Molecular and Electronic Structure of the Complexes formed by the Schiff Base *N*-(*o*-Hydroxybenzylidene)ferroceneamine with Co^{II}, Ni^{II}, Cu^{II}, and Zn^{II}†

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The Schiff base (HL) formed by condensation of ferrocenylamine with salicylaldehyde has been used for the preparation of complexes with Co^{II}, Ni^{II}, Cu^{II}, and Zn^{II} of formula $[ML_2]$. The ligand HL is stable in the solid state and easily hydrolyzed in solution with formation of the free N-base. This hydrolysis has been studied kinetically in a water–acetone acidic medium. A single-crystal *X*-ray study of HL [orthorhombic, space group $Pca2_1$, a = 16.229(2), b = 5.914(1), c = 14.516(2) Å, $\alpha = \beta = \gamma = 90°$, and Z = 4] indicates almost coplanarity between the chelating N–C–C–O moiety and the adjacent cyclopentadienyl ring of ferrocene, with the H atom of the hydroxyl group bridging between the N and O atoms. An *X*-ray study has been also carried out on the complex $[CuL_2]$ [monoclinic, space group $P2_1/c$, a = 12.668(2), b = 10.422(2), c = 20.921(3) Å, $\alpha = \gamma = 90$, β = 91.10(1)°, and Z = 4] in which Cu^{II} has a distorted tetrahedral environment. On the basis of the available information, *i.e.* *X*-ray, visible spectral, and magnetic susceptibility data, all the $[ML_2]$ complexes can be assigned a tetrahedral or pseudo-tetrahedral structure. Cyclic voltammetric experiments in dimethylformamide have been performed mainly to examine the $Fe^{II} \longrightarrow Fe^{III}$ one-electron oxidation in HL and its $[ML_2]$ complexes, and the results are compared to those previously obtained for ferrocenylamine and other monosubstituted ferrocene derivatives.

A vast amount of work has been carried out on the characterization of mono- and di-substituted derivatives of ferrocene, $[Fe(\eta^5-C_5H_5)_2]$, as typical organometallic species.[1] Extension of this work has been only partly directed to ferrocene-containing metal chelate complexes which, in themselves, can be regarded as multicentre molecules involving various aspects of both organometallic and co-ordination chemistry.[2] The presence in these systems of proximal metals with different environments and oxidation and/or spin states might determine mutual co-operation in: (*a*) intramolecular electron-transfer processes between the organometallic and co-ordination centres, and (*b*) new forms of reactivity towards external substrates.

The present work is intended as a preliminary contribution to the general problem exposed above. When this work was started there appeared to be rare examples reported of ferrocenyl groups combined to a Schiff-base metal chelate.[3] Ferrocenylamine has recently become more easily accessible[4,5] and has been used here as an appropriate N-base for condensation with *o*-hydroxybenzaldehyde, with formation of a Schiff-base bidentate chelating (N,O) system having an adjacent ferrocenyl group. We report here the synthesis and properties of *N*-(*o*-hydroxybenzylidene)ferroceneamine (HL) and its complexes of formula $[ML_2]$ with Co^{II}, Ni^{II}, Cu^{II}, and Zn^{II}. The molecular and electronic structure and redox properties of the complexes have been mainly investigated by single-crystal *X*-ray diffraction, i.r. and u.v.–visible spectroscopy, room-temperature magnetic susceptibility measurements, and cyclic voltammetry. A summary of this work was previously anticipated.[6] Whilst this work was being further developed, we learned of a short report[7] dealing mainly with the synthetic aspects of HL and its zinc(II) and cobalt(II) derivatives, with no reference to their molecular and electronic structure and redox behaviour.

Experimental

Ferrocenecarboxylic acid, triethylamine, ethyl chloroformate, NaN_3, salicylaldehyde, and the other common chemicals used for the preparation of ferrocenylamine, its Schiff-base derivative (HL), and the $[ML_2]$ complexes were all reagent grade. Dimethylformamide (dmf) was dried over $CaSO_4$ and then fractionally distilled twice under vacuum. Tetrabutylammonium perchlorate, NBu_4ClO_4, was a crystalline material used without further purification.

Ferrocenylamine.—This compound was prepared from ferrocenecarboxylic acid by the method described by Herberhold *et al.*,[4] later improved by the same authors.[5] The acid derivative is transformed into the corresponding azide and then into the diacetyl derivative of ferrocenylamine. The diacetamide is then hydrolyzed to give the free N-base. By this method 1.5 g of ferrocenylamine were normally obtained starting from 10 g of ferrocenecarboxylic acid. The compound is often contaminated by the monoacetamide, due to incomplete hydrolysis. The ground material can be used as such for the preparation of the Schiff base (see below).

Schiff Base (HL).—This was prepared by heating a solution of ground ferrocenylamine (700 mg, 3.48 mmol) and salicylaldehyde (424 mg, 3.48 mmol) in absolute ethanol in the presence of K_2CO_3 (100 mg). After cooling and filtration, the solution was evaporated to dryness. The solid residue was dissolved in the minimum amount of $CHCl_3$ and the solution passed through a column of silica gel using $CHCl_3$ as eluant.

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

The eluted chloroform solution obtained (red-brown) was evaporated to dryness, leaving HL as a reddish brown solid (400 mg, 38%). Crystallization from 95% ethanol gave pure needles of the Schiff-base, 1 cm long (Found: C, 66.7; H, 4.95; N, 4.45. Calc. for $C_{17}H_{15}FeNO$: C, 66.9; H, 4.95; N, 4.6%).

Kinetic Study of the Hydrolysis of HL.—The hydrolysis of HL was investigated in a mixed aqueous solvent, due to solubility problems. Preliminary investigation indicated that 50% v/v acetone–water was the best medium.

