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ELECTROCHEMICAL SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF NICKEL(II) AND COPPER(II) COMPLEXES OF TRIDENTATE SCHIFF BASES: MOLECULAR STRUCTURE OF THE FIVE-COORDINATED COPPER(II) COMPLEX: 1,10-PHENANTHROLINE {2-[(2-OXYPHENYL)IMINOMETHYL]PHENOLATO}COPPER(II)

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Abstract—Electrochemical oxidation of metal anodes (copper and nickel) in acetonitrile solutions of Schiff bases (H_2L) (synthesized from salicylaldehydes and 2-aminophenols) gave CuL and NiL complexes. When 1,10-phenanthroline (phen) or 2,2′-bipyridine (bipy) was added to the electrolytic cell, the mixed complexes CuLL′ and NiLL′ (L′ = phen or bipy) were obtained. The crystal structure of 1,10-phenanthroline {2-[(2-oxyphenyl)iminomethyl]phenolato}copper(II) was determined by X-ray diffraction. The structure consists of monomeric molecules in which the copper atom has a distorted square-pyramidal CuN_3O_2 kernel.

The growing interest in copper complex ligands containing phenolic ligands is due to the presence of such moities in a number of mono- (e.g. galactose oxidase[1]) or dinuclear (e.g. tyrosinase,[2] haemocyanin[3]) copper proteins. In recent years, a number of binuclear[4] and, to a lesser extent, mononuclear[5] copper complexes containing the phenolate ion have been investigated as models of copper proteins.

The present work is a continuation of our studies on the preparation of metal complexes by electrochemical oxidation of metal anodes in solutions of Schiff bases bearing weakly acidic groups, e.g. salicylaldimines (phenolic OH)[6–11] or pyrrolaldimines (pyrrole NH),[12–15] or with a disulphide bond [Schiff bases of bis(aminoalkyl/aryl) disulphides].[16,17] By following a similar procedure, complexes were prepared containing copper or nickel and 2-[(2-hydroxyphenyl)iminomethyl] phenols (H_2L^n; Scheme 1), which are Schiff bases capable of forming phenoxy bridges between metal ions (where $R = R' = H$, H_2L^1; $R = 4,6\text{-}(OCH_3)_2$ $R' = H$, H_2L^2; $R = 3\text{-}OCH_2CH_3$ $R' = H$, H_2L^3; $R = 5\text{-}OCH_3$ $R' = H$, H_2L^4; $R = 5\text{-Br}$ $R' = H$, H_2L^5; $R = H$ $R' = 4\text{-}CH_3$, H_2L^6; $R = H$ $R' = 5\text{-}CH_3$, H_2L^7; $R = H$ $R' = 4,6\text{-}(CH_3)_2$, H_2L^8).

EXPERIMENTAL

Acetonitrile, aldehydes and amines were used as supplied. Copper and nickel (Ega Chemie) were used in the form of plates (*ca* 2 × 2 cm^2).

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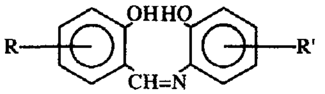

Scheme 1.

Schiff bases were prepared by refluxing an ethanol solution of equimolar amounts of aldehyde and amine in a Dean–Stark apparatus for several hours until the theoretical amount of water collected in the trap. After cooling the solution, precipitated solids were filtered out, washed with diethyl ether, dried *in vacuo* and their purity was checked by recording their IR and ^1H NMR spectra prior to use in the electrochemical synthesis. The IR spectra of these ligands have a medium intensity band at 2700 cm^{-1} corresponding to intramolecularly hydrogen-bonded OH; a high intensity band at *ca* 1620 cm^{-1} attributable to $\nu(C{=}N)$; and a band at *ca* 1280 cm^{-1} due to the phenolic C—O vibration. The ^1H NMR spectra showed four signals at 13.54–13.14, 9.76–9.57, 8.95–8.89 and 7.6–6.8 ppm which were attributed to salicylidene OH, amine phenol OH, HC=N and phenyl ring hydrogens respectively. Ligands with methyl, ethoxy or methoxy substituents gave additional signals due to the substituent protons.

