

a given over-all energy separation of the d orbitals, the orbital energy stabilization achieved by spin pairing is considerably less in the square-planar case than in the octahedral case. Since it is observed that in gillespite all the 3d orbitals lie within a range of 20,000  $\text{cm}^{-1}$ , the observation that the ferrous ion in gillespite is in a high-spin state is exactly what one would expect.

### Conclusions

The electronic spectra of gillespite are consistent with the ground state of  $\text{Fe}^{2+}$  in the gillespite structure being  ${}^5A_{1g}$ , corresponding to the configuration  $d^2_{z^2}d^1_{xz}d^1_{yz}d^1_{xy}d^1_{x^2-y^2}$ . The transitions observed may be assigned to electronic transitions from the  ${}^5A_{1g}$  state to other quintet states of the  $\text{Fe}^{2+}$ , occurring by the mechanism of vibronic coupling.

The first excited state,  ${}^5E_g$  (corresponding to  $d^1_{z^2}(d_{xz}d_{yz})^3d^1_{xy}d^1_{x^2-y^2}$ ), appears to lie between 500 and 1500  $\text{cm}^{-1}$  above the  ${}^5A_{1g}$  ground state. The remaining quintet excited states,  ${}^5B_{2g}$  ( $d^1_{z^2}d^1_{xz}d^1_{yz}d^2_{xy}d^1_{x^2-y^2}$ ) and

${}^5B_{1g}$  ( $d^1_{z^2}d^1_{xz}d^1_{yz}d^1_{xy}d^2_{x^2-y^2}$ ), lie approximately 7500 and 19,000  $\text{cm}^{-1}$  above the ground state, respectively. These energies are estimates of the energies of vibrationally unexcited states, based on the estimates of vibrational frequencies made above.

**Acknowledgments.**—The gillespite for this study was kindly given by Dr. J. T. Alfors, California Division of Mines, and Professor A. Pabst, University of California, Berkeley, Calif. We are most grateful to Mr. K. Murray and to Professor J. Lewis for the temperature study of the magnetic susceptibility of gillespite, which was carried out at the University of Manchester. The water analysis was kindly performed by Mr. J. H. Scoon of the Department of Mineralogy and Petrology, University of Cambridge. We also thank Dr. D. M. L. Goodgame of the University of London for helpful discussions. M. G. C. thanks the SRC for financial assistance.

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## Electron Spin Resonance of Pentamethylenetetrazole Manganese(II) and Copper(II) Complexes<sup>1</sup>

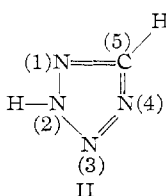
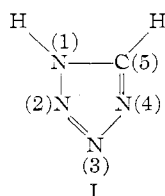
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Electron spin resonance spectra of the pentamethylenetetrazole (PMT) complexes  $\text{Mn}(\text{PMT})_6(\text{ClO}_4)_2$ ,  $\text{Cu}(\text{PMT})_6(\text{ClO}_4)_2$ , and  $\text{Cu}(\text{PMT})_4(\text{ClO}_4)_2$  were obtained. For  $\text{Mn}(\text{PMT})_6(\text{ClO}_4)_2$  complex dispersed in  $\text{Zn}(\text{PMT})_6(\text{ClO}_4)_2$  the data indicate that the metal-ligand bonds are highly ionic (91%) and that the distortion from octahedral symmetry ( $D = 41 \times 10^{-4} \text{ cm}^{-1}$ ) is small. For  $\text{Cu}(\text{PMT})_4(\text{ClO}_4)_2$  and  $\text{Cu}(\text{PMT})_6(\text{ClO}_4)_2$  it was possible to obtain high-resolution spectra of the copper nuclear splittings from the undiluted powder. Nitrogen superhyperfine splittings were observed in dilute solid solutions of  $\text{Cu}(\text{PMT})_6(\text{ClO}_4)_2$ . The  $\text{Cu}(\text{PMT})_6(\text{ClO}_4)_2$  data indicate that the Jahn-Teller distortion resonates along the three equivalent octahedral axes at room temperature when the compound is in a suitable diamagnetic host, but in the undiluted powder the compound has a permanent tetragonal distortion. The copper PMT complexes are approximately 80% ionic. The bonding of the PMT ligand appears to be similar to that of pyridine with the PMT nitrogen slightly less basic than the pyridine nitrogen in 4-cyanopyridine.

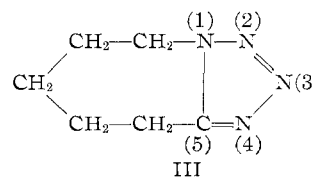
### Introduction

Tetrazoles are five-membered, heterocyclic ring compounds which contain one carbon and four nitrogen atoms linked by three single and two double bonds. The parent compound may exist in tautomeric forms I and II.<sup>3</sup> It is found that 97% of a mixture of I and



II exists in the form I.<sup>4</sup>

The tetrazole ring is unusual among cyclic systems in that it offers only two points of substitution—in positions 1 or 2 and 5. Pentamethylenetetrazole, III (hereafter abbreviated as PMT), represents a special group of dialkyl-substituted tetrazole derivatives in which the two alkyl substituents form a second cyclic system.



(1) Presented before the 151st Meeting of the American Chemical Society, Pittsburgh, Pa., March 31, 1966.

(2) (a) The University of Akron; (b) Michigan State University.

(3) D. W. Moore and A. G. Whittaker, *J. Am. Chem. Soc.*, **82**, 5007 (1960).

(4) J. B. Lounsbury, *J. Phys. Chem.*, **67**, 721 (1963).

