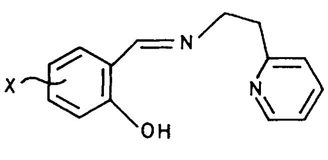
The Electrochemical Synthesis of Neutral Copper(II) Complexes of Schiff Base Ligands: The Crystal Structure of Bis{*N*-[2′-(2″-pyridyl)ethyl]-4,6-dimethoxysalicylideneiminato}copper(II)†

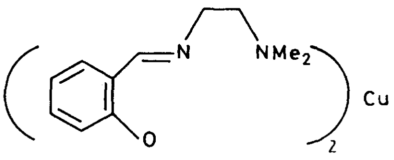
Neil M. Atherton, David E. Fenton,* Geoffrey J. Hewson, and Colin H. McLean
Department of Chemistry, The University, Sheffield S3 7HF
Rufina Bastida, Jaime Romero, and Antonio Sousa*
Departamento de Quimica Inorganica, Universidad de Santiago, Santiago de Compostela, Spain
Eduardo E. Castellano
Istituto de Fisica e Quimica, Universidade de Sao Paulo, C.P.369 13.560, Sao Carlos, Sao Paulo, Brazil

The electrochemical synthesis and physico-chemical properties of neutral copper(II) complexes of Schiff bases derived from 2-(2-aminoethyl)pyridine and substituted salicylaldehydes are presented together with the *X*-ray structure of bis{*N*-[2′-(2″-pyridyl)ethyl]-4,6-dimethoxysalicylideneiminato}-copper(II). The crystals are monoclinic, with a = 9.871(3), b = 8.208(8), c = 18.230(4) Å, β = 93.85(2)°, space group $P2_1/c$, 1 577 reflections with $|I_o| > 3\sigma|I_o|$, R = 0.039. The copper atom has a square-planar geometry and the pyridyl nitrogen atoms are not co-ordinated. An extension of the electrochemical synthesis to metal complexes of Schiff bases derived from 4(5)-[(2-aminoethyl)thiomethyl]imidazole and *o*-hydroxyacetophenones is also reported.

The ligand system (1) has previously been investigated as a potentially tridentate ligand. Taylor and Coleman[1] prepared the monoligated complexes [Cu(L)Cl] [L = anion of (1) where X = H, 5-NO_2, 5-Cl, or 5-OMe] by the reaction of the ligand HL with $CuCl_2$, and from the magnetic and spectroscopic properties suggested that the copper(II) was in a five-co-ordinate environment. This implied that a dimerisation had occurred, which was later corroborated by Latour *et al.*[2] who found that in the chloro- and acetato-complexes of copper(II) with L (X = H) dinuclear and trinuclear species were available.



(1)



(2)

Taylor and Coleman[1] noted that by introducing NaOH into their reaction mixture complexes of the type [CuL_2] were available. Again a five-co-ordinate copper(II) environment was predicted from the physicochemical studies and it was proposed that the geometry of such complexes should be similar to that found in the structure of (2).[3] In this complex one ligand is tridentate and the second is bidentate with a pendant, non-bonded NMe_2 group present. Yamanouchi and Yamada,[4] who also prepared complexes of [CuL_2], suggested, from optical spectroscopic data, that the complexes would be square planar. Although a bonding mode was not defined it was suggested that in related [CoL_3] and [PdL_2] complexes the pyridine nitrogen is non-bonding.

The electrochemical syntheses described herein gave a novel and facile route to the neutral [CuL_2] complexes and it was therefore of interest to determine the structure of one such complex in order to establish the facultative properties of the ligand. The wider application of the synthetic procedure was demonstrated by application of the electrochemical method to the syntheses of neutral complexes of Schiff bases derived from an (aminoethyl)thiomethylimidazole and *o*-hydroxyacetophenones.

