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Coordination compounds of copper, nickel and iron with Schiff bases derived from hydroxynaphthaldehydes and salicylaldehydes

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CONTENTS

A. INTRODUCTION

(i) Information associated with biological aspects

It is a well-known fact that several metalloproteins and metalloenzymes play important roles in natural biological systems. These functions are related to catalytic activity in reactions such as hydrogen exchange, hydrolysis of esters, fluorophosphates, nitriles or amides, formation of Schiff bases and carboxylation or decarboxylation [1–4].

The functions of a metal ion in a metalloprotein are determined by structural

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characteristics which include, among others, the nature of its coordination sphere. These functions also depend on the structural arrangement in the vicinity of the metallic ion but outside its coordination sphere [5,6].

There is an enormous amount of information about the quest for synthetic models which compare more or less successfully with biological compounds [7–15]. On the other hand, a great deal of information regarding the properties of synthetic Schiff bases of potential biological interest has arisen during the last few years. Several of these compounds were characterized and used as models for a series of systems [16–31]. These include nickel which has been found in few biological systems but has recently been detected in very low amounts in jack-bean urease [32] and in some hydrogenases [33,34]. The use of these compounds in catalytic reactions has also been considered [35–41].

(ii) Information associated with redox properties

Some biological responses of the metal ion in a metalloprotein may be enhanced or diminished by small changes in the ligand structure. Moreover, these changes are probably related to the redox activity of the metal ion.

An engaging problem in inorganic species with biomimetic properties has been the quantitative evaluation of the effect that small changes in the ligand structure have on redox potentials. Furthermore, redox properties are related to structural and electronic parameters which are typical of a specific complex [42–47].

The semiquantitative evaluation of the effect of the ligands upon metal redox properties has been widely studied in cyclic and acyclic structures with extensive conjugated π-electron systems [42,43,46].

The earliest synthetic macrocyclic compounds were obtained several years ago [48], the number rising rapidly from the 1960s [49–51]. Since then, interest in their preparation has increased enormously [52–55].

It is possible through adequate design of a ligand to obtain better knowledge of the factors that modify the coordination sphere and the electronic properties of the central atom in order to match some characteristics with the behaviour of a natural product [56,57]. For example, synthetic complexes in which it is likely to stabilize Cu(III) have been prepared to explain the reaction mechanisms of some copper metalloenzymes [14,58,59]. In this respect, some electrochemical properties of copper(II) complexes with several polydentate Schiff bases have been exploited successfully [60].

On the other hand, it has been shown experimentally that the Fe^{III}/Fe^{II} redox potential must be around 0.0 V (vs. SCE) for an iron-containing system to react reversibly with dioxygen. Several detailed studies on synthetic iron complexes which show redox values around this value have appeared [7,61–63].

The nature of the redox process in this kind of complex has also been studied extensively, showing that, in some cases, this process is detected on the metal centre and in others on the ligand [64–71]. For example, iron, cobalt and nickel tetraphenyl porphyrins exhibit oxidation on the metal while copper and zinc derivatives do so on the ligand [72].

Redox potentials can be modified by the introduction of suitable substituents on the ligands [73–77] or by subtle changes in the medium [77,78]. The influence that ring size, number of members in chelate rings and the presence of imino and α-diimino groups, among others, have upon the redox potentials have been studied [5,68,77]. A quantitative contribution of some of the above-mentioned factors for predicting redox potentials was recently reported [79]. It is worthwhile mentioning that suitable correlations between half-wave potentials and structural parameters have also been found for many macrocyclic complexes [5,57,66,67,71,77].

The information available on the redox behaviour of complexes with acyclic Schiff bases is rather limited. The composition, symmetry, chemical and physical properties of compounds with these bases are mainly determined by steric and electronic effects of the ligand substituents [5,74,75,80–87]. These effects have been studied in greater detail for nickel(II) and copper(II) complexes [52,88,89]. Patterson and Holm [44] and Pletcher and co-workers [58,90] have studied the relationship between electrochemical behaviour and structure for some copper(II) and nickel(II) complexes with this kind of ligand.

Information relating to coordination compounds of the first transition series with some bidentate and tetradentate Schiff bases derived *exclusively* from salicylaldehyde and α-hydroxynaphthaldehydes (see Figs. 1 and 2) is presented in this review [91–100]. The more relevant structural, spectroscopic and electrochemical properties [81,101] are discussed; comparisons are made with certain metalloproteins.

B. GENERAL REMARKS ON THE LIGANDS

During the last few years, a significant amount of information related to the characterization of Schiff bases and their complexes with several metals has appeared [102–109]. Only the ligands indicated in Fig. 1, i.e. salicylaldimines and α-hydroxynaphthaldimines, were selected to account for some aspects of their properties, mainly those derived from several classical spectroscopies (IR, UV–VIS, NMR and EPR) and electrochemistry. Properties of copper, nickel and iron complexes with these ligands will be presented in the following sections.

In these ligands, the breadth of the band assigned to the O–H stretching transition was explained in terms of the formation of an intramolecular hydrogen bond, OH···N, which was confirmed by NMR spectroscopy and isotopic substitution [110–113].

NMR results have shown the presence of keto-amine versus enol-imine equilibria [114–118] (Fig. 1), detected even in the solid state by photochromic and thermochromic studies [119,120] and confirmed by electronic and vibrational spectral analysis [121–123].