Buffer solutions of 0.1 mol dm^{-3} ionic strength, transparent in the visible region and thus suitable for spectrophotometric investigation, were prepared according to the literature.[8] Aliquots of each buffer solution in water were mixed with equal volumes of water or acetone. The acidity values[8] in water (pH) and those in aqueous acetone (pH*) were measured with a Radiometer pH meter using glass and saturated calomel electrodes; pH* values were reproducible and constant with time.

Kinetic measurements were performed spectrophotometrically, with a thermostatted Cary 219 apparatus. An acetone solution (1 cm^3) of the Schiff base and the aqueous buffer solution (1 cm^3) were introduced separately into the two compartments of a silica cell filled with a septum. After allowing the temperature to equilibrate in the spectrophotometer cell holder, the solutions were mixed and the absorbance decrease of the substrate maximum (λ = 476 nm) was measured with time. All the runs were duplicated. First-order rate constants were obtained, with the reaction followed to 75—95% completion, and correlation coefficients equal to or better than 0.9999.

In HCl solution (pH 1.0, pH* 2.50), upon mixing, the solution turned violet ($\lambda_{max.}$ 579 nm) and then slowly gave the spectrum of protonated ferrocenylamine ($\lambda_{max.}$ = 410 nm), with an isosbestic point at 398 nm. The reaction, followed either at 579 or 476 nm, gave the same first-order rate coefficient in both cases.

Preparation of Complexes $[ML_2]$.—(*a*) *Of* Cu^{II}. The ligand HL (609 mg, 2 mmol) was suspended in absolute ethanol (50 cm^3) and the mixture brought to boiling temperature. To the hot solution KOH (122 mg, 2.2 mmol) dissolved in the minimum amount of absolute ethanol was added, followed by a solution of $Cu(O_2CMe)_2 \cdot H_2O$ (199 mg, 1 mmol) in the same solvent. On cooling at room temperature the dark brown crystalline complex precipitated (590 mg, 87.5%) (Found: C, 60.60; H, 4.25; N, 4.15. Calc. for $C_{34}H_{28}CuFe_2N_2O_2$: C, 60.80; H, 4.20; N, 4.15%). The complex can be recrystallized from warm benzene. It is unstable in hot benzene as well as in $CHCl_3$ where the free Schiff base is slowly formed.

(*b*) *Of* Co^{II}. The procedure is identical to that used for $[CuL_2]$. Amounts used: HL (609 mg, 2 mmol in 50 cm^3 of hot absolute EtOH), KOH (2 mmol in hot absolute EtOH), $CoCl_2 \cdot 6H_2O$ (237 mg, 1 mmol in hot absolute EtOH). Red-brown crystalline $[CoL_2]$ was obtained on cooling (540 mg, yield 81%) (Found: C, 60.65; H, 4.15; N, 3.95. Calc. for $C_{34}H_{28}CoFe_2N_2O_2$: C, 61.20; H, 4.25; N, 4.20%). This complex is well soluble in $CHCl_3$ and benzene, but only scarcely soluble in EtOH.

(*c*) *Of* Zn^{II}. The ligand HL (501 mg, 1.64 mmol) was dissolved in hot absolute EtOH (50 cm^3). To this solution were added KOH (92 mg, 1.64 mmol) dissolved in absolute EtOH (5 cm^3) and $ZnCl_2$ (112 mg, 0.82 mmol) dissolved in the same solvent (6 cm^3). After cooling, the crystalline complex formed. It was separated from the mother-liquors by filtration, dissolved in chloroform, filtered, and the solution evaporated to dryness. Further purification of the complex was obtained by dissolving it in hot acetone (120 cm^3). After filtration, the hot solution was left to stand, yielding 270 mg (47%) of the complex (Found: C, 60.60; H, 4.30; N, 3.95. Calc. for $C_{34}H_{28}Fe_2N_2O_2Zn$: C, 60.60; H, 4.20; N, 4.15%). Complete hydrolysis of the complex with formation of the free N-base is observed from the visible spectrum in $CHCl_3$ solution.

(*d*) *Of* Ni^{II}. Some irreproducibility was noticed in the preparation of this complex. The best method was as follows: HL (499 mg, 1.64 mmol) was dissolved in hot absolute EtOH (30 cm^3). To this solution was added KOH (104 mg, 1.64 mmol) dissolved in absolute EtOH (5 cm^3) and then $NiCl_2$ (104 mg, 0.82 mmol) dissolved in the same solvent (8 cm^3). The mixture was rapidly filtered and left to stand. A microcrystalline material formed and was separated from the solution by filtration (yield *ca.* 70%). Crystallization from benzene led to a species which contains occluded benzene. Benzene and excess of Schiff base, present as impurity, can be both eliminated by heating the complex under vacuum for 2 h (150 °C; 10^{-2} mmHg, 1.33 Pa) (Found: C, 61.60; H, 4.40; N, 3.80. Calc. for $C_{34}H_{28}Fe_2N_2NiO_2$: C, 61.25; H, 4.25; N, 4.20%). Hydrolysis of this complex occurs in benzene or $CHCl_3$ with formation of the free Schiff base.

Single-crystal X-Ray Diffraction Analysis of HL *and* $[CuL_2]$.—Suitable crystals of HL and $[CuL_2]$ were mounted in glass capillaries and sealed under nitrogen. Data were collected at room temperature on a single-crystal four-circle diffractometer. Crystal data and details of the parameters associated with the data collection and structure refinement are given in Table 1. The reduced cells quoted were obtained with the use of TRACER.[9] For intensities and background the 'three-point' technique was used. The structure amplitudes were obtained after the usual Lorentz and polarization corrections. Data reduction, structure solution, and refinement were carried out on a Gould 32/77 computer using SHELX 76.[10] The crystal quality was tested by scans which showed that crystal effects could not be neglected. An absorption correction was then applied using semiempirical method.[11] The function minimized during the full-matrix least-squares refinement was $\Sigma w|\Delta F|^2$.[10] A weighting scheme based on counting statistics was applied. Anomalous scattering corrections were included in all structure-factor calculations.[12a] Scattering factors for neutral atoms were taken from ref. 12*b* for non-hydrogen atoms and from ref. 13 for H. Among the low-angle reflections no correction for secondary extinction was deemed necessary. For both HL and $[CuL_2]$ all the hydrogen atoms were located from Fourier difference maps and introduced in the refinement as fixed contributors ($U_{iso} = 0.08$ Å^2). Fractional atomic co-ordinates, selected bond distances and angles are given in Tables 2—5.