Results and Discussion

The analytical data reported in Table 1 show that an electrochemical procedure can be satisfactorily used for the synthesis of compounds of general formula [CuL_2] (L = L^1—L^5). In the case of ligands HL^1—HL^3 a current of 10 mA produces crystalline compounds but the complexes obtained from ligands HL^4 and HL^5 are recovered as powders. The electrochemical yield, defined as the quantity of metal dissolved per Faraday of charge, is close to 1 mol F^{-1} indicating that the synthesis of this complex involves the processes (1) and (2), followed by the oxidation reaction (3).

$$\text{Cathode: LH} + e^- \longrightarrow L^- + \tfrac{1}{2}H_2 \qquad (1)$$

$$\text{Anode: } L^- + \text{Cu} \longrightarrow [\text{CuL}] + e^- \qquad (2)$$

$$[\text{CuL}] + \text{HL} \longrightarrow [\text{CuL}_2] + \tfrac{1}{2}H_2 \qquad (3)$$

A stereoscopic projection of the structure of [$Cu(L^3)_2$] is given in the Figure. Final atomic co-ordinates are given in Table 2 and selected bond distances and angles accompany the Figure. The Cu ion is located on a crystallographic symmetry centre and is co-ordinated to the phenolate oxygen and imine nitrogen atoms of two symmetry-related moieties. The configuration is exactly square planar to within experimental accuracy with Cu–O 1.871 and Cu–N 1.998 Å. These bond distances are similar to those found in related salicylaldiminato complexes.[5] The pyridyl N atom is not co-ordinated to the copper. The C–N bond length is in agreement with the value of

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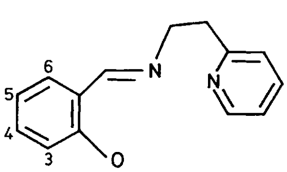
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.
Non-S.I. unit employed: G = 10^{-4} T.

1.30 Å proposed for a C=N bond,[6] and the C–O bond length is shorter than that for a C–O single bond but in excess of that for a C=O double bond.[7] The C–C bonds in the benzene ring which are most distant from the metal are shorter than the C–C bonds near to the metal; this is in accord with observations made by Lingafelter and Braun.[5]

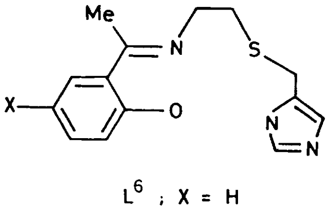
Table 1. Analytical data (%)*

Complex	C	H	N
$[Cu(L^1)_2]$	65.1 (65.4)	5.1 (5.1)	10.8 (10.9)
$[Cu(L^2)_2]$	65.5 (63.9)	6.1 (5.7)	9.4 (9.3)
$[Cu(L^3)_2]$	60.3 (60.6)	5.5 (5.4)	8.8 (8.8)
$[Cu(L^4)_2]$	50.2 (50.3)	3.5 (3.5)	8.2 (8.3)
$[Cu(L^5)_2]$	40.4 (40.5)	2.6 (2.6)	6.6 (6.7)
$[Cu(HL^6)]ClO_4{\cdot}2H_2O$	35.6 (35.5)	3.9 (4.3)	9.2 (8.9)
$[Cu(HL^6)]O_2CMe{\cdot}2H_2O$	44.0 (44.6)	4.3 (4.6)	9.3 (9.8)
$[Cu(HL^6)]O_2CMe{\cdot}H_2O$	46.6 (46.7)	4.7 (5.1)	10.5 (10.2)
$[Zn(HL^6)]O_2CMe{\cdot}0.75H_2O$	44.2 (44.6)	5.0 (4.3)	9.6 (9.8)
$[CuL^6]{\cdot}H_2O$	47.4 (47.4)	4.5 (4.8)	11.9 (11.8)
$[CuL^7]{\cdot}0.5H_2O$	50.1 (50.1)	4.9 (5.0)	12.0 (11.7)

* Calculated values in parentheses.