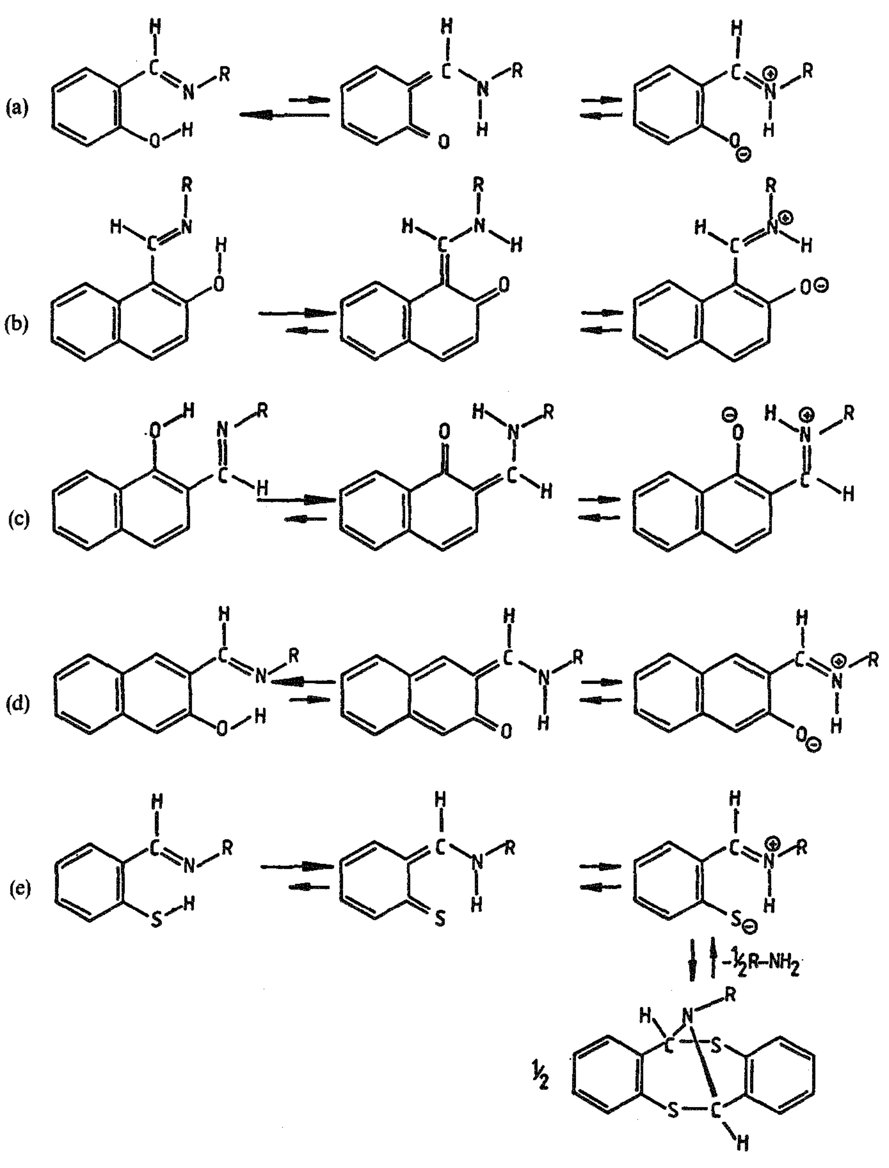


Fig. 1. Keto-amine/enol-imine tautomeric equilibria for the ligands discussed in the text. R = alkyl or aryl. (a) Salicylaldimines; (b) 2-hydroxy-1-naphthaldimines; (c) 1-hydroxy-2-naphthaldimines; (d) 3-hydroxy-2-naphthaldimines; (e) *o*-mercaptobenzaldimines [110–129].

Salicylaldimines frequently show enol-imine tautomerism in solution, with few exceptions. 2-Hydroxy-1-naphthaldimines generally show keto-amine predominance while 3-hydroxy-2-naphthaldimines are almost exclusively in the enol-imine form (Fig. 1 (a)–(d)). The behaviour of 1-hydroxy-2-naphthaldimines depends on the nature of the solvent [124,125]. In addition, thio-derivatives such as *N*-alkyl-*o*-mercapto-

