

3030 (w), 2915 (w), 2545 (vs), 1481 (m), 1466 (w), 1449 (w), 1418 (w), 1370 (w), 1285 (w), 1266 (w), 1203 (w), 1149 (w), 1018 (s), 944 (m), 765 (w), 735 (w), 704 (m)  $\text{cm}^{-1}$ . *Anal.* Calcd  $\text{C}_{16}\text{H}_{38}\text{B}_{18}\text{CoN}$ : C, 38.58; H, 7.69; B, 39.07; Co, 11.83; N, 2.81. Found: C, 38.62; H, 7.72; B, 38.76; Co, 11.58; N, 3.12.

**Tetramethylammonium Tricarbonyl(benzodicarbollyl)manganate(I) (14).** A solution of 2 mmol of potassium sodium benzodicarbollide (6) in 75 ml of tetrahydrofuran was added to 650 mg (2 mmol) of bromomanganese pentacarbonyl. After stirring, the mixture was filtered and the solvent was evaporated under vacuum. The orange residue was dissolved in a minimum amount of methanol and 2 g of tetramethylammonium chloride in 10 ml of water was added, followed by more water to complete the precipitation. The precipitated product was collected and dried in air and then chromatographed on silica gel using acetonitrile as the eluent. The yellow band was collected and crystallized from acetonitrile-water to yield 561 mg (88%) of 14 as bright yellow plates, mp 285° dec. The product was recrystallized from acetone-water. Nmr (DMSO- $d_6$ ):  $\delta$  3.11 (s, 12,  $\text{NCH}_3$ ), 6.11 (m of  $\text{A}_2\text{B}_2$  type, 4,  $\text{CH}=\text{CH}-\text{CH}=\text{CH}$ ). Uv-vis (methanol): 216 nm ( $\epsilon$  23,800), 260 nm (sh,  $\epsilon$  6950), 368 nm ( $\epsilon$  1650). *Anal.* Calcd for  $\text{C}_{13}\text{H}_{22}\text{B}_9\text{MnNO}_3$ : C, 39.47; H, 6.37; B, 24.59; Mn, 13.88; N, 3.54. Found: C, 39.38; H, 6.36; B, 24.31; Mn, 13.66; N, 3.35.

**Tetramethylammonium Bis(benzodicarbollyl)nickelate(III) (19).** A solution of 2 mmol of potassium sodium benzodicarbollide and 0.08 mmol of piperidine in 75 ml of diglyme was added to 1 mmol of anhydrous nickel(II) iodide and was heated 22 hr at 110° under nitrogen. The mixture was filtered through Celite and the solvent was evaporated under vacuum. The residue was dissolved in a small amount of methanol and filtered and then treated with excess tetramethylammonium chloride and water. The 335 g of crude material contained a large proportion of tetramethylammonium hydrogen benzodicarbollide. Chromatography on silica gel with 5% acetonitrile in methylene chloride led to the elution of a purple band of 20, the work-up of which is described in the following paragraph. The

product (19) was eluted with 10% acetonitrile in dichloromethane. The solvent was removed under vacuum and the brown residue was dissolved in a minimum amount of methanol and filtered. Addition of water and then sodium chloride crystallized the product (19); 75 mg (15%). Ir (KBr): 3021 (w), 2915 (w), 2849 (w), 2519 (vs), 1481 (s), 1441 (w), 1418 (w), 1200 (w), 1183 (w), 1142 (w), 1064 (w), 1007 (s), 968 (w), 941 (m), 905 (w), 762 (w), 714 (m), 694 (m)  $\text{cm}^{-1}$ . Uv-vis (methanol): 204 nm ( $\epsilon$  12,210), 210 nm ( $\epsilon$  12,460), 248 nm ( $\epsilon$  9998), 330 nm, ( $\epsilon$  5820), 380 nm ( $\epsilon$  5700), 428 nm (sh,  $\epsilon$  3320), 472 nm (sh,  $\epsilon$  2023). The analytical sample was again chromatographed on silica gel and recrystallized from methanol-water. *Anal.* Calcd for  $\text{C}_{16}\text{H}_{38}\text{B}_{18}\text{Ni}$ : C, 38.60; H, 7.69; B, 39.09; N, 2.81; Ni, 11.79. Found: C, 38.77; H, 7.65; B, 35.36; N, 3.11; Ni, 15.60.

**Bis(benzodicarbollyl)dinickel(II) (20).** The solution of the rapidly eluted purple band from the chromatography of the nickel(III) salt 19 was concentrated and the residue was triturated with methanol to yield 27 mg (5%) of 20 as dark purple crystals, which did not melt below 300°. Nmr (DMSO- $d_6$ ):  $\delta$  1.54 (m,  $\text{A}_2\text{B}_2$  pattern,  $\text{CH}=\text{CH}-\text{CH}=\text{CH}$ ). Ir (KBr): 3333 (w), 2865 (w), 2597 (vs), 2525 (vs), 1418 (w), 1364 (w), 1212 (m), 1136 (m), 1002 (s), 927 (w), 911 (w), 887 (w), 849 (m), 830 (w), 824 (w), 791 (w), 758 (w), 723 (m)  $\text{cm}^{-1}$ . Uv-vis (acetonitrile): 224 nm ( $\epsilon$  13,080), 248 nm (sh,  $\epsilon$  9920), 265 nm ( $\epsilon$  11,000), 283 nm (sh,  $\epsilon$  9830), 388 nm ( $\epsilon$  6380), 468 nm ( $\epsilon$  2500), 552 nm ( $\epsilon$  1840). *Anal.* Calcd for  $\text{C}_{12}\text{H}_{26}\text{B}_{18}\text{Ni}_2$ : C, 29.88; H, 5.43; B, 40.34; Ni, 24.34. Found: C, 30.09; H, 5.64; B, 28.10; Ni, 26.26.

**Registry No.** 1, 20505-39-9; 2, 39472-28-1; 3, 39472-25-8; 4, 20505-38-8; 5, 39472-24-7; 6, 39472-22-5; 7, 49564-22-9; 8, 39472-27-0; 10, 39472-26-9; 11, 49564-23-0; 13, 39472-23-6; 14, 49564-26-3; 15, 49613-21-0; 16, 49613-22-1; 17, 49564-25-2; 18, 49664-78-0; 19, 49564-27-4; 20, 49683-29-6; 21, 49564-24-1; bromomanganese pentacarbonyl, 14516-54-2.

