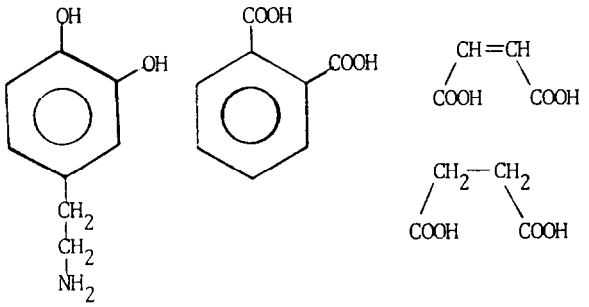
It is well known that the spin–lattice relaxation rates cannot often be rationalized in terms of the Solomon-Bloembergen equation, in its original form, because of the important contribution arising from the unpaired spin density onto the ligand molecule [1]. Thus a modified S.B. equation, where both the metal-centered and ligand-centered dipolar contributions are taken into account, must be employed.

In this work the Ni(II) complexes of dopamine [2], a molecule of biological relevance, phthalic acid [3], maleic and succinic acid [4] were examined. The common feature of these differently flexible ligands is a potential bidentate binding site.



From the analysis of the proton and carbon paramagnetic shifts, induced on the nuclei of the different ligands bound to Ni^{2+}, a delocalization mechanism was hypothesized with the aid of an INDO M.O. analysis, performed on suitable radical models of the ligand. The radical model giving hyperfine coupling constants in the best agreement with the experimental shifts was then used to obtain a complexation model. The reliability of the model chosen was tested introducing the metal–nucleus distances in the reduced and modified S.B. equation and veryfying whether the calculated total unpaired spin densities and correlation times satisfy the experimental nuclear relaxations.

In the case of ligands having a partially rigid skeleton (dopamine, phthalic and maleic acids) the approach led to a unique complexation model, consistent with the experimental data, while for the more flexible succinic acid the result were not so encouraging.

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R8

Cu(II)–Mn(II)–Imidazole Competing Equilibria. ESR Study.

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The interaction between divalent metal ions and nucleobases is very important in many biochemical reactions [1].

The metal ions affinity toward different ligands is strongly related to the extent of the metal-ligand equilibrium. The aim of this report is to apply the ESR analysis carried out by means of the Mn(II) and Cu(II) paramagnetic probes to study the competion equilibrium of the Me-nucleobases complexes [2–4].

Cu(II)–Imidazole System

The Cu(II)–imidazole interaction is analyzed in terms of the X-band ESR hyperfine structure resolution. Due to the interaction of $S_{Cu} = ½$ with $I_{Cu} = 3/2$ four lines of equal intensity are expected in the presence of imidazole. The Hamiltonian of such an interaction is represented by [5]:

$$\mathcal{H} = \beta_o[g_{\parallel}H_zS_z + g_{\perp}(H_xS_x + H_yS_y)] + \\ + A_{\parallel}I_zS_z + A_{\perp}(I_xS_x + I_yS_y) \qquad (1)$$

The well-resolved hpf structure of the Cu(II)–Imidazole system at low metal ligand molar ratios (Cu(II)/[L] = 1:20) suggests a very strong interaction between the paramagnetic metal ion and the base.

The ESR analysis shows that the following equilibrium:

$$Cu(II)(H_2O)_6 + 4\ Imid \overset{K}{\rightleftarrows} \\ Cu(II)–(Imid)_4(H_2O)_2 + 4H_2O \qquad (2)$$

is pH independent for pH values up to 5.2; in more acidic conditions, the hpf structure reduces and the Cu(II)–H_2O broadline appears (Fig. 1(a) and (b)).

The superhyperfine structure in the Cu(II)–Imid spectrum is absent and the nitrogen atoms interacting with the cupric ions are equivalent. The value of $a_{Cu-N} = 7.45$ mT found, is consistent with a four planar imidazole molecule and two axial water molecules.