Electrochemical synthesis

The procedure used is similar to that described by Tuck.[18] The electrochemical cell comprised an elongated beaker containing the Schiff base and supporting electrolyte (10 mg of tetraethylammonium perchlorate) dissolved in 50 cm^3 of acetonitrile. This was fitted with a rubber bung through which leads from a purpose-built d.c. power supply passed to the anode, a metal foil plate suspended from a platinum wire, and the cathode, a platinum wire. The cell can be summarized as follows:

$$Pt(-)/MeCN + H_2L''/M(+)$$

where M is Cu or Ni, and H_2L'' is the Schiff base; or

$$Pt(-)/MeCN + H_2L'' + L'/M(+)$$

where L′ is 1,10-phenanthroline or 2,2-bipyridine, added to the acetonitrile solution to allow synthesis of mixed complexes. Details of solution compositions and electrochemical conditions are given in Table 1. As the electrolysis proceeded, hydrogen was evolved at the cathode and at the end of electrolysis an insoluble solid formed in solution. The solids were washed with acetonitrile, then ether, and dried *in vacuo*. Crystals of the compound CuL^1phen obtained after recrystallization from methanol were suitable for X-ray analysis.

X-Ray data collection and reduction

A green crystal of $[Cu(C_{13}H_9NO_2)(phen)]\cdot 3CH_3OH$ mounted on a glass fibre was used for data collection. Cell constants and an orientation matrix for data collection were obtained by least-squares refinement of the diffraction data from 25 reflections on an Enraf–Nonius CAD4 automatic diffractometer.[19] Data were collected at 243 K using Cu K_α radiation ($\lambda = 1.54056$ Å) and were corrected for Lorentz and polarization effects. An empirical absorption correction was also made.[20] Crystal data, experimental details and refinement results are summarized in Table 2.

Structure solution and refinement

The structure was solved by direct methods,[21] which revealed the position of all non-hydrogen atoms, and refined on F by a full-matrix least squares procedure using anisotropic displacement parameters for all non-hydrogen atoms. Methyl alcohol molecules are disordered as demonstrated by their larger than normal mean-square displacement parameters. Hydrogen atoms were positioned according to idealized geometry (C—H = 0.95 Å), and given isotropic B values which were 1.3 times that of the atom attached and added to the structure factor calculation but their positional parameters were not refined. The secondary-extinction coefficient was refined to $g = 1.569 \times 10^{-7}$ $\{F_c = F_c/[1+g(F_c)^2L_p]\}$.[22] The final cycle of refinement, including 346 variables, converged to $R = 0.096$ and $R_w = 0.096$. The structural disorder of the methanol molecules explains the relatively high R factors. Atomic scattering factors were from the *International Tables for X-Ray Crystallography*,[23] molecular graphics from SCHAKAL.[24] Atom positions, bond lengths and bond angles, and other crystallographic data have

Table 1. Experimental conditions for the electrochemical syntheses[a]

Ligand (H_2L_2)						Metal	
R	R′	Compound	Amount of H_2L_2(g)[b]	Amount of L′(g)	Time (h)	dissolved (mg)	E_F (mol F^{-1})
H	H	CuL^1	0.154	—	2	45.0	0.95
		CuL^1phen	0.154	0.43	2	46.1	0.97
		NiL^1	0.159	—	4	41.8	0.48
		NiL^1phen	0.159	0.148	4	44.2	0.50
		NiL^1bipy	0.159	0.116	3	29.4	0.45
4,6-OCH_3	H	CuL^2	0.305	—	3	74.3	1.0
		NiL^2	0.217	—	4	46.7	0.53
		NiL^2phen	0.217	0.148	4	41.2	0.47
		NiL^2bipy	0.217	0.116	4	42.8	0.49
3-OCH_2CH_3	H	CuL^3	0.383	—	4	99.4	1.0
		NiL^3	0.192	—	4	41.7	0.48
		NiL^3phen	0.192	0.148	4	39.6	0.45
		NiL^3bipy	0.192	0.116	4	46.2	0.53
5-OCH_3	H	CuL^4	0.183	—	2	43.5	0.91
		NiL^4	0.217	—	4	46.7	0.53
		NiL^4phen	0.217	0.148	4	40.5	0.46
		NiL^4bipy	0.217	0.116	4	46.0	0.53
5-Br	H	CuL^5	0.190	—	3	72.0	1.0
		NiL^5	0.218	—	3.5	35.7	0.42
		NiL^5phen	0.218	0.148	3.5	37.9	0.45
		NiL^5bipy	0.218	0.116	3.75	41.1	0.49
H	4-CH_3	CuL^6	0.331	—	4	95.1	1.0
		CuL^6phen	0.331	0.286	4	91.2	0.96
		NiL^6bipy	0.169	0.116	4	41.4	0.47
H	5-CH_3	CuL^7	0.329	—	4	96.3	1.0
		CuL^7phen	0.329	0.286	4	93.9	0.99
		NiL^7bipy	0.169	0.116	4	43.6	0.50
H	4,6-$(diCH_3)_2$	CuL^8	0.349	—	3	74.2	1.0
		CuL^8phen	0.349	0.286	3.5	81.5	0.98
		NiL^8	0.251	—	3	32.4	0.49
		NiL^8bipy	0.265	0.280	3	35.6	0.54