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## Electron Paramagnetic Resonance Spectrum of Dinitratotris(pyridine)copper(II) Doped into Single Crystals of Dinitratotris(pyridine)zinc(II) and -cadmium(II). Electronic Structure of Dinitratotris(pyridine)copper(II)

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The electron paramagnetic resonance spectra of dinitratotris(pyridine)copper(II) doped into single crystals of the analogous zinc and cadmium complexes have been studied at room and liquid nitrogen temperatures. At liquid nitrogen temperature, hyperfine splittings from the  $^{14}\text{N}$  nuclei of the pyridine ligands as well as the  $^{63}\text{Cu}$  and  $^{65}\text{Cu}$  nuclei are easily resolved. The principal values of the  $g$  and copper hyperfine tensors exhibit a very pronounced rhombic symmetry. An analysis of the hyperfine and  $g$  values suggests that the ground state can be described as mostly  $d_{z^2}$  with a small admixture of  $d_{x^2-y^2}$ . Detailed considerations of the copper and ligand hyperfine tensors indicate the unpaired electron is delocalized from the metal to the pyridine ligands to the extent of 25-30%. The orientation of  $g$  and hyperfine tensors can easily be rationalized in terms of the known crystal and molecular structures of the dinitratotris(pyridine) complexes.

### Introduction

There has been considerable interest in complexes which contain coordinated nitrate ions. Crystallographic studies have shown that nitrate ions can function as monodentate,<sup>1,2</sup> bidentate,<sup>3</sup> or bridging<sup>4</sup> ligands. Pyridine complexes of di-

valent transition metal nitrates have been known for some time, but the first systematic attempt to characterize these complexes was made by Haendler and coworkers.<sup>5-7</sup> More recently, Cameron and coworkers have determined the crystal structures of a number of the pyridine-metal(II) nitrate complexes.<sup>1,2,4,8,9</sup> The tris(pyridine) complexes in particular

(1) A. F. Cameron, D. W. Taylor, and R. H. Nuttall, *J. Chem. Soc. A*, 3402 (1971).

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(8) A. F. Cameron, D. W. Taylor, and R. H. Nuttall, *J. Chem. Soc., Dalton Trans.*, 1603 (1972).

have an interesting and unusual geometry (see Figure 1).<sup>8,9</sup> The metal ion can be considered to be five-, six-, or seven-coordinate depending on how the binding of the nitrate ligands is interpreted. We have investigated the electron paramagnetic resonance spectra of  $\text{Cu}(\text{py})_3(\text{NO}_3)_2$  doped into the analogous zinc and cadmium complexes in order to study the electronic structure of a copper complex having this unusual geometry.

### Experimental Section

**Compound Preparation and Crystal Growth.** The  $\text{Cu}(\text{py})_3(\text{NO}_3)_2$  and  $\text{Zn}(\text{py})_3(\text{NO}_3)_2$  were prepared by the method of Nuttall, *et al.*,<sup>10</sup> while  $\text{Cd}(\text{py})_3(\text{NO}_3)_2$  was prepared by the procedure of Ouellette and Haendler.<sup>7</sup> Crystals of the zinc and cadmium complexes containing a small amount of the copper complex were grown from acetonitrile solution. Approximately 1 g of the zinc or cadmium complex and a smaller amount (~0.1 g) of the copper complex were dissolved in a small quantity (~10 ml) of dry acetonitrile. A few milliliters of dry petroleum ether was then added to the acetonitrile solution and the resulting solution was put into a stoppered flask and allowed to stand overnight in a refrigerator. During this time crystals with a slight bluish tint appeared at the bottom of the flask. The doped crystals were washed with petroleum ether and dried under vacuum at room temperature.

**Mounting and Orientation Procedures.** The crystals that were obtained exhibited a variety of crystal habits. The crystals chosen for these studies were all diamond-shaped plates. The orientation of the crystallographic axes with respect to the external shape (see Figure 2) was determined by taking X-ray precession photographs of fairly large, well-developed crystals. The samples for epr study were aligned with the aid of a polarizing microscope. They were mounted on 3-mm quartz rods so that either the *a* or *b* crystallographic axis was parallel to the long axis of the rod. The samples were dipped into a solution of "Formvar" in 1,2-dichloroethane to give them a moisture-protective coating. These orienting and mounting procedures were carried out as rapidly as possible, since the crystals slowly decompose in moist air.

**Electron Paramagnetic Resonance Measurements.** The electron paramagnetic resonance spectra were recorded at room and liquid nitrogen temperatures on a Varian E-3 spectrometer using 100-kHz modulation. The *g* values were determined by comparison with polycrystalline DPPH (*g* = 2.0036). The angular dependences of the spectra in the (010) and (100) crystallographic planes were studied.

### Analysis of the Spectra

The dinitratotris(pyridine) complexes of copper, zinc, and cadmium crystallize in space group  $C_2/c$ , with four molecules per unit cell.<sup>8,9</sup> All four molecules have twofold symmetry ( $C_2$  parallel to *b*) and are magnetically equivalent. At room temperature the spectra exhibit only a broad four-line multiplet; however, considerably more detail appears at liquid nitrogen temperature. Hyperfine splittings from the <sup>14</sup>N nuclei of the three pyridine ligands as well as the <sup>63</sup>Cu and <sup>65</sup>Cu nuclei are easily resolved at 77°K.

The spectra can be described by the spin Hamiltonian

$$\mathcal{H} = \vec{H} \cdot \vec{g} \cdot \vec{S} + \vec{S} \cdot \vec{A}_{\text{Cu}} \cdot \vec{I}_{\text{Cu}} + \sum_L \vec{S} \cdot \vec{A}_L \cdot \vec{I}_L$$

where *L* represents the nitrogen nuclei of the pyridine ligands. Unfortunately, at certain crystal orientations the spectra are quite complex, and the evaluation of the spin-Hamiltonian parameters is not straightforward. The *g* values are the simplest of the parameters to determine. They were calculated from the expression  $g = 2.0036 H_{\text{DPPH}} / H_0$  (where  $H_0$  is the field at the copper resonance and  $H_{\text{DPPH}}$  is the field at which the reference resonance appears). The values of  $H_0$  were corrected for second-order effects in the

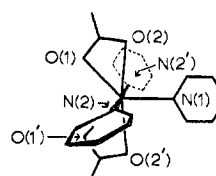


Figure 1. Perspective drawing of a dinitratotris(pyridine) complex.

