

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.

- 1 A. H. Alberts, R. Annunziata and J.-M. Lehn, *J. Am. Chem. Soc.*, **99**, 8502 (1977).
- 2 L. Siegfried and Th. A. Kadon, to be published.

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Kinetics and Mechanism of Ligand Substitution in Tetrahedral Zinc Complexes

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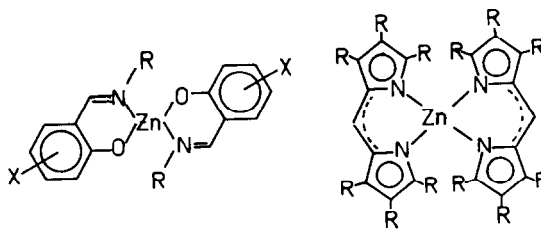
Zinc(II) complexes are of major importance for biological systems. Compared with other divalent transition metal complexes there is relatively little information on the kinetics and mechanism of ligand substitution in zinc(II) complexes. This is probably due to the fact that in the case of zinc(II) there 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)



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 $ZnA_2 \hat{=} I \hat{=} Zn(X\text{-sal-R})_2 \hat{=} \text{bis-(N-alkylsalicylaldiminato)-Zn(II)}$, $ZnA_2 \hat{=} II \hat{=} Zn(\text{HMDP})_2 \hat{=} \text{bis-(hexamethyldipyromethenido)-Zn(II)}$, and for ligands HB such as acetylacetonone $\hat{=} \text{Hacac}$, 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 $\hat{=} Zn(X\text{-sal-R})_2$

II $\hat{=} Zn(\text{HMDP})_2$

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:

$$v = k_{\text{obs}} \cdot [\text{complex}] = (k_s + k_{\text{HB}}[\text{HB}]) \cdot [\text{complex}] \quad (2)$$

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 $X^4 = \text{OMe}$ and R = nPr prove tetrahedral coordination geometry in the solid state.
- (ii) Complexes $Zn(X\text{-sal-R})_2$ react much faster than complexes $Zn(\text{HMDP})_2$, for which $k_s = 0$.
- (iii) For the salicylaldiminato complexes $Zn(X\text{-sal-R})_2$ the relative contributions of k_s and $k_{\text{HB}} \cdot [\text{HB}]$ 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} .

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Synthesis and Reactivity towards Dioxygen of a Series of Five-coordinated Complexes between *N,N'*-(3,3'-Dipropylmethylamine)bis(2-hydroxy-1-naphthylideneamine) 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.