	3	4	5	6
L^1 ;	H	H	H	H
L^2 ;	OEt	H	H	H
L^3 ;	H	OMe	H	OMe
L^4 ;	H	H	Br	H
L^5 ;	Br	H	Br	H



L^6 ; X = H

L^7 ; X = Me

The e.s.r. spectra were found to be typical of Cu^{II} with axially symmetric *g*- and *A*-tensors. The e.s.r. parameters of $[CuL_2]$ ($L = L^1$—L^5) are listed in Table 3. Comparison of these parameters with those of related compounds of known geometries have been made. Yokoi[8] studied a number of bis(*N*-alkylsalicylideneiminato)copper(II) complexes using e.s.r. and visible spectroscopy. In conjunction with *X*-ray data he concluded that as the size of the alkyl group increased the geometries moved from slightly distorted square planar to distorted tetrahedral copper(II) environments. As this degree of distortion increased $g_{\parallel}$ increased and $A_{\parallel}$ decreased; this could also be predicted from a crystal field treatment of the spin Hamiltonian. On comparison of these data, obtained for solutions in toluene, with those reported in this paper it is apparent that our complexes fall into the planar category. This is supported, in the case of $[Cu(L^3)_2]$, by the *X*-ray crystal structure. Furthermore Maki and McGarvey[9] obtained e.s.r. parameters of $g_{\parallel} = 2.200$, $g_{\perp} = 2.045$, $A_{\parallel} = 180.1$ G, and $A_{\perp} = 22.0$ G from single-crystal studies on the square-planar complex $[Cu(sal)_2]$(sal = salicylideneiminate). In the series of complexes $[CuL_2]$ the distortion from planarity appears to increase in the order $L^3 < L^2 < L^1 < L^5$.

The i.r. spectra of the complexes are consistent with the structural data presented above. The spectra show no bands attributable to ν(OH) and the characteristic ν(CO) of the phenolic group undergoes a shift to higher frequencies. The band attributable to ν(CN) of the azomethine group is shifted 15—20 cm^{-1} to lower frequencies in all of the metal complexes. The bands at *ca.* 630 cm^{-1} which may be attributed to pyridine ring vibrations have not been shifted at all in the metal complexes. This indicates that the pyridine is not involved in co-ordination to the copper. This is corroborated by the structure analysis.

Although electronic spectra of copper(II) complexes with multidentate ligands are not in general good indicators of geometry it has been stated that an absorption band in the region 550—670 nm is indicative of five-co-ordinate square-pyramidal geometry whereas a band at 800—850 nm is characteristic of five-co-ordinate trigonal-bipyramidal geometry;[10,11] some direct correlations have been summarised by Taylor and Coleman.[1] In the above $[CuL_2]$ complexes (Table 4) the absorption bands appear at *ca.* 560—600 nm; these have been related to square-planar complexes by Yokoi[8] with the exception of the 3-ethoxy derivative. The *X*-ray structure confirms the geometry for the 4,6-dimethoxy derivative and by implication the remaining complexes should also be square planar. The band for the 3-ethoxy complex appears at 710 nm, intermediate in the classification noted above but strongly suggestive of a five-co-ordinate geometry. It is possible that there are steric constraints imposed by the introduction of the

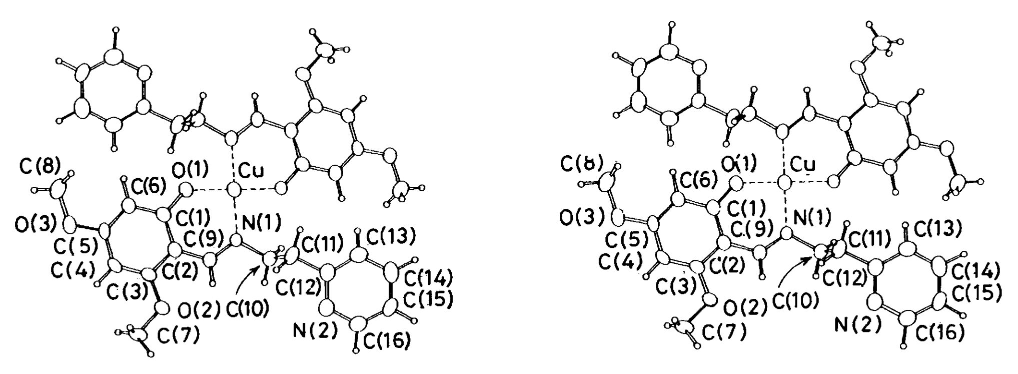


Figure. Stereoscopic projection of the structure of $[Cu(L^3)_2]$. Selected bond lengths (Å): Cu–O(1) 1.871, Cu–N(1) 1.998, C(1)–O(1) 1.302, C(1)–C(2) 1.416, C(2)–C(9) 1.423, C(9)–N(1) 1.295, C(10)–N(1) 1.484, C(10)–C(11) 1.529. Selected bond angles (°): O(1)–C(1)–C(2) 122.0, C(1)–C(2)–C(9) 122.0, C(2)–C(9)–N(1) 127.40