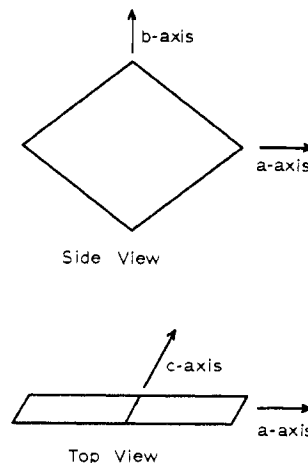


Figure 2. Orientation of the crystallographic axes with respect to the external morphology of the crystals of the dinitratotris(pyridine)-zinc(II) and -cadmium(II) complexes.

hyperfine structure according to the equations of Bleaney, Bowers, and Ingram.<sup>11</sup>

Symmetry requires one of the principal axes of both the *g* and copper hyperfine tensors of the dinitratotris(pyridine)-copper(II) complex to lie along the molecular twofold axis, parallel to *b*. This direction is taken as *y* in the coordinate system which we found most convenient. The *x* and *z* axes are then constrained to lie in the *ac* (010) crystallographic plane. The angular variations of the *g* factor of the copper complex doped into the zinc lattice in the (100) and (010) planes are shown in Figure 3. The calculated *g* values were obtained from the expression

$$g(\theta, \eta) = ((g_y \cos \theta)^2 + (g_x \sin \theta \cos(\eta - \varphi))^2 + (g_z \sin \theta \sin(\eta - \varphi))^2)^{1/2}$$

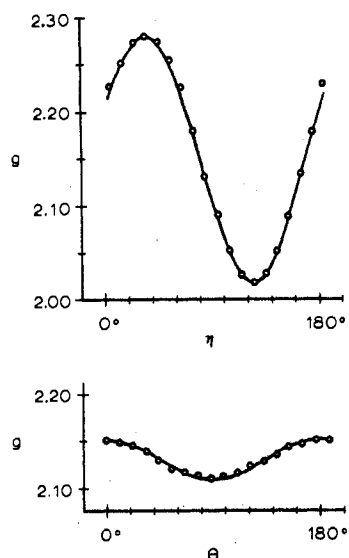
In this equation  $\theta$  is the angle between the *b* axis and the magnetic field,  $\eta$  is the angle between the *a* axis and the projection of the magnetic field onto the *ac* plane, and  $\varphi$  is the angle between the *g* tensor, *x* axis, and the crystallographic *a* axis. For the zinc lattice the angle  $\varphi$  is about 35°. Similar angular variation curves were obtained for the cadmium lattice using a  $\varphi$  angle of 58°. From these angular dependence studies the orientations of the *x* and *z* axes of the *g* tensor with respect to the molecular structure of the complex shown in Figures 4 and 5 were determined. (The orientation of the copper complex was assumed to be determined by the host lattice.) Unfortunately, our apparatus did not allow an extremely accurate absolute determination of the  $\eta$  angle. Although, the locations of the *x* and *z* directions shown in Figures 4 and 5 represent the average of a number of determinations, these locations could be in error by as much as 5–10°.

Although the *y* directions of the *g* and copper hyperfine tensors are coincident by symmetry, the *x* and *z* directions

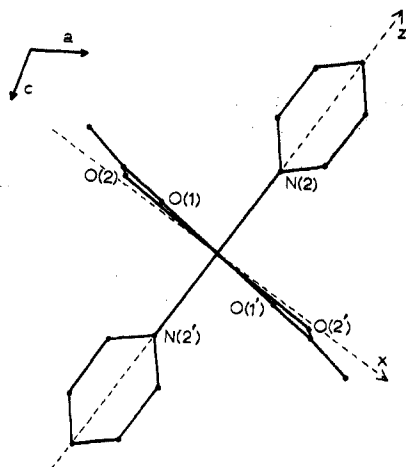
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(11) B. Bleaney, K. D. Bowers, and D. J. E. Ingram, *Proc. Roy. Soc., Ser. A*, 228, 147 (1955).



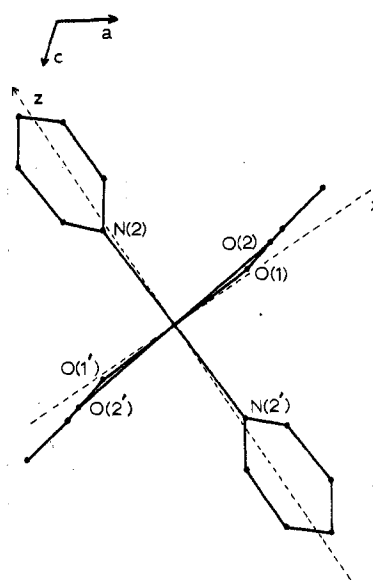
**Figure 3.** The angular dependence of the  $g$  value of the spectrum of  $\text{Cu}(\text{py})_3(\text{NO}_3)_2$  doped into the  $\text{Zn}(\text{py})_3(\text{NO}_3)_2$  lattice. The upper drawing shows the variation in the  $ac$ , (010), plane and the lower drawing shows the variation in the (100) plane. The open circles are the experimental values while the solid curves represent calculated values. In the (010) plane the  $\theta$  angle is constant at  $90^\circ$  and in the (100) plane the  $\eta$  angle is always  $90^\circ$ .



**Figure 4.** A projection of the dinitratotris(pyridine)zinc(II) molecule in the  $ac$  plane showing the orientation of the  $x$  and  $z$  axes. The pyridine ring on the twofold axis (the ring which contains  $\text{N}(1)$ ) has been omitted. The atom coordinates were taken from ref 8.

are not necessarily the same for the two tensors. It was noticed that the overall width of the spectrum (the separation between the first and last lines) showed an angular dependence very similar to that of the  $g$  factor. In the (010) plane the maximum width is observed at the same  $\eta$  angle as the maximum  $g$  value. Assuming that the largest contribution to the width of the spectrum comes from the hyperfine coupling with the  $^{65}\text{Cu}$  and  $^{63}\text{Cu}$  nuclei, one would conclude that the orientation of all three principal directions of the hyperfine tensor is the same or very nearly the same as that of the  $g$  tensor.