Chemical investigation of 1,5-substituted tetrazoles have shown that they are nucleophilic reagents and that their nucleophilic character varies with the nature of the groups substituted on the ring. In this respect, substituted tetrazoles present an especially interesting problem both for the pharmacologist and the chemist. As drugs, they possess a wide spectrum of neurological activities from strong convulsants (such as PMT) to depressants (1-methyl-5-aminophenyltetrazole).<sup>5</sup> As electron donors they form complexes with halogens, interhalogens, and transition metal ions.<sup>6</sup> It seems quite plausible that there may be some correlation between the nucleophilic properties of tetrazoles and their physiological activity.<sup>7</sup> A comprehensive study of the donor properties of 1,5-substituted tetrazoles has been initiated some time ago. This paper is a part of that study.

Recently, transition metal complexes with 1-substituted tetrazoles have been reported.<sup>8</sup> Although the complexes were well characterized, the method of coordination between the central metal ion and the tetrazole ligands was not known. Three possible modes of coordination were suggested.<sup>9</sup> (1) One of the nitrogens of the tetrazole ring acts as a Lewis base and donates its pair of electrons to the central metal ion. (2) Since the tetrazolate anion seems to satisfy two coordination sites on the copper ion, coordination could occur by the formation of bonds to two different nitrogen atoms of the tetrazole ring. (3) The central metal ion may coordinate to the  $\pi$ -electron system of the tetrazolate anion.

Jonassen and his co-workers<sup>10,11</sup> prepared microcrystalline complexes of iron(II) conforming to the general formula  $\text{Fe}(\text{tetrazolato})_2 \cdot 2\text{H}_2\text{O}$ . They used the anions of 5-chlorotetrazole, 5-trifluoromethyltetrazole, and 5-nitrotetrazole. Using infrared and Mössbauer studies they proposed the formation of an analog to ferrocene when the tetrazole had strongly electronegative groups on the carbon. However, in a recent paper<sup>12</sup> they have concluded from optical studies that their earlier  $\pi$ -complex model is incorrect and that the coordination is actually distorted octahedral with each 5-trifluoromethyltetrazole bonded to two metal atoms through  $\sigma$  bonds from the nitrogens and with the other two coordination positions occupied by water molecules.

A powerful tool for the study of metal-ligand bonding is electron spin resonance spectroscopy (esr); however,

(5) Pharmacological properties of 1,5-substituted tetrazoles have been investigated in detail by Gross and Featherstone; cf. F. W. Schuller, S. C. Wang, R. M. Featherstone, and E. G. Gross, *J. Pharmacol. Exptl. Therap.*, **97**, 266 (1949), and references cited therein.

(6) J. W. Vaughn, T. C. Wehman, and A. I. Popov, *J. Inorg. Nucl. Chem.*, **26**, 2027 (1964), and references cited therein.

(7) B. Pullman and A. Pullman, *Proc. Natl. Acad. Sci. U. S.*, **44**, 1197 (1958).

(8) C. H. Brubaker and G. L. Gilbert, *Inorg. Chem.*, **2**, 1216 (1963).

(9) C. H. Brubaker and N. A. Daugherty, *J. Am. Chem. Soc.*, **83**, 3779 (1961).

(10) A. D. Harris, R. H. Herber, H. B. Jonassen, and G. K. Wertheim, *ibid.*, **85**, 2927 (1963).

(11) H. B. Jonassen, J. O. Terry, and A. D. Harris, *J. Inorg. Nucl. Chem.*, **25**, 1239 (1963).

(12) A. D. Harris, H. B. Jonassen, and R. D. Archer, *Inorg. Chem.*, **4**, 147 (1965).

the previously known paramagnetic transition metal tetrazole complexes were insoluble in organic solvents, presumably owing to a polymeric structure, and were therefore not amenable to study by esr methods. During the past year a number of transition metal complexes of PMT have been prepared and characterized.<sup>13</sup> Since these complexes appeared to be monomeric as evidenced by their solubility in polar organic solvents, an esr investigation was undertaken to determine the nature of the metal-ligand bonds.

### Experimental Section

**Reagents.**—Transition metal perchlorates were obtained as hydrates from the G. F. Smith Chemical Co. Pentamethylenetetrazole was obtained from the Knoll Pharmaceutical Co. and purified as described previously.<sup>14</sup> The solvents were of reagent grade quality and were used without further purification.

**Preparation of Hexakis(pentamethylenetetrazole)copper(II) Perchlorate.**—A solution was prepared containing 3.72 g (0.01 mole) of vacuum-dried copper(II) perchlorate hexahydrate in 50 ml of 2,2'-dimethoxypropane. The mixture was stirred to disperse the copper salt which has a limited solubility in this solvent. An excess of pentamethylenetetrazole (11.04 g) was added to the solution and a light blue precipitate was formed after about 5 min. The precipitate was filtered, washed several times with chilled ethyl ether, and dried at room temperature under vacuum. The product was obtained in 96% yield; mp 117.5°.

*Anal.* Calcd for  $\text{Cu}(\text{PMT})_6(\text{ClO}_4)_2$ : Cu, 5.80; C, 39.65; H, 5.55; N, 30.83;  $\text{ClO}_4^-$ , 18.20. Found: Cu, 5.71; C, 39.62; H, 5.63; N, 31.10;  $\text{ClO}_4^-$ , 18.75.