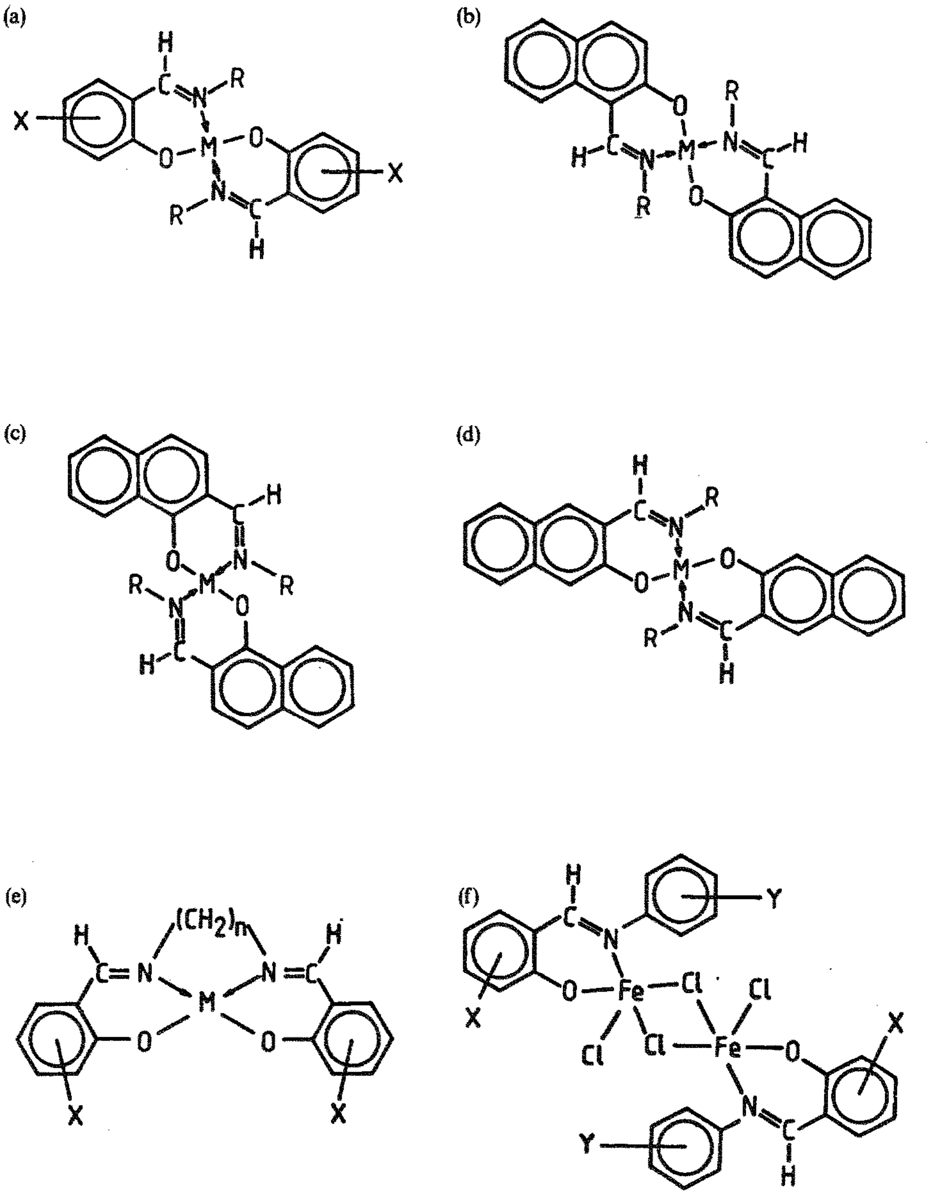


Fig. 2. Coordination compounds derived from the ligands shown in Fig. 1 and discussed in the text. R = alkyl or aryl; M = divalent ion; X = halogen, nitro; Y = halogen, alkyl, alkoxy. Note that structure (*e*) for $n = 2$ derivatives shows three fused rings of six, five, and six members [84,101,106,122,169–182, 205,206].

benzaldimines show a predominance of the thioketo form which normally condenses to form dithiocine (Fig. 1 (e) [126–129].

The ^{1}H-NMR spectra of α-hydroxynaphthaldimines show a complicated coupling pattern for the aromatic protons. The chemical shifts have been unambiguously assigned by 2-D correlated ^{13}C-^{1}H NMR spectroscopy and by the use of lanthanide shift reagents [129–133]. The average molecular geometry and the optimum location of the lanthanide ion for complex formation with the Schiff base has been established [134–138]. It was found that some 3-hydroxy-2-naphthaldimines show a net reaction with the lanthanide shift reagent [129,134,139,140].

Some structural features were found in substituted bases; for example, the influence of halogen substitution on the electronic distribution of salicylaldimine ligands has been evaluated through a detailed analysis of vibrational bands [141,142].

On the other hand, the substitution of hydroxy-naphthaldimines by nitro groups has shown an increase in the acidity of the phenolic hydrogen. The predominance of the enol-imine or keto-amine tautomer was not significantly changed upon substitution [143,144]. In addition, substitution by nitro groups splits the proton aromatic signals and makes their assignment easier [143].

The presence of nitro groups allows the formation of stable radicals [145–150]. Characterization by EPR has confirmed some observed properties and allowed the interpretation of the behaviour of some living systems [151–155].

The EPR spectra of *N*-alkyl-4-nitro-3-hydroxy-2-naphthaldimines showed hyperfine splittings, which might be due to the delocalization of the free electron that excludes the azomethine group, and with the absence of hydrogen bonds [150,156]. The same delocalization was observed in *N*-alkyl-4-nitro-1-hydroxy-2-naphthaldimines but in this case hydrogen-bonded interactions with nitro groups were detected [143].

The donor capacity of these nitro-substituted ligands has been shown to correlate with their electrochemical properties, which have also been widely studied in analogous organic ligands [157–160].

Nitro-substituted hydroxynaphthaldimines showed several more or less complicated cathodic processes [161,162]; it has been observed that the reduction of nitro groups generally occurs at lower potentials than that of azomethine groups [163–167].

Electrochemical research on these nitro compounds has led to the determination of the partial redox processes shown in eqns. (1)–(6) [162]. The potentials that can be assigned to the reduction of the azomethine group may show, in some aqueous solvents, an irreversible protonation of the reduced compounds, as is indicated in eqns. (7)–(9) [166].