Evaluation of the hyperfine coupling constants required computer simulation techniques which involved a number of assumptions. Only the hyperfine interactions from the copper nuclei and the nitrogen nuclei of the three pyridine ligands were considered. The coupling constant for  $^{63}\text{Cu}$  was taken as 0.934 that of  $^{65}\text{Cu}$ . This factor was determined from the gyromagnetic ratios of the two nuclei. Relative



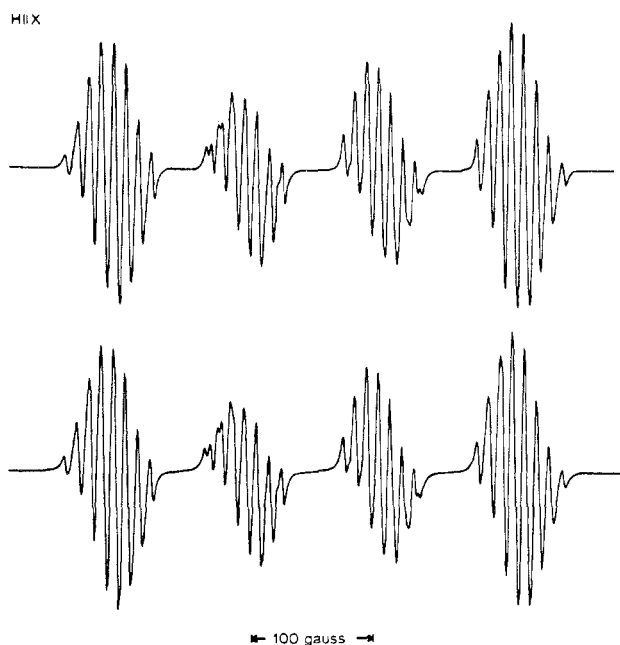
**Figure 5.** A projection of the dinitratotris(pyridine)cadmium(II) molecule in the  $ac$  plane showing the orientation of the  $x$  and  $z$  axes. The pyridine ring on the twofold axis (the ring which contains  $\text{N}(1)$ ) has been omitted. The atom coordinates were taken from ref 9.

intensities of the  $^{65}\text{Cu}$  and  $^{63}\text{Cu}$  lines were assigned according to the natural abundances of the two isotopes. The coupling constants of the  $^{14}\text{N}$  nuclei in the two symmetry-related pyridine ligands ( $\text{N}(2)$  and  $\text{N}(2')$ ) were assumed to be equal. All the lines were given a lorentzian shape and a constant width. Only the allowed ( $\Delta M_s = \pm 1$ ,  $\Delta M_l = 0$ ) transitions were calculated. Since the coupling constants for the copper nuclei are fairly large, the second-order terms given by Bleaney, Bowers, and Ingram<sup>11</sup> were included in the calculation of line positions. The second-order term,  $d$  (see ref 11), which could not be easily evaluated from the spectra, was treated as a variable but was in no case allowed to exceed reasonable limits ( $5 \times 10^{-4} \text{ cm}^{-1}$ ). (This term has the effect of increasing the separation between the two center lines of the copper hyperfine structure.) The coupling constants for the copper and ligand nuclei were varied until good agreement between the calculated and observed spectra was obtained. Simulations were attempted only for the spectra taken with the field applied along principal directions of the  $g$  tensor. The calculated and observed spectra for  $\text{Cu}(\text{py})_3(\text{NO}_3)_2$  in  $\text{Zn}(\text{py})_3(\text{NO}_3)_2$  are shown in Figures 6-8. Similar results were obtained for the spectra of the doped cadmium complex. The coupling constants for both lattices are given in Table I.

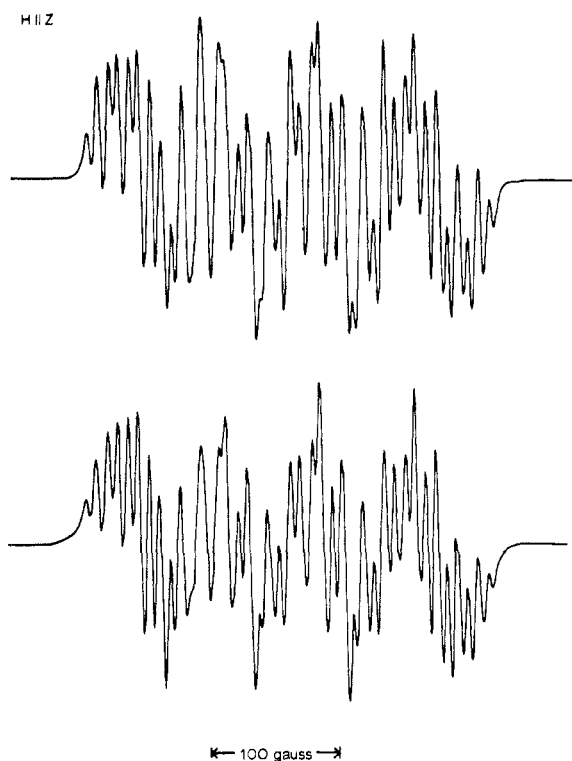
On the whole the agreement between the calculated and observed spectra is very good. Even fairly subtle spectral features are reproduced; however, there are a few minor but noticeable discrepancies. It is quite possible that the actual line shapes of the resonances are not perfectly lorentzian. This could account for the slight disagreement observed at the outer edges of the  $H \parallel y$  spectrum. Small errors in the treatment of the second-order effects in the copper hyperfine structure could cause the discrepancies between the observed and calculated intensities in the  $H \parallel z$  spectrum.

#### Spin-Hamiltonian Parameters and the Electronic Structure of Dinitratotris(pyridine)copper(II)

**Copper Hyperfine and  $g$  Tensors.** The  $g$  and copper hyperfine tensors of most copper(II) complexes exhibit nearly axial symmetry; however, those of the dinitratotris(pyridine) complex show very definite rhombic symmetry. In analyzing

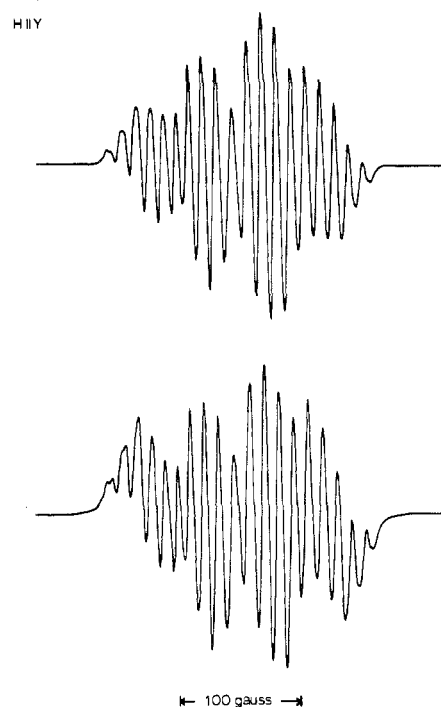


**Figure 6.** Comparison of the observed and calculated spectra for  $\text{Cu}_x\text{Zn}_{1-x}(\text{py})_3(\text{NO}_3)_2$  at 77°K with the magnetic field applied along the x axis. The lower trace is the simulated spectrum. A peak to peak line width of 3.3 G was used in the calculation of the simulated spectrum.



