with the spacing between lines equal to twice the spinning frequency.

It must be noted that this technique is very different from the fast magic-angle spinning used in high-resolution NMR spectroscopy in solids. Here the spinning is solely for the purpose of orienting the nematic director and need only be rapid compared with the rate of director relaxation. The very rapid tumbling motions within the liquid crystal are sufficient to time average the residual dipolar interactions which depend only on the angle α between the director and the magnetic field as specified by the $3 \cos^2 \alpha - 1$ dependence from which magic-angle considerations arise.

The above technique will allow study of the geometry of nonsymmetrical molecules or parts of large molecules. This should thus be of great use in chemical-structure elucidation and intramolecular dynamic studies. Further applications of this technique in thermotropic and lyotropic liquid crystal are now under way and will be published along with a detailed analysis of the director dynamics.

Synthetic Model Approach to the Active Site Structure of Cytochrome Oxidase. Novel Porphyrin-Containing Heterobinuclear Fe(III)–Cu(II) Complexes

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The active site structure and related function of cytochrome c oxidase still remains one of the most enigmatic and controversial problems in biophysical chemistry.[1] This is despite extensive application of a wide variety of physical techniques over almost half a century since Warburg's discovery of this very important enzyme. We,[2] and several other groups,[3–7] have adopted the synthetic model approach in an effort to elucidate at a molecular level the structural requirements which might explain the observed properties of the natural system. Heterobinuclear complexes containing antiferromagnetically coupled Fe(III) and Cu(II) ions
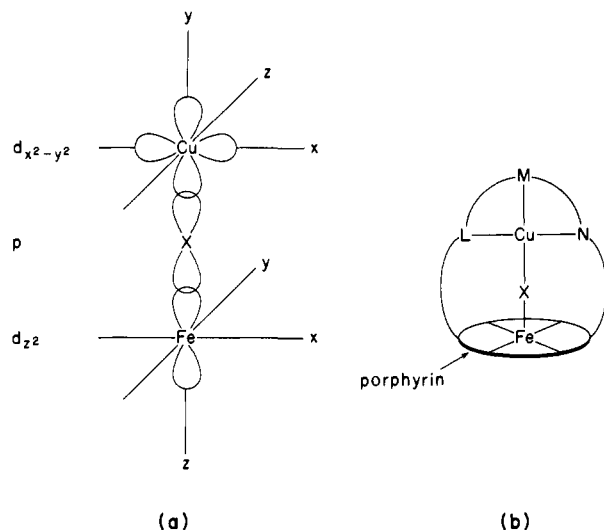
(1) Recent reviews on the present state of knowledge of cytochrome c oxidase include: "Cytochrome Oxidase"; King, T. E., Orii, Y., Chance, B., Okunuki, K., Eds.; Elsevier: New York, 1979. Malstrom, B. G. "Metal Ion Activation of Dioxygen"; Spiro, T. G., Ed.; Wiley: New York, 1980; Chapter 5, p 181. Wilson, D. F.; Erecińska, M. in "The Porphyrins"; Dolphin, D., Ed.; Academic Press: New York, 1979; Vol. VII, Chapter 1, p 1.

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(4) Landrum, J. T.; Reed, C. A.; Hatano, K.; Scheidt, W. R. *J. Am. Chem. Soc.* **1978**, 100, 3232. Landrum, J. T.; Hatano, K.; Scheidt, W. R.; Reed, C. A. *Ibid.* **1980**, 102, 6729.

(5) Okawa, H.; Kanda, W.; Kida, S. *Chem. Lett.* **1980**, 1281.

(6) Jaud, J.; Journaux, Y.; Galy, J.; Kahn, O. *Nouv. J. Chim.* **1980**, 4, 629.

(7) Chang, C. K. In "Biochemical and Clinical Aspects of Oxygen"; Caughey, W. S., Ed.; Academic Press: New York, 1979; p 437.