$$\mathrm{R{-}NO_2 + e \rightarrow R{-}NO_2^{-\cdot}} \tag{1}$$

$$\mathrm{R{-}NO_2^{-\cdot} + 2H^+ + e \rightarrow R{-}NO + H_2O} \tag{2}$$

$$\mathrm{R{-}NO + H^+ + e \rightarrow R{-}NOH^\cdot} \tag{3}$$

$$\mathrm{R{-}NOH^{\cdot} + H^+ + e \rightarrow R{-}NHOH} \tag{4}$$

$$\mathrm{R{-}NHOH + 2H^+ + e \rightarrow R{-}NH_2^{+\cdot} + H_2O} \tag{5}$$

$$\mathrm{R{-}NH_2^{+\cdot} + e \rightarrow R{-}NH_2} \tag{6}$$

$$\mathrm{{-}CH{=}N{-} + e \rightarrow {-}\bar{C}H{-}\dot{N}{-}} \tag{7}$$

$$\mathrm{{-}\bar{C}H{-}\dot{N}{-} + e \rightarrow {-}\bar{C}H{-}\bar{N}{-}} \tag{8}$$

$$\mathrm{{-}\bar{C}H{-}\bar{N}H{-} + H^+ \rightarrow {-}CH_2{-}NH{-}} \tag{9}$$

C. SOME ELECTRONIC AND ELECTROCHEMICAL PROPERTIES IN SOLUTION

(i) Nickel complexes. General aspects

No substantial solvent effects were found in the electronic spectra of nickel(II) complexes with tetradentate Schiff bases (Fig. 2(e)), while copper(II) analogues showed noticeable changes in some cases [101,168,169]. These facts can be explained by the molecular orbitals involved in the transitions [170,171]. In addition, the stereochemistry of these complexes exhibited marked differences, depending on the substituent in the bases or the length of the methylene chain [101,106,172–174].

There is a lot of information in the literature relating to nickel(II) complexes with bidentate Schiff bases [84,106,174–177]. The effect of substitution by nitro groups in nickel(II) complexes with Schiff bases derived from salicylaldehydes and α-hydroxynaphthaldehydes and anilines has been the subject of recent reports [101,178,179]. These compounds showed intramolecular hydrogen bonds and tautomeric equilibria in some cases [180]. The electronic effects due to the presence of nitro groups on salicylaldimines were not similar to those observed for α-hydroxynaphthaldimines [122]. Electronic spectroscopy results indicated that, in these cases the nickel(II) complexes change their structures on going from solution to solid phase, the changes depending on the donor character and polarity of the solvent [178,181,182].

(a) ^{1}H NMR of nickel complexes

Several nickel(II) complexes with Schiff bases have shown paramagnetic species in solution; in some cases, planar diamagnetic–tetrahedral paramagnetic equilibria have been found [183]. ^{1}H NMR spectroscopy of nickel(II) and cobalt(II) complexes, among other ions, showed substantial changes in the chemical shift of ligand proton signals upon complexation as a consequence of contact or pseudocontact shift phenomenon [184,185]. Holm et al. and others reported, several years ago, the temperature-dependent probable association or conformational equilibrium in solution between planar and tetrahedral species for nickel(II) *N*-alkyl-salicylaldiminates [186–192]. This phenomenon has allowed the binuclear character of some complexes to be studied [193]. In addition, the presence of enantiomeric and meso forms in the complex bis (*N*-sec-butyl-1-hydroxy-2-naphthaldiminate) nickel(II) has been detected [194–196].

(b) Electrochemistry of nickel complexes

It has been observed that, for nickel(II) complexes with tetradentatate Schiff bases (Fig. 2(e)), the stabilization of nickel(I) and nickel(III) oxidation states depends on the structure of the complex in solution; pseudotetrahedral species only stabilized the nickel(III) oxidation state while planar species stabilized nickel(I) and nickel(III) oxidation states [172,197]. Some nickel(II) complexes showed additional peaks in the anodic region, which were interpreted in terms of the probable oxidation of the ligand [198]. Correlation between the cyclic voltammetry results and the electronic structures have led to the conclusion that the hole size and the geometry of the coordination site occupied by the nickel(II) ion play an important role in the observed behaviour [6,70,199]. This conclusion has also been reached for bidentate ligands (vide infra). In this case (Fig. 2(a)–(d)) substantial differences in the value of the reduction potential to nickel(I) due to electronic and steric effects of the substituents in the ligands were found [200–203]]. Some stabilization of nickel(I) has been observed by nitro-substitution [161,162,204].

(ii) Copper complexes. General aspects

Copper(II) complexes, illustrated in Fig. 2(a)–(d), generally show monomeric planar or tetrahedral structures in solution. Tetrahedral geometry was observed for ligands with bulky substituents in the solid phase [205]. The solution structure of these complexes depends on the polarity and donor capacity of the solvent [101,168,169]. The magnitude of the distortion of the complex can be interpreted in terms of the relative intensity observed for the electronic transition of the azomethyne double bond of the ligand [206].

(a) Electrochemistry of copper complexes

For copper(II) complexes with tetradentatate Schiff bases (Fig. 2(e)), only stabilization of copper(I) has been found; the monomeric state has been confirmed spectroscopically [207]. Sakura et al. [6] have established that copper(III), due to its size, is only stabilized by structures with five-membered fused rings, which is not the case with these ligands (see Fig. 2(e)). It is interesting to mention here that bis-5-bromo-salicyliden-ethylenediamine copper(II) showed an additional cathodic wave due to its reduction to metallic copper. A subsequent anodic process led to the original copper(II) complex, a fact which has made its electrosynthesis possible [141].