**Figure 7.** Comparison of the observed and calculated spectra for  $\text{Cu}_x\text{Zn}_{1-x}(\text{py})_3(\text{NO}_3)_2$  at 77°K with the magnetic field applied along the y axis. The lower trace is the simulated spectrum. A peak to peak line width of 5.0 G was used in the calculation of the simulated spectrum.

the tensors, we have found it convenient to take a somewhat idealized view of the geometry of the dinitratotris(pyridine) complexes. The coordination sphere about the metal ion can be treated as a highly distorted rhombic octahedron (see Figure 9). The N(2)-Cu-N(2') and O(2)-Cu-O(2') bond angles in the copper complex of 176.0 and 168.8°, respective-



**Figure 8.** Comparison of observed and calculated spectra for  $\text{Cu}_x\text{Zn}_{1-x}(\text{py})_3(\text{NO}_3)_2$  at 77°K with the magnetic field applied along the z axis. The lower trace is the simulated spectrum. A peak to peak line width of 5.0 G was used in the calculation of the simulated spectrum.

**Table I.** Spin-Hamiltonian Parameters of Dinitratotris(pyridine)copper(II)

	$\text{Cu}_x\text{Zn}_{1-x}(\text{py})_3(\text{NO}_3)_2$	$\text{Cu}_xCd_{1-x}(\text{py})_3(\text{NO}_3)_2$
Room Temperature		
<i>g</i> values		
$g_x$	$2.25 \pm 0.02$	$2.20 \pm 0.02$
$g_y$	$2.19 \pm 0.02$	$2.22 \pm 0.02$
$g_z$	$2.03 \pm 0.02$	$2.04 \pm 0.02$
Hyperfine constants, $\times 10^{-4} \text{ cm}^{-1}$		
$\text{Cu}^a \begin{cases} A_x \\ A_y \\ A_z \end{cases}$	$\begin{matrix} \sim 90 \\ \sim 55 \\ \sim 65 \end{matrix}$	$\begin{matrix} \sim 65 \\ \sim 75 \\ \sim 50 \end{matrix}$
77°K		
<i>g</i> values		
$g_x$	$2.279 \pm 0.003$	$2.279 \pm 0.003$
$g_y$	$2.151 \pm 0.003$	$2.162 \pm 0.003$
$g_z$	$2.017 \pm 0.003$	$2.012 \pm 0.003$
Hyperfine constants, $\times 10^{-4} \text{ cm}^{-1}$		
$^{65}\text{Cu}^b \begin{cases} A_x \\ A_y \\ A_z \end{cases}$	$\begin{matrix} 127 \pm 1 \\ 49 \pm 1 \\ 78 \pm 1 \end{matrix}$	$\begin{matrix} 116 \pm 1 \\ 49 \pm 1 \\ 79 \pm 1 \end{matrix}$
$^{14}\text{N}(1) \begin{cases} A_x \\ A_y \\ A_z \end{cases}$	$\begin{matrix} 9.4 \pm 0.2 \\ 12.9 \pm 0.4 \\ 9.4 \pm 0.2 \end{matrix}$	$\begin{matrix} 8.4 \pm 0.2 \\ 11.9 \pm 0.4 \\ 8.4 \pm 0.2 \end{matrix}$
$^{14}\text{N}(2) \begin{cases} A_x \\ A_y \\ A_z \end{cases}$	$\begin{matrix} 11.2 \pm 0.2 \\ 10.9 \pm 0.4 \\ 15.0 \pm 0.2 \end{matrix}$	$\begin{matrix} 11.0 \pm 0.2 \\ 10.9 \pm 0.4 \\ 14.9 \pm 0.2 \end{matrix}$

<sup>a</sup> Represents a weighted average of the <sup>65</sup>Cu and <sup>63</sup>Cu coupling constants. <sup>b</sup> The <sup>63</sup>Cu coupling constants are equal to 0.934 times the <sup>65</sup>Cu constants.

ly, are not too different from the 180° required by our assumption of octahedral geometry. The other two oxygen atoms of the nitrate ions (O(1) and O(1')) are treated as having the effect of a single ligand placed halfway between them. This single ligand would then be trans to the third pyridine nitrogen (N(1)). This description of the bonding has been previously proposed by Cameron and coworkers.<sup>8,9</sup> Clearly, the treatment of O(1) and O(1') is the weakest aspect of the

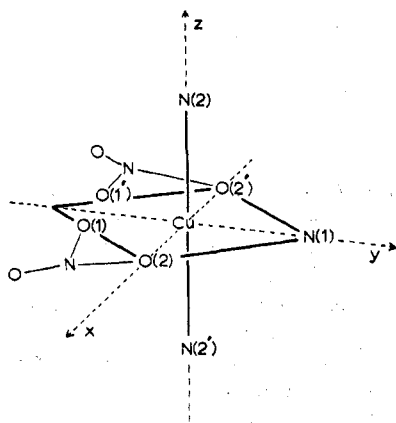


Figure 9. An idealized view of the bonding in the dinitratotris(pyridine) complexes. The  $x$ ,  $y$ , and  $z$  axes correspond to the principal directions of the  $g$  tensor.

idealized model. It should be pointed out that the analysis of the  $g$  and hyperfine tensors does not really require the assumption of any model; however, such an idealization is quite useful in gaining physical insight from the results.

