

(the line perpendicular to the Ni–Cu–Cl ‘plane’, see ref. 1) parallel to the one at origin and the others are nearly parallel (within 7.5°). The second material has not yet been obtainable in suitable single crystal form for X-ray or EPR studies.

Two aspects of the epr studies are of importance in non-diluted studies: (A) the intramolecular magnetic parameters and (B) the intermolecular interactions. The former reflects a growing awareness of the need for correlation of epr data with other properties on structurally well-characterized materials [3, 4], and the latter (B) is of importance here largely because of the potential influence on the former (A) [5].

The room temperature X-band epr of *1* produced an axially symmetrically g tensor with $g_z = g_{\parallel} = 2.00$ and $g_{\perp} = 2.17$ in sensible agreement with the frozen solution measurements [1]. The lineshape was Lorentzian and the width was nearly isotropic with a peak-to-peak linewidth of about 30 gauss. Since the X-ray results suggest that g averaging should be minimal, the g factors as measured in this pure material should reflect the molecular parameters. Some small measurement frequency dependent effects were noted which are consistent with exchange averaging in which the exchange and observation frequencies are comparable. These have been discussed elsewhere [5].

In *2*, the polycrystalline epr spectrum could be analyzed, for the most part, with standard methods. The parameters $g_{\parallel} = 2.00$ and $g_{\perp} = 2.16$ were obtained directly from the undiluted material and are in good agreement with solution results. The computer fitting of the spectrum indicates that the line is Lorentzian and somewhat narrower than in *1*. Some extra-absorption appeared between the parallel and perpendicular spectra which could be fitted with appropriate intermolecular dipolar interactions. Furthermore, the epr lineshape, calculated linewidth and effective g -values were independent of measurement frequency. These results suggest that the effective exchange field in *2* is higher than *1* and that it is higher than the highest measurement frequencies (60 GHz).

In addition, to a good first approximation, the measured magnetic parameters in the pure material should reflect those for the molecular complex [4]. Finally, we conclude that the ligand arrangement of *2* is similar to *1* and that tmpa effectively constrains the copper(II) site to a trigonal bipyramidal geometry.

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Chelation of Ferrous Sulphate Solutions by Pyridoxal Isonicotinoyl Hydrazone

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In an attempt to improve upon desferrioxamine B (‘desferal’, DF) as an agent for the treatment of iron overload, the non-toxic and inexpensive pyridoxal isonicotinoyl hydrazone (PINH) emerged as an effective iron mobilizer which compares with DF when given parenterally or orally to mice. PINH was noted for its enhanced affinity for ferrous ions, functioning as a tridentate ligand, in which the phenolic group, the double-bonded nitrogen, and the oxygen atom of the carbonyl group were observed to participate in metal binding. At around pH 7.0 a dark brown iron-complex was crystallized out from aqueous solution and analyzed as a $(\text{PINH})_2\text{Fe}\cdot 2\text{H}_2\text{O}$ compound. To ascertain the oxidation and the spin states of iron chelated by PINH, the latter was subjected to a Mössbauer spectroscopic study in the polycrystalline state. It exhibited a broad doublet at 88 K with δ 0.51 mm/s, quadrupole splitting, $\Delta\epsilon$ 0.63 mm/s, and at 300 K, δ = 0.41 mm/s and $\Delta\epsilon$ = 0.57 mm/s, suggesting a μ -oxo complex, with non-equivalent locations for the two iron atoms. These correspond to the presence of high-spin tri-valent iron in the complex. We could not however, exclude at this stage the possibility of the presence of low-spin di-valent iron atoms.

The spatial structure of the complex and its resemblance to the air-sensitive iron-porphyrin complexes will be discussed.