$\text{Mn}(\text{PMT})_6(\text{ClO}_4)_2$ ,  $\text{Zn}(\text{PMT})_6(\text{ClO}_4)_2$ , and  $\text{Fe}(\text{PMT})_6(\text{ClO}_4)_2$  were also prepared by precipitation as anhydrous microcrystalline powders in 2,2-dimethoxypropane and  $\text{Cu}(\text{PMT})_4(\text{ClO}_4)_2$  complex by a similar technique in anhydrous acetic acid.<sup>15</sup>

**Measurements.**—Electron spin resonance measurements were carried out with a Varian V-4500 spectrometer equipped with 100-Kc/sec modulation. The magnetic field was measured with a proton magnetic resonance gaussmeter. The  $\text{Mn}(\text{PMT})_6(\text{ClO}_4)_2$  in  $\text{Zn}(\text{PMT})_6(\text{ClO}_4)_2$  and in  $\text{Fe}(\text{PMT})_6(\text{ClO}_4)_2$  spectra were obtained from powder samples prepared by evaporation of solutions containing the paramagnetic and diamagnetic species in a 1:1000 mole ratio. This is necessary to prevent exchange and dipolar broadening of the esr lines. For  $\text{Cu}(\text{PMT})_6(\text{ClO}_4)_2$  a solid solution in  $\text{Zn}(\text{PMT})_6(\text{ClO}_4)_2$  could be prepared by rapid evaporation from  $\text{CH}_2\text{Cl}_2$ . Both the  $\text{PMT}_4$  and  $\text{PMT}_6$  complexes of Cu(II) gave good undiluted powder and frozen solution spectra; however, accurate values of the isotropic esr parameters could not be obtained from the liquid solutions owing to the large variation of line width with nuclear spin quantum number.

The peak intensities were measured with a Keuffel and Esser Co. compensating polar planimeter.

### Theoretical Section

**$\text{Mn}(\text{PMT})_6(\text{ClO}_4)_2$ .**—Mn(II) is  $d^5$  and in this case is high spin.<sup>15</sup> The ground state is an orbital singlet  $^6S_{5/2}$  which to first order should not interact with the crystalline electric field. However, to higher order the combined action of an electric field gradient and the spin-spin interaction does split the energy levels.<sup>16</sup> The magnitude of this zero field splitting is expressed by the axial field splitting parameter,  $D$ , for the case

(13) F. M. D'Itri and A. I. Popov, to be published.

(14) A. I. Popov, C. C. Bisi, and M. Craft, *J. Am. Chem. Soc.*, **80**, 6513 (1958).

(15) F. M. D'Itri, Master's Degree Thesis, Michigan State University, 1966.

(16) A. S. Chakravarty, *J. Chem. Phys.*, **39**, 1004 (1963).

of an axial distortion of the octahedral field. The spin Hamiltonian is

$$H = g\beta\mathbf{H}\cdot\mathbf{S} + D[S_z^2 - \frac{1}{3}S(S+1)] + A\mathbf{S}\cdot\mathbf{I} \quad (1)$$

In this equation  $\mathbf{H}$  is the magnetic field vector,  $g$  is the spectroscopic splitting factor ( $g$  value),  $\beta$  is the Bohr magneton,  $A$  is the manganese nuclear hyperfine splitting constant,  $\mathbf{S}$  is the electronic spin vector,  $\mathbf{I}$  is the nuclear spin vector,  $S = 5/2$ , and  $S_z$  is the diagonal spin operator. Neglecting the nuclear hyperfine splittings, five transitions corresponding to  $\Delta M_s = 1$  would be expected in an orientated single crystal since  $M_s$  can have the values  $\pm 5/2$ ,  $\pm 3/2$ , and  $\pm 1/2$ . The transitions are

$$\pm 5/2 \rightarrow \pm 3/2 \quad h\nu = g\beta H \pm 2D(2\cos^2\theta - 1) \quad (2)$$

$$\pm 3/2 \rightarrow \pm 1/2 \quad h\nu = g\beta H \pm D(3\cos^2\theta - 1) \quad (3)$$

$$1/2 \rightarrow -1/2 \quad h\nu = g\beta H \quad (4)$$

where  $\theta$  is the angle between the applied magnetic field and the direction of the axial distortion. In a powder only the  $\Delta M_s 1/2 \rightarrow -1/2$  transition is observed since the angular dependence of the  $\Delta M_s \pm 5/2 \rightarrow \pm 3/2$  and  $\pm 3/2 \rightarrow \pm 1/2$  transitions broadens these peaks beyond resolvability. The  $1/2 \rightarrow -1/2$  transition is affected to second order by a term proportional to  $D^2/g\beta H$ . However, for small axial distortions this term can be neglected.

Thus, in a powder spectrum one expects to see only the  $\Delta M_s 1/2 \rightarrow 1/2$  absorption. For Mn(II) this line is split into six lines by the nuclear hyperfine splitting due to  $^{55}\text{Mn}$  ( $I = 5/2$ ). In addition to the six allowed transitions, it is sometimes possible to observe a low-intensity pair of forbidden lines between each pair of allowed lines. These lines are due to simultaneous changes of both the electronic and nuclear spin by  $\pm 1$ . From the intensity ratio of the forbidden lines to the allowed lines one can obtain an approximate value of the distortion from octahedral symmetry,  $D$ , with the equation<sup>17</sup>

IR (intensity ratio) =

$$\frac{8}{15} \left( \frac{3}{4} \frac{D}{g\beta H} \right)^2 \left[ \frac{1 + S(S+1)}{3M(M-1)} \right]^2 [I(I+1) - m^2 + m] \quad (5)$$

where  $S = 5/2$  (total electron spin),  $I = 5/2$  (total nuclear spin),  $m = 1/2$  (component of electron spin), and  $M = 1/2$  (component of nuclear spin). As an alternate method of determining  $D$  one can utilize the published graphs of Allen<sup>18</sup> which give  $D$  as a function of the relative intensities of the allowed transitions. Although for other transition metal complexes the interpretation of esr metal hyperfine splittings in terms of ionicity of the metal-ligand bonds is presently too complex to have a quantitative significance,<sup>19</sup> for Mn-

(II) the plot of the per cent ionicity of the host lattice as determined by Pauling's equation<sup>20</sup> for the ionic character of a bond

$$I = 1 - \exp \frac{-(X_A - X_B)^2}{4} \quad (6)$$

(where  $X_A$  and  $X_B$  refer to the values of the electronegativity of the two atoms in the bond) gives an extrapolated value at 100% ionicity in good agreement with the theoretical value.<sup>21</sup> Unfortunately, one cannot distinguish between the covalency contribution of the electrons while involved in  $\sigma$  orbitals and while involved in  $\pi$  orbitals.