[a] Initial current of 10 mA.

[b] Plus $[NMe_4]\ ClO_4$ (*ca* 10 mg.).

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Instrumentation

Microanalytical data were determined by a Perkin–Elmer 240B microanalyser and are listed in Table 3. IR spectra of samples in KBr disc were recorded on a Perkin–Elmer spectrometer. ^1H NMR spectra of the Schiff bases were recorded on a Bruker WM 250 with TMS as the internal standard. EI-mass spectra were performed in a Kratos MS50TC spectrometer connected to a DS90 data system. Diffuse reflectance spectra were recorded on a Perkin–Elmer Lambda 9 spectrophotometer, and magnetic moments were measured in a Vibrating Sample Magnetometer (Digital Measurements System 1660) operating to 5000 G.

RESULTS AND DISCUSSION

In all cases, the products were solids and were easily isolated from the electrolyte solution by filtration. Analytical data (Table 3) suggest that the electrochemical procedure is a satisfactory one for

Table 2. Crystal data, data collection and structure refinements parameters of [CuL^{1}phen] · 3CH$_3$OH

Crystal shape	Prismatic
Size (mm)	0.30 × 0.25 × 0.30
Chemical formula	$C_{28}H_{26}CuN_3O_5$
Formula weight	548.8
Crystal system	triclinic
Space group	P(−)1
Unit cell dimensions	
a (Å)	8.560(4)
b (Å)	11.275(6)
c (Å)	13.254(5)
α (°)	101.35(3)
β (°)	90.81(4)
γ (°)	99.47(3)
Volume of unit cell (Å^3)	1235.6(6)
Z	2
D_X (g cm^{-3})	1.473
F(000)	568
Linear absorption coefficient (cm^{-1})	15.820
Minimum, maximum and average absorption correction	0.692/1.233/0.977
Maximum value of (sin θ)/λ reached in intensity measured (Å^{-1})	0.593
Range of h, k, l	$0 \rightarrow 7; -13 \rightarrow 13; -15 \rightarrow 15$
Total no. refl. measured (θ range,°)	4076, 4−66
No. of unique refl. (R_{int})	3438, 0.039
No. of observed reflections	2805
Criterion for observed reflections	$I > 1\sigma(I)$
Weighting scheme	$1/\sigma^2(F)$
Parameters refined	346
Value of R	0.096
Value of R_ω	0.096
Ratio of max. LS shift to e.s.d. (Δ/σ)	0.79
Max. $\Delta\rho$ in final diff. electron density map (e Å^{-3})	0.672
Error in observation of unit weight	2.104
Secondary-extinction coefficient	1.569×10^{-7}

the synthesis of compounds of general formula ML^n (where M = Cu or Ni, n = 1 to 8), and confirm that mixed complexes ML^{n}L′ were formed with electrolyte solutions containing phenanthroline or bipyridine (L′ is phen or bipy).

For a copper anode, the electrochemical efficiency, E_f (defined as moles of metal dissolved per Faraday of charge), was close to 1.0 mol F^{-1}. This value of E_f and the evolution of hydrogen at the cathode suggest the following reaction scheme.

