

Fig. 4

Quadrupole splittings for high-spin (x) low-spin (•) and «intermediate» (+) doublet as a function of temperature

with increasing temperature while the other two doublets show a continuous decrease explainable by second order Doppler shift.

ACKNOWLEDGEMENTS

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PS4.13 — MO

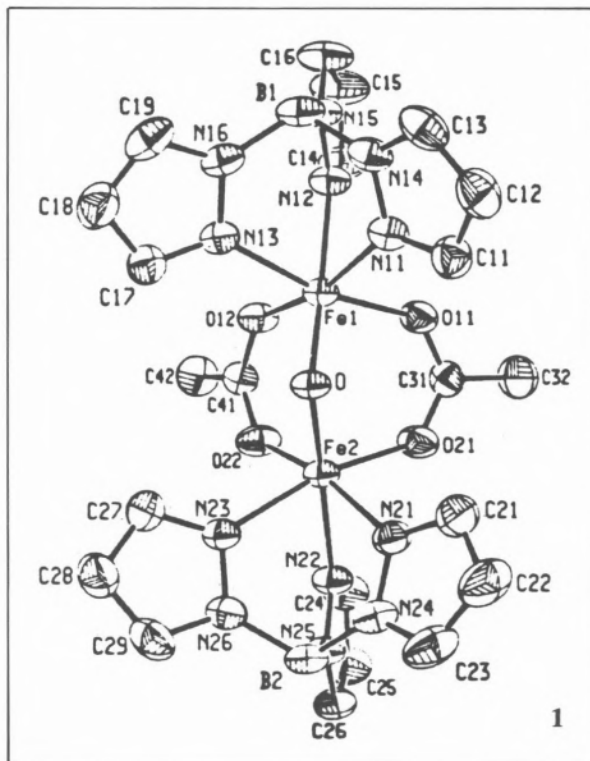
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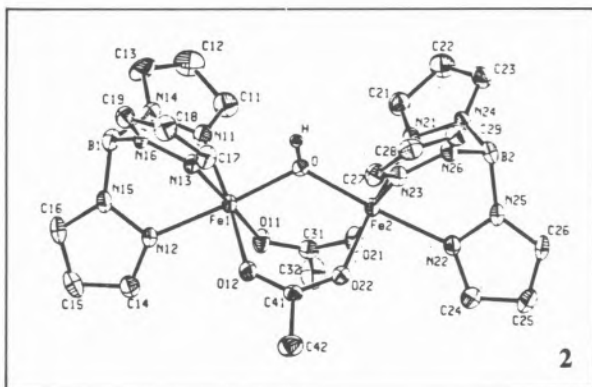
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NEW CHEMISTRY OF BINUCLEAR IRON COMPLEXES — MODELS FOR HEMERYTHRIN AND RELATED PROTEINS

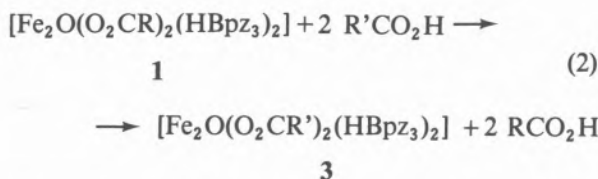
Previously we described the synthesis of $[\text{Fe}_2\text{O}(\text{O}_2\text{CR})_2(\text{HBpz}_3)_2]_2$ complexes [$\text{R} = \text{Me}$, Et, Ph; $\text{HBpz}_3 = \text{hydrotris(1-pyrazolyl)borate}$], **1**, and showed that their magnetic and spectroscopic properties closely resemble those of the met forms of hemerythrin as well as ribonucleotide reductase [1]. The analogs where HBpz_3 is replaced



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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PS4.14 — TU

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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).