

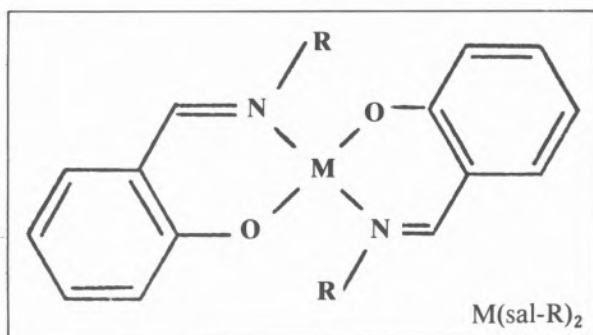


PS5.26 — TH

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KINETICS OF LIGAND SUBSTITUTION IN CHELATE COMPLEXES OF DIVALENT TRANSITION METALS OF BIOLOGICAL IMPORTANCE

The bis chelate complexes $M(\text{sal-R})_2$ of divalent transition metals M^{2+} ($M = \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}$) with various *N*-alkyl salicylaldimines Hsal-R ($R = \text{Et}, n\text{-Pr}, i\text{-Pr}, t\text{-Bu}, \text{neo-Pe}, \text{Ph}$) have been prepared by standard procedures and characterized.



Stopped-flow spectrophotometry has been used to study the reactivity of these complexes towards ligand substitution with acetylacetone (Hacac) in methanol under pseudo first-order conditions ($[\text{Hacac}]_0 \gg [\text{M}(\text{sal-R})_2]_0$) according to (1):



The experimental rate law is a two-term rate law:

$$\text{rate} = (k_S + k_{\text{Hacac}}[\text{Hacac}])[M(\text{sal-R})_2] \quad (2)$$

The substitution of the first ligand in $M(\text{sal-R})_2$ is rate determining, *i.e.*, the conversion

$M(\text{sal-R})(\text{acac}) \rightarrow M(\text{acac})_2$ is a fast consecutive step.

The relative contributions of the terms k_S and $k_{\text{Hacac}}[\text{Hacac}]$ in (2) to the overall rate are mainly controlled by two factors, namely, (i) by the type of the *N*-alkyl group R for a given metal M , and, (ii) by the type of metal M for a given *N*-alkyl group R .

The data obtained for k_S and k_{Hacac} at 25°C for the 24 reactions studied are presented. The rate constants range from $k_S \approx 0$ ($M = \text{Ni}$; $R = \text{Et}, i\text{-Pr}, \text{neo-Pe}$) to $k_S = 18.5 \text{ s}^{-1}$ ($M = \text{Zn}$; $R = \text{Ph}$) and from $k_{\text{Hacac}} \approx 0$ ($M = \text{Cu}, \text{Zn}$; $R = t\text{-Bu}$) to $k_{\text{Hacac}} = 2070 \text{ M}^{-1} \text{ s}^{-1}$ ($M = \text{Ni}$; $R = \text{Et}$). The trends observed for the reactivity of the various complexes are correlated with their coordination geometry (as controlled by the *N*-alkyl group R) and with the intimate mechanism of both the solvent-induced pathway k_S and the ligand-dependent pathway $k_{\text{Hacac}}[\text{Hacac}]$.



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COORDINATING PROPERTIES OF PYRIDOXAL THIOSEMICARBAZONE IN METAL COMPLEXES

The study of transition metal complexes of thiosemicarbazones is of great interest because of their pharmacological properties [1-3]. As part of a continuing interest in the chelating behaviour of ligands which have biological activities and the