The structure of HL was solved by the heavy-atom method starting from a three-dimensional Patterson map. Refinement was first isotropically, then anisotropically for the non-hydrogen atoms down to R = 0.044 (R_g = 0.060), by full-matrix least squares. At this point, since the space group is polar, the chirality of the crystal was tested by inverting all the co-ordinates (x, y, z to $-x, -y, -z$) and refinement to convergence once again. The resulting values (R = 0.042, R_g = 0.059) indicated that the inverted structure should be accepted. So, the atomic co-ordinates given in Table 2 refer to this. In the final difference map there were no significant peaks above the general background.

The structure of $[CuL_2]$ was solved and refined as described for HL, except for the use of blocked full-matrix least squares. The final difference map showed no unusual feature with no peaks above the general background.

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

Other Physical Measurements.—I.r. spectra were measured on a Perkin-Elmer 783 spectrophotometer by using Nujol mulls

Table 1. Experimental data for the *X*-ray diffraction studies on crystalline HL and $[CuL_2]$ [a]

Compound	HL	$[CuL_2]$
	$C_{17}H_{15}FeNO$	$C_{34}H_{28}CuFe_2N_2O_2$
M	305.2	671.8
Crystal dimensions/mm	0.11 × 0.51 × 0.69	0.08 × 0.40 × 0.48
Crystal system	Orthorhombic	Monoclinic
Space group	$Pca2_1$	$P2_1/c$
Cell parameters at 295 K [b]		
a/Å	16.229(2)	12.668(2)
b/Å	5.914(1)	10.422(2)
c/Å	14.516(2)	20.921(3)
$\alpha,\gamma/^\circ$	90	90
$\beta/^\circ$	90	91.10(1)
U/Å^3	1 393.2(4)	2 805.2(8)
D_c/g cm^{-3}	1.455	1.591
$F(000)$	158	343
μ/cm^{-1}	10.74	18.09
Scan speed/°s^{-1}	0.100	0.075
Scan width/°	1.40	1.20
2θ Range/°	6—56	6—48
Reflections measured	hkl	$\pm hkl$
Unique total data	1 745	4 561
Unique observed data (N_o)	1 054	2 569
Parameters varied (N_v)	180	361
N_o/N_v	5.9	7.1
Max. shift/error on last cycle	0.04	0.05
$R = \Sigma\lvert\Delta F\rvert/\Sigma\lvert F_o\rvert$	0.042	0.039
$R' = \Sigma w^{\frac{1}{2}}\lvert\Delta F\rvert/\Sigma w^{\frac{1}{2}}\lvert F_o\rvert$	0.047	0.041
Goodness of fit = $[\Sigma w\lvert\Delta F\rvert^2/(N_o - N_v)]^{\frac{1}{2}}$	0.68	0.95

[a] Details pertaining to both complexes: graphite-monochromated Mo-K_α radiation (λ = 0.7107 Å); Philips PW 1100 diffractometer; equatorial diffraction geometry; scan type ω—2θ; Z = 4; criterion for observed reflections, $I > 3\sigma(I)$. [b] Unit-cell parameters were obtained by least-squares analysis of the setting angles of 25 carefully centred reflections chosen from diverse regions of reciprocal space.

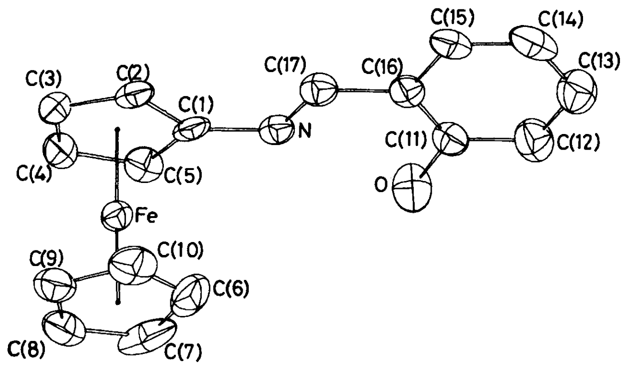

Figure 1. An ORTEP drawing of HL

and NaCl or CsI windows, visible reflectance spectra on a Beckman DK2A instrument, and visible solution spectra on a Perkin-Elmer 330 spectrophotometer. Room-temperature magnetic susceptibility measurements were obtained by the Gouy method by using a permanent magnet (7 000 G, 0.7 T) and a solution of $NiCl_2$ as calibrant. *X*-Ray powder photographs were obtained with a Debye powder camera (diameter 114.6 mm) and Cu-K_α (nickel-filtered) radiation. Room-temperature cyclic voltammetric experiments were performed in dimethylformamide containing 0.1 mol dm^{-3} NBu_4ClO_4 by using a 471 Amel multipolarograph. The working electrode was a platinum disc (diameter 2 mm), the counter electrode was a platinium wire, and the reference electrode was a saturated calomel electrode (s.c.e.) with a special salt bridge for use in dmf.[14] Elemental analyses were obtained by the Servizio di Microanalisi at the Area della Ricerca (Consiglio Nazionale delle Ricerche, Monterotondo Stazione).

