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Correlation of K-Absorption Edge and EXAFS Spectra of Human Ferric Transferrin with Those of Model Iron(III) Complexes

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The nature of the iron(III) binding sites in plasma transferrin, the iron transport protein of vertebrates, is still not known, despite the considerable spectroscopic effort which has been expended on the problem [1]. In the diferric form, the two sites are believed to be very similar (although not identical) in nature, although substitution of other metal ions provides evidence (from e.p.r. spectra) for site flexibility [2].

The results obtained from a K-absorption edge and EXAFS spectroscopic study of human ferric transferrin and several low mol. wt. complexes of Fe(III) ($S = 5/2$) carried out at the ADONE Synchrotron (Frascati) will be reported. The K-absorption edge spectrum of human diferric transferrin, measured as a lyophilised sample (Fe_2HTR) is well-defined, with a weak 1s→3d absorption at $7117.8_5 \pm 0.9$ eV, followed by a high-intensity 1s→4p absorption at 7137.4 ± 0.8 eV (inflection point, presumably assignable to the transition 1s→4s, at $7130.6_5 \pm 0.3$ eV). Table I lists some spectra of tetrahedral, octahedral six-coordinate, and seven coordinate complexes [3] with mainly N,O donor ligands.

From the data available, a tetrahedral structure can be excluded. $(Ph_4As)FeCl_4$, with a virtually regular tetrahedral structure, shows a relatively strong 1s→3d band, followed by a well-defined 1s→4s transition, which then merges into a very broad ill-defined band containing the 1s→4p transition. Although shifts going from one stereochemistry to another are relatively large (*i.e.* the spectra are of diagnostic value) a choice between octahedral six-coordinate and pentagonal bipyramidal seven-coordinate is not easy. However, despite the similarity in spectra between Fe_2HTR and $Fe(acac)_3$ (Table I), that Fe_2HTR probably is not simply octahedral six-coordinate is demonstrated by the fact that $Fe(acac)_3$ gives an e.p.r. spectrum (77K, $CHCl_3$ gel, X-band) entirely different from that of Fe_2HTR.

TABLE I. K-Absorption Edge Spectra (in eV; low mol. wt. compounds ±0.1 eV).

Compound	$A_{max}^{1s\rightarrow 3d}$	Inflection point	$A_{max}^{1s\rightarrow 4p}$
Fe_2HTR	7117.8_5 (±0.9)	7130.6_5 (±0.3)	7137.4 (±0.8)
$[Fe(dapsc)(OH_2)_2](NO_3)_2OH$	7118.3	7130.6	7135.2
$\{Fe(daptrien)(NCS)_2\}(SCN)$	7117.7	7130.9	7134.0
$[Fe(daptsc)(OH_2)_2](NO_3)_2OH$	7116.2	7126.4	7130.4
$[Fe(saltrien)](PF_6)$	7117.3	7128.0	7139.8
$[Fe(acac)_3]$	7117.0	7131.2	7137.0
$(Ph_4As)[FeCl_4]$	7114.8	7123.0	7133.7

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Complexes of Dioxouranium(VI) with Pyridoxal and Glycine

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The catalytic effect of metal ions upon transamination reactions of aminoacids by pyridoxal and its