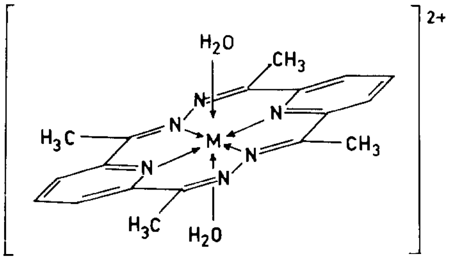
of the condensation reactions, which ultimately end with ring closure.

As a continuation of our studies on the effectiveness of metal ions of varying radius and electron configuration in the synthesis of macrocyclic compounds [1–5], we now report the template action of Ni(II) and Co(II) ions in the synthesis of a planar hexaaza quadridentate macrocycle. The free title ligand L has also been prepared without the aid of metal, albeit with very low yield [1].

The macrocyclic complexes of stoichiometry $[NiL(H_2O)_2](ClO_4)_2 \cdot 4H_2O$ and $[CoL(H_2O)_2](ClO_4)_2 \cdot 4H_2O$ were prepared by reacting 2,6-diacetylpyridine with hydrazine in the presence of metal salts with yields of 83 and 89% respectively. The formulations of these complexes follow from spectral data (i.r., uv–vis, e.s.r.) and thermal and elemental analyses. The infrared spectra of these complexes confirm the formation of the macrocyclic compounds by the absence of uncondensed functional group stretching modes of starting materials and the appearance of a strong absorption band at *ca.* 1600 cm^{-1} attributable to the coordinated C=N stretching mode. The high and low energy pyridine bands are observed at *ca.* 1570, 1460, 635, and 420 cm^{-1} suggesting coordination of pyridine. The presence of non-coordinated perchlorates in the complexes is inferred from the broad, intense band centered at 1100 cm^{-1} and a strong sharp band at 625 cm^{-1}, and also from the absence of splitting of the degenerate stretching and bending modes of ClO_4^- ion, which is indicative of coordinated species. A broad diffuse band in the 3500–3200 cm^{-1} region is assigned to O–H stretching modes for lattice water. A weak absorption observed at 530 cm^{-1} may suggest that coordinated water is also present. The electronic spectra of solutions of the complexes exhibit bands at *ca.* 37,000 and 280,000 cm^{-1}, attributable to the $\pi \rightarrow \pi^*$ transitions of the coordinated macrocycle. The electron spin resonance spectra of the cobalt complex taken in solution and in the solid state at room and liquid nitrogen temperatures give the value of $g = 2.2$, characteristic of low-spin complexes of Co(II) with square-planar or octahedral symmetry. The thermogravimetric analysis indicates for these two complexes loss of four molecules of water at 30–60 °C, and two water molecules at 120–160 °C.



On the basis of spectral and analytical data, along with the molecular model analysis, it seems reasonable to assume that these complexes have a six-coordinate octahedral structure with the macrocycle occupying the equatorial plane and the axial positions being filled with water. This structure is highly stabilized by the formation of two five- and two six-membered chelate rings upon coordination, which allows the high resonance of the system. The complexes satisfy the Hückel criterion having 14 π electrons in the inner ring and are therefore chemically stable and comparable in this regard with the derivatives of phthalocyanines and porphyrins.

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R3

EPR of Trigonal Bipyramidal Copper(II) Complexes with Tripod Ligands

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Very recent studies in one of our laboratories (KDK) have emphasized the usefulness of some tripod ligands in studying and modeling certain aspects of the coordination chemistry and structure properties of 5-coordinate copper(I) and copper(II) complexes [1]. Furthermore, the general features of the EPR spectra of 5-coordinate copper(II) complexes covering the full range from trigonal bipyramidal to square pyramidal are also now reasonably well understood [2]. In this paper we report the results of a single crystal and polycrystalline epr study of a well characterized complex: $[Cu(tmpa)X]PF_6$ with tmpa = tris (2-pyridyl)-methylamine and X = Cl^- (*1*) and a polycrystalline multifrequency (9–60 GHz) study of a related complex: $[Cu(tmpa)X]PF_6$ with X = N_3^- (*2*). The former material has a nearly trigonal bipyramidal geometry about a Cu(II) center and, of the 14 Cu(II) centers which lie within a radius 12 Å of one placed at an origin, 7 have their Z axes (the line perpendicular to the N1–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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R4

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 $(PINH)_2Fe \cdot 2H_2O$ 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, $\delta = 0.41$ 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.