Cathode: $H_2L + e^- \longrightarrow HL^- + 1/2\,H_2$

Anode: $Cu \longrightarrow Cu^+ + e^-$

$Cu^+ + HL^- \longrightarrow CuL + 1/2\,H_2$

or $Cu^+ + HL^- + L' \longrightarrow CuLL' + 1/2\,H_2$.

For a nickel anode values of E_f were close to 0.5, which suggests anodic oxidation as follows.

Cathode: $H_2L + 2e^- \longrightarrow L^{-2} + H_2$

Anode: $Ni + L^{-2} \longrightarrow NiL + 2e^-$

or $Ni + L^{-2} + L' \longrightarrow NiLL' + 2e^-$.

Structure of (CuL^{1}phen)

Figure 1 shows the molecular structure of CuL^{1}phen and the atom numbering system used. Bond distances and angles are listed in Table 4.

Comparison of the data in Table 4 with ideal values for coordination polyhedra, and the value of 0.092 found for the geometric parameter τ [$\tau = (\beta - \alpha)/60$, where α and β are the O(1)—Cu—O(2) and N(18)—Cu—N(31) bond angles, respectively],[25] together suggest that the complex has a geometry closer to square-pyramidal ($\tau = 0$) than trigonal-bipyramidal ($\tau = 1$). The

Table 3. Analytical data for the complexes

R	R′	Compound	%C	%N	%H
H	H	CuL^1	56.8(56.8)	5.7(5.2)	3.5(3.3)
		CuL^1phen	65.4(66.0)	9.2(9.2)	4.4(3.7)
		$NiL^1 \cdot 3H_2O$	48.1(48.2)	4.5(4.3)	5.1(4.6)
		NiL^1phen $\cdot 5/2H_2O$	60.1(60.6)	9.1(8.5)	4.4(4.4)
		NiL^1bipy $\cdot 4H_2O$	56.0(55.5)	8.4(8.4)	4.2(5.0)
4,6-$(OCH_3)_2$	H	CuL^2	54.4(53.8)	4.3(4.2)	4.0(3.9)
		$NiL^2 \cdot 2H_2O$	49.5(49.2)	4.1(3.8)	5.1(4.6)
		NiL^2phen $\cdot 4H_2O$	55.2(55.6)	7.7(7.2)	4.3(4.9)
		NiL^2bipy $\cdot 2H_2O$	58.0(57.5)	7.9(8.0)	5.8(4.8)
3-OCH_2CH_3	H	CuL^3	56.5(56.5)	3.9(4.3)	3.7(4.0)
		$NiL^3 \cdot 5/2H_2O$	50.2(50.2)	3.9(3.9)	4.8(5.0)
		NiL^3phen $\cdot 5/2H_2O$	60.0(60.1)	7.8(7.8)	5.1(4.8)
		NiL^3bipy $\cdot 5/2H_2O$	58.7(58.3)	8.2(8.2)	5.4(5.1)
5-OCH_3	H	CuL^4phen $\cdot 3/2H_2O$	61.1(60.9)	7.9(8.1)	4.3(4.3)
		$NiL^4 \cdot 7/2H_2O$	45.5(46.3)	4.1(3.9)	4.3(4.9)
		NiL^4phen $\cdot 3H_2O$	57.7(58.4)	8.3(7.9)	4.9(4.7)
		NiL^4bipy $\cdot H_2O$	60.8(60.8)	8.6(8.8)	6.4(4.4)
5-Br	H	$CuL^5 \cdot 3/2H_2O$	40.6(41.0)	4.2(3.7)	3.0(2.9)
		$NiL^5 \cdot H_2O$	42.3(42.5)	4.5(3.8)	2.5(2.2)
		NiL^5phen	56.8(56.8)	7.8(7.9)	3.3(3.0)
		NiL^5bipy $\cdot 3/2H_2O$	51.9(51.9)	7.9(7.9)	3.5(3.5)
H	4-CH_3	CuL^6	58.1(58.2)	5.1(4.9)	4.2(3.8)
		CuL^6phen	66.6(66.6)	8.4(8.9)	4.2(4.1)
		NiL^6bipy $\cdot H_2O$	62.9(62.9)	8.8(9.1)	4.8(4.6)
H	5-CH_3	CuL^7	58.3(58.2)	4.2(4.8)	5.1(4.8)
		CuL^7phen $\cdot 3/2H_2O$	63.0(63.0)	8.2(8.4)	4.6(4.4)
		NiL^7bipy $\cdot H_2O$	62.3(62.9)	8.8(9.1)	4.7(4.6)
H	2,6-$(CH_3)_2$	CuL^8	59.0(59.5)	5.0(4.6)	4.6(4.3)
		CuL^8phen $\cdot 5/2H_2O$	61.4(61.4)	7.7(7.9)	4.9(4.9)
		$NiL^8 \cdot 5/2H_2O$	52.8(52.5)	4.3(4.1)	5.0(5.2)
		NiL^8bipy	61.8(61.26)	8.4(8.5)	4.7(5.1)

