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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 ± 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 ± 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.

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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

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

derivatives has been demonstrated through formation of intermediate metal complexes of Schiff bases [1–5].

In our laboratory the role of dioxouranium(VI) ions in biochemical processes is under investigation and several complexes between UO_2^{2+} and biomolecules have been hitherto prepared and studied. Recently, the interaction of dioxouranium(VI) acetate with the ligand pyridoxal has been studied and the bonding of dioxouranium(VI) to phenolic and aldehydic oxygen atoms of pyridoxal has been proved [6, 7]. The influence of uranyl ions on amino-acid–pyridoxal complexes has been investigated as well.

The pyridoxal–glycine–uranyl acetate system has been studied both in solution and in solid state by electronic spectra and i.r. measurements respectively. The electronic spectra of an equimolar mixture of methanolic pyridoxal and glycine show peaks near 360 nm and 320 nm. The peaks markedly increase, when uranyl is added in equimolar amount, as a function of time with a red shift to 390 nm and 343 nm respectively. The band at 278 nm, due to the phenolic group of pyridoxal, appears also slightly shifted to 275 nm and two isosbestic points are present at 290 nm and 275 nm. The resulting spectrum of methanolic pyridoxal–glycine–uranyl complex is identical to that of a pyridoxylidene–glycine–dioxouranium(VI) mixture.

The results obtained in the solid state indicate that ternary complexes 1:1:1 are formed and the elemental analysis is in agreement with the formulation: $UO_2(C_8H_8NO_2)(C_2H_3NO_3)(CH_3COO)2H_2O$.

The i.r. spectrum of the uranyl solid complex was compared with the spectra of the free components. Changes in the i.r. absorptions are observed in particular in the regions where the azomethine C=N stretching, the phenolic carbon–oxygen stretching and the asymmetric carboxyl stretching respectively occur. In fact, the azomethine stretch, ν_{CN}, is assignable to the strong band near 1610 cm^{-1} and the ν_{COO} and ν_{CO} to the absorption peaks near 1570 cm^{-1} and 1510 cm^{-1} respectively.

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Behavior of Copper Complexes in Very Restricted Fields Provided by Reversed Micelles

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Copper ion, in its various forms, plays an important role in many biological reactions. This versatility of copper stems from its feasible redox property and possibility of coordination to a number of common ligands to form complexes of different structure, *e.g.*, octahedral, tetrahedral or square-planar, and mononuclear or polynuclear structures. To date, numerous studies have been performed on the preparation and characterization of model copper complexes in conjunction with the structure and function of the copper metallo–enzymes. However, metal ions in reversed micelles, one of enzyme pocket models, have not attracted much attention. As part of our investigations on the metal ion behavior in reversed micelles [1] correlating with the activity of water and the restricted field effect provided in the micelles, we recently explored redox properties of copper ion and chelation of common ligands of biochemical interest such as imidazole to Cu(I) or Cu(II) ion.

When aqueous Cu(II) chloride is solubilized in chloroform containing 0.20 *M* hexadecyltrimethylammonium chloride (CTACl) and 0.20 *M* or less of water, the predominant species formed is the chloride-bridged polymeric complex. This complex shows absorption bands at 294 and 408 nm. Upon the addition of imidazole to this system, the intensity of both bands decreases and a new band appears at about 280 nm. From an analogous experiment in aqueous media, this was assigned to a charge-transfer band of the copper–imidazole complex. The change of the band intensity as a function of imidazole concentration showed a clear break at the point where $[Im]/[Cu(II)] \doteqdot 2$. In contrast, the presence of 1.0 *M* water abolished the break, just like in the bulk aqueous solution.

In chloroform containing CTACl, Cu(I) chloride is also readily solubilized and the Cu(I) ion is subject to a very slow oxidation by oxygen present in the medium. The oxidation is drastically facilitated by the addition of aqueous hydrogen peroxide. Interestingly, the resulting absorption spectrum was exactly the same as that of Cu(II) chloride itself dissolved in the reversed micelles except the apparent extinction coefficients at λ_{max}'s. On the other hand, Cu(II) chloride complex is reduced instantaneously by the addition of 2-mercaptoethanol as evidenced by a disappearance of 294 and 408 nm bands. Chelation