Nickel(II) and copper(II) complexes show electrochemical properties that depend on the substituents in the Schiff base ligands [5]. However, the effect of substituents on the redox potentials is different. Figure 3 shows the effect on the

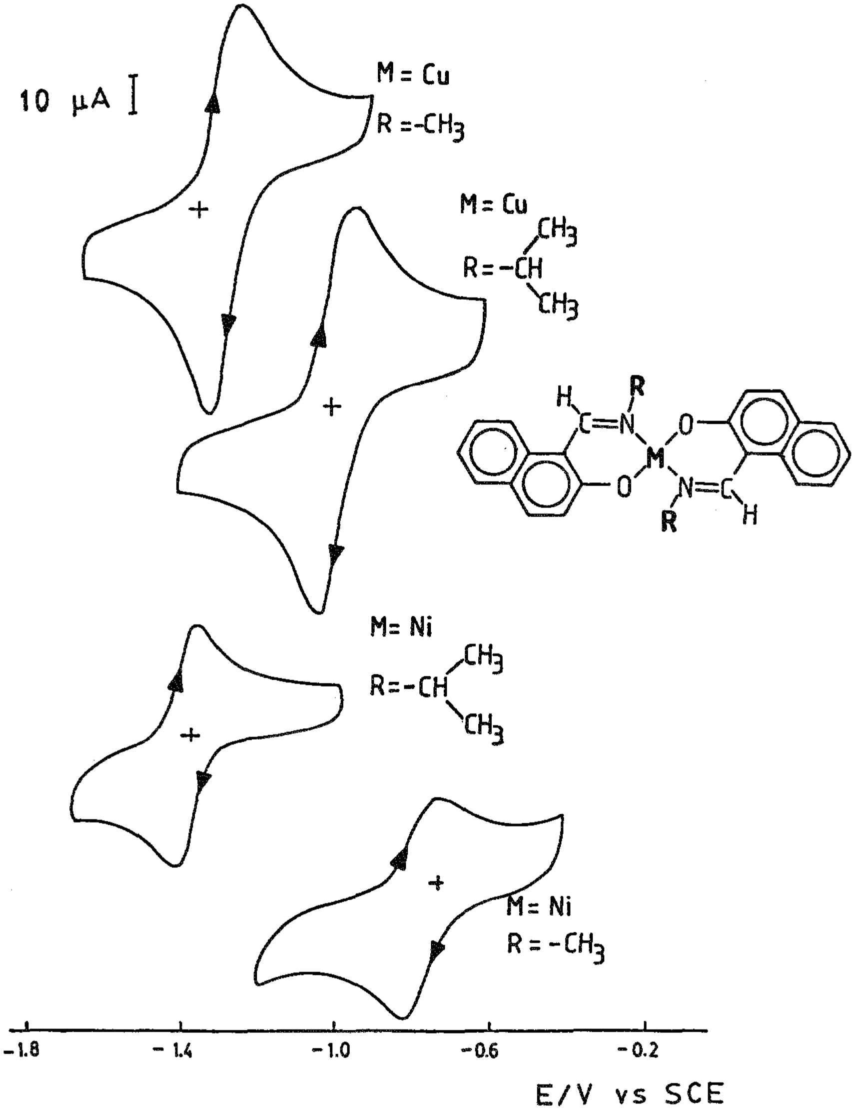


Fig. 3. A comparison of the cyclic voltammograms of similar Cu(II) and Ni(II) complexes with Schiff base ligands derived from 2-hydroxy-1-naphthaldehyde and methyl and isopropyl amine. Solvent: *N*, *N'*-dimethylformamide [5,44].

half-wave potential for the metal(II)–metal(I) process for copper(II) and nickel(II) complexes with ligands derived from 2-hydroxy-1-naphthaldehyde and methyl and isopropylamine in *N*,*N'*-dimethylformamide solution. It has been shown that the isopropyl group stabilizes copper(I) better than the methyl group, while the contrary is true with nickel complexes. These facts were interpreted in terms of the electronic configuration of each metal ion [44].

The reduction reaction for the copper(II) complexes (Fig. 2(a)–(d)) showed a first-order kinetic process with a moderately fast one-electron transfer controlled solely by diffusion of the electroactive species and with no complications due to further chemical reaction [5,82]. Since these copper(II) complexes generally show monomeric structures in solution and one-electron reduction processes, they are described as potential catalysts for the electrochemical synthesis of interesting compounds [58,208].

It is possible to control the Cu(II)/Cu(I) redox potential by means of adequate synthetic design. In this particular case, structural effects such as structure distortion or the number of rings have played an important role. In addition, some combined studies, which include theoretical HOMO-LUMO calculations have recently been published [208a,209].

The following relationships related to redox processes of copper(II) complexes have been found [210]:

(a) A linear relationship as shown in Fig. 4 between d–d transitions and half-wave potentials for a series of copper(II) complexes with some 3-hydroxy-2-naphthaldimines and 2-hydroxy-1-naphthaldimines [75,82]. According to these results and the comparison of electronic spectra in *N,N'*-dimethylformamide solution, it is evident that the copper(II) complexes change from planar to non-planar geometry on reduction [44,211]. These complexes showed a decrease of their distortion on going from *tert*-butyl to hydrogen and a subsequent destabilization of Cu(I) (Fig. 4).

(b) The dependence of the half-wave potential on the position of the substituent in the aniline moiety is shown in Fig. 5 for *N,N'*-dimethylformamide solutions of copper(II) complexes with bromosalicylaldimines derived from anilines [5]. This fact merits some comments: (i) the potential shifts to more positive values by ca. 100 mV on changing from a monobromo- to a dibromosalicylaldehyde derivative with a given aniline; (ii) the additional bromine at position 3 generates an electronic effect which stabilizes copper(I); (iii) moreover, for the same complex series, either mono- or dibrominated, and with the same aldehyde and varying the aniline, a destabilization of copper(I) was observed regardless of the ortho substituent.