Figure 1. Schematic representation of (a) the orientation of metal atomic orbitals predicted for significant exchange interaction between a single electron in the d_{z^2} orbital of a high-spin Fe(III) ion in a porphyrin with an electron in the singly occupied $d_{x^2-y^2}$ orbital of a Cu(II) ion in a square-planar, square-pyramidal, or tetragonal ligand field, via the p orbitals of a single bridging ligand X. The labeling of the axes around Cu as shown are to indicate the orthogonality of the ligand field of the Cu with respect to Fe and the singly-occupied orbital as $d_{x^2-y^2}$. Alternative labeling of the axes to match those of the Fe requires the appropriate Cu orbital to be designated $d_{x^2-z^2}$. (b) A ligand system which could maximize such orbital overlap.

generally have been the focus of these model studies, since it seems likely that such a situation exists in the enzyme;[8] proposed bridging groups between the Fe of heme a_3 and Cu_{a_3} have included imidazolate,[9a] oxo,[9b] and thioether (methionine).[9c] An alternative postulate[9d] involving the Fe(IV) and Cu(I) centers to explain the lack of observable ESR signals has recently received some attention.

We[2] have synthesized a model system containing an iron(III) porphyrin with an appended Cu(II)-containing tetrapyridine ligand system with a variety of bridging ligands. However, we have shown recently[10,11] that this system has limited applicability as a model to describe the magnetic properties of the fully oxidized or resting state of the enzyme. The lack of significant antiferromagnetic coupling has been attributed to a mismatch of the appropriate singly occupied atomic orbitals.[10] In the light of these observations, we have synthesized a model system containing an iron(III) porphyrin with an appended Cu(II)-containing ligand system which should allow correct orientation for significant exchange coupling between the two metal centers. We now describe the synthesis and properties of some Fe/Cu heterobinuclear complexes of this system.

In the light of our observations on the previous model system,[2,10,11] we expected that the most effective exchange pathway would result from σ overlap (via the p orbitals of a bridging ligand) of the singly occupied $d_{x^2-y^2}$ Cu(II) orbital in a tetragonal, square-pyramidal, or square-planar ligand field with the d_{z^2} orbital of the high-spin Fe(III) (Figure 1a).[12] This requires a ligand system such as that represented in Figure 1b where the average

(8) Tweedle, M. F.; Wilson, L. J.; García-Iñiguez, L.; Babcock, G. T.; Palmer, G. *J. Biol. Chem.* **1978**, 253, 8065.

(9) (a) Palmer, G.; Babcock, G. T.; Vickery, L. E. *Proc. Natl. Acad. Sci. U.S.A.* **1976**, 73, 2206. (b) Reed, C. A.; Landrum, J. T. *FEBS Lett.* **1979**, 106, 265. (c) Chance, B.; Powers, L. *Biophys. J.* **1981**, 33, 95a. Powers, L.; Chance, B.; Ching, U.; Angiolillo, P. *Ibid.* **1981**, 33, 95a. (d) Seiter, C. H. A.; Angelos, S. G. *Proc. Natl. Acad. Sci. U.S.A.* **1980**, 77, 1806.

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(11) Gunter, M. J.; Mander, L. N.; Berry, K. J.; Murray, K. S.; Clark, P. E., manuscript in preparation.
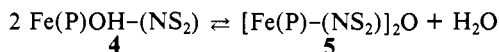
(12) The most effective pathways for exchange coupling in terms of orbital symmetry properties has been discussed in detail: Ginsberg, A. P. *Inorg. Chim. Acta. Rev.* **1971**, 5, 45.

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ligand plane around the Cu is orthogonal to the porphyrin mean plane. Ideally, X should be an exogenous ligand to allow study of a variety of potentially bridging ligands. This type of system then requires as a basis a suitably disubstituted porphyrin to which might be attached an appropriate tridentate ligand "strap".

We have now developed an efficient synthesis and atropisomer separation of such a porphyrin, viz., 5,15-bis(o-aminophenyl)-2,3,7,8,12,13,17,18-octamethylporphyrin (1).[13] The α,α isomer was condensed with 2,6-pyridylbis(4'-thia-5'-pentanoyl chloride) to give the "strapped" porphyrin 2, (P)–(NS$_2$), in 70% yield.[13,14]

