

as is the case in Mb and MnHRP, binding of H_2O_2 to the metal ions would be somewhat 'hindered', which will decrease the rate compared to that if the site were vacant, as in LPO, HRP and modified Mb. This is exactly what is experimentally observed here. The nature of the coordination geometry around the metal centre is therefore important in controlling the catalytic activity of the enzymes. The redox properties of the metal ion would also make some difference as is observed between Mb and MnHRP with similar coordination geometry but dissimilar metal ions at the centre.

4. Concluding remarks

Spin-lattice relaxation time measurements of bulk water in paramagnetic metal-enzymes promises to be useful in deciding if the water molecule is coordinated to the metal centre. The coordination geometry around the metal ion in these enzymes appears to modulate their catalytic activity, though other factors such as redox properties of the metal ion and heme cavity structure must be significant contributory factors in this process.

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References

- Behere D V, Marathe V R and Mitra S 1981 *Chem. Phys. Lett.* **81** 57
 Bloembergen N 1957 *J. Chem. Phys.* **27** 572
 Dugad L B, Behere D V, Marathe V R and Mitra S 1984 *Chem. Phys. Lett.* **104** 353
 Dunford H B and Stillman J S 1976 *Coord. Chem. Rev.* **19** 187
 Dwek R A, Williams R J P and Xavier A V 1974 *Metal ions in biological systems* (ed.) H Sigel (Marcel Dekker, New York) **4** 62
 Lanir A and Schejter A 1975 *Biochem. Biophys. Res. Commun.* **62** 199
 Lukat G S, Rogers R and Goff H M 1987 *Biochemistry* **26** 6927
 Mitra S 1982 In *Iron porphyrins II* (eds) A B P Lever and H B Gray (Reading, MA/New York: Addison-Wesley/Benjamin)
 Modi S, Behere D V and Mitra S 1989a *Biochemistry* **28** 4689
 Modi S, Behere D V and Mitra S 1989b *Biochem. Biophys. Acta* **996** 214
 Modi S, Behere D V and Mitra S 1989c *J. Biol. Chem.* **264** 19677
 Modi S, Behere D V and Mitra S 1990a *J. Inorg. Biochem.* **38** 17
 Modi S, Behere D V and Mitra S 1990b *Biochem. Biophys. Acta* **1038** 164
 Modi S, Behere D V, Mitra S and Bendal S D 1991a *Chem. Commun.* **830**
 Modi S, Deodhar S, Behere D V and Mitra S 1991b *Biochemistry* **30** 118
 Morishima I, Ogawa S, Inubushi T, Yonezawa T and Iizuka 1977 *Biochemistry* **16** 5109
 Perutz M F 1990 *Mechanism of cooperativity and allosteric regulation in proteins* (Cambridge: University Press)
 Perutz M F, Fermi G, Luisi B, Shaanam B and Liddington R C 1987 *Acc. Chem. Res.* **20** 309
 Saunders B C 1973 In *Inorganic biochemistry* (ed.) G L Eichhorn (Amsterdam: Elsevier) p. 988
 Saxena A K, Modi S, Behere D V and Mitra S 1990 *Biochem. Biophys. Acta* **1041** 83
 Shiro Y and Morishima I 1986 *Biochemistry* **25** 1986
 Solomon I 1955 *Phys. Rev.* **99** 559
 Takano T 1977 *J. Mol. Biol.* **110** 537
 Wuthrich K 1970 *Struct. Bonding* **8** 53