(c) A larger number of aromatic rings stabilizes copper(I) complexes [75]. Figure 6 shows the empirical dependence between the half-wave potential and the total number of aromatic rings for a series of copper(II) complexes measured under similar experimental conditions.

In Scheme 1, the half-peak potential values for copper(II) with a series of related Schiff base ligands are shown. It can be seen that the copper(II)–copper(I) potential value varies from −1.21 to −0.37 V [73]. The effect of the number of bromine atoms, shown in structures VII and VIII, and the effects of the substituent on the aromatic ring, shown in structures VI–VIII, were commented on in earlier figures.

These results have contributed to the synthesis of inorganic models that have helped our understanding of the functioning of copper metalloproteins related to electron transport. In addition, the study of these models has indicated that, in order

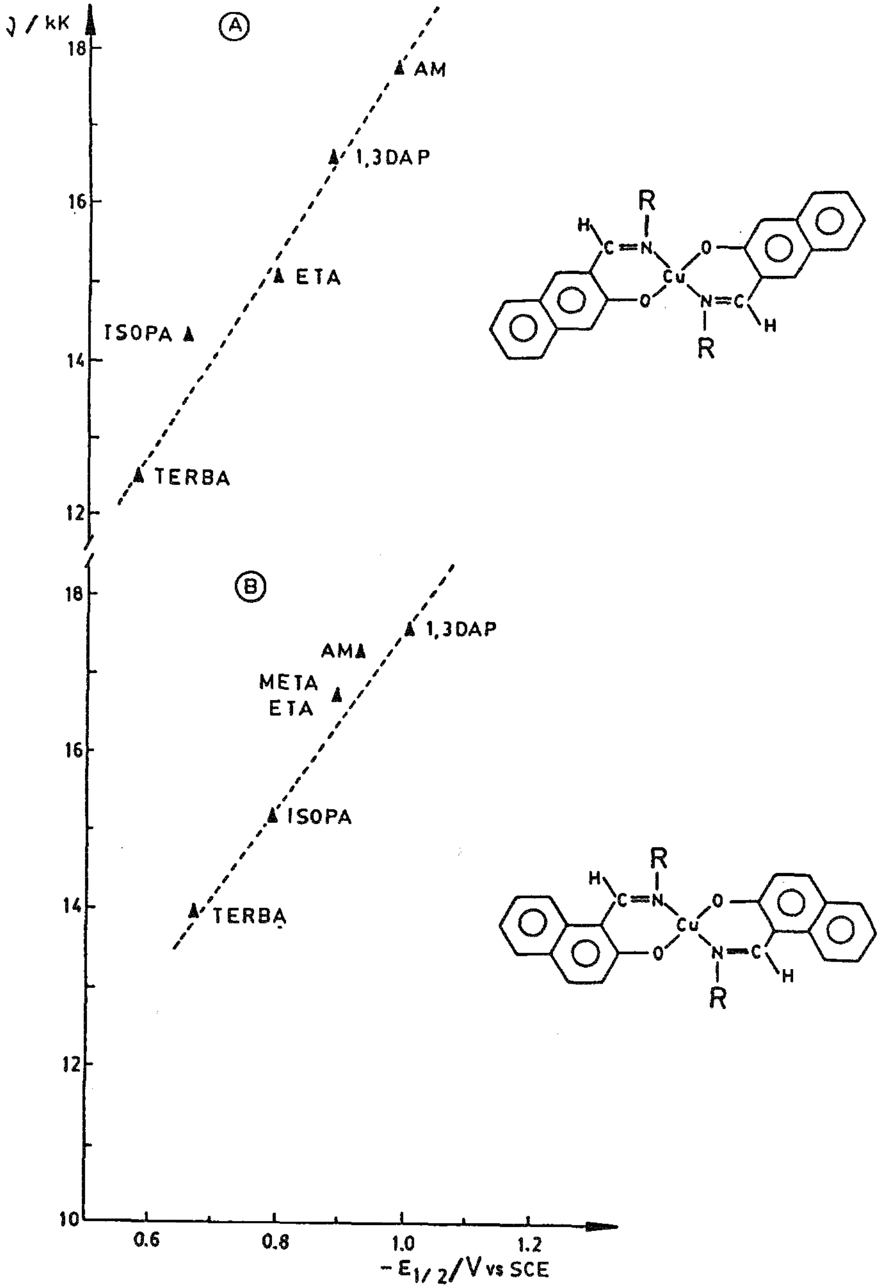


Fig. 4. Relationship between d-d transitions and half-wave reduction potentials for a series of Cu(II) complexes with some 3-hydroxy-2-naphthaldimines and 2-hydroxy-1-naphthaldimines for $R = t\text{-}C_4H_9$ (TERBA), $n\text{-}C_3H_7$ (ISOPA), C_2H_5 (ETA), $CH_2-CH_2-CH_2$ (1,3DAP) and H (AM) [44,75,82,210,211].