2

(P)-(NS$_2$)
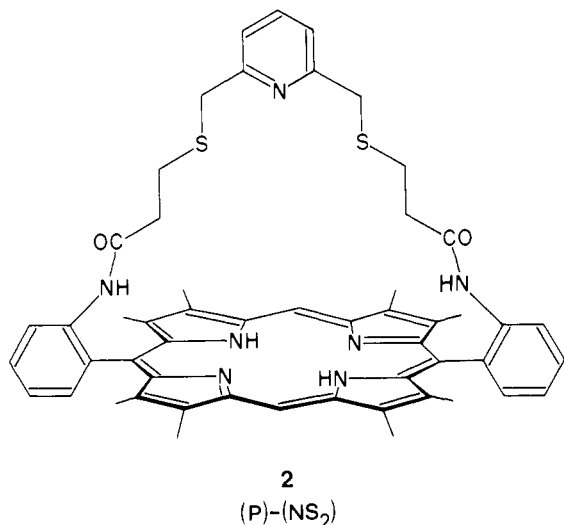
The ferrous sulfate method[15] was used to insert iron into the porphyrin (2) to give the high-spin Fe(III) complex Fe(P)Cl–(NS$_2$) (3).[16] After treatment of a CHCl$_3$ solution of 3 with aqueous NaOH and subsequent chromatography and recrystallization from CHCl$_3$–MeOH, the hematin hydrate Fe(P)OH–(NS$_2$)·H$_2$O (4) was obtained. The hydroxo formation was established by analytical [Anal. (C$_{53}$H$_{52}$N$_7$O$_3$S$_2$Fe·H$_2$O) C, H, N, Fe], IR (no bands, 840–925 cm^{-1}), magnetic (μ_{eff} = 5.8 μ_B at 300 K) and ESR ($g \sim$ 6, 2 at 4.2 K) measurements.[17,18] However, the uncrystallized product has an infrared band at 890 cm^{-1} and a μ_{eff} = 2.5 μ_B at 300 K, consistent with a μ-oxo-oligomeric structure [Fe(P)–(NS$_2$)]$_2$O (5). Indeed, solution studies show a solvent-dependent equilibrium:

$$2 \; \text{Fe(P)OH–(NS}_2) \rightleftharpoons [\text{Fe(P)–(NS}_2)]_2\text{O} + \text{H}_2\text{O}$$
$$ \textbf{4} \phantom{\text{Fe(P)OH–(NS}_2) \rightleftharpoons} \textbf{5}$$

For example, in THF [λ_{max} 401, 502 (sh), 565, 593 (sh) nm; μ_{eff} = 3.9 μ_B per Fe] the equilibrium lies clearly to the right, whereas in 10% MeOH/CHCl$_3$ [λ_{max} 406, 488, 505 (sh), 575 (sh), 590 nm; μ_{eff} = 5.9 μ_B], 4 is the predominant species[19] (Figure 2). Acid

Figure 2. UV–visible spectra of (a) Fe(P)OH–(NS$_2$) $\rightleftharpoons$ [Fe(P)–(N-S$_2$)]$_2$O (4 $\rightleftharpoons$ 5) in 10% MeOH/CHCl$_3$ (---) and THF (—) and (b) Fe(P)Cl–(NS$_2$) (3) (---) and [Fe(P)BF$_4$–Cu(NS$_2$)OH]BF$_4$·H$_2$O (8) (—) in 10% MeOH/CHCl$_3$.

(HCl or HCN) treatment of solutions of either 4 or 5 gives 3 and Fe(P)CN–(NS$_2$) (6), respectively.

Treatment of solutions (THF or CHCl$_3$/MeOH) of any of 3, 4, 5, or 6 with Cu(ClO$_4$)$_2$, Cu(BF$_4$)$_2$, or Cu(triflate)$_2$ solutions resulted in each case in spectroscopically (UV–visible) similar solutions, different from any of 3, 4, 5, or 6; however, a solution of 3, 4, or 5 when treated with CuCl$_2$ solution in each case gave a spectrum similar to that of 3 (Figure 2). Thus, the iron porphyrin chromophore is influenced by the nature of the anion of the added Cu salt, consistent with the reaction

$$\text{Fe(P)Y–(NS}_2) + \text{CuX}_2 \rightarrow [\text{Fe(P)X–Cu(NS}_2)\text{Y}]\text{X}$$
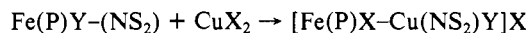
Indeed, from the reactions of 5 in 1% aqueous THF with Cu(ClO$_4$)$_2$ or Cu(BF$_4$)$_2$ solutions were isolated complexes formulated as [Fe(P)ClO$_4$–Cu(NS$_2$)OH]ClO$_4$ 7 and [Fe(P)BF$_4$–Cu(NS$_2$)-OH]BF$_4$·H$_2$O 8, respectively.[20]