Results and Discussion

Schiff Base (HL).—*X-Ray crystal structure.* The structure of HL is depicted in Figure 1, with pertinent bond distances and angles in Table 4. It consists of discrete monomeric HL molecules, in which the potentially bidentate Schiff base is bonded to a carbon atom of the ferrocene system through the nitrogen atom. The geometry of the organometallic residue is very similar to that observed in ferrocene itself with the two rings nearly parallel to each other [dihedral angle 3.2(3)°], and does not deserve further comment. The Schiff-base residue is nearly planar, the maximum displacement from the mean plane being 0.039(9) Å for C(11). It is approximately parallel to the cyclopentadienyl rings, the mean dihedral angle between them being 10.7(3)°. Nevertheless, there is no appreciable delocalization, as indicated by the remarkable single-bond character of N–C(1) [1.405(14) Å]. The nitrogen atom lies nearly in the plane of the C(1)—C(5) ring, being out of it by 0.043(7) Å on the opposite side to iron. Along the C–N=C–Ph system the iminic double bond N–C(17) = 1.278(11) Å is markedly localized. Accordingly, the C(16)–C(17) distance [1.447(12) Å] approximates to a single bond. The planarity of the Schiff base is consistent with the presence of a strong OH ••• N intramolecular hydrogen bond: O ••• N 2.593(9), O–H 0.83, N ••• H 1.84 Å, O–H ••• N 149°.

Kinetic behaviour. First-order rate constants for the hydrolysis of HL in 50% v/v acetone–water solutions were measured at different pH* values (see Experimental section). We can compare the results (Table 6) with those reported for the corresponding benzene-containing molecule, *i.e.* *N*-(*o*-hydroxybenzylidene)aniline, after allowance is made for the different solvent system.[15]

On a qualitative basis, we note that the reaction is slower with the ferrocene derivative than with the benzene compound, at any acidity of the medium: ratio of rate constants = 0.014 at pH* 2.05 and pH 2.05, 0.035 at pH* 6.09 and pH 6.09, and 0.020

Table 2. Fractional atomic co-ordinates (× 10^4) for HL

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Fe	−1 927(1)	−1 259(2)	0(−)	C(8)	−677(5)	−914(17)	−160(8)
O	−3 542(4)	−7 322(11)	−1 825(5)	C(9)	−1 056(5)	1 156(15)	−262(6)
N	−3 434(4)	−3 925(10)	−702(5)	C(10)	−1 611(6)	1 029(18)	−997(7)
C(1)	−3 037(4)	−2 857(12)	40(10)	C(11)	−4 191(5)	−6 246(15)	−2 213(6)
C(2)	−3 098(5)	−515(14)	368(6)	C(12)	−4 583(6)	−7 212(18)	−2 955(7)
C(3)	−2 587(5)	−309(13)	1 146(6)	C(13)	−5 211(7)	−6 132(18)	−3 391(7)
C(4)	−2 195(5)	−2 450(15)	1 306(5)	C(14)	−5 468(5)	−3 964(20)	−3 087(9)
C(5)	−2 466(5)	−3 971(12)	606(6)	C(15)	−5 078(5)	−96(16)	−2 372(7)
C(6)	−1 590(8)	−1 108(26)	−1 350(9)	C(16)	−4 432(5)	−4 059(13)	−1 908(6)
C(7)	−986(8)	−2 418(17)	−810(9)	C(17)	−4 022(5)	−2 973(14)	−1 141(6)

Table 3. Fractional atomic co-ordinates (× 10^4) for [CuL_2]

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Cu	1 645(1)	1 283(1)	4 056(0)	C(15)	3 972(5)	2 528(8)	4 269(3)
Fe(1)	1 617(1)	2 792(1)	5 994(0)	C(16)	4 383(5)	610(6)	2 885(4)
Fe(2)	4 737(1)	2 159(1)	3 447(0)	C(17)	5 029(6)	239(7)	3 396(4)
O(1)	276(3)	1 722(4)	3 779(2)	C(18)	5 971(5)	944(8)	3 361(5)
O(2)	2 569(3)	−91(4)	3 944(2)	C(19)	5 869(6)	1 735(8)	2 825(5)
N(1)	2 336(3)	2 728(4)	3 608(2)	C(20)	4 903(6)	1 535(7)	2 528(4)
N(2)	1 285(3)	807(4)	4 927(2)	C(21)	13(4)	2 574(5)	3 342(3)
C(1)	832(4)	1 741(5)	5 324(3)	C(22)	−1 011(5)	2 584(6)	3 105(3)
C(2)	377(5)	1 585(6)	5 934(3)	C(23)	−1 337(5)	3 470(7)	2 651(3)
C(3)	55(5)	2 813(7)	6 132(3)	C(24)	−662(6)	4 371(7)	2 432(3)
C(4)	311(5)	3 723(6)	5 668(3)	C(25)	341(5)	4 383(6)	2 651(3)
C(5)	798(5)	3 069(6)	5 156(3)	C(26)	727(5)	3 485(5)	3 096(3)
C(6)	3 128(5)	2 144(6)	6 044(3)	C(27)	1 804(5)	3 542(5)	3 274(3)
C(7)	3 100(5)	3 456(6)	5 875(3)	C(31)	2 512(4)	−1 185(6)	4 253(3)
C(8)	2 588(5)	4 126(6)	6 376(3)	C(32)	3 060(5)	−2 257(7)	4 001(3)
C(9)	2 316(5)	3 233(7)	6 847(3)	C(33)	3 005(6)	−3 445(7)	4 295(4)
C(10)	2 642(5)	2 005(6)	6 639(3)	C(34)	2 434(6)	−3 608(6)	4 841(4)
C(11)	3 392(4)	3 020(6)	3 737(3)	C(35)	1 914(5)	−2 607(6)	5 101(3)
C(12)	4 043(5)	3 902(6)	3 410(4)	C(36)	1 957(4)	−1 364(5)	4 818(3)
C(13)	4 994(6)	3 978(8)	3 746(5)	C(37)	1 409(4)	−363(5)	5 147(3)
C(14)	4 963(6)	3 161(10)	4 273(4)				