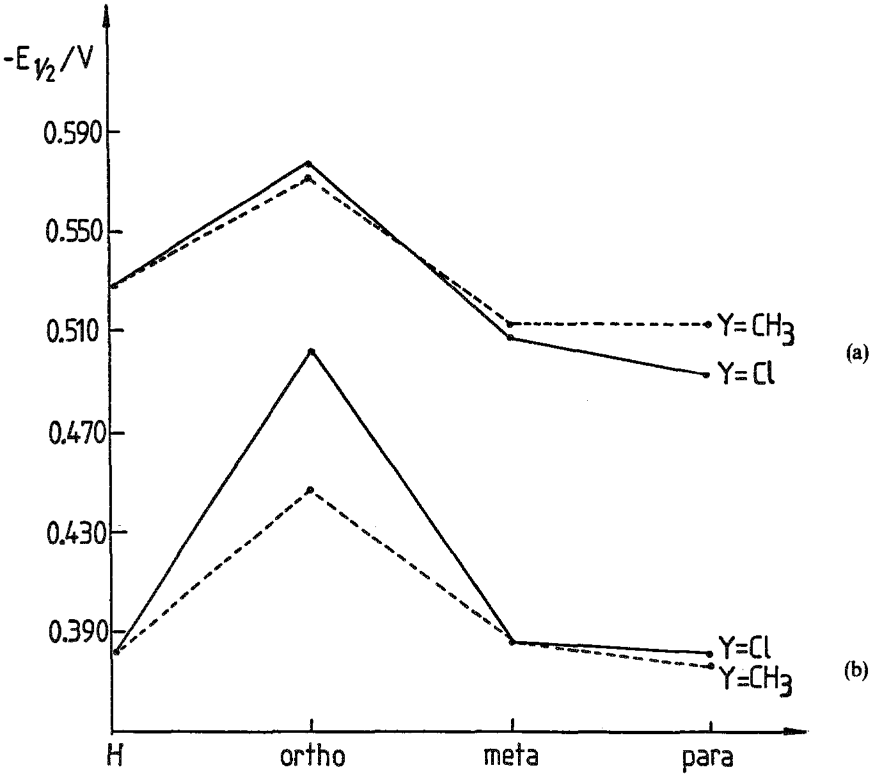
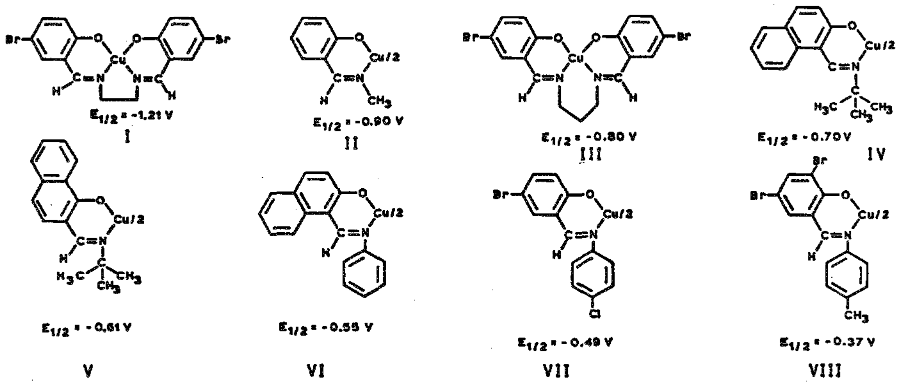


Fig. 5. Half-wave reduction potentials versus the substituent position on the aniline for copper(II) complexes with bromosalicylaldimines. Substituents: C, CH_3; solvent: *N*,*N'*-dimethylformamide. (a) Bis-*N*-(substituted)aryl-5-bromo-salicylald-iminate copper(II); (b) bis-*N*-(substituted)aryl-3,5-dibromo-salicylald-iminate copper(II) [5,210].



Scheme 1. Summary of half-wave reduction potentials for copper(II) with a series of related Schiff base ligands [73,210].

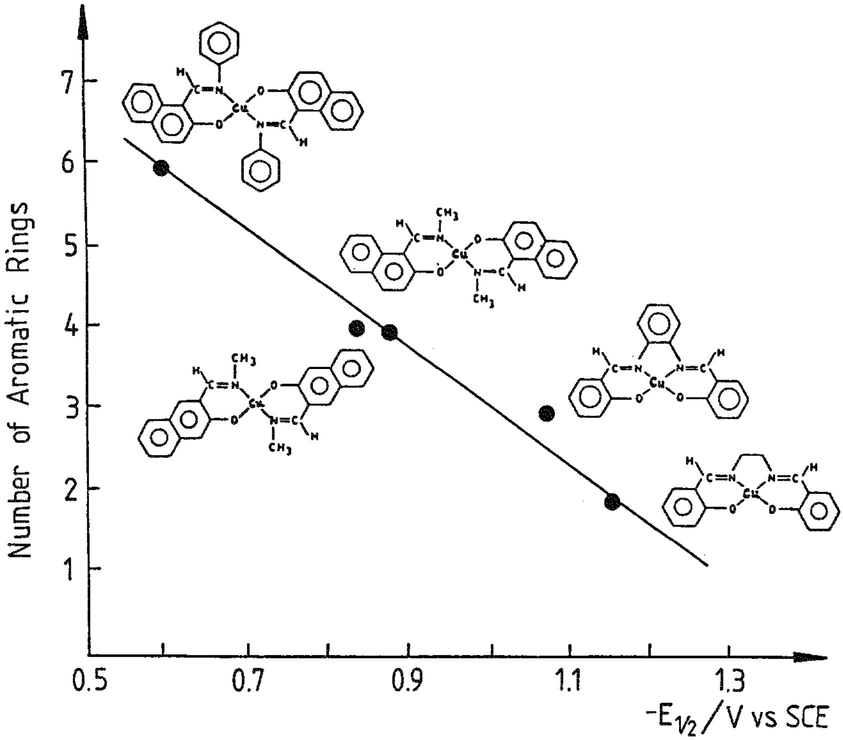


Fig. 6. Relationship between the number of aromatic rings in the copper(II) complexes shown and the half-wave reduction potentials, all measured under similar experimental conditions [75,210].

to decrease the energy of the reduction process, it is necessary to generate a highly distorted ligand field around the copper(II) ion or to surround it with an extended π electron system. Studies with softer bases as ligands have shown that a shift of the Cu(II)/Cu(I) half-wave potential to more positive values is obtained, the values being closer to those found in some blue copper proteins [209].