The ESR spectrum of 7 at 4.2 K in frozen solution (CHCl$_3$/MeOH or Me$_2$SO) shows signals typical of a rhombically

(13) Compound 1 was prepared by condensation of 3,3',4,4'-tetramethyl-2,2'-dipyrromethane with o-nitrobenzaldehyde to give the porphyrinogen and subsequent oxidation and reduction to the diaminoporphyrin (1). Separation of the atropisomers was achieved by chromatography of the derived diacetates. Full experimental details including the synthesis of 2 together with proof of structure will appear elsewhere,[14] and have been supplied to the referees.

(14) Gunter, M. J.; Mander, L. N. *J. Org. Chem.*, in press.

(15) "Porphyrins and Metalloporphyrins"; Smith, K. M., Ed.; Elsevier: New York, 1975; p 803.

(16) Anal. (C$_{53}$H$_{51}$N$_7$O$_2$S$_2$FeCl) C, H, N, Fe. Mass spectrum (70 eV); m/z 936–937, M$^+$; calcd 937. λ_{max} (10% MeOH/CHCl$_3$): 395, 507, 540 (sh), 588 (sh), 645 nm. μ_{eff} (10% MeOH/CHCl$_3$) = 6.1 μ_B at 300 K. ESR (10% MeOH/CHCl$_3$, 4.2 K): g = 6.31, 5.61, and 2.00.

(17) We have recently reported a futher example of an isolated and well-characterized iron(III) porphyrin–hydroxo complex.[18] Except for this case and certain protein derivatives (e.g., methemoglobin and metmyoglobin) in which dimerization to a μ-oxo complex is sterically prevented, such monomeric hydroxo complexes have not been isolated. All iron(III) porphyrin μ-oxo oligomers studied to date show a band in the IR region between 850 and 900 cm^{-1}, a μ_{eff} between 1.6 and 1.9 μ_B per Fe, and no ESR signals. See: White, W. I. In "The Porphyrins", Dolphin, D., Ed.; Academic Press: New York, 1979; Vol. V, p 318.

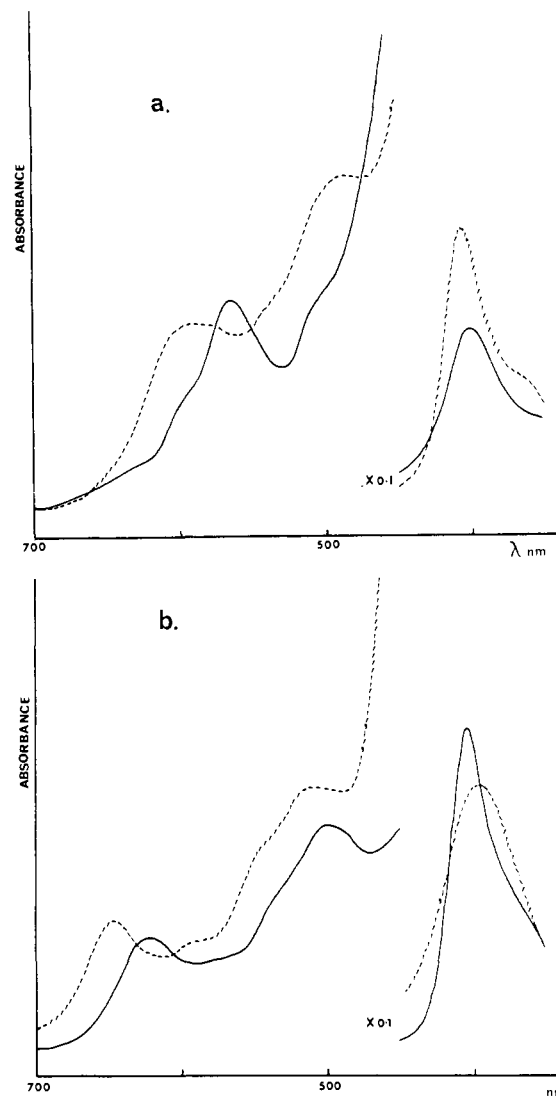(18) Gunter, M. J.; Mander, L. N.; Murray, K. S.; Clark, P. E. *J. Chem. Soc., Chem. Commun.* 1981, 799.