**Cu(PMT)<sub>6</sub>(ClO<sub>4</sub>)<sub>2</sub> and Cu(PMT)<sub>4</sub>(ClO<sub>4</sub>)<sub>2</sub>.**—Cu(II) is  $d^9$ . In octahedral symmetry the unpaired electron is expected in the degenerate  $x^2 - y^2$  and  $z^2$  energy levels. Since these two orbitals contain three electrons, an additional *net* stabilization is expected if the symmetry is lowered such that the two paired electrons go into the resulting lower energy orbital and the single unpaired electron occupies the now higher energy orbital.<sup>22</sup> The higher energy orbital is expected to be the  $\sigma$  orbital to those ligands which are closest to the metal. The resulting distortion is normally tetragonal with the two axial ligands moving outward. At higher temperatures it is found that the distortion resonates along the three symmetry axes while at lower temperatures the distortion freezes in along one of the axes.<sup>23</sup> This type of behavior can be expected for Cu(PMT)<sub>6</sub>(ClO<sub>4</sub>)<sub>2</sub>. However, for Cu(PMT)<sub>4</sub>(ClO<sub>4</sub>)<sub>2</sub> the difference in the crystal field between PMT and ClO<sub>4</sub><sup>-</sup> should lead to a tetragonal crystal field even at room temperature. The spin Hamiltonian for a tetragonal crystal field is

$$H = g\beta H_z S_z + g_{\perp} \beta (H_x S_x + H_y S_y) + A_{\parallel}^{\text{Cu}} I_z S_z + A_{\perp}^{\text{Cu}} (I_x S_x + I_y S_y) + A_{\parallel}^{\text{N}} (I_x S_x \text{ or } I_y S_y) + A_{\perp}^{\text{N}} (I_y S_y \text{ or } I_x S_x + I_z S_z) \quad (7)$$

where the tetragonal distortion is along the  $z$  axis. The relationships between the nitrogen hyperfine splittings and the molecular orbital that the unpaired electron is in are

$$A_{\parallel}^{\text{N}} = A_s^{\text{N}} + 2A_D \quad (8)$$

$$A_{\perp} = A_s + \frac{4}{5} n^2 \frac{\mu_I \beta_I}{I} \left\langle \frac{1}{r^3} \right\rangle \frac{N_{\sigma}^2 \lambda^2}{4} + 2A_D N_{\sigma}^2 \quad (9)$$

$$A_{\perp}^{\text{N}} = A_s^{\text{N}} - A_D \quad (10)$$

$$A_{\perp}^{\text{N}} = A_s^{\text{N}} - \frac{2}{5} n^2 \frac{\mu_I \beta_I}{I} \left\langle \frac{1}{r^3} \right\rangle \frac{N_{\sigma}^2 \lambda^2}{4} - A_D N_{\sigma}^2 \quad (11)$$

$$\psi^* = N_{\sigma} (\phi_{x-y} - \lambda \phi_{N\sigma}) \quad (12)$$

where  $A_s^{\text{N}}$  is the isotropic splitting,  $A_s^{\text{N}} = \frac{1}{3} A_{\parallel}^{\text{N}} + \frac{2}{3} A_{\perp}^{\text{N}}$ ,  $n^2$  is the fraction of p character in the nitrogen

(20) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 98. See also B. Welber, *Phys. Rev.*, **138**, A1481 (1956), for a discussion of the application of Pauling's equation.

(21) R. S. Title, *Phys. Rev.*, **131**, 623 (1963), and references cited therein.

(22) H. A. Jahn and E. Teller, *Proc. Roy. Soc. (London)*, **A164**, 117 (1938).

(23) See R. S. Drago, "Physical Methods in Inorganic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1965, pp 356, 357, and H. C. Allen, G. F. Kokoszka, and R. G. Inskeep, *J. Am. Chem. Soc.*, **86**, 1023 (1964), and references cited therein.

(17) B. Bleaney and R. S. Rubins, *Proc. Phys. Soc. (London)*, **77**, 103 (1961). The corresponding equation for a cubic field is given by J. E. Drumheller and R. S. Rubins, *Phys. Rev.*, **133**, A1099 (1964).

(18) B. T. Allen, *J. Chem. Phys.*, **43**, 3820 (1965).

(19) See, for example, H. A. Kuska and M. T. Rogers, *ibid.*, **43**, 1744 (1965).

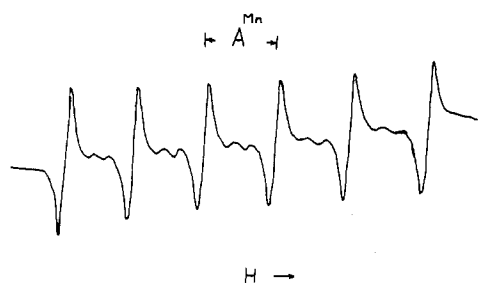


Figure 1.—First-derivative power spectrum of  $\text{Mn(PMT)}_6(\text{ClO}_4)_2$  in  $\text{Fe(PMT)}_6(\text{ClO}_4)_2$ .