coordination polyhedron comprises one phenanthroline nitrogen, the azomethine nitrogen and the two phenolate oxygens of the Schiff base (which form the base of the pyramid), and the remaining phenanthroline nitrogen (which occupies the axial position). The maximum deviation of the base from the best plane through the N_2O_2 atoms is 0.06 Å, and the Cu atom is displaced 0.15 Å out of this plane towards the axial nitrogen. The angles N(18)—Cu—N(42) (107°) and N(31)—Cu—N(42) (77.2°) are wider and narrower, respectively, than in an ideal square pyramidal complex (90°) due to the small bite angle of the bidentate phenanthroline ligand.

The Cu—O bonds are of similar length (1.944 and 1.957 Å) and are close to values observed for other five-coordinate copper(II) Schiff-base complexes, e.g. bis(N-dimethylamino-salicylaldiminato)copper(II) (mean value 1.936 Å).[26] The Cu—N(azomethine) bond length (1.93 Å) is unexceptional and also similar to the corresponding value for the latter complex (mean 1.946 Å); the shorter Cu—N(phen) bond (2.018 Å) is normal,[27,28] but the longer axial bond (2.268 Å) is comparable only to that found in $Cu(phen)_3$ (2.32 Å), which shows a considerable Jahn–Teller distortion.[28]

Each phenyl ring of the Schiff base lies in a plane including its phenolate oxygen, and the four atom set comprising the azomethine bridge (C—C=N—C) lies in a third plane. The dihedral angles between these planes fall in the range 4–6°, so the entire ligand is practically planar. The

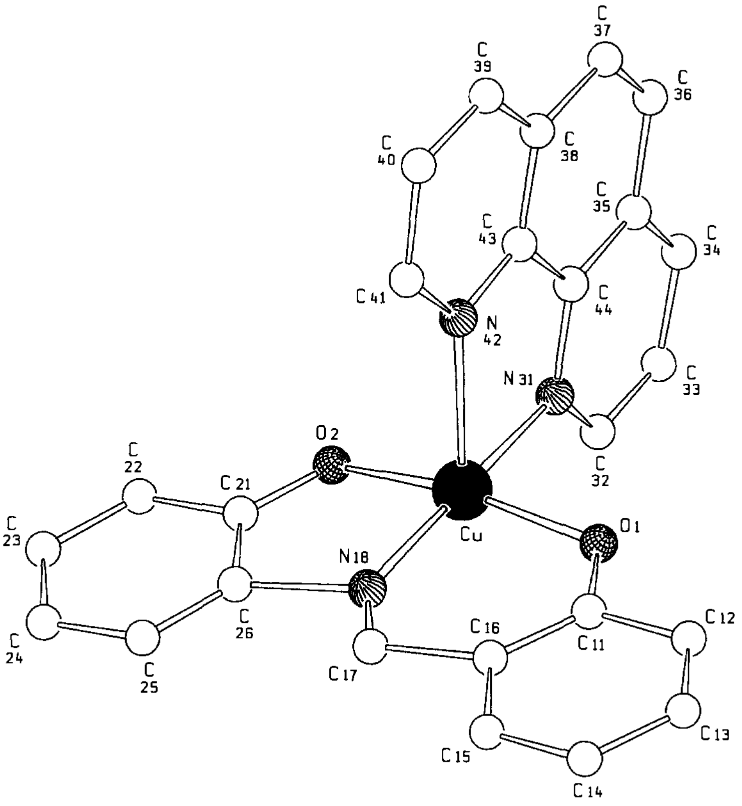

Fig. 1. The molecular structure of CuL^1phen.

