254	2.064	80	186	27
[CuL^{10}]	2.136	2.252	2.078	79	174	32

* The parameters $g_\perp$ and $A_\perp$ were calculated from the equations $g_0 = (g_\parallel + g_\perp)/3$ and $A_0 = (A_\parallel + 2A_\perp)/3$ using the observed values of g_0, $g_\parallel$, A_0, and $A_\parallel$.

E.S.R. Spectra.—These were measured in *NN*-dimethylformamide solution at room temperature and at liquid nitrogen temperature. The *g* and *A* values are given in Table 5. Based on these data, the complexes can be classified into two groups: $\overline{NCH_2CH_2CH_2NCu}$ and $\overline{NCH_2CH_2NCu}$ chelated complexes. The former exhibit larger $g_\parallel$ values and smaller $A_\parallel$ values than the latter complexes. This tendency can be explained in terms of the distortion of the co-ordination geometry from square planar to tetrahedral, as known from previous studies of well established complexes,[12] although there is no linear correlation between the *d–d* band maxima and the $g_\parallel$ or $A_\parallel$ values for the complexes studied.

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