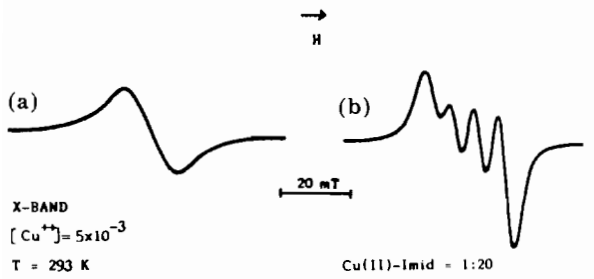

Fig. 1.

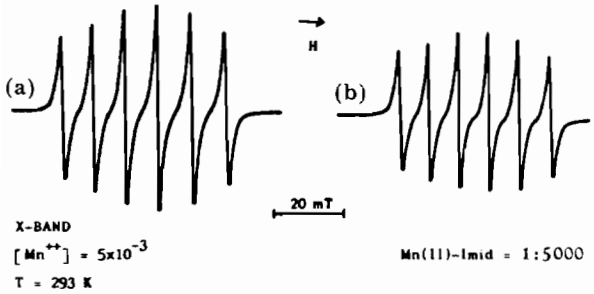

Fig. 2.

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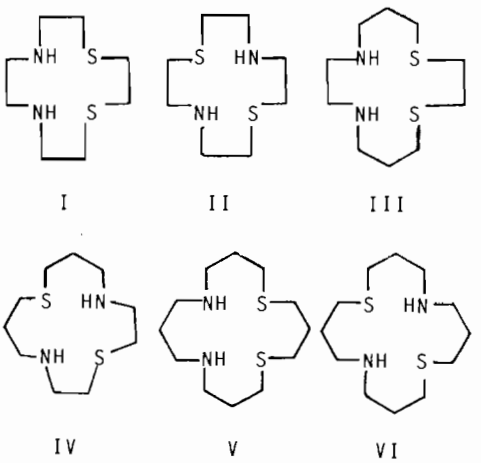
A combination of sulfur and nitrogen donor atoms is well-known in the active center of copper enzymes and may be essential for the specific properties of biological copper. Little is known, however, about the redox properties of corresponding low-molecular copper complexes.

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

of the pH and of the concentrations of buffers and acetonitrile. With the *trans*-14-macrocycle IV the kinetics are completely described by a second order rate constant: $-d[O_2]/dt = k \cdot [O_2][CuL^+]$, $k = 40\ M^{-1}\ s^{-1}$.

For the other ligands, the same rate law is obtained from initial rates. Stability constants and standard potentials of the CuL^{2+}/CuL^+ couples are correlated to the kinetics of autoxidation. As an example, with V the electrode potential is too high to allow the accumulation of H_2O_2 under our experimental conditions (pH = 6–8), in line with the insignificant rate of autoxidation. The correlation of redox potentials with the kinetics of autoxidation will be discussed in detail.

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R10

Kinetics and Mechanism of Ligand Substitution in Tetrahedral Zinc Complexes

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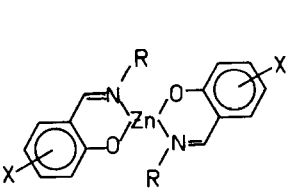
Zinc(II) complexes are of major importance for biological systems. Compared with other divalent transition metal complexes there is relatively little information on the kinetics and mechanism of ligand substitution in zinc(II) complexes. This is probably due to the fact that in the case of zinc(II) there are no ligand field stabilization effects. Hence, zinc(II) systems are in general kinetically labile and not coloured, which makes monitoring more difficult.

Ligand substitution in systems such as (1)

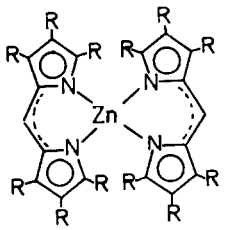
$$ZnA_2 + 2HB \rightleftharpoons ZnB_2 + 2HA \qquad (1)$$

can be easily followed spectrophotometrically if the absorption of ZnA_2 in the UV/VIS range is stronger than that of HA, HB, and ZnB_2. This is so for the tetrahedral complexes $ZnA_2 \triangleq I \triangleq Zn(X\text{-sal-}R)_2 \triangleq$ bis-(N-alkylsalicylaldiminato)-Zn(II), $ZnA_2 \triangleq II \triangleq Zn(HMDP)_2 \triangleq$ bis-(hexamethyldipyrromethenido)-Zn(II), and for ligands HB such as acetylacetone ≙ Hacac, even if present in large excess.

The kinetics of ligand substitution in complexes *I* and *II* were studied by SF spectrophotometry (*I*) and normal spectrophotometry (*II*) in organic solvents. Mechanistic information was obtained through variation of the substituent X, of the alkyl group R and of the nature of the attacking ligand HB.



I ≙ $Zn(X\text{-sal-}R)_2$



II ≙ $Zn(HMDP)_2$

In protic solvents ligand substitution according to (1) follows the general rate law (2), in which k_s describes a ligand independent pathway induced by the solvent:

$$v = k_{obs}^* [complex] = (k_s + k_{HB}[HB])^* [complex] \qquad (2)$$

The results obtained can be summarized as follows:

(i) X-ray structures of complexes $Zn(X\text{-sal-}R)_2$ with X = H and R = Et, iPr, nBu and with X^4 = OMe and R = nPr prove tetrahedral coordination geometry in the solid state.

(ii) Complexes $Zn(X\text{-sal-}R)_2$ react much faster than complexes $Zn(HMDP)_2$, for which $k_s = 0$.

(iii) For the salicylaldiminato complexes $Zn(X\text{-sal-}R)_2$ the relative contributions of k_s and $k_{HB} \cdot [HB]$ to k_{obs} as well as the size of k_{obs} are governed by the nature of R.

(iv) The kinetic effect of substituents X in the 5-position is not very significant in protic solvents.

(v) Variation of the nature of HB clearly reveals the associative character of the ligand pathway k_{HB}.

R11

Synthesis and Reactivity towards Dioxygen of a Series of Five-coordinated Complexes between N,N′-(3,3′-Dipropylmethylamine)bis(2-hydroxy-1-naphthylidenamine) and the Metal Ions Mn(II), Fe(II), Co(II), Ni(II) and Cu(II)

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The study of metal complexes able to react with dioxygen has aroused great interest in recent years.