Table 2. Final atomic co-ordinates for $[Cu(L^3)_2]$

Atom	*X/a*	*Y/b*	*Z/c*
Cu	0.0000	0.5000	0.5000
O(1)	−0.126 1(3)	0.598 0(4)	0.432 6(1)
C(1)	−0.249 0(3)	0.652 1(5)	0.438 1(2)
C(2)	−0.317 1(3)	0.636 9(5)	0.503 7(2)
C(3)	−0.449 7(4)	0.704 2(5)	0.504 7(2)
C(4)	−0.511 6(3)	0.777 9(5)	0.444 2(2)
C(5)	−0.441 6(4)	0.789 3(5)	0.380 6(2)
C(6)	−0.313 8(4)	0.730 1(5)	0.376 4(2)
O(2)	−0.507 0(3)	0.691 6(4)	0.570 6(2)
C(7)	−0.638 3(4)	0.762 4(6)	0.576 6(2)
O(3)	−0.511 5(3)	0.868 1(4)	0.322 9(2)
C(8)	−0.444 4(5)	0.891 8(7)	0.257 6(2)
N(1)	−0.136 3(3)	0.496 5(4)	0.576 2(2)
C(9)	−0.257 2(4)	0.558 0(5)	0.567 4(2)
C(10)	−0.099 1(4)	0.433 8(5)	0.651 2(2)
C(11)	−0.020 0(5)	0.566 2(6)	0.694 8(2)
C(12)	0.023 6(4)	0.514 7(5)	0.772 2(2)
C(13)	0.159 1(4)	0.497 6(6)	0.795 2(2)
C(14)	0.194 3(5)	0.454 4(5)	0.867 2(3)
C(15)	0.093 6(5)	0.433 9(6)	0.914 1(2)
C(16)	−0.039 2(5)	0.454 5(6)	0.887 3(2)
N(2)	−0.074 9(3)	0.494 2(5)	0.817 3(2)

Table 3. E.s.r. parameters for $[CuL_2]$ complexes in thf

L	$\langle g\rangle$	$\langle A\rangle$/G	$g_{\parallel}$[a]	$g_{\perp}$	$A_{\parallel}$/G[b]	$A_{\perp}$/G
L^1	2.114	74.5	2.239	2.051	177.7	22.91
L^2	2.114	79.0	2.228	2.057	183.5	26.8
L^3	2.113	78.0	2.217	2.061	189.6	22.2
L^4[c]	2.126	73.7	—	—	—	—
L^5	2.119	76.15	2.259	2.049	172.5	28.0

[a] Values accurate to ±0.001. [b] Values accurate to ±1 G. [c] The frozen thf solution spectrum of this complex showed signals in the out-of-plane region due to two types of complex; this could be due to an impurity or possibly from co-ordination of ligand in an axial position. The lines were not well resolved and so the parallel coupling could not be accurately measured.

Table 4. Electronic spectroscopic data for $[CuL_2]$ complexes (c.t. = charge transfer)

	CHCl$_3$ solution		Solid state	
L	$\lambda_{max.}$/nm (ε/dm^3 mol^{-1} cm^{-1})	c.t. (nm)	$\lambda_{max.}$/nm	c.t. (nm)
L^1	590 (86)	368	657	375
L^2	710 (38)	366	699	373
L^3	566 (80)	340	625	370
L^4	586 (96)	378	625	364
L^5	594 (113)	380	625	373

longer alkyl chain which preclude achievement of a square-planar form.