$\sigma$  orbital ( $n^2 = 2/3$ , assuming  $sp^2$  hybridization),  $I$  is the nuclear spin of the ligand ( $I = 1$  for nitrogen),  $\beta_I$  is the nuclear magneton,  $\mu_I$  is the magnetic moment of the ligand nucleus, and  $A_D$  is the direct dipole term. For nitrogen

$$2/5 \frac{\mu_I \beta_I}{I} \left\langle \frac{1}{r^3} \right\rangle = 17.05 \text{ gauss} \quad (13)$$

using  $\langle 1/r^3 \rangle_{2p} = 3.10 \text{ au.}^{24}$

The spin density can also be determined from the  $A_s^N$  values by the equation

$$A_s = \frac{8\pi\mu_I\beta_I}{3I} (1 - n^2) \frac{N_\sigma^2 \lambda^2}{4} |\psi(0)|^2 \quad (14)$$

For nitrogen

$$\frac{8\pi}{3} \frac{\mu_I \beta_I}{I} |\psi(0)|^2 = 550 \text{ gauss} \quad (15)$$

### Results and Discussion

**$\text{Mn(PMT)}_6(\text{ClO}_4)_2$ .**—The esr data are given in Table I along with some literature data for comparison. A typical powder spectrum is given in Figure 1. The intensity ratio of the forbidden to the allowed transition is 1:18. This gives a value of  $D = 41 \times 10^{-4} \text{ cm}^{-1}$ . From the ratio of the allowed  $I = 5/2$  line to the  $I = 1/2$  line (1.12) and Allen's graph,<sup>18</sup>  $D$  is determined to be  $\approx 40 \times 10^{-4} \text{ cm}^{-1}$ . A  $D$  value of this magnitude indicates that the distortion from octahedral symmetry is small. From Title's plot<sup>21</sup> of ionicity *vs.*  $A^{\text{Mn}}$ , the manganese-ligand bonds are determined to be 91% ionic ( $N^2 = 0.91$ ). The line width (peak-to-peak width on the derivative curve) is approximately 10 gauss in  $\text{Zn(PMT)}_6(\text{ClO}_4)_2$  and  $\text{Fe(PMT)}_6(\text{ClO}_4)_2$ . This puts an *upper limit* on the isotropic nitrogen splitting of approximately 4 gauss assuming that there are six equivalent nitrogens bonded to the Mn(II). A 4 gauss nitrogen splitting for Mn(II) is equivalent to a 20 gauss nitrogen splitting in Cu(II) owing to the inverse dependence of  $A$  on the number of unpaired electrons; see eq 16.

The  $A$  value for  $\text{Mn(CN)}_6^{3-}$  is included in Table I; however, it cannot be directly compared with the other  $A$  values since  $\text{Mn(CN)}_6^{3-}$  is a low-spin complex. The  $A$  value is inversely proportional to the total electron spin of the complex ( $2S$ )<sup>25</sup> shown in eq 16

(24) J. R. Morton, J. R. Rowlands, and D. H. Whiffen, *Mol. Phys.*, **5**, 248 (1962).

$$A \text{ (in gauss)} = \frac{8\pi}{3} \frac{\mu_I \beta_I}{2SI} |\psi(0)|^2 \quad (16)$$

where  $|\psi(0)|^2$  is the Fermi contact term and is calculated from unrestricted Hartree-Fock theory.<sup>26</sup> Correcting this  $A$  value for the  $S = 1/2$  value gives an ionicity ( $N^2$ ) of 0.5 from Title's graph. This value, although reasonable, cannot be considered quantitatively significant since the graph is constructed for the high-spin case where the five unpaired electrons are in both  $\sigma$  and  $\pi$  orbitals while in the spin-paired configuration the unpaired electron is only in a  $\pi$  orbital; also, the  $|\psi(0)|^2$  part of eq 16 is expected to change as has been shown for iron by Mössbauer spectroscopy.<sup>27</sup>

TABLE I  
ELECTRON SPIN RESONANCE DATA FOR SOME  
 $\text{Mn}^{2+}$  COMPLEXES

	$A, 10^{-4}$ $\text{cm}^{-1}$	$g$	$D, 10^{-4}$ $\text{cm}^{-1}$	$N^2$	Ref
$\text{Mn(PMT)}_6(\text{ClO}_4)_2$ in $\text{Zn(PMT)}_6(\text{ClO}_4)_2$	84.4	2.001	$\approx 41$	0.91	<i>a</i>
$\text{Mn(PMT)}_6(\text{ClO}_4)_2$ in $\text{Fe(PMT)}_6(\text{ClO}_4)_2$	84.	2.00	$\approx 41$	0.91	<i>a</i>
$\text{Mn(PMT)}_6(\text{ClO}_4)_2$ in $\text{CH}_3\text{NO}_2$	87.1	2.001		0.93	<i>a</i>
$\text{Mn(H}_2\text{O)}_6^{2+}$	89.0			0.94	<i>b</i>
$\text{Mn(CN)}_6^{3-}$	78.3			$(\approx 0.5)^d$	<i>c</i>

<sup>a</sup> This investigation. <sup>b</sup> G. E. Pake, "Paramagnetic Resonance," W. A. Benjamin, Inc., New York, N. Y., 1962, p 77. <sup>c</sup> J. M. Baker, B. Bleaney, and K. D. Blowers, *Proc. Phys. Soc. (London)*, **B69**, 1205 (1956). <sup>d</sup> See Discussion section.

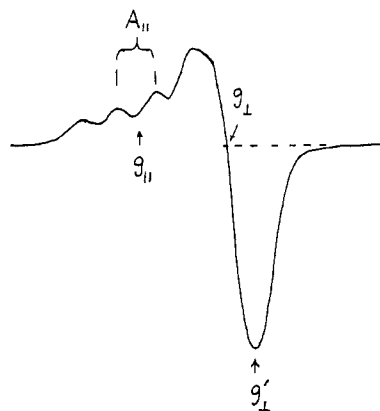


Figure 2.—First-derivative power spectrum of undiluted  $\text{Cu(PMT)}_6(\text{ClO}_4)_2$  at room temperature.  $g_{\perp}$  gives the location of  $g_{\perp}$  as found from the analysis of F. K. Kneubühl, *J. Chem. Phys.*, **33**, 1074 (1960).  $g_{\perp}'$  is the approximate location of  $g_{\perp}$  found by T. Vännegard and R. Aasa, "Proceedings of the First International Conference on Paramagnetic Resonance, Jerusalem, 1962," Vol. 2, 1963, p 509.