D. SOME PROPERTIES IN THE SOLID PHASE

(i) Analysis of M(II) complexes by IR spectroscopy

The $\nu_{C=N}$ and $\nu_{C=C}$ frequencies of a series of bidentate and tetradentate salicylaldimines or α-hydroxynaphthaldimines (Fig. 1) were located at higher values than those of their nickel(II), copper(II) and cobalt(II) complexes [81,121,212–217] while the ν_{C-O} frequency lay at lower values. The assignment of the ν_{C-O} frequency led to some controversy in the past but it has been confirmed by isotopic substitution and normal coordinate analysis [216–218]. These observations can be explained by the formation of a π delocalized six-member chelate ring and by the existence of a cross-resonance phenomenon [80,173,219].

Some of the low-intensity bands which appear in the 630–370 cm^{-1} region have been assigned to metal–ligand vibrations [220–227] and have been characterized as mixed bands [122].

(a) Infrared spectra of iron(III) complexes

Iron(III) complexes with Schiff bases derived from bromosalicylaldehydes and substituted anilines: bis-*N*-(substituted)aryl-5-bromo-salicylaldiminate iron(III) chloride and μ-dichloro-bis-chloro-*N*-(substituted)aryl-5-bromo-salicylaldiminate iron-(III) (Fig. 2(*f*)) [227,228] show that the ligand $\nu_{C=N}$ and ν_{C-O} frequencies are respectively shifted to higher and lower energies upon complexation [228]. These results are the opposite of those observed earlier (vide supra) [212–219].

These differences can be attributed to stoichiometry changes in the complex that induce a greater Lewis acid character on the iron(III) ion; thus, the azomethine nitrogen hybridization changes [229] to a greater enol-imine contribution upon coordination [228].

An increase in the $\nu_{C=N}$ stretching frequency has been observed when some Schiff bases react with Lewis acids, such as boron trifluoride, leading to a change in the hybridization of the azomethine nitrogen. This result has been confirmed by ab initio calculations [230].

The metal-ligand vibrations are consistent with the presence of chlorine atoms in terminal and bridge positions in the complexes shown in Fig. 2(f) [231–233]. These vibrations were characterized as mixed bands and were interpreted in terms of normal modes of vibration which showed harmonic coupling of the aromatic rings. In addition, no contributions of bridging species have been found in this kind of complex: the existence of neither superoxide or peroxide (1100–800 cm^{-1} region) nor oxide bridges (780–570 cm^{-1} region) was observed [234].

(ii) Magnetic properties of iron(II) complexes

Antiferromagnetic properties have been found almost exclusively in some binary compounds containing first transition series elements [235–244].

However, some solid state effects have been observed in iron(II) and iron(III) complexes with bidentate Schiff bases derived from salicylaldehydes and anilines [245–247]: for example, magnetic moment values at different temperatures for some iron(II) complexes are higher than those reported for other iron(II) Schiff bases complexes [248–252], suggesting the existence of ferromagnetic interactions in the solid phase.

On the other hand, high values for magnetic moments have been reported only for ferrites and similar inorganic compounds [240,242]. Furthermore, some complexes of iron(II), such as $[\mathrm{Fe(pyridine)_2(SCN)_2}]$ [253], showed ferromagnetic behaviour at low temperatures.

The variation of the molar magnetic susceptibility with temperature in the range 3–360 K for the above-mentioned complexes suggests ferrimagnetic, rather than ferromagnetic, behaviour at some temperatures followed by antiferromagnetism at lower temperatures. In some complexes, an additional "residual paramagnetism" is observed at low temperatures [254].

The proposed ferrimagnetic phenomenon is supported by Mössbauer spectroscopy results [254], which suggest the existence of at least two sites for the iron atoms.

(a) Electronic and magnetic properties of iron(III) complexes

The electronic spectra of the dimeric species μ-dichloro-bis-chloro-*N*-(substituted)anil-5-bromo-salicylald-iminate iron(III) (Fig. 2(f)) in the solid phase have been explained in terms of metal–ligand charge transfer and/or intraligand bands [255,256].

Electronic transitions in high-spin iron(III) complexes are forbidden [257]. Nevertheless, lower-energy bands of middling intensity appeared in dimeric species that have been assigned [258] to forbidden spin transitions with increased intensity due to simultaneous pair excitation.

The effective magnetic moments at room temperature are slightly lower than those found for high-spin Fe(III); their variation with temperature showed [259] antiferromagnetic interactions with coupling and residual paramagnetic parameters related to those obtained in similar complexes [245,260]. Dimeric systems with dihydroxy-, dialkoxy- and *p*-quinone [261–264] bridges showed weaker coupling than in the former cases [228].

On the other hand, the solid state structure is not retained when the complexes go into solution: electronic spectra, magnetic moments and osmometric measurements in dimethylformamide showed monomeric high-spin iron(III) structures [256,258].

Mössbauer spectra of these dimeric species at 77 K showed a doublet not quite different to those observed in pseudo-octahedral N_2O_2 complexes [258]. The isomer shifts and quadruple splittings are typical of high-spin iron(III) and depend on the nature of the substituent in the aniline group [228,265].

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