Table 4. Selected bond distances (Å) and angles (°) for CuL^1phen

Cu—O(1)	1.957(6)	Cu—O(2)	1.944(7)
Cu—N(18)	1.93(1)	Cu—N(31)	2.018(7)
Cu—N(42)	2.268(7)		
O(1)—Cu—O(2)	167.8(3)	O(1)—Cu—N(18)	94.2(4)
O(1)—Cu—N(31)	89.6(3)	O(1)—Cu—N(42)	97.1(3)
O(2)—Cu—N(18)	84.7(4)	O(2)—Cu—N(31)	90.5(4)
O(2)—Cu—N(42)	94.8(3)	N(18)—Cu—N(31)	173.3(5)
N(18)—Cu—N(42)	107.7(3)	N(31)—Cu—N(42)	77.2(3)

phenanthroline ligand is also planar, lying at a dihedral angle of *ca* 90° to the best plane through the tridentate ligand.

Spectroscopic and magnetic studies

The IR spectra of the complexes show no bands attributable to ν(O—H), confirming loss of the phenolic hydrogens during electrolysis, but do show bands attributable to phenolic ν(C—O) and the azomethine ν(C=N), though at higher and lower frequencies, respectively, than those of the corresponding bands of the free ligand. These observations suggest that the complexed Schiff bases are dianions coordinated via the two phenolate oxygens and the azomethine nitrogen, and so confirm the tridentate nature of the ligands; this being the case, it would not be unreasonable to suggest that the CuL″ and NiL″ complexes are at least dimeric, or possibly polymeric, in the solid state.

In the IR spectra of the compounds with L′, additional bands corresponding to those typical of coordinated bipy and phen ligands are observed (740 and 760 cm^{-1}, and 730, 850 and 1510 cm^{-1}, respectively),[29,30] which confirms that the metal atom is five coordinate in these complexes.

The magnetic moments of copper(II) complexes [CuL] at room temperature lie in the range 1.22–1.57 BM. These values are lower than expected for a d^9 Cu complex, which may be due to an exchange interaction occurring between two metal ions connected by a phenoxide bridge. The diffuse reflectance spectra of the compounds show a band at *ca* 15 000 cm^{-1}, in agreement with those reported for square-planar copper(II) complexes. A square-planar dimeric structure is therefore tentatively assigned to the copper(II) complexes. The poor solubility of these compounds in common organic solvents prevented confirmation of this by determination of their molecular mass, but their mass spectra show molecular ion peaks corresponding to dinuclear complexes (for example, 548 amu for CuL^1 and 576 amu for CuL^6). The mixed copper compounds, [CuLL′], show magnetic moments in the range expected for copper(II) complexes, and their diffuse reflectance spectra show a broad asymmetric band at *ca* 13 000 cm^{-1}, suggesting the five coordinate geometry found in the CuL^{1}phen complex.

The magnetic moments of the [NiL] complexes fall within the range 2.97–3.10 BM, which is consistent with the expected value for an octahedral nickel(II) complex. This coordination geometry is also suggested by the diffuse reflectance spectra of the complexes, which exhibit two *d–d* bands well within the range for six-coordinate octahedral complexes of nickel(II) (*ca* 11 000 and 16 000 cm^{-1}), and can be assigned to the $^3A_{2g} \rightarrow {}^3T_{2g}$ and $^3A_{2g} \rightarrow {}^3T_{1g}$ transitions respectively.[31] A six-coordinate polymeric structure is therefore tentatively assigned to the nickel(II) complexes but, for the same reason given in the case of CuL complexes, this cannot be substantiated by molecular weight determination. However, contrary to these observations, the magnetic moments of the mixed nickel(II) complexes, [NiLL′], were 3.50–3.80 BM at room temperature, and are compatible with a five-coordinate central nickel(II) atom. The diffuse reflectance spectra also show four bands at 7200–7500, 8100–8700, 10 500–12 200 and 16 700–18 600 cm^{-1}, which are typical of five-coordinated nickel(II) complexes.[31]

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