**$\text{Cu(PMT)}_6(\text{ClO}_4)_2$  and  $\text{Cu(PMT)}_4(\text{ClO}_4)_2$ .**—The esr data are given in Table II along with some literature data for comparison. A surprising result of this investigation is that it was possible to resolve the copper nuclear hyperfine splittings in the undiluted samples. See Figure 2. As discussed by Assour and Harrison,<sup>28</sup>

(25) I. Chen, C. Kikuchi, and H. Watanabe, *J. Chem. Phys.*, **42**, 186 (1965); J. M. Pendlebury, *Proc. Phys. Soc. (London)*, **84**, 857 (1964); E. König, *Z. Naturforsch.*, **19a**, 1139 (1964).

(26) R. E. Watson and A. J. Freeman, *Phys. Rev.*, **123**, 2027 (1961).

(27) N. E. Erickson and A. W. Fairhall, *Inorg. Chem.*, **4**, 1320 (1965), and references cited therein.

(28) J. M. Assour and S. E. Harrison, *Phys. Rev.*, **136**, A1368 (1964).

TABLE II  
 ESR DATA FOR Cu(II) COMPLEXES WITH NITROGEN-BONDING LIGANDS

	$g_{\parallel}^a$	$A_{\parallel}^{\text{Cu}},$ $10^4 \text{ cm}^{-1} \text{ }^b$	$g_{\perp}$	$A_{\perp}^{\text{N}},$ $10^4 \text{ cm}^{-1}$	$A_{\perp}^{\text{N}},$ $10^4 \text{ cm}^{-1}$	Ref
Cu(py) <sub>4</sub> <sup>+2</sup>						
in Pt(py) <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub>	2.236	192	2.050	16	12.6	<i>a</i>
in undiluted Cu(py) <sub>4</sub> (ClO <sub>4</sub> ) <sub>2</sub>	2.265	190	2.06( $g_{\perp}$ ) <sup><i>f</i></sup>			<i>b</i>
in Cd(py) <sub>4</sub> (Ts) <sub>2</sub>	2.290	162	2.050	13	11.2	<i>a</i>
Cu(4-CNC <sub>6</sub> H <sub>4</sub> N) <sub>6</sub> (ClO <sub>4</sub> ) <sub>2</sub>						
in Cd(4-CNC <sub>6</sub> H <sub>4</sub> N) <sub>6</sub> (ClO <sub>4</sub> ) <sub>2</sub>	2.274	173	2.065	14	11.2	<i>a</i>
Cu(PMT) <sub>6</sub> (ClO <sub>4</sub> ) <sub>2</sub>						
undiluted powder at 20°	2.331	122				<i>c</i>
at -70°	2.339	138				<i>c</i>
at -130°	2.344	146				<i>c</i>
at -170°	2.354	152				<i>c</i>
in CH <sub>2</sub> Cl <sub>2</sub>	2.299	164		15.6	14.2	<i>c</i>
in CH <sub>3</sub> NO <sub>2</sub>	2.305	164	2.08( $g_{\perp}$ ) <sup><i>f</i></sup> 2.04( $g_{\perp}'$ ) <sup><i>f</i></sup>			<i>c</i>
in Zn(PMT) <sub>6</sub> (ClO <sub>4</sub> ) <sub>2</sub> at -173°	2.348	147		12.7	12.1	<i>c</i>
in solid PMT at -160°		148				<i>c</i>
Cu(PMT) <sub>4</sub> (ClO <sub>4</sub> ) <sub>2</sub>						
undiluted powder	2.283	180	2.07( $g_{\perp}$ ) <sup><i>f</i></sup>			<i>c</i>
in nitrobenzene	2.285	177	2.08( $g_{\perp}$ ) <sup><i>f</i></sup>			<i>c</i>
Cu(8HQ) <sub>2</sub> ·2H <sub>2</sub> O	2.287	171	2.066	(9) <sup><i>e</i></sup>		<i>d</i>

<sup>a</sup> W. Schneider and A. V. Zelewsky, *Helv. Chim. Acta*, **48**, 1529 (1965); Ts = *p*-toluenesulfonate anion. <sup>b</sup> H. A. Kuska, unpublished data. <sup>c</sup> The present investigation. <sup>d</sup> G. F. Kokoszka, H. C. Allen, Jr., and G. Gordon, *J. Chem. Phys.*, **42**, 3730 (1965); 8HQ = 8-hydroxyquinolate. <sup>e</sup> Average of  $A_{\parallel}^{\text{N}}$  and  $A_{\perp}^{\text{N}}$ . <sup>f</sup> See Figure 2. <sup>g</sup>  $\pm 0.005$ . <sup>h</sup>  $\pm 5$ .

interactions between neighboring ions are expected to broaden the hyperfine lines so that normally only a resolution of the parallel ( $g_{\parallel}$ ) and perpendicular ( $g_{\perp}$ ) absorptions is obtained.<sup>29</sup> Copper porphyrin complexes also give high-resolution esr spectra in the undiluted powder.<sup>30</sup> The corresponding Mn(II) PMT complexes do not show this resolution presumably due to the greater dipolar interaction of five unpaired electrons in Mn(II) compared to the one unpaired electron in Cu(II).

