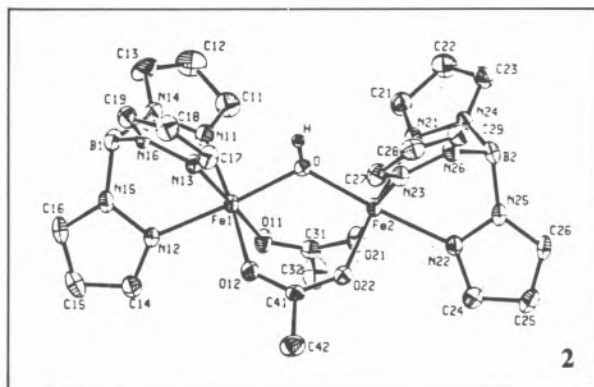
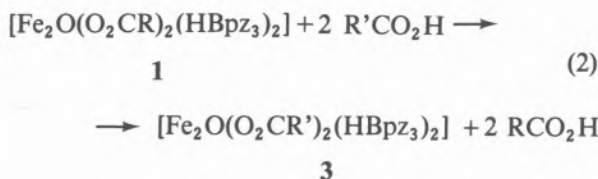


by TACN (1,4,7-triazacyclononane) exhibit similar behavior [2]. The discovery [3] that **1** can be reversibly protonated to form $[\text{Fe}_2(\text{OH})(\text{O}_2\text{CR})_2(\text{HBpz}_3)_2]_2^+$, **2**, eq. (1), suggested that it might be possible to exchange the brid-



ging carboxylate groups in **1** with other carboxylic acids, eq. (2). This exchange reaction has now been demonstrated by NMR and optical spectroscopic studies. The mechanism presumably involves



protonation of the oxo bridge to form **2**, a reaction that lengthens the Fe-O bridge bond by 0.18 Å [3], followed by hydroxide bridge cleavage upon attack by the $\text{R}'\text{CO}_2^-$ anion on one of the iron centers. Closure of the $\text{R}'\text{CO}_2^-$ bridge displaces one oxygen of an originally bridging RCO_2^- ligand, and loss of RCO_2H together with closure of the Fe-O-Fe bridge completes the first substitution reaction. This process is then repeated to form the product **3**. Using related chemistry we have prepared and structurally characterized by X-ray crystallography the phosphate bridged analog of **1**, $[\text{Fe}_2\text{O}(\text{O}_2\text{P}(\text{OPh})_2)_2(\text{HBpz}_3)_2]$, **4**. These results demonstrate that carboxylate groups and phosphate esters can be readily exchanged into the bridging positions of the μ -oxodiiron(III) center, presumably by means of μ -hydroxodiiron(III) intermediates. This new chemistry raises interesting

possibilities for the catalytic mechanisms of ribonucleotide reductase, uteroferrin, and the purple acid phosphatases.

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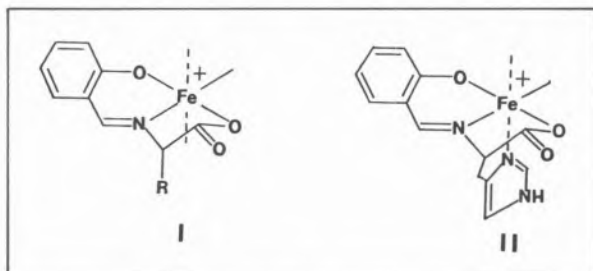
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MODELS FOR IRON-TYROSINATE COORDINATION IN PROTEINS. SPECTRAL AND STEREOCHEMICAL STUDIES OF IRON(III) COMPLEXES OF N-SALICYLIDENE-L-AMINO ACIDS

The iron-tyrosinate proteins are a heterogeneous group of non-heme iron proteins that includes the transferrins, the catechol dioxygenases and the purple acid phosphatases [1]. These proteins display, as a common spectral feature, a moderately intense absorption band that dominates the visible spectrum and is attributed to a charge transfer transition from the tyrosinate residue to iron(III).

The position and intensity of this band depend on many factors, such as the metal geometry and the number of phenolate groups bound to iron(III), but it is also sensitive to the nature of the other ligands in the iron environment. Only limited information is available on the nature and number of these additional ligands in the various proteins; hence the importance of model studies [2-5] that serve to provide the necessary data for a correct interpretation of the spectral features of the metal sites in the proteins.