The  $g_x$  and  $g_y$  values of copper(II) complexes which have the usual  $d_{x^2-y^2}$  ground state typically lie between 2.04 and 2.07, while the  $g_z$  values fall in the 2.15–2.40 range. In contrast, one of the  $g$  values of the dinitratotris(pyridine)copper(II) complex ( $g_z$ ) is close to the free-electron value (2.002). Low values such as this have been observed for a few other copper(II) complexes and have been taken as an indication of a  $d_{z^2}$  ground state.<sup>12</sup> The three  $g$  values are similar to those reported by Schatz and McMillan for copper(II) in zinc-3-pyridinesulfonate<sup>13</sup> and those presented by Sroubek and Zdansky for copper(II) doped into cadmium tungstate.<sup>14</sup> Following the procedure of Sroubek and Zdansky, the copper portion of the wave function of the unpaired electron can be written as<sup>14</sup>

$$\psi = \alpha(|3z^2 - r^2\rangle + \beta|x^2 - y^2\rangle)/\sqrt{1 + \beta^2}$$

This wave function has been slightly modified to include the  $\sqrt{1 + \beta^2}$  normalization factor. (The ligand contribution to the wave function will be considered later.) Using a somewhat modified form of the expressions which Sroubek and Zdansky derived from the work of Bleaney, Bowers, and Pryce,<sup>15</sup> the hyperfine constants can be related to the  $g$  values in the equations

$$A_x = P(-\kappa\alpha^2 + \Delta g_x + (1/14)\Delta g_y - 2\alpha^2/7 - 4\sqrt{3}\alpha^2\beta/7 + 6\alpha^2\beta^2/7)$$

$$A_y = P(-\kappa\alpha^2 + \Delta g_x + (1/14)\Delta g_y - 2\alpha^2/7 + 4\sqrt{3}\alpha^2\beta/7 + 6\alpha^2\beta^2/7)$$

$$A_z = P(-\kappa\alpha^2 + \Delta g_z - (1/14)(\Delta g_x + \Delta g_y) + 4\alpha^2/7)$$

$$P = g_e\beta_e g_n \beta_n \langle r^{-3} \rangle$$

$$\Delta g = g - 2.0023$$

(12) B. J. Hathaway and T. E. Billing, *Coord. Chem. Rev.*, **5**, 143 (1970).

(13) G. C. Schatz and J. A. McMillan, *J. Chem. Phys.*, **55**, 2342 (1971).

(14) Z. Sroubek and K. Zdansky, *J. Chem. Phys.*, **44**, 3078 (1966).

(15) B. Bleaney, K. D. Bowers, and M. H. L. Pryce, *Proc. Roy. Soc., Ser. A*, **228**, 166 (1955).

These expressions have been modified to include the  $\beta^2$  terms dropped in Sroubek and Zdansky's treatment. The term is a dimensionless factor which represents the contact (polarization of "s" shells) contribution to the hyperfine tensor. Using a  $\langle r^{-3} \rangle$  value of  $5.57 \times 10^{25} \text{ cm}^{-3}$  calculated from Watson and Freeman's Hartree-Fock computations,<sup>16</sup>  $P$  for  $^{65}\text{Cu}$  was determined to be  $0.0417 \text{ cm}^{-1}$ . Unfortunately, the signs of the hyperfine constants in the above equations are not known.

The relative signs of the coupling constants of a molecule can be determined with the aid of that molecule's liquid solution spectrum by making use of the relation

$$A_{\text{soln}} = A_{\text{av}} = (1/3)(A_x + A_y + A_z)$$

Solutions of dinitratotris(pyridine)copper(II) in acetonitrile and methylene chloride (with or without excess pyridine) exhibit nearly identical epr spectra which at room temperature consist of a poorly resolved four-line pattern ( $A \approx 60 \times 10^{-4} \text{ cm}^{-1}$ ). Unfortunately, the frozen solution spectra (77°K) do not resemble those of polycrystalline samples of the copper-doped zinc and cadmium complexes indicating that the solid-state and solution species are not the same. Thus, the solution data are useless for our purpose and a number of possible sign combinations must be considered.

Taking  $A_z$  to be positive,<sup>14</sup>  $A_x$  and  $A_y$  may be either positive or negative giving four possible sign combinations. Two of the sign combinations ( $A_x > 0, A_y > 0$  and  $A_x < 0, A_y > 0$ ) lead to values of  $\alpha^2$  which are much smaller than those which have been reported previously for copper(II) complexes ( $\alpha^2 < 0.5$ ). The other two combinations give reasonable values of  $\alpha^2$ , and the solutions to the equations using both sign combinations are given in Table II. The two sets of results can be tested by attempting to calculate  $\delta_{xy}$  ( $\delta_{xy} = g_x - g_y$ ) from the expression<sup>14</sup>

$$\delta_{xy} = (\Delta g_x + \Delta g_y)(2\beta/\sqrt{3})$$

For the zinc lattice  $\delta_{xy}$  is 0.128 and the  $\delta_{xy}$  value calculated from the case I data is 0.099 while that for case II is 0.191. This indicates that the sign combination in case I is more likely to be correct, but the choice is by no means clear-cut. The  $\alpha^2$  and  $\kappa$  values in both cases are quite comparable to the values which have been reported for other copper(II) complexes such as copper(II) doped into cadmium, zinc, and magnesium tungstate,<sup>14</sup> bis(3-pyridinesulfonato)copper(II),<sup>13</sup> bis(acetylacetonato)copper(II),<sup>17</sup> bis(benzoylacetonato)copper(II),<sup>18</sup> and bis(salicylaldimino)copper(II).<sup>19</sup> The  $\alpha^2$  values for these complexes lie in the 0.7–0.9 range while the  $\kappa$  parameters range roughly from 0.2 to 0.35. (The last four complexes mentioned have a  $d_{x^2-y^2}$  rather than a  $d_{z^2}$  ground state.)

A very reasonable physical picture results from considering the ground-state wave function derived from the  $g$  and  $A$  tensor analysis in terms of our idealized view of the coordination in these complexes. In a  $d^9$  system such as copper(II) the unpaired electron can be treated as a positively charged hole in a filled d subshell. In a complex, such a hole will distribute itself in space so that it has a maximum density in the region of the most strongly interacting ligands. The wave

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(17) A. H. Maki and B. R. McGarvey, *J. Chem. Phys.*, **29**, 31 (1958).

(18) M. A. Hitchman and R. L. Belford, "Electron Spin Resonance of Metal Complexes," T. F. Yen, Ed., Plenum Press, New York, N. Y., 1969, pp 97–109.

(19) A. H. Maki and B. R. McGarvey, *J. Chem. Phys.*, **29**, 35 (1958).

function for the unpaired electron (or hole) in the  $\text{Cu}(\text{py})_3(\text{NO}_3)_2$  complex has predominantly  $d_{z^2}$  character (in either case I or case II). Thus, the region of greatest density is along the  $z$  axis toward the nitrogen atoms of the two symmetry-related pyridines (N(2) and N(2')). It is reasonable to assume that these two pyridines have the greatest interaction with the copper(II) ion since the crystal structure shows the metal-nitrogen bond length for these two ligands (2.02 Å) to be shorter than any of the other metal-ligand distances.<sup>8</sup>

The effect of adding a small amount of  $d_{x^2-y^2}$  to the wave function is to increase the density along the  $y$  axis and reduce it along  $x$ . This also seems quite reasonable since the ligands on the  $x$  axis (O(2) and O(2')) have the largest metal-ligand distance (2.73 Å) indicating that they interact the least with the copper ion. The ligands along the  $y$  direction, N(1), O(1), and O(1'), have metal to ligand distances of 2.06 and 2.15 Å, respectively. (The metal-ligand distances have been taken from the crystal structure of the copper complex. We feel that in molecular solids such as these complexes the packing forces do not greatly alter the molecular structure of a molecule. Thus, the host lattice does not affect the structure of an impurity molecule but does determine the orientation of the molecule in the crystal. It should be noted that the copper, zinc, and cadmium complexes have similar enough structures that the argument given above would not change even if the structural parameters of the host lattices were used.)