The esr data indicate that the environment of Cu(PMT)<sub>4</sub>(ClO<sub>4</sub>)<sub>2</sub> in frozen nitrobenzene is similar to the environment in the pure powder with the complexes having definite tetragonal symmetry. A comparison of the PMT<sub>4</sub> esr parameters with those for the bis-8-hydroxyquinolate complex (larger  $A_{\parallel}$  value, smaller  $g_{\parallel}$  value) indicates<sup>19</sup> that the PMT ligand is slightly more basic. This conclusion is supported by the shift in the low-energy optical spectrum from 15,400 cm<sup>-1</sup> for copper(II) bis-8-hydroxyquinolate to 16,100 cm<sup>-1</sup> for the PMT<sub>4</sub> complex.<sup>15,31</sup> (Both spectra are for the solid.) The  $N_{\sigma}^2$  value for the bis-8-hydroxyquinolate complex was found to be 0.82.<sup>31</sup>

For Cu(PMT)<sub>6</sub>(ClO<sub>4</sub>)<sub>2</sub> in Zn(PMT)<sub>6</sub>(ClO<sub>4</sub>)<sub>2</sub> and in a solid solution of PMT only one line was observed at room temperature indicating an effective octahedral crystal field apparently due to resonance of the tetragonal distortion along the three crystal axes.<sup>23</sup> At low temperature a typical spectrum for the tetragonal case is obtained indicating that the tetragonal distortion remains fixed along one of the three axes. The

variation of the spectrum with temperature is similar to the published spectra of Allen, *et al.*<sup>23</sup>

For undiluted Cu(PMT)<sub>6</sub>(ClO<sub>4</sub>)<sub>2</sub> it appears that the distortion is fixed along one axis even at room temperature. This is not unexpected since each complex is surrounded by complexes that also distort with the apparent result that the distortion is influenced both by the local Jahn-Teller effect and the lattice distortion.

The temperature dependence of the undiluted Cu(PMT)<sub>6</sub>(ClO<sub>4</sub>)<sub>2</sub>  $A_{\parallel}$  and  $g_{\parallel}$  data is not what one would expect. If the tetragonal distortion would increase as the temperature is lowered, one would expect  $A_{\parallel}$  to increase (as observed) and  $g_{\parallel}$  to decrease (which is opposite to what is observed). A similar temperature dependence has recently been reported for Cu(II) in AgCl.<sup>32</sup>

For Cu(PMT)<sub>6</sub>(ClO<sub>4</sub>)<sub>2</sub> it was possible to observe the nitrogen superhyperfine splittings. From the  $g_{\parallel}$  part of the spectrum one obtains  $A_{\perp}^{\text{N}}$  since the electron is in the Cu-N  $\sigma$  bonds which are perpendicular to the magnetic field in this orientation. From the  $g_{\perp}$  part of the spectrum, according to the analysis of Kon and Sharpless,<sup>33</sup> it is possible to obtain  $A_{\parallel}^{\text{N}}$ . In the  $A_{\parallel}$  part of the spectrum the nitrogen splittings consisted of nine lines indicating four equivalent nitrogens in the plane of the unpaired electron's molecular orbital. This gives additional evidence in support of the tetragonal distortion since there would be six equivalent nitrogens if the crystal field was octahedral (degenerate  $x^2 - y^2$  and  $z^2$  orbitals). The unpaired electron spin densities reaching the nitrogen,  $N^2\lambda^2/4$ , are given in Table III for a number of copper complexes. A direct comparison between the PMT and pyridine complexes will only

(29) A. L. Poznyak, V. N. Tadeush, and L. A. Ilyukevich, *Zh. Strukt. Khim.*, **6**, 779 (1965).

(30) D. J. E. Ingram, J. E. Bennett, P. George, and J. M. Goldstein, *J. Am. Chem. Soc.*, **78**, 3545 (1956).

(31) See reference given in footnote *d* Table II.

(32) D. C. Burnham, *Bull. Am. Phys. Soc.*, **11**, 186 (1966).

(33) H. Kon and N. E. Sharpless, *J. Phys. Chem.*, **70**, 105 (1966).

TABLE III  
 COMPARISON OF NITROGEN SPIN DENSITIES FOR COPPER COMPLEXES

	$A_{  }^N$ , $10^4 \text{ cm}^{-1}$	$A_{\perp}^N$ , $10^4 \text{ cm}^{-1}$	$A_s^N$ , $10^4 \text{ cm}^{-1}$	$A_p$ , $10^4 \text{ cm}^{-1}$	$A_D$ , $10^4 \text{ cm}^{-1}^b$	$N^2\lambda^2/4$		Ref for $A_{  }^N$ and $A_{\perp}^N$ values
						From $A_s$	From $A_p - A_D$	
Cu(phthalocyanine)	17.8	14.5	15.6 <sup>d</sup>	1.1	0.28	0.085	0.072	a
Cu(C <sub>6</sub> H <sub>5</sub> N) <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub>	16	12.6	13.7 <sup>d</sup>	1.1	0.27	0.075	0.073	b
Cu(PMT) <sub>6</sub> (ClO <sub>4</sub> ) <sub>2</sub> in CH <sub>2</sub> Cl <sub>2</sub>	15.6	14.2	14.7 <sup>d</sup>	0.5	0.27	0.080	0.020	c
Cu(C <sub>6</sub> H <sub>5</sub> N) <sub>4</sub> S <sub>2</sub> O <sub>8</sub>	(15.6)	12.7						d
Cu(4-(CH <sub>3</sub> ) <sub>2</sub> N-C <sub>6</sub> H <sub>4</sub> N) <sub>4</sub> (Ts) <sub>2</sub>	15	12.5	13.3 <sup>d</sup>	0.8	0.26	0.073	0.047	b
Cu(4-CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub> N) <sub>4</sub> (Ts) <sub>2</sub>	14	12.5	13.0 <sup>d</sup>	0.5	0.26	0.071	0.021	b
Cu(4-NC-C <sub>6</sub> H <sub>4</sub> N) <sub>6</sub> (ClO <sub>4</sub> ) <sub>2</sub>	14	11.2	12.1 <sup>d</sup>	0.9	0.26	0.066	0.056	b
Cu(C <sub>6</sub> H <sub>5</sub> N) <sub>4</sub> (Ts) <sub>2</sub>	13	11.2	11.8 <sup>d</sup>	0.6	0.25	0.064	0.031	b
Cu(PMT) <sub>6</sub> (ClO <sub>4</sub> ) <sub>2</sub> in Zn(PMT) <sub>6</sub> (ClO <sub>4</sub> ) <sub>2</sub>	12.7	12.1	12.3 <sup>d</sup>	0.2	0.26	0.067	0.0	c
Cu(phen) <sub>3</sub> (NO <sub>3</sub> ) <sub>2</sub>	12	10	10.7 <sup>d</sup>	0.7	0.25	0.058	0.039	e
Cu(dipy) <sub>3</sub> (NO <sub>3</sub> ) <sub>2</sub>	12	9	10.0 <sup>d</sup>	1.0	0.24	0.055	0.067	e
Cu(glycinate) <sub>2</sub>	10	7.2	8.1 <sup>d</sup>	0.9	0.23	0.044	0.059	f

