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. Kaden, to be published.

R10

Kinetics and Mechanism of Ligand Substitution in Tetrahedral Zinc Complexes

M. DREHER and H. ELIAS

Anorganische Chemie III, Eduard-Zintl-Institut, Technische Hochschule Darmstadt, Hochschulstr. 4, 6100 Darmstadt, F.R.G.

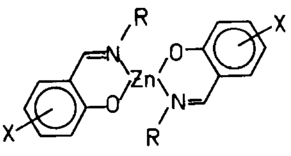
Zinc(II) complexes are of major importance for biological systems. Compared with other divalent transition metal complexes there is relatively little information on the kinetics and mechanism of ligand substitution in zinc(II) complexes. This is probably due to the fact that in the case of zinc(II) there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

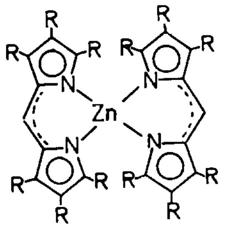
$$ZnA_2 + 2HB \rightleftharpoons ZnB_2 + 2HA \qquad (1)$$

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 $ZnA_2 \hat{=} I \hat{=} Zn(X\text{-sal-}R)_2 \hat{=}$ bis-(N-alkylsalicylaldiminato)-Zn(II), $ZnA_2 \hat{=} II \hat{=} Zn(HMDP)_2 \hat{=}$ 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.



$I \hat{=} Zn(X\text{-sal-}R)_2$



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

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-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)

R. CINI, P. ZANELLO, A. CINQUANTINI

Istituto di Chimica Generale, Università di Siena, Piano dei Mantellini 44, 53100 Siena, Italy

A. COLLIGIANI, C. PINZINO

Laboratorio di Chimica Quantistica ed Energetica Molecolare del C.N.R. (National Research Council), Via Risorgimento 35, 56100 Pisa, Italy

and G. VALENTINI

Istituto di Chimica Industriale, Università di Pisa, Via Risorgimento 35, 56100 Pisa, Italy

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

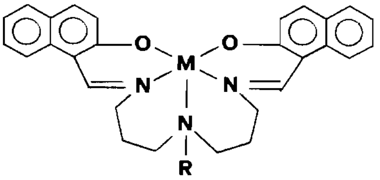
TABLE I. Oxidation Potential of the [M(NAPRDPT)] Complexes from Cyclic Voltammetry.

Complex	$E^{\circ\prime}_{II/III}$/V
[Mn(NAPHDPT)]	−0.31
[Mn(NAPMeDPT)]	−0.31
[Fe(NAPHDPT)]	−0.32
[Fe(NAPMeDPT)]	−0.27
[Co(NAPHDPT)]	−0.37
[Co(NAPMeDPT)]	−0.23
[Ni(NAPHDPT)]	+0.35
[Ni(NAPMeDPT)]	+0.40
[Cu(NAPHDPT)]	+0.75*
[Cu(NAPMeDPT)]	+0.86*

*Peak potential values at 0.2 V sec^{-1}.

Particular attention has been paid to those derivatives which take up dioxygen reversibly because they can mimic biological oxygen carriers [1]. In an attempt to find the parameters able to give some rationalization on the oxygenation reactions we have previously studied the behaviour towards dioxygenation of a series of five-coordinated metal complexes with O_2N_3 donor set (namely [M(SALRDPT)]) by electrochemical and X-ray diffraction techniques [2–5].

We wish to report here on the behaviour of the complexes [M(NAPRDPT)] having the same O_2N_3 donor set.



M = Mn(II), Fe(II), Co(II), Ni(II), Cu(II)
R = H, Me

As in the case of SAL derivatives, all the NAP compounds undergo in DMSO solution a quasi-reversible one-electron anodic oxidation, except for copper(II) compounds, which are irreversibly oxidized (Table I). The comparison with SAL complexes shows that NAP derivatives are more easily oxidizable.

The reaction with dioxygen in DMSO solution was followed by voltammetric techniques. The results indicate that [Co(NAPRDPT)] compounds are able to add dioxygen reversibly. For the manganese(II) and iron(II) complexes irreversible addition occurs, with formation of different oxygenated products. Copper(II) and nickel(II) complexes do not react with dioxygen.

The equilibrium constant of the reaction:

$$[Co(NAPMeDPT)] + O_2 \rightleftarrows [Co(NAPMeDPT)] \cdot O_2$$

in DMSO at 20 °C resulted $(1.0 \pm 0.5) \times 10^4$ dm^3 mol^{-1}.

At least for these types of pentadentate complexes it is possible to state that the location of the oxidation potential allows one to predict whether a compound is able to react with dioxygen but it is not sufficient to predict whether the dioxygenation reaction proceeds reversibly.

The manganese(II), iron(II) and cobalt(II) complexes were ESR inactive both as powders or in degassed solutions.

By exposure to O_2 of toluene solutions of the [Co(NAPMeDPT)] or [Co(NAPHDPT)] complexes strong ESR signals were recorded, characterized by g-factor values of 2.022 and 2.037 respectively. The [Co(NAPHDPT)] adduct signal exhibited a Co hyperfine interaction, whereas the [Co(NAPMeDPT)] one did not, due to the rotation of the methyl group in this latter system. The ESR spectra have been related to metal species reversibly coordinating O_2 which also showed a different spontaneous decaying process.

The IR spectra of solid samples or homogeneous solutions of the different complexes showed significant changes due to O_2 coordination. Hypotheses on the nature of the reversibly and irreversibly coordinating O_2 species have been made on the basis of the frequencies of the IR absorption.

1 R. D. Jones, D. A. Summerville and F. Basolo, *Chem. Rev.*, *79*, 139 (1979).
2 R. Cini and P. Orioli, *J. Chem. Soc., Chem. Comm.*, 196 (1981).
3 R. Cini and P. Orioli, *Inorg. Chim. Acta*, *63*, 243 (1982).
4 P. Zanello, R. Cini, A. Cinquantini and P. Orioli, *J. Chem. Soc. Dalton Trans.*, in press.
5 P. Zanello, R. Cini and A. Cinquantini, submitted for publication.