**Ligand Hyperfine Structure.** The observation of well-developed ligand hyperfine structure is an indication of some amount of metal to ligand delocalization. An analysis of the hyperfine interaction can lead to an estimation of the extent of delocalization and a description of the molecular orbital containing the unpaired electron.

The  $^{14}\text{N}$  hyperfine tensors of copper(II) complexes containing nitrogen donor ligands usually exhibit axial or nearly axial symmetry about the copper-nitrogen bond. This appears to be the case in the dinitratotris(pyridine)copper(II). The coupling constants for N(1) show nearly axial symmetry about the  $y$  axis while those for N(2) and N(2') are nearly symmetric about the  $z$  axis (see Table I). The crystal structure shows the Cu-N(1) bond to be exactly coincident with  $y$  while the Cu-N(2) and Cu-N(2') bonds are nearly but not exactly parallel with  $z$ . Taking the ligand hyperfine tensors as axial the coupling constants can be expressed in the following equations: for N(1),  $A_{\parallel} = A_y$ ,  $A_{\perp} = (A_x + A_z)/2$ ; for N(2) and N(2'),  $A_{\parallel} = A_z$ ,  $A_{\perp} = (A_x + A_y)/2$ . (The values for N(2) and N(2') are subject to some error, since the copper-nitrogen bonds are not exactly parallel to  $z$ .) These coupling constants can be resolved into isotropic and anisotropic or dipolar parts according to the equations

$$A_{\parallel} = K + 2T$$

$$A_{\perp} = K - T$$

where  $K$  is the isotropic part and  $T$  is the dipolar part. The isotropic portion results from contact interaction in which the unpaired electron has a finite density at the nucleus. Large contact interactions are expected only if the molecular orbital containing the unpaired electron has some  $s$  character. The dipolar part arises from through-space effects and  $p$ -orbital contributions to the molecular orbital. Assuming that only the  $2s$  and  $2p_1$  orbitals ( $2p_1$  is directed along the Cu-N bond) of the nitrogen participate in bonding with the copper ion, isotropic and dipolar coupling constants can be expressed as

$$K (\text{cm}^{-1}) = \epsilon^2 (8\pi g_e \beta_e g_n \beta_n |\psi_{2s}(0)|^2) / 3hc$$

$$T (\text{cm}^{-1}) = \gamma^2 (2g_e \beta_e g_n \beta_n \langle r^{-3} \rangle_{2p}) / 5hc + \alpha^2 g_e \beta_e g_n \beta_n / R^3 hc$$

In these expressions  $\epsilon$  and  $\gamma$  are the molecular orbital coefficients of the nitrogen  $2s$  and  $2p_1$  orbitals, respectively. The second term of the equation for  $T$  is the direct dipole-dipole term in which  $\alpha^2$  is the unpaired electron density on the copper ion and  $R$  is the distance between the copper and nitrogen nuclei. The MO coefficients,  $\epsilon$  and  $\gamma$ , can be calculated from the equations above, using the observed values of  $K$  and  $T$  along with values of  $R$  taken from the crystal structure,  $|\psi_{2s}(0)|^2$  taken from Hartree-Fock calculations,<sup>20</sup> and  $\langle r^{-3} \rangle_{2p}$  determined from epr studies of atomic nitrogen.<sup>21</sup> The results are presented in Table III. The values of  $\epsilon^2$  and  $\gamma^2$  indicate that there is a small but significant delocalization of the unpaired electron from the copper(II) ion to the nitrogen atoms of the three pyridine ligands. The amounts of metal to nitrogen delocalization determined for this complex are similar to those which have been reported for other complexes which contain copper(II) ions bound to ligands which coordinate through  $sp^2$ -hybridized nitrogen atoms. Examples of such complexes are bis(3-pyridinesulfonato)copper(II),<sup>13</sup> bis(salicylaldimino)copper(II),<sup>19</sup> and tetraphenylporphyrincopper(II).<sup>22</sup> It is interesting to note that our computations indicate that the extent of delocalization onto N(1) is somewhat less than onto N(2) and N(2'). This observation is certainly in agreement with the qualitative description of the electron distribution in the complex given in the previous section.

The  $\epsilon^2/\gamma^2$  ratios should be mentioned since this ratio is, at least in principle, a measure of the hybridization of the nitrogen atom. One would expect the  $sp^2$ -hybridized nitrogen of a pyridine ligand to have an  $\epsilon^2/\gamma^2$  ratio of 2.0; however, the computed ratios for both types of nitrogen atoms in the dinitratotris(pyridine) complex are approximately 3. We feel that this discrepancy probably arises from the many approximations used in computing the  $\epsilon$  and  $\gamma$  values and does not indicate an unusual electronic structure of the pyridine ligands of this complex.

## Conclusions

Combining the results of the two previous sections the following wave functions are obtained for the unpaired electron (electron hole) of the dinitratotris(pyridine)copper(II) molecule

$$\begin{aligned} \text{case I: } \psi = & 0.86(|3z^2 - r^2\rangle + 0.20|x^2 - y^2\rangle) - \\ & 2(0.16|2s\rangle\text{N}(2) + 0.26|2p\rangle\text{N}(2)) - \\ & (0.14|2s\rangle\text{N}(1) + 0.25|2p\rangle\text{N}(1)) \end{aligned}$$

$$\begin{aligned} \text{case II: } \psi = & 0.78(|3z^2 - r^2\rangle + 0.389|x^2 - y^2\rangle) - \\ & 2(0.16|2s\rangle\text{N}(2) + 0.26|2p\rangle\text{N}(2)) - \\ & (0.14|2s\rangle\text{N}(1) + 0.25|2p\rangle\text{N}(1)) \end{aligned}$$

(These wave functions are for copper doped into the zinc complex. The wave functions for the cadmium lattice can be readily obtained from the data in Tables II and III.) The signs of the coefficients of the nitrogen orbitals are taken as negative since the unpaired electron is presumed to reside in an antibonding molecular orbital. The spin density on the

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(21) H. E. Radford and K. M. Evenson, *Phys. Rev.*, **168**, 70 (1968).