<sup>a</sup> S. E. Harrison and J. M. Assour, *J. Chem. Phys.*, **40**, 365 (1964). <sup>b</sup> See reference given in footnote a of Table II. <sup>c</sup> Present investigation. <sup>d</sup> H. G. Hecht and J. P. Frazier, III, *J. Chem. Phys.*, **44**, 1718 (1966). In this paper the authors assign, for  $g_{\perp}$ , the 15.6  $10^{-4} \text{ cm}^{-1}$  splitting as a copper splitting and assign a nitrogen splitting of  $10^{-4} \text{ cm}^{-1}$ . However, this assignment predicts an unusually low  $A_s^N$  value ( $\approx 5 \times 10^{-4} \text{ cm}^{-1}$ ). Both the anisotropic data in ref 35 and the reported solution  $A_s^N$  value [ $14 \times 10^{-4} \text{ cm}^{-1}$ : H. R. Gersmann and J. D. Swalen, *J. Chem. Phys.*, **36**, 3221 (1962)] indicate that this assignment is unlikely. A K-band esr spectrum would resolve this ambiguity since the assigned  $g_2$  to  $g_3$  separation would increase if the assignment is correct but a nuclear hyperfine separation would remain the same. <sup>e</sup> See ref 23, H. C. Allen, *et al.* phen = 1,10-phenanthroline; dipy = 2,2'-dipyridine. <sup>f</sup> See ref 19. <sup>g</sup> Calculated from  $A_s = \frac{1}{3}A_{||} + \frac{2}{3}A_{\perp}$ . <sup>h</sup> Estimated from  $A_s^N$  values, knowing the  $A_D$  values for the glycinate and phthalocyanine complexes since their internuclear distances are known; ref 19.

be valid if the sp hybridization is the same for both. It appears that the PMT nitrogen-copper orbitals contain a greater percentage of s character than the assumed sp<sup>2</sup> hybridization. Since the PMT data were obtained from powder samples while the pyridine data were obtained from orientated single crystals,<sup>35</sup> it is possible that the lack of p character in the PMT case is not real but just a reflection of the limitations of the powder method. However, if real, this data appears to support some preliminary X-ray work on single crystals of Ni(PMT)<sub>6</sub>(ClO<sub>4</sub>)<sub>2</sub> which indicate that the metal-ligand bond is not coplanar with the tetrazole structure.<sup>34</sup> Another possible explanation is that there is appreciable  $\pi$  bonding since the  $A_p$  values in Table III represent the net difference between  $\sigma$  and  $\pi$  delocalization.

The behavior of the Cu(PMT)<sub>6</sub>(ClO<sub>4</sub>)<sub>2</sub> system in going from the undiluted powder to CH<sub>2</sub>Cl<sub>2</sub> is consistent with the optical data.<sup>15</sup> In solution the low-energy peak is at 14,600  $\text{cm}^{-1}$  while in the powder it is at 13,500  $\text{cm}^{-1}$ . This indicates a stronger equatorial crystal field in solution in agreement with the larger  $A_{||}^N$  value, smaller  $g_{||}$  value, and, from ref 19, a larger  $A_{||}^{\text{Cu}}$  value. The Cu(4-CNC<sub>5</sub>H<sub>4</sub>N)<sub>6</sub>(ClO<sub>4</sub>)<sub>2</sub> low-energy

peak<sup>35</sup> is at 16,800  $\text{cm}^{-1}$  indicating that it has a stronger crystal field than Cu(PMT)<sub>6</sub>(ClO<sub>4</sub>)<sub>2</sub>, in agreement with its smaller  $g_{||}$  value and larger  $A_{||}^{\text{Cu}}$  value.

In conclusion, this investigation shows that bonding mode 1 (see Introduction) is consistent with the observed octahedral Mn(II) and Jahn-Teller tetragonal Cu(PMT)<sub>6</sub><sup>2+</sup> behavior. The Mn(II) complex is 91% ionic while the copper PMT complexes from the observed nitrogen splittings and the comparisons with optical and esr data for other copper complexes have  $N_{\sigma}^2 \approx 0.8$ . The difference in covalency is not unexpected as Cu(II) normally forms more covalent complexes than Mn(II); for example, with 8-hydroxyquinoline in 50% dioxane the stability constants for Mn(II) are  $K_1 = 8.28$  and  $K_2 = 7.17$ , while for Cu(II) they are  $K_1 = 13.49$  and  $K_2 = 12.73$ .<sup>36</sup>

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(35) See reference given in footnote a of Table II.

(36) W. D. Johnston and H. Freiser, *J. Am. Chem. Soc.*, **74**, 5239 (1952).

(34) R. C. Srivastava, personal communication.