Table 4. Selected bond distances (Å) and angles (°) for HL

Fe–Cp(1)	1.642(9)	Fe–Cp(2)	1.662(12)
Fe–C(1)	2.035(7)	C(2)–C(3)	1.406(12)
Fe–C(2)	2.022(8)	C(3)–C(4)	1.436(12)
Fe–C(3)	2.057(8)	C(4)–C(5)	1.427(11)
Fe–C(4)	2.069(7)	C(6)–C(7)	1.475(18)
Fe–C(5)	2.028(8)	C(6)–C(10)	1.364(18)
Fe–C(6)	2.036(13)	C(7)–C(8)	1.390(16)
Fe–C(7)	2.046(13)	C(8)–C(9)	1.378(13)
Fe–C(8)	2.052(8)	C(9)–C(10)	1.398(13)
Fe–C(9)	2.045(9)	C(11)–C(12)	1.375(13)
Fe–C(10)	2.047(10)	C(11)–C(16)	1.422(12)
O–C(11)	1.353(11)	C(12)–C(13)	1.359(15)
N–C(1)	1.405(14)	C(13)–C(14)	1.419(16)
N–C(17)	1.278(11)	C(14)–C(15)	1.344(15)
C(1)–C(2)	1.468(12)	C(15)–C(16)	1.396(12)
C(1)–C(5)	1.403(13)	C(16)–C(17)	1.447(12)
Cp(1)–Fe–Cp(2)	178.6(5)	O–C(11)–C(12)	119.4(8)
C(1)–N–C(17)	121.8(7)	C(12)–C(11)–C(16)	119.6(8)
N–C(1)–C(5)	122.7(7)	C(11)–C(16)–C(15)	117.8(8)
N–C(1)–C(2)	129.9(7)	C(15)–C(16)–C(17)	121.1(7)
C(2)–C(1)–C(5)	107.3(7)	C(11)–C(16)–C(17)	121.1(7)
O–C(11)–C(16)	120.8(7)	N–C(17)–C(16)	122.1(7)

Cp(1) and Cp(2) refer to the C(1)—C(5) and C(6)—C(10) cyclopentadienyl rings respectively.

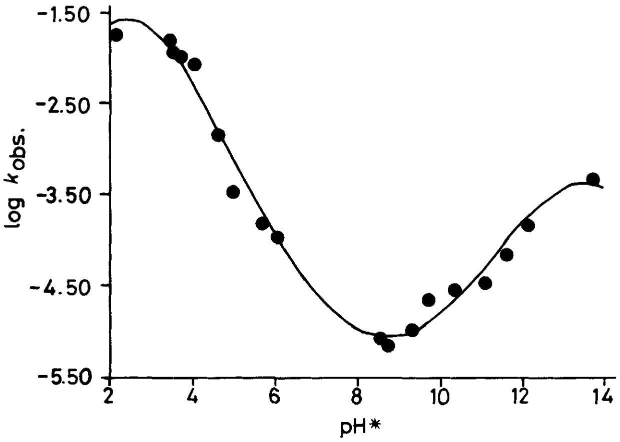

Figure 2. Variation of hydrolysis rate of HL with pH*

at pH* 13.74 and pH 13.74. This result is in agreement with a process where the rate-determining step is a nucleophilic attack (either by water or OH^-), since the ferrocenyl ring is known to act as an electron-releasing group (*e.g.* a ferrocene side-chain is *ca.* 100 fold more reactive than a benzene side-chain with electrophilic reagents[16]).

Consistently with a lower reactivity, HL is more selective than (*o*-hydroxybenzylidene)aniline: *k*(pH 2)/*k*(pH 7.5) = 500 with the benzene derivative and *k*(pH* 2.05)/*k*(pH* 8.72) = 2 500 with the ferrocene derivative; where pH 7.5 and pH* 8.72 correspond to the mininum reactivity with the benzene and ferrocene system, respectively. By plotting log $k_{obs.}$ *vs.* pH*

Table 5. Selected bond distances (Å) and angles (°) for $[\mathrm{CuL}_2]$

Fe(1)–Cp(1)	1.644(7)	Fe(2)–Cp(3)	1.638(8)
Fe(1)–Cp(2)	1.649(7)	Fe(2)–Cp(4)	1.653(8)
Cu–O(1)	1.900(4)	C(22)–C(23)	1.384(9)
Cu–O(2)	1.879(4)	C(23)–C(24)	1.364(10)
Cu–N(1)	1.992(4)	C(24)–C(25)	1.361(10)
Cu–N(2)	1.953(4)	C(25)–C(26)	1.404(8)
O(1)–C(21)	1.314(7)	C(26)–C(27)	1.429(9)
O(2)–C(31)	1.313(7)	C(31)–C(32)	1.427(9)
N(1)–C(11)	1.413(6)	C(31)–C(36)	1.405(8)
N(1)–C(27)	1.288(7)	C(32)–C(33)	1.385(10)
N(2)–C(1)	1.413(7)	C(33)–C(34)	1.380(12)
N(2)–C(37)	1.312(7)	C(34)–C(35)	1.359(9)
C(21)–C(22)	1.399(8)	C(35)–C(36)	1.426(8)
C(21)–C(26)	1.424(8)	C(36)–C(37)	1.441(8)
Cp(1)–Fe(1)–Cp(2)	179.2(3)	Cp(3)–Fe(2)–Cp(4)	178.5(4)
N(1)–Cu–N(2)	138.3(2)	N(1)–C(11)–C(15)	124.0(5)
O(2)–Cu–N(2)	94.9(2)	N(1)–C(11)–C(12)	128.2(5)
O(2)–Cu–N(1)	103.2(2)	C(12)–C(11)–C(15)	107.6(5)
O(1)–Cu–N(2)	96.3(2)	O(1)–C(21)–C(26)	122.8(5)
O(1)–Cu–N(1)	95.4(2)	O(1)–C(21)–C(22)	118.7(5)
O(1)–Cu–O(2)	137.0(2)	C(22)–C(21)–C(26)	118.5(5)
Cu–O(1)–C(21)	126.9(3)	C(25)–C(26)–C(27)	118.3(5)
Cu–O(2)–C(31)	124.0(4)	C(21)–C(26)–C(27)	124.2(5)
Cu–N(1)–C(27)	121.0(4)	C(21)–C(26)–C(25)	117.5(5)
Cu–N(1)–C(11)	120.6(3)	N(1)–C(27)–C(26)	128.1(5)
C(11)–N(1)–C(27)	117.4(5)	O(2)–C(31)–C(36)	124.3(5)
Cu–N(2)–C(37)	122.3(4)	O(2)–C(31)–C(32)	117.7(5)
Cu–N(2)–C(1)	118.8(3)	C(32)–C(31)–C(36)	118.0(5)
C(1)–N(2)–C(37)	118.9(5)	C(35)–C(36)–C(37)	115.8(5)
N(2)–C(1)–C(5)	122.3(5)	C(31)–C(36)–C(35)	119.6(5)
N(2)–C(1)–C(2)	129.0(5)	C(31)–C(36)–C(37)	124.5(5)
C(2)–C(1)–C(5)	108.7(5)	N(2)–C(37)–C(36)	124.2(5)