Tetradentate Schiff bases derived from (aminoethyl)thiomethylimidazoles and salicylaldehydes have been shown to act as versatile ligands for metal complexation.[12–15] The condensation of *o*-hydroxyacetophenone and 4(5)-[(2-aminoethyl)-thiomethyl]imidazole (Hatim) gave the tetradentate Schiff base (H_2L^6) which was characterised by chemical analysis, i.r. and n.m.r. spectroscopies, and mass spectrometry. The reaction, in ethanolic solution, of H_2L^6 with equimolar amounts of $Cu(ClO_4)_2$·$6H_2O$ and methanolic NaOH gave the cationic complex $[Cu(HL^6)]ClO_4$·$2H_2O$ as a grey-brown solid. The i.r. spectrum gave a medium intensity band at 3 360 cm^{-1}, attributed to the imidazole N–H stretch, and an imine stretch at 1 600 cm^{-1}, the latter being shifted from 1 616 cm^{-1} in the free ligand. The optical spectrum showed a *d–d* band at 581 nm (solid state) suggestive of a distorted co-ordination geometry around the copper(II) atom. It is not unreasonable to propose that the structure of this compound resembles that of the corresponding salicylaldehyde-derived complex in which the copper(II) atom is four-co-ordinate but distorted from square-planar geometry by displacement of the thioether sulphur atom out of the equatorial ligating plane by 0.85 Å.[16]

Attempts to form neutral complexes by reaction of the pre-formed cationic complex with excess methanolic NaOH, or by addition of $Cu(ClO_4)_2$·$6H_2O$ and two equivalents of methanolic NaOH to an ethanolic solution of H_2L^6 were unsuccessful as were reactions starting from $Cu(NO_3)_2$. Using the technique successfully employed in the synthesis of neutral complexes derived from salicylaldehydes and Hatim, the reaction of $Cu(O_2CMe)_2$ with the ligand in acetonitrile[16] gave only the cationic complex $[Cu(HL^6)]O_2CMe$. Two hydrates were isolated; the green monohydrate was recovered from reactions carried out in acetonitrile and the brown dihydrate was isolated from reactions performed in methanol. The corresponding zinc complex $[Zn(HL^6)]O_2CMe$·$0.75H_2O$ was prepared using this route. The neutral complexes were finally prepared by application of the electrochemical synthesis described above.

The optical spectra of the $[Cu(L^6)]$·H_2O and $[Cu(L^7)]$·$0.5H_2O$ (where H_2L^7 is the ligand derived from Hatim and 5-methyl-*o*-hydroxyacetophenone) show *d–d* bands at 602 and 584 nm respectively (solid state). The slight shift to lower energy from the position noted for the cationic complexes suggests that there is an overall similarity in structure and that the imidazolate anion is a weaker field ligand than the imidazole itself.

Experimental

Microanalyses were determined using a Perkin-Elmer 240B microanalyser. I.r. spectra were recorded as Nujol mulls on a Perkin-Elmer 180 spectrophotometer.The optical spectra were recorded using a Perkin-Elmer Lambda 3 spectrophotometer (solution) and a Unicam SP735 diffuse reflectance spectrophotometer (solid state). Proton n.m.r. spectra were recorded using a Bruker WH250 FT spectrometer. The e.s.r. spectra were recorded on a Bruker ER200D-Src spectrometer in tetrahydrofuran (thf) to obtain the average spin Hamiltonian parameters $\langle g\rangle$ and $\langle A\rangle$. The solutions were then frozen in liquid N_2 and the spectra recorded at 130 K. Spin Hamiltonian parameters were obtained for the parallel orientations from these spectra while the perpendicular parameters were calculated from the relationships (4) and (5).

$$\langle g\rangle = \tfrac{1}{3}(g_{\parallel} + 2g_{\perp}) \qquad (4)$$

$$\langle A\rangle = \tfrac{1}{3}(A_{\parallel} + 2A_{\perp}) \qquad (5)$$

Acetonitrile was dried by refluxing over phosphorus pentoxide and distilled immediately prior to use. The aldehydes and amine were used as supplied. Copper (Ega Chemie) was used as plates (*ca.* 2 × 2 cm square). The ligands HL^1—HL^5 were prepared by reaction of equimolar amounts of the appropriate aldehyde and amine in benzene until the theoretical amount of water was

Table 5. Experimental conditions for the electrochemical syntheses

Ligand	Amount of ligand (g)[a]	Initial potential (V)[b]	Time (h)	Metal dissolved (mg)	E_f (mol F^{-1})
HL^1	1.0	20	2	51	1.07
HL^2	0.5	10	1	23	0.97
HL^3	0.65	15	2.5	65	1.00
HL^4	1.0	15	1	26	1.09
HL^5	0.5	20	1.5	35	0.98
HL^6	0.2	20	2	45	0.94
HL^7	0.22	20	2	48	1.01

[a] Plus $[NMe_4]ClO_4$ (*ca.* 10 mg). [b] Voltage to produce a current of 10 mA.