(19) The ESR spectra of 4 in CHCl$_3$/MeOH and THF both show signals at g $\sim$ 6, 2 typical of high-spin iron(III) porphyrins. However, the signal intensity in CHCl$_3$/MeOH is ca. 10 times greater than that in THF under identical conditions.

(20) 7: Anal. (C$_{53}$H$_{52}$N$_7$O$_3$S$_2$FeCu(ClO$_4$)$_2$) C, H, N, Fe, Cu. λ_{max} (10% MeOH/CHCl$_3$) 405, 502, 535 (sh), 575, 630 nm. 8: Anal. (C$_{53}$H$_{52}$N$_7$O$_3$-S$_2$FeCu(BF$_4$)$_2$H$_2$O) C, H, N, Fe, Cu. λ_{max} (10% MeOH/CHCl$_3$) 405, 500, 535 (sh), 575 (sh), 624 nm.
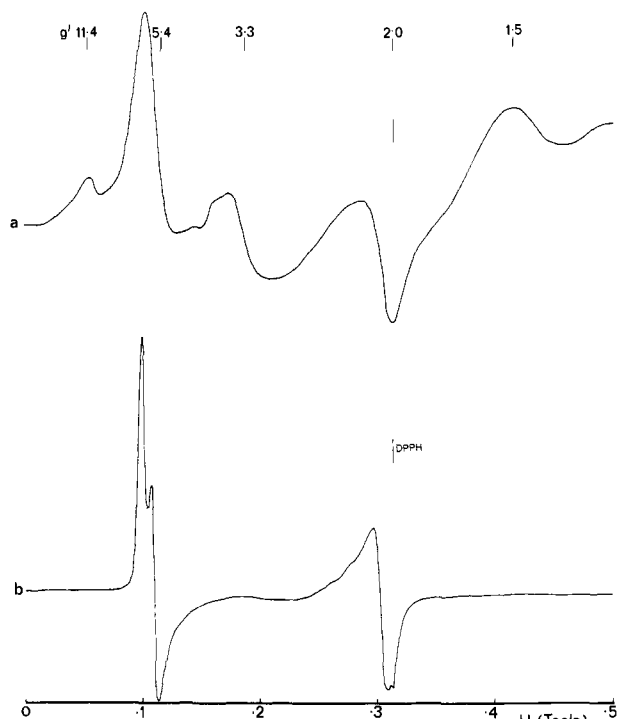
Figure 3. ESR spectra at 4.2 K and 8.778 GHz of [Fe(P)ClO₄–Cu(N-S₂)OH]ClO₄ (7) (a) as a powder and (b) in 10% MeOH/CHCl₃ solution. The designation g' is used to describe the field-frequency relationship of the spectral lines and are not necessarily true g tensors of the Zeeman terms in the spin Hamiltonian.
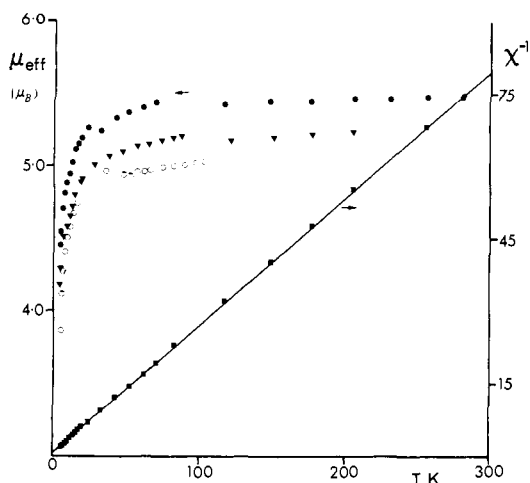

Figure 4. Temperature dependence of the magnetic moment (μ_{eff}) for the heterobinuclear Fe–Cu complexes: (●) [Fe(P)ClO₄–Cu(NS₂)OH]·ClO₄ (7); (○) [Fe(P)BF₄–Cu(NS₂)OH]BF₄·H₂O (8); (▼) Fe(P)OH–Cu(NS₂)OH·ClO₄ (9). Also represented is the reciprocal molar susceptibility, χ^{-1}, vs. T for 7 (■). The solid line is the Curie–Weiss plot with the following parameters: slope = 0.264, θ = 2.62 K.