Cp(1), Cp(2), Cp(3), and Cp(4) refer to the cyclopentadienyl rings C(1)—C(5), C(6)—C(10), C(11)—C(15), and C(16)—C(20) respectively.

Table 6. First-order rate constants for the hydrolysis of HL in 50% v/v acetone–water at different pH and 25 °C (buffer solutions with the same ionic strength)

Run	pH[a]	pH*[b]	$k_{\mathrm{obs.}}/\mathrm{s}^{-1}$
1	2.85	3.50	$(1.53 \pm 0.06) \times 10^{-2}$
2	2.76	3.60	$(1.19 \pm 0.21) \times 10^{-2}$
3	3.04	3.78	$(1.10 \pm 0.04) \times 10^{-2}$
4	3.10	4.01	$(9.1 \pm 0.9) \times 10^{-3}$
5	3.52	4.64	$(1.51 \pm 0.08) \times 10^{-3}$
6	3.81	4.99	$(3.42 \pm 0.17) \times 10^{-4}$
7	4.46	5.75	$(1.65 \pm 0.02) \times 10^{-4}$
8	5.25	6.04	$(1.2 \pm 0.1) \times 10^{-4}$
9	4.82	6.09	$(1.15 \pm 0.02) \times 10^{-4}$
10	5.00	6.24	$(1.80 \pm 0.09) \times 10^{-4}$
11	5.24	6.49	$(1.68 \pm 0.08) \times 10^{-4}$
12	7.44	8.65	$(8.88 \pm 0.10) \times 10^{-6}$
13	8.97	8.72	$(8.00 \pm 0.10) \times 10^{-6}$
14	7.99	9.26	$(1.08 \pm 0.09) \times 10^{-5}$
15	8.40	9.76	$(2.35 \pm 0.11) \times 10^{-5}$
16	8.30	10.39	$(3.00 \pm 0.10) \times 10^{-5}$
17	9.07	11.10	$(3.77 \pm 0.34) \times 10^{-5}$
18	10.08	11.60	$(7.83 \pm 0.27) \times 10^{-5}$
19	10.59	12.14	$(1.56 \pm 0.10) \times 10^{-4}$
20	12.38	13.74	$(5.00 \pm 0.03) \times 10^{-4}$
21[c]	1.00	2.05	$(1.80 \pm 0.03) \times 10^{-2}$

[a] In aqueous solution. [b] In 50% acetone–water. [c] 0.1 mol dm^{-3} HCl.

(Figure 2) the pattern is similar for both species, with a difference in the region pH* 8—10.5.

Complexes $[\mathrm{ML}_2]$.—*The structure of* $[\mathrm{CuL}_2]$. The structure of this complex consists of discrete $[\mathrm{CuL}_2]$ molecules with the oxygen and nitrogen donor atoms of two ligand anions bonded to $\mathrm{Cu^{II}}$ in a distorted tetrahedral co-ordination (Figure 3). Selected bond distances and angles are given in Table 5. The ligands show some distortions with respect to the neutral ligand HL (see above), the two nitrogen atoms being out of the respective cyclopentadienyl rings, N(1) by 0.310(4) Å on the opposite site to iron. In addition, N(1) is markedly out of the C(21)—C(26) ring [0.267(4) Å]. The two six-membered chelation rings show half-chair conformations, Cu being displaced by 0.110(1) and 0.458(1) Å from the plane through O(1)–C(21)–C(26)–C(27)–N(1) and O(2)–C(31)–C(36)–C(37)–N(2), respectively, with the pertinent aromatic rings. As observed in HL, in each ligand the best plane through the Schiff-base residue is nearly parallel to the cyclopentadienyl rings [mean dihedral angles 15.3(2) and 8.8(2)° for the ligands O(1)–N(1) and O(2)–N(2), respectively]. As a result of the tetrahedral co-ordination for $\mathrm{Cu^{II}}$, the corresponding planar moieties of the two ligands are approximately perpendicular to each other.

The Cu–O and Cu–N bond distances fall in the range of values usually observed for copper(II) complexes.[17] Bond distances and angles within the two ligands are not significantly different and agree well with those of the free HL molecule. Of note is that the ferrocene moiety is practically unmodified upon chelation of the central metal ion. The Fe(1)···Cu and Fe(2)···Cu distances are 4.350(1) and 4.300(1) Å, respectively, thus excluding any significant direct interaction.

