the $^2B_2$ level with the $^2E_\pm$ levels which yields a triclinic electron distribution. The $^2E_\pm$ levels admix to the $^6A_1$ ground state by spin–orbit coupling. The electron distribution is therefore predominantly spherically symmetric with a small rhombic component C_{2v}. Ferric low spin Fe in Mb(CN) has for C_{4v} symmetry a ^2E ground state and low lying $^2E_2$ and $^4A_2$ levels at about 300 and 800 cm^{-1}. A triclinic perturbation splits the ^2E doublet into $^2E_+$ and the new ground state $^2E_-$. The electron distribution is therefore always of rhombic symmetry C_{2v}.

It is intended to discuss also the symmetry properties of hemes and heme proteins for the $3d^6$ configuration of Fe.

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Jack Bean Urease: the First Nickel Enzyme

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Jack bean urease is the first example of a nickel metalloenzyme [1–3]. Reassessment of the molecular properties of the enzyme shows that the native enzyme has a molecular weight (M_r) of 590,000 ± 30,000, and that under denaturing conditions, urease breaks down to identical subunits with M_r = 90,000–100,000 [4]. The molecular weight of subunits is 96,600, as determined by titration with radioactive inhibitors (acetohydroxamic acid [5] and phosphoramidate) [2, 4]. Thus the native enzyme consists of six identical subunits, and these are arranged in the form of a regular octahedron [6]. Each subunit contains one cystine disulfide bond and a total of fifteen cysteine residues [7].

Each subunit contains 2.0 ± 0.1 very tightly bound nickel ions [1, 2, 8–10]. After the electronic absorption spectrum of native urease has been corrected for effects of light scattering, the peaks associated with nickel ion (λ_{max}: ~407 nm, 745 nm, 1060 nm) are consistent with Ni(II) in an octahedral environment [6, 11]. β-Mercaptoethanol binds rapidly and reversibly to urease to produce marked reversible changes in the absorption spectrum of the enzyme [12]. New absorption peaks in the difference spectrum (324 nm, 1550 M^{-1} cm^{-1}; 380 nm, 890 M^{-1} cm^{-1}; 420sh nm, 460 M^{-1} cm^{-1}) are consistent with charge transfer transitions of a thiolate anion coordinated to Ni(II).

A detailed mechanism was developed in which urea is activated towards nucleophilic attack by virtue of O-coordination to Ni(II) ion [13], and has been subsequently successfully modelled [14].

The competitive inhibitors acetohydroxamic acid, phosphoramidate and fluoride [4, 12, 15], produce small, reversible changes near 400 nm in the absorption spectrum of urease, consistently with their direct coordination to Ni(II) ion.

These and other aspects of the chemistry of this system will be discussed.

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Ions and Ionophores

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It will be shown using typical examples that it is possible to account, by explicit computations, for the complexing preferences of ionophores for certain cations. In the case of valinomycine, the preference observed for complexing the alkali cations is in the order $Rb^+ \sim> K^+ > Cs^+ \gg Na^+$, and can be accounted for by making an energy balance between the ener-