split high-spin ($S = {}^5/_2$) iron(III) porphyrin at $g = 6.27$ and 5.70 and a broad signal showing poorly resolved hyperfine splitting around $g = 2$ assigned to Cu(II) (Figure 3b).[21] However, the magnetic moment in CHCl₃/MeOH solution at 303 K is 5.5 μ_B per binuclear molecule, which is lower than the expected value of 6.16 μ_B for an uncoupled $S = {}^5/_2$, $S = {}^1/_2$ system. Figure 4 shows the χ^{-1} vs. T and the μ_{eff} vs. T plots for 7 and 8 in the solid state. For 7 the moment decreases gradually from a room temperature value of around 5.5 to 5.37 μ_B at 50 K; below 20 K it

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(21) Similar spectra are observed for 8. No signals are observed above ca. 35 K, presumably due to relaxation broadening; the measured signal intensities at 4.2 K correspond to 1 ± 0.2 spins for Fe and Cu. Similar effects were observed by us for the related Fe(P)X–Cu(N₄)²⁺ systems where we have demonstrated no exchange coupling between the two metal ions.[2,10,11]

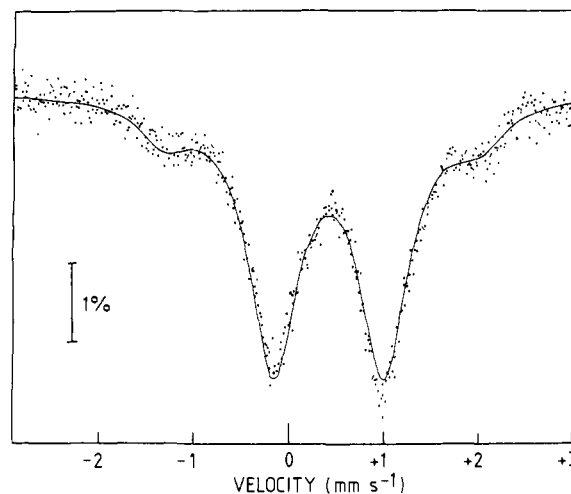**Figure 5.** Zero-field Mössbauer spectrum of 7 at 4.2 K.

falls rapidly to 4.45 μ_B at 4.28 K. A similar trend is observed for 8, although the absolute values are slightly lower. The χ^{-1} vs. T plots of 7 and 8 show Curie–Weiss behavior (θ = 2.62 and 2.73 K, respectively) and obviously cannot be fitted to a $-2J\vec{S}_1\cdot\vec{S}_2$ exchange-coupled Hamiltonian.[22] Nevertheless, if an estimated Curie component of 1.90 μ_B for Cu(II) is subtracted from the observed susceptibility, moments at 300 K of 5.16 μ_B per Fe for 7 and 4.90 μ_B per Fe for 8 are obtained. These values are too low for high-spin Fe(III) ($S = {}^5/_2$, μ_{eff} typically 5.9–6.1 μ_B) and indicate a situation involving quantum mixing or equilibrium of $S = {}^3/_2$ and $S = {}^5/_2$ spin states. The shapes of the μ_{Fe-Cu} vs. T (K) plots for 7 and 8 are characteristic of A states, either spin sextets or quartets, having considerable zero-field splitting.

The zero-field Mössbauer spectrum of 7 at 4.2 K (Figure 5) shows two quadrupole doublets, a major one (85% of area) with δ = 0.44 mm·s⁻¹ (with respect to α-Fe) and ΔE = 1.16 mm·s⁻¹ and a minor one (15% of area) with δ = 0.36 mm·s⁻¹ and ΔE = 3.32 mm·s⁻¹. The features are generally similar to those obtained for the related [Fe(P)–Cl–Cu(N₄)](ClO₄)₂ complex and can be similarly interpreted.[2,10,11] Thus, the major doublet is assigned to $S = {}^5/_2$ Fe(III) and the minor doublet to $S = {}^3/_2$ Fe(III).[23] These two states are both populated at 4.2 K, each having a lifetime longer than the Mössbauer time scale of 10⁻⁷ s. The ESR spectrum of 7 in the solid state (powder) at 4.2 K (Figure 3a) gives some further evidence for intermediate spin state on Fe. Besides broad absorptions at $g' \sim 11.4$ and 3.3 assigned to intermolecular interactions[24,2] and a broad absorption at $g' \sim 2$ for the Cu(II) ion, signals at $g' \sim 5.4$, 2.0, and 1.5 are consistent with the calculated values for $S = {}^3/_2$ Fe(III) in a rhombic field with $\lambda = {}^1/_3$.[25,26]