U.V.-Visible Spectral and Magnetic Behaviour of $[\mathrm{ML}_2]$ *Complexes.*—The ligand HL and complexes $[\mathrm{ML}_2]$ are solid stable crystalline materials. They are all strongly coloured (brownish red or dark brown) as is normal for ferrocenyl-containing complexes, since these have highly intense absorptions in the u.v.–visible reflectance spectra in the region below 500 nm. As a consequence, *d–d* transitions of the central metal ions in $[\mathrm{ML}_2]$ complexes are detectable only in the visible (> 500 nm)–near-i.r. region and obscured at lower wavelengths. Table 7 summarizes the spectral data for the $[\mathrm{ML}_2]$ complexes. Solutions of $[\mathrm{ML}_2]$ in non-donor or weak donor solvents, such as benzene, $\mathrm{CHCl_3}$, or dmf, are not stable and tend slowly to hydrolyze with formation of the free Schiff base. Thus, the estimated ε values reported in Table 7 should be regarded as somewhat approximate.

The visible spectra of $[\mathrm{ML}_2]$ complexes, in combination with room-temperature magnetic susceptibility measurements and *X*-ray information, substantially confirm the assignment of a four-co-ordinate pseudo-tetrahedral structure for all the complexes examined. The complex $[\mathrm{CuL}_2]$, unequivocally pseudo-tetrahedral from *X*-ray data, receives scarce additional information from its visible spectrum, the *d–d* bands of $\mathrm{Cu^{II}}$ being almost completely obscured by the bands due to ferrocene. Only a weak shoulder at *ca.* 700 nm seems to be ascribable as a *d–d* transition. The $\mu_{\mathrm{eff.}}$ value for solid $[\mathrm{CuL}_2]$, 1.87, indicates the presence of one unpaired electron, as expected. The complex $[\mathrm{CoL}_2]$ is also almost certainly pseudo-tetrahedral, as suggested by its isomorphism with the corresponding zinc(II) complex. Its visible spectrum strongly supports this assignment, showing a near-i.r. absorption at 1 270 nm (accompanied by a shoulder at 925 nm) which can be assigned as a $^4T_1(F) \longrightarrow {}^4A_2(F)$ transition in a tetrahedral or pseudo-tetrahedral symmetry.[18] The transition $^4T_1(P) \longrightarrow {}^4A_2(F)$, expected at lower wavelengths, is very likely obscured by ferrocene absorptions. The position, shape, and intensity of the band at 1 270 nm are very similar to those found for bis(dipivaloylmethanido)cobalt(II), also suggested to be four-co-ordinated and pseudo-tetrahedral.[18] The $\mu_{\mathrm{eff.}}$ value for $[\mathrm{CoL}_2]$, 4.91, is substantially in line with expectation for high-

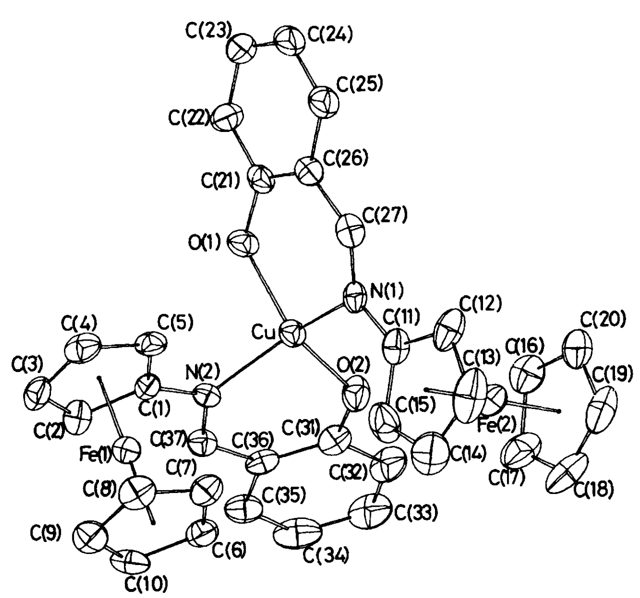

Figure 3. An ORTEP drawing of $[CuL_2]$

Table 7. Visible spectral data for complexes $[ML_2]$*

	$[CoL_2]$	$[NiL_2]$	$[CuL_2]$	$[ZnL_2]$
S	304 (28 400)	303 (11 710)	301 (27 000)	308 (26 500)
R	370	380	395	380
S	394 (14 300)	395 (10 500)	405 (15 400)	403 (18 000)
R	475	480	500	490
S	490 (5 000)	480 (3 850)	476 (5 200)	490 (6 000)
R	875 (sh)	1 000	700 (sh)	
S	925 (35)	1 170 (sh) (12)	700 (sh) (380)	
R	1 260	1 600		
S	1 270 (60)	1 600 (17)		

* λ/nm (ε/dm^3 mol^{-1} cm^{-1}). R = Reflectance, S = solution spectra in $CHCl_3$.

spin Co^{II}. There is no structural reference for $[NiL_2]$, since this complex is not isomorphous either with the complexes of Co^{II} and Zn^{II} or with that of Cu^{II}. Its $\mu_{eff.}$ value, 2.83, excludes a square-planar structure which should determine a low-spin state (d^8, diagmagnetic). We tentatively assign a pseudo-tetrahedral structure to this complex because of the presence of near-i.r. absorptions located at 1 600 and 1 170 nm (sh) which would not be compatible with the occurrence of a pseudo-octahedral structure. In this case too, however, the most intense absorption expected in the visible region could not be detected as it is probably obscured by the ferrocene bands.