Table 6. Summary of crystal data

Formula	$C_{32}H_{34}CuN_4O_6$
M	633.5
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	9.871(3)
b/Å	8.208(8)
c/Å	18.230(4)
β/°	93.85(2)
U/Å^3	1 474(2)
Z	2
D_c/g cm^{-3}	1.429
F(000)	670
μ/mm^{-1}	0.741
Radiation (λ)	Mo-K_α (0.710 73 Å)
Total reflections	2 885
Observed reflections	1 577
R[a]	0.039
R'[b]	0.041

[a] $R = \Sigma(|F_o|-|F_c|)/\Sigma F_o$. [b] $R' = \Sigma w^{\frac{1}{2}}(|F_o|-|F_c|)/\Sigma w^{\frac{1}{2}}F_o$, $w = [\sigma^2(F_o) + 0.002F_o^2]^{-1}$.

collected in a Dean-Stark trap; the solid product was washed with dry diethyl ether and the purity checked by recording the i.r. and ^{1}H n.m.r. spectra.[1,4]

The Schiff bases and cationic complexes derived from Hatim were prepared by the methods described in ref. 16. The electrochemical method used in the syntheses of the metal complexes is similar to that described by Habeeb *et al.*[17] The cell was a 'tall-form' beaker (100 cm^3) fitted with a rubber bung through which the electrical leads entered the cell. The anode, in foil form, was suspended from a platinum wire; the cathode was also a platinum wire. The ligand was dissolved in acetonitrile and tetramethylammonium perchlorate (*ca.* 10 mg) was added to the solution as the supporting electrolyte. Nitrogen was bubbled through the solution to ensure an inert atmosphere and also to agitate the solution during the electrolysis. Direct current was obtained from a home-made d.c. power supply. The cell can be summarised as $Pt(-)/CH_3CN + HL/Cu(+)$. During the electrolysis hydrogen was evolved at the cathode. In the case of ligands HL^4 and HL^5 insoluble compounds were visible within a few minutes but with the other ligands crystals are formed slowly and appear at the bottom of the beaker. At the completion of the reaction the compounds were collected, washed with diethyl ether and acetonitrile and dried under vacuum. The experimental conditions for the reactions are detailed in Table 5.

Crystal Structure Analysis.—A dark blue prismatic crystal having dimensions 0.11 × 0.14 × 0.40 mm was mounted in an Enraf-Nonius CAD-4 four-circle diffractometer. The cell constants were determined from setting angles for 25 reflections in the range $9.9 < \theta < 18.2°$. The systematic absences observed suggested the space group to be $P2_1/c$. With $\omega/2\theta$ scan mode a total of 3 059 reflections were collected in the range $\theta = 3$—26°. From 2 885 symmetry-independent reflections ($R_{int.} = 0.025$), 1 577 with $|I_o| > 3\sigma|I_o|$ were considered as observed and used for refinement. Lorentz polarisation corrections and an absorption correction were performed (maximum and minimum transmission factors 0.942 and 0.848). The crystal data are summarised in Table 6.

The structure was solved by the Fourier method, revealing the positions of all non-hydrogen atoms. Full-matrix least-squares refinement with anisotropic thermal parameters for heavy atoms, an overall isotropic thermal parameter (which refined to $U = 0.06$ Å^2) for the hydrogen atoms which were located from difference maps, and an extinction correction of the form $F_{corr.} = F_c(1 - kF_c^2/\sin\theta)$, with $k = 6.3 \times 10^{-8}$, converged for 197 variable parameters to $R = 0.039$ and $R' = 0.041$. Scattering factors and anomalous dispersions were taken from refs. 18—20. All calculations were performed on a VAX 11/780 computer using the programs SHELX 76[21] and ORTEP.[22] Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters, H-atom co-ordinates, and remaining bond lengths and angles.

Acknowledgements

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