The existence of intermediate-spin Fe(III) porphyrins is now well established for mononuclear complexes such as Fe(TPP)-ClO₄[27] and Fe(OEP)ClO₄[28] as well as for the binuclear complexes of (P)–(N₄).[2,10,11] Thus, in 7 and 8 it is likely that one of the perchlorate or tetrafluoroborate groups, respectively, is bonded to Fe. In the absence of a crystal structure, we are unable to

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(22) A description of the magnetic properties of the first well-characterized exchange-coupled $S = {}^1/_2$, ${}^5/_2$ Fe/Cu system has appeared recently. Jaud, J.; Journaux, Y.; Galy, J.; Kahn, O. *Nouv. J. Chim.* **1980**, *4*, 629.

(23) Although the area ratios of the doublets indicate that the $S = {}^5/_2$ species predominates at 4.2 K, this is not necessarily so if the Debye–Waller factors for the two states are unequal. See: Haddad, M. S.; Lynch, M. W.; Federer, W. D.; Hendrickson, D. N. *Inorg. Chem.* **1981**, *20*, 123 and references therein.

(24) Chikira, M.; Kon, H.; Smith, K. M. *J. Chem. Soc., Dalton Trans.* **1980**, 526.

(25) Maltempo, M. M. *Chem. Phys. Lett.* **1979**, *60*, 441.

(26) The broad absorption around $g' \sim 5$–6 may also contain unresolved components of a rhombically split $S = {}^5/_2$ Fe(III) spectrum.

(27) Reed, C. A.; Mashiko, T.; Bentley, S. P.; Kastner, M. E.; Scheidt, W. R.; Spartalian, K.; Lang, G. *J. Am. Chem. Soc.* **1979**, *101*, 2948.

(28) Masuda, H.; Taga, T.; Osaki, K.; Sugimoto, H.; Yoshida, Z.; Ogoshi, H. *Inorg. Chem.* **1980**, *19*, 950. Dolphin, D. H.; Sams, J. R.; Tsin, T. B. *Ibid.* **1977**, *16*, 711.

establish the existence of any bridge bonding between Fe and Cu or whether the ClO_4^- or BF_4^- groups are axially coordinated to the Fe on the side distal to the Cu. Although a detailed interpretation of the magnetic and Mössbauer data will appear elsewhere, we make the following preliminary comments on the electronic situation in **7** and **8**: (i) there is little or no exchange coupling between Fe and Cu; (ii) a thermally dependent spin equilibrium between closely spaced $^5/_2$ and $^3/_2$ states on Fe would not be expected to give rise to the Curie-like χ^{-1} vs. T behavior observed; (iii) a quantum-mechanically mixed-spin ($^5/_2/^3/_2$) ground-state model is more compatible with the magnetic data, but again some curvature in the high-temperature region of the μ vs. T plots would be expected;[2,27] (iv) the presence of two distinct molecular species with spin ground states $^3/_2$ and $^5/_2$ could exist in the solid sample and give rise to overall Curie behavior. The Mössbauer data at 4.2 K of **7** would be more compatible with models ii and iv. However, a recent report[29,30] of spin crossover behavior in 6-coordinate adducts of the type [Fe·OEP·py₂]ClO₄ uses spin admixture model iii to interpret the magnetic data and suggests that separate quadrupole doublets are possible in the Mössbauer spectrum. Further Mössbauer studies over a wider temperature range are required to help resolve the electronic picture in the present species.

If the reaction between **4** and $Cu(ClO_4)_2$ is carried out in 10% $MeOH/CHCl_3$ there is isolated by fractional crystallization, besides **7**, a second product. From the analytical data and the fact that its UV–visible spectrum[31] closely resembles that of **4**, this product may be formulated as $Fe(P)OH–Cu(NS_2)OH·ClO_4$ (**9**) or $Fe(P)–O–Cu(NS_2)·ClO_4·H_2O$ (**10**). Lack of infrared bands in the 840–920-cm⁻¹ region favor the hydroxo formulation **9**. Indeed, a spectrum identical with that of **9** is obtained on treating **7** with a solution of $Bu_4N·OH$ (1 mol), although only a mixture of **7** and **9** is obtained on crystallization.