Cyclic Voltammetric Data.—Cyclic voltammetric experiments on HL, the $[ML_2]$ complexes, and the reference species ferrocene and ferrocenylamine were carried out in dmf at room temperature in the presence of NBu_4ClO_4. Attention was essentially centred on the first one-electron oxidation, which changes the ferrocenyl group into the ferrocenium cation. Data are summarized in Table 8. It can be seen that the more easily oxidized species is ferrocenylamine which has a value of −0.40 V *versus* ferrocene and 0.05 V *versus* the s.c.e. Good agreement is found between these data and those obtained by Britton *et al.*[19] in acetonitrile, in which a value of −0.37 V was obtained for ferrocenylamine *versus* ferrocene. This value is anomalous, being lower by 0.4—0.6 V compared to those measured for a series of monosubstituted ferrocene derivatives $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4R)]$ (R = Cl, Br, I, or various organic substituents).[19]

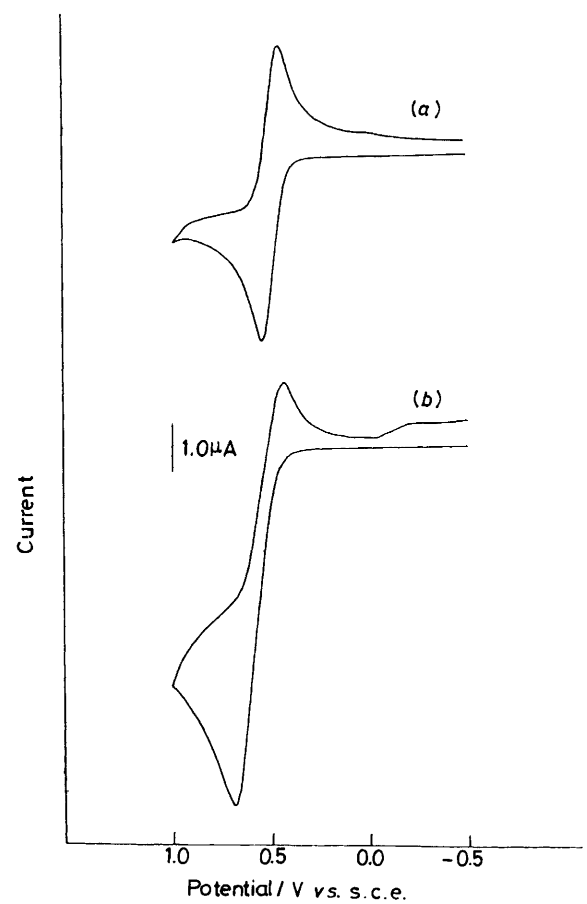

Figure 4. Cyclic voltammograms obtained in dmf (0.102 mol dm^{-3} in NBu_4ClO_4) at room temperature at a potential sweep rate of 100 mV s^{-1} for (*a*) HL (2.32 mmol dm^{-3}) and (*b*) $[ZnL_2]$ (2.52 mmol dm^{-3}). The initial potential was set at −0.50 V and the switching potential was 1.00 V

It can also be seen from Table 8 that the values found for HL and $[ML_2]$ are all in the range found for ferrocene or higher. Apparently, then, in going from ferrocenylamine to the Schiff base HL, or to the $[ML_2]$ species, the same effect is produced as that obtained upon formally exchanging ferrocenylamine with the other already mentioned monosubstituted derivatives. The potentials indicate that oxidation depends appreciably on the nature of the central metal ion. Whilst HL is as easily oxidizable as $[NiL_2]$, the oxidation process for the $[ML_2]$ species is facilitated in the order Ni^{II} > Cu^{II} > Co^{II} > Zn^{II}. Since apparently there is no significant π conjugation between the ferrocenyl group and the Schiff base chelating ring through the C(1)–N bond in HL and the C(1)–N(2) and C(11)–N(1) bonds in $[CuL_2]$, electronic effects, which make more difficult the $Fe^{II} \longrightarrow Fe^{III}$ oxidation process, are likely to be propagated through the skeletal system of the sigma bonds.

Figure 4 shows the cyclic voltammograms for HL and $[ZnL_2]$ under the specified experimental conditions. Due to the instability of the zinc complex in dmf, the experiments were conducted by direct dissolution of the complex in the cell and voltammograms run immediately after. Figure 4 shows that the current amplitude of the cyclic voltammogram for $[ZnL_2]$ is double, within the experimental error, that observed for HL. This demonstrates that in $[ZnL_2]$ both ferrocenyl groups are simultaneously oxidized; hence they are perfectly equivalent and non-interacting. Although the metal atom has an unequivocal effect on the absolute value of the potential for the ferrocenyl groups, no significant electronic contact occurs between the two ferrocenyl groups within the complex.

Table 8. Cyclic voltammetric data in dmf

Compound	10^3 Concentration/ mol dm^{-3}	Concentration of NBu_4ClO_4/mol dm^{-3}	First oxidation potential/V *
Ferrocene	1.94	0.12	0.45
Ferrocenylamine	1.0	0.12	0.05
HL	1.44	0.125	0.51
[CoL$_2$]	0.84	0.11	0.58
[NiL$_2$]	1.125	0.12	0.45
[CuL$_2$]	0.89	0.13	0.53
[ZnL$_2$]	1.13	0.115	0.69

* *vs.* s.c.e.

Conclusion

Ferrocenylamine and salicylaldehyde have been combined together in a new Schiff-base chelating molecule (HL) for the formation of multimetallic systems of formula [ML$_2$]. Single-crystal *X*-ray work on [CuL$_2$] seems to indicate that π-electron conjugation between the peripheral ferrocenyl groups and the central Schiff-base chelating system is not significant. Electrochemical data, on the other hand, show a dependence of the first oxidation potential ($Fe^{II} \longrightarrow Fe^{III}$) on the nature of the central metal ion, which might mean that electronic contact is possible *via* the σ-bonding system. The two ferrocenyl groups within [ZnL$_2$] are electrochemically indistinguishable and are simultaneously oxidized. *X*-Ray data also indicate that, although no direct contact between the Fe and the central metal ion is possible, the Fe $\cdots$ M distance may be appropriate for the binding of a bridging ligand for the possible investigations of new forms of reactivity in the one-electron oxidized materials. Presently, attempts at the synthesis and characterization of derivatives of [ML$_2$] complexes containing the ferricenium cation are being carried out.

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