Mn(II)–Imidazole System

The presence of different molecular species in a manganous solution can be detected by means of the study of ESR parameters like a, the hyperfine coupling constant and ΔT, linewidth [6]. The ESR

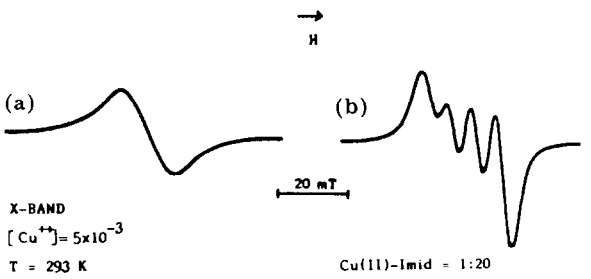

Fig. 1.

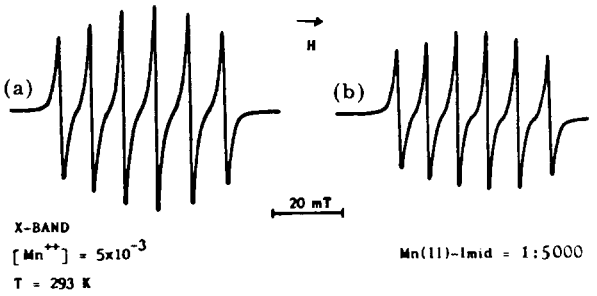

Fig. 2.

$Mn(II)-H_2O$ spectrum is characterized at room temperature by $a_{Mn(II)-H_2O}$ = 3.8 mT and $\Delta H_{Mn(II)-H_2O}$ = 1.5 mT values. For molar ratios [Mn(II)]/[Imidazole] = 1:900, $a_{Mn(II)-Imid}$ = 9.4 mT, and ΔH = 2.1 mT. For molar ratios [Mn(II)]/[Imid] = 1:5000, $a_{Mn(II)-Imid}$ = 8.94 mT and ΔH = 1.4 mT.

The consistent variations of the coupling constant as the ligand, increase (Fig. 2(a) and (b)) as interpreted with a charge in the first coordination sphere of the metal ion. At high ligand concentration the value of the coupling constant and linewidth suggest a very symmetric arrangement of the ligands around the manganous ion, like a tetrahedric complex. Also steric considerations suggest the following equilibrium [7]:

$$[Mn(II)(H_2O)_6]^{++} + 4\ Imid \overset{K}{\rightleftarrows} [Mn(II)(Imid)_4]^{++} + 6H_2O \qquad (3)$$

The equilibrium (3) becomes quantitative for metal ligand molar ratios much higher than the Cu(II)–Imid equilibrium; this underlines the major affinity of the cupric ion for the imidazole ligand.

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R9

Oxidation Potentials and Autoxidation of Copper(I) Complexes with a Series of $[N_2S_2]$-Macrocycles

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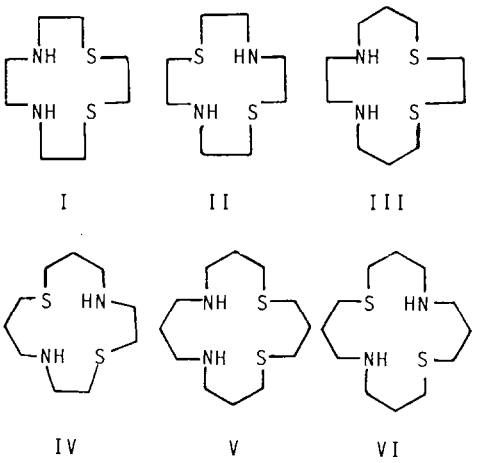
A combination of sulfur and nitrogen donor atoms is well-known in the active center of copper enzymes and may be essential for the specific properties of biological copper. Little is known, however, about the redox properties of corresponding low-molecular copper complexes.

The macrocyclic ligands I–VI were obtained by high-dilution cyclisation via the corresponding amides and reduction with diborane [1, 2].



These ligands, while structurally very similar, span a considerable range of cavity sizes which in turn are strongly reflected in the susceptibilities of the corresponding Cu(I) complexes toward autoxidation. Reactions with O_2 are very fast with the twelve-membered macrocycles I–II and with III, and they can only be followed by stopped-flow techniques. Complexes with the 14-macrocycle IV can be studied conveniently with an oxygen electrode. The complexes with the 16-membered macrocycles V–VI show no significant reactivity.

The kinetics of autoxidation are relatively simple. Under conditions where the formation of the complexes is essentially complete, the rate is independent