Although the ESR spectra of **9** in the solid state and 10% $MeOH/CHCl_3$ solution at 4.2 K show signals similar to **7**, the measured signal area in the frozen solution spectrum is less than 5% of that of **7** or **8** at the same temperature and at 4.2 K accounts for <5% of the Fe and Cu present, when integrated against equimolar FeTPPCl and $Cu(ClO_4)_2$ solutions. Nevertheless, the μ_{eff} vs. T plot of **9** (Figure 4) resembles those of **7** and **8** and again shows Curie–Weiss behavior ($\theta = 2.81$ K). Hence, in the solid state, it appears that a similar electronic environment exists for all three complexes **7–9**. The magnetic moment of **9** in $CHCl_3/MeOH$ solution at 330 K is 5.4 μ_B (Evans NMR method), close to the solid-state value. The significantly reduced intensities of the ESR resonances of **9** could reflect a conformation in solution different to the solid state which allows some exchange coupling[32] (and hence the ESR signals would be due to <5% impurity or ESR-detectable component of an equilibrium situation, cf. **4** ⇌ **5**), or alternatively to increased dipolar relaxation broadening in **9** compared to **7** or **8**.[33]

Thus, despite our efforts to induce spin coupling between Fe and Cu with two differently orientated coordination arrangements for Cu, viz., the previously reported[2] (P)–(N₄) and the present (P)–(NS₂) system, the results reported here show that exchange coupling effects are minimal in the complexes so far studied, at least in the solid state. To date, we have best evidence for coupling occurring within the low-spin iron–copper porphyrin system [Fe(P)–CN–Cu(N₄)](ClO₄)₂.[10,11] Others have recently achieved strong antiferromagnetic coupling between $S = {}^5/_2$ Fe and $S =$ $^1/_2$ Cu in a binuclear Schiff-base complex where the metal atoms are bridged in a coplanar arrangement by phenoxide oxygen atoms.[22] Translating these and the present results brings us some way closer to defining the requirements for the situation purported to exist in cytochrome *c* oxidase.[8] We are currently investigating other Fe–Cu complexes of **2** which can be expected to display exchange coupling between $S = {}^5/_2$ Fe and $S = {}^1/_2$ Cu.

Novel Linear Al–H–Al Electron-Deficient Bond in Na[(CH₃)₃Al–H–Al(CH₃)₃]

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Electron-deficient molecules have played an important role in the development of valence theory. The elucidation of the structures of B_2H_6[1] and $Al_2(CH_3)_6$[2] were early triumphs of diffraction experiments, and the bridging of the monomeric units together has been the subject of many investigations.[3,4] The bonding is commonly referred to in terms of the classic two-electron three-center interaction in the bridge. This description invariably requires two structural features: (1) an elongated M–X bond in the bridge compared to an electron-precise terminal bond and (2) a sharp M–X–M bridge angle. The former is taken as evidence of the intrinsic weakness of the electron-deficient bond, while the latter promotes a close M···M approach. In trimethylaluminum the Al···Al distance is 2.60 Å,[5] and theoretical descriptions of the bonding include a substantial metal–metal interaction.[6,7] The anion of the title compound demonstrates a new type of electron-deficient bond for aluminum compounds which bears directly on the basic tenets of the phenomenon in general. The Al–H–Al angle is 180°, and the metal–metal interaction (Al···Al = 3.30 Å) is insignificant. However, the Al–H bond length, 1.65 Å, is comparable to that found in the "normal" electron-deficient bridge for [(CH₃)₂AlH]₂, 1.68 Å.[8]

The title compound also has a direct relationship to the postulated linear B–H–B bond in the $B_2H_7^-$ ion. This substance was first reported by Brown, Stehle, and Tierney in 1957[9] and has subsequently been subjected to numerous studies.[10–12] The only crystal structure to show a single hydrogen bridge mode of bonding between two boron atoms was that of K[(C₄H₈)₂B₂H₃].[13] Here the B–H–B bond angle was 140°.

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