We have synthesized and characterized a series of high spin iron(III) complexes of the *N*-salicylidene derivatives of L-amino acids, Fe(sal-L-aa)Cl, having the structure **I** when the amino acid is non



polar or **II** in the case of histidine. The stereochemical properties of these complexes have been deduced on the basis of detailed studies performed on the corresponding zinc(II), copper(II) and cobalt(II) systems [6-8]. Systems of this type seem particularly convenient for the investigation of adduct formation with additional ligand molecules, since both equatorial and axial coordination positions are in principle available to the added ligands. The electronic spectra in methanol of the complexes of type **I** (aa = ala, val, phe) display the phenolate-to-iron charge transfer band in the narrow range 530-540 nm ($\epsilon \sim 1200 \text{ M}^{-1} \text{ cm}^{-1}$), while additional absorptions occur at ~ 430 ($\epsilon \sim 1000$), 318 (~ 5000), 295 (~ 5000), 262 (~ 13000) and 235 nm (~ 17000). Coordination of a pseudoaxial imidazole group, as in **II**, produces an ipsochromic shift of the visible bands, particularly that near 500 nm, but has almost negligible effects on the other electronic transitions. Shifts to higher energy of the phenolate-to-iron charge transfer bands can be observed in the spectra of either **I** or **II** upon addition of various bases, the extent of the shift being dependent on the nature of the added base. Comparable changes occur in the CD

spectra of the systems. Of particular interest are the adducts between **I** or **II** and the catecholate monoanion (catH) that may be compared with other models proposed [3] for substrate binding to the catechol dioxygenase enzymes [1]. The adducts [Fe(sal-L-ala)(catH)] and [Fe(sal-L-his)(catH)] exhibit phenolate-to-iron charge transfer bands at 480 and 470 nm, respectively, with a broad shoulder between 650 and 700 nm, that is attributed to a catecholate-to-iron charge transfer band [9]. Although the match may be accidental, the similarity between these spectra and those of the corresponding dioxygenase-substrate complexes (465 and ~ 680 nm for catechol dioxygenase, 475 and ~ 690 nm for protocatechuate 3,4-dioxygenase) [1] is surprisingly good (for [Fe(salen)(catH)] the corresponding bands occur at 418 and ~ 590 nm) [1] and bear on the relevance of the Fe(sal-L-aa)X complexes in model studies of iron-tyrosinate proteins.

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PS4.15 — TH

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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 rhodoturulic 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

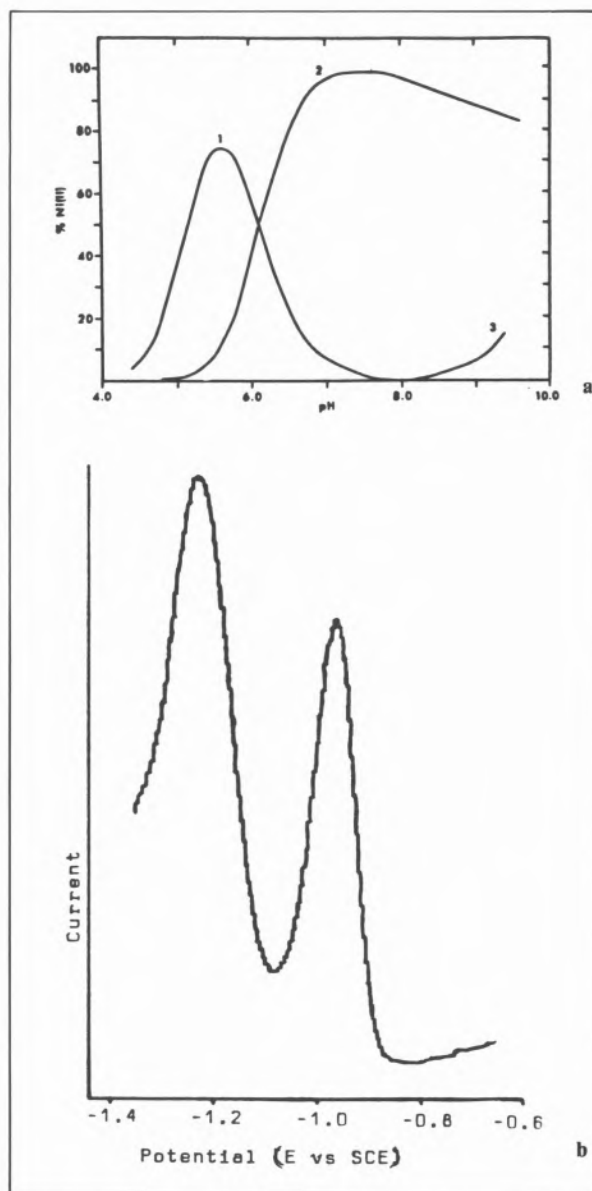


Fig. 1

- 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 NaNO₃ at pH 6.2

acids, HOHN-CO-(CH₂)_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 Fe₂L₃ (Fig. 2). The insolubility of the orange complex at higher concentrations is also atypical of simple hydro-