(22) P. T. Monohavan and M. T. Rogers, "Electron Spin Resonance of Metal Complexes," T. F. Yen, Ed., Plenum Press, New York, N. Y., 1969, pp 143-173.

Table II. Analysis of the Copper Hyperfine and  $g$  Tensors

	$\text{Cu}_x\text{Zn}_{1-x}$ $(\text{py})_3(\text{NO}_3)_2$	$\text{Cu}_x\text{Cd}_{1-x}$ $(\text{py})_3(\text{NO}_3)_2$
Case I ( $A_x, A_y < 0; A_z > 0$ )		
$\kappa$	0.322	0.301
$\alpha$	0.875	0.877
$\beta$	0.201	0.176
$\alpha^2$	0.765	0.770
$\beta^2$	0.040	0.031
Case II ( $A_x < 0; A_y, A_z > 0$ )		
$\kappa$	0.301	0.274
$\alpha$	0.839	0.838
$\beta$	0.389	0.362
$\alpha^2$	0.704	0.702
$\beta^2$	0.151	0.131

copper ion ( $\alpha^2$ ) is calculated to be 0.76 (case I) or 0.70 (case II) while the total density on the three nitrogen atoms is computed to be 0.26. If these values are reasonably correct, the results suggest that the extent of delocalization of the unpaired electron onto the oxygen atoms of the nitrate ions is small (case II) or insignificant (case I), since the three nitrogen atoms and the copper ion account for essentially all of the electron density. Unfortunately,  $^{16}\text{O}$  has no nuclear spin; therefore, one cannot obtain an experimental measure of the spin density on the oxygen atoms. It should be mentioned that Smith has recently criticized the use of epr constants,  $g$  values specifically, for the calculation of the molecular orbital parameters of copper(II) complexes.<sup>23</sup> While he specifically discussed tetragonal complexes, the criticisms undoubtedly apply to copper(II) complexes of other geometries as well. Although the present study makes use of the ligand and copper hyperfine constants in addition to the  $g$  values, it is probably unwise to expect the molecular orbital parameters which have been derived to be more than qualitatively accurate.

There are some small but significant differences in the spectral parameters of the copper complex obtained from the two different host lattices. The analysis of the copper hyperfine and  $g$  tensors indicates that the amount of  $d_{x^2-y^2}$  orbital mixed into the unpaired electron's wave function ( $\beta$ ) is somewhat smaller in the cadmium lattice (both case I and case II).

(23) D. W. Smith, *J. Chem. Soc. A*, 3108 (1970).

Table III. Analysis of Ligand Hyperfine Constants

	$\text{Cu}_x\text{Zn}_{1-x}$ $(\text{py})_3(\text{NO}_3)_2$	$\text{Cu}_x\text{Cd}_{1-x}$ $(\text{py})_3(\text{NO}_3)_2$
N(1): $\gamma^2 = K/513, \epsilon^2 = (T - 0.165)/16.9$		
$K, \times 10^{-4} \text{ cm}^{-1}$	10.5	9.6
$T, \times 10^{-4} \text{ cm}^{-1}$	1.20	1.20
$\gamma^2$	0.020	0.018
$\epsilon^2$	0.061	0.061
N(2) and N(2'): $\gamma^2 = K/513, \epsilon^2 = (T - 0.173)/16.9$		
$K, \times 10^{-4} \text{ cm}^{-1}$	12.4	12.3
$T, \times 10^{-4} \text{ cm}^{-1}$	1.32	1.35
$\gamma^2$	0.024	0.024
$\epsilon^2$	0.068	0.070

According to our previous argument, a decrease in  $\beta$  would indicate a reduction in electron density along the  $y$  axis of the molecule. This supposition is supported by the fact that the coupling constants for N(1), which lies along the  $y$  axis, are about 10% smaller in the copper-doped cadmium lattice than in the zinc lattice. The differences in spectral parameters for the two lattices indicate that the molecular structure of the copper complex is at least somewhat affected by the host lattice. Unfortunately, the estimation of the amount of structural change necessary to account for the observed differences in spectra is a very difficult problem.

On the whole, this spectral analysis has given an internally consistent and physically reasonable description of the ground-state electronic structure of the dinitratotris(pyridine)copper(II) complex. The inability to determine with certainty the relative signs of the copper hyperfine constants (cases I and II) is an obvious weakness of this treatment, but fortunately the same physical picture results in both cases. It appears that a highly distorted octahedron is a very plausible description of the coordination sphere of dinitratotris(pyridine)copper(II).

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**Registry No.**  $\text{Cu}(\text{py})_3(\text{NO}_3)_2$ , 49664-79-1;  $\text{Zn}(\text{py})_3(\text{NO}_3)_2$ , 32124-88-2;  $\text{Cd}(\text{py})_3(\text{NO}_3)_2$ , 49564-51-4.

Contribution from the Department of Chemistry, University of Natal, Durban, South Africa

## Binary Silver Bromide-Alkali Bromide Melts. Calculated and Measured Energies of Mixing

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Excess Gibbs free energies of mixing, calculated using the Davis-Rice theory, for silver bromide-alkali bromide melts are found to agree with the experimental values. Precise measurements of energies of mixing for the  $\text{AgBr-ABr}$  ( $A = \text{Li, Na, K, Rb, Cs}$ ) systems are presented which also enable, for the first time, satisfactory theoretical predictions of excess entropies of mixing to be made. The excess entropies of mixing are such that  $\Delta G^E$  cannot be approximated by  $\Delta H^M$  as usually assumed, especially for  $\text{AgBr-LiBr}$ . The importance of a silver-graphite thermocouple emf correction is explained and the Pelton-Flengas theory is tested.

### Introduction

As outlined in a preliminary communication,<sup>1</sup> measurements

(1) R. L. Paul and H. C. Brookes, *Inorg. Nucl. Chem. Lett.*, **8**, 629 (1972).

of energies of mixing of molten  $\text{AgBr-ABr}$  ( $A = \text{Na, K, Rb, Cs}$ ) systems have been obtained using emf formation cells. The  $\text{AgBr-LiBr}$  system, which displays a large negative excess entropy of mixing, has since been investigated in our labora-