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ANALYTICAL TECHNIQUES IN THE STUDY OF Ni AND Fe MODEL COMPLEXES OF BIOLOGICAL SIGNIFICANCE

There is increasing awareness of the need for analytical probes that can determine the complex species of a metal without disturbance of the matrix. The task is made somewhat easier by using model compounds, designed to mimic the properties of the complex of interest. The elucidation of the Ni(II)-binding site of human serum albumin involved the use of computer-assisted potentiometric analysis of the interaction of the *N*-terminal native-sequence tripeptide, L-aspartyl-L-alanyl-L-histidine *N*-methylester with Ni(II). The low-molecular-weight Ni(II) binding constituent in human serum, L-histidine, forms only two major complex species in the pH range 4-9, Ni(Hist) and Ni(Hist)₂ [1]. The species distribution is verified by examining the system by differential pulse polarography at the same metal:ligand ratio. Fig. 1 shows in a single scan the two kinetically inert complex species, at pH 6.2, and serves as a useful comparison of the information that can be obtained by the application of current-measuring and potentiometric methods of analysis.

As an extension of our previous studies on Fe(III)-monohydroxamate complexes, investigations into the synthesis and analysis of simple model compounds of the naturally occurring rhodoturlic acid were undertaken [2,3]. A strong indication of similar Fe(III)-binding comes from an examination of the visible absorption spectra of the Fe(III) complexes of the synthesised dihydroxamic

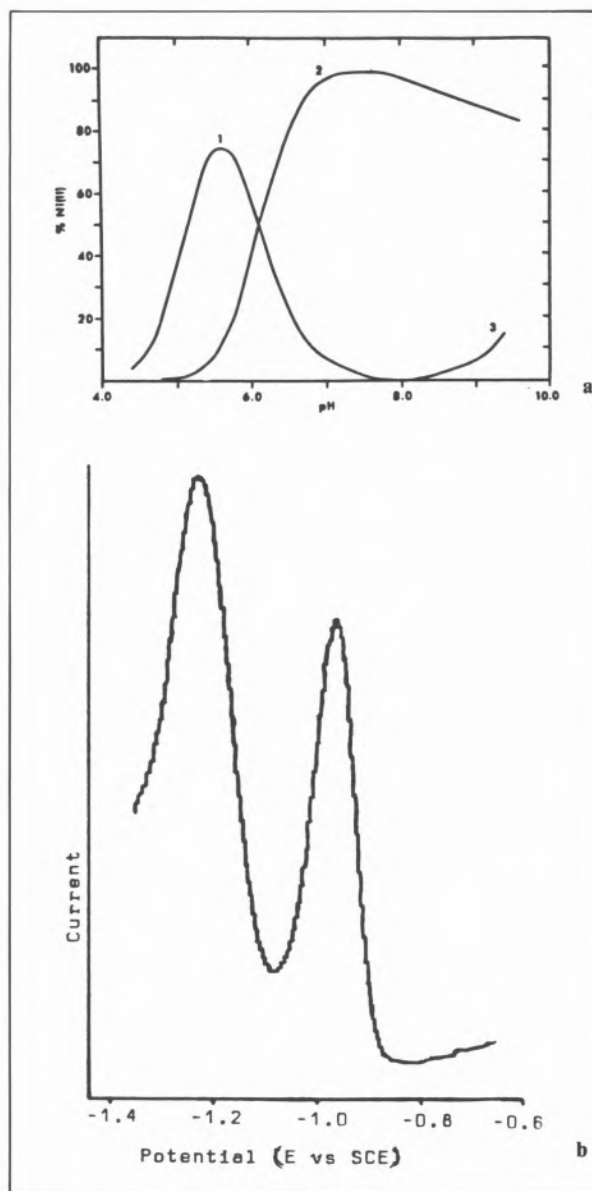


Fig. 1

- a) Species distribution diagram for the Ni(II)-L-His system, $C_M = 1.09 \times 10^{-4} M$, $C_L = 4.81 \times 10^{-4} M$, curve 1, ML ; curve 2, ML_2 ; curve 3, $MH_{-1}L_2$
b) Differential pulse polarogram of Ni(II)-L-His system in $0.6 M NaNO_3$ at pH 6.2

acids, $HOHN-CO-(CH_2)_n-CONHOH$ [4]. A clear isobestic point at 480 nm is evident suggesting that two complex species exist in the pH range 3.6 to 9.0. Results from the potentiometric analysis for $n=3$ indicates a levelling of \bar{n} at a value of 1.5 supporting a formulation of Fe_2L_3 (Fig. 2). The insolubility of the orange complex at higher concentrations is also atypical of simple hydro-

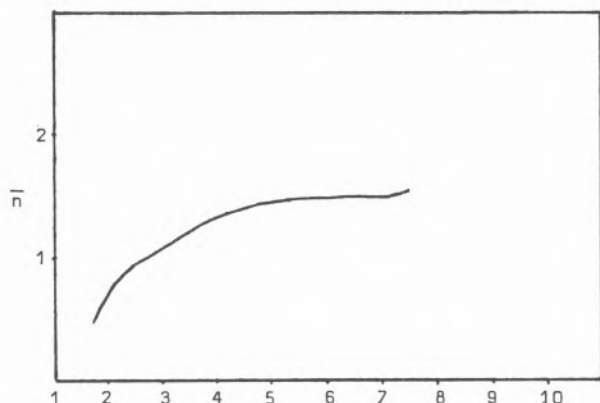


Fig. 2

Plot of \bar{n} versus pH for the Fe(III)-glutaryl dihydroxamic acid system ($n=3$)

xamate complexation of Fe(III). Further investigations are being carried out.

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PS4.16 — MO

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SYNTHETIC APPROACH TO THE MONONUCLEAR ACTIVE SITES OF MOLYBDOENZYMES

EXAFS results for several molybdoenzymes responsible for oxidation of substrates X/XO by oxygen atom transfer with concomitant changes

of central molybdenum oxidation states from VI to IV (*via* V) indicate the minimal coordination spheres $\text{Mo}^{\text{VI}}\text{O}_2(\text{SR})_{2,3}$ and $\text{Mo}^{\text{IV}}\text{O}(\text{SR})_{3,4}$ for the oxidised and fully reduced forms, respectively. Numerous molybdenum-containing model complexes have been prepared to mimic the structural as well as the functional properties of the molybdoenzymes [1]. To date none of these model complexes appears to have all these properties very similar to the molybdoenzymes. We have synthesized some monomeric complexes of the general formula: $[\text{MoS}(\text{S}_2)(\text{DTC})]$, $[\text{MoO}(\text{DTC})(\text{cat})]$ and $[\text{MoO}_2(\text{DTC})(\text{cat})]^-$ (DTC = dialkyldithiocarbamate, cat = catecholatedianion). These complexes catalyze the oxidation of xanthine and sulfite and can reduce molecular oxygen to superoxide. Typical EPR parameters for the complex $[\text{MoOEt}_2(\text{DTC})(\text{cat})]$ (g_{xx} , 1.951; g_{yy} , 1.979; g_{zz} , 1.995; $\langle g \rangle = 1.975$; $\langle A \rangle$, 31.0) suggest the structural closeness of this model compound to xanthine oxidase [2]. EPR and other spectral data along with C.V. results are presented and their relevance to enzymatic processes is discussed.

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