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Electron Paramagnetic Resonance Study of Bis(N-methyl-2 amino-1-cyclopentenedithiocarboxylato) Copper (II)

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The electron paramagnetic resonance (EPR) spectrum of the copper (II) complex with the 2-methylamino-1-cyclo-pentene-1-dithiocarboxylate(acdc) anion, $Cu(N-CH_3 \ acdc)_2$ has been studied in the diamagnetic host lattices afforded by the corresponding divalent nickel, zinc, cadminum and mercury complexes. EPR parameters of the complex support the exclusive use of sulfur atoms by the ligand in metal binding. A combination of host lattice structure and covalency effects can be account for the observed spin-Hamiltonian parameters.

Introduction

One of the most interesting biological molecules that contains Cu(II) is the "blue" copper(II) protein. Both the optical and ESR spectra are quite unusual for copper in this oxidation state. It appears that the unusual characteristics of these copper centers results from the coordination environment of the metal ion which is distorted from square planar structure to pseudo-tetrahedral one[1].

One of the more unusual aspects of the blue copper enzyme and proteins is the value of A_{11} (hyperfine splitting constant) in the ESR spectra[2]. It has been reported that the value of A_{11} for copper enzymes is very small compared with other ordinary copper(II) complexes. Bereman et al.[3] prepared the distorted copper(II) complexes and found that there is a good correlation between the value of A_{11} and twist angle. Although the coordination environment of those complexes is quite different from that found for blue copper in biological systems, its tendency to become lower in A_{11} value as the twist angle increases seems clear.

The ligand N-methyl-2-amino-1-cyclopentenedithiocarboxylate anion (N-CH$_3$ acdc), 1, forms dark brown colored complex

(1)
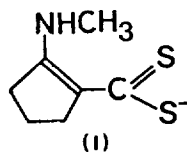
with copper(II) and preliminary experiments indicate that the spin Hamiltonian parameters for this complex were lattice dependent. It was therefore deemed worthwhile to execute the present study of lattice effects on the ESR spectrum of $Cu(N-CH_3 \ acdc)_2$.

Experimental

The ligand, N-methyl-2-amino-1-cyclopentenedithiocarboxylate was prepared by the method of Bordas et al.[4]. The copper complex was prepared in methanol by the method of Mondal and coworkers[5]. The complex prepared was isolated as a dark brown solid. Anal. Calcd. for $C_{14}H_{10}N_2S_4Cu$: C, 41.20; 4.94; N, 6.86. Found: C, 40.14; H, 4.77; N, 6.64.

Doping samples were prepared by adding the ammonium salt of N-CH$_3$ acdc anion to the stoichiometric mixture of the $CuCl_2$ in methanol. ESR spectra were measured with a Varian E109 X-Band spectrometer (9.370 GHz, 100 KHz field modulation). The frequency was monitored with a calibrated absorption wavemeter in corporated in the microwave unit. Field calibration was checked using diphenylpicrylhydrazyl (DPPH) free radical for which g = 2.003. The EPR spectra were interpreted by standard techniques. Some of spectra were simulated using the computer program described by Venable[6].

Results and Discussion

ESR Spectra. The ESR spectra of $Cu(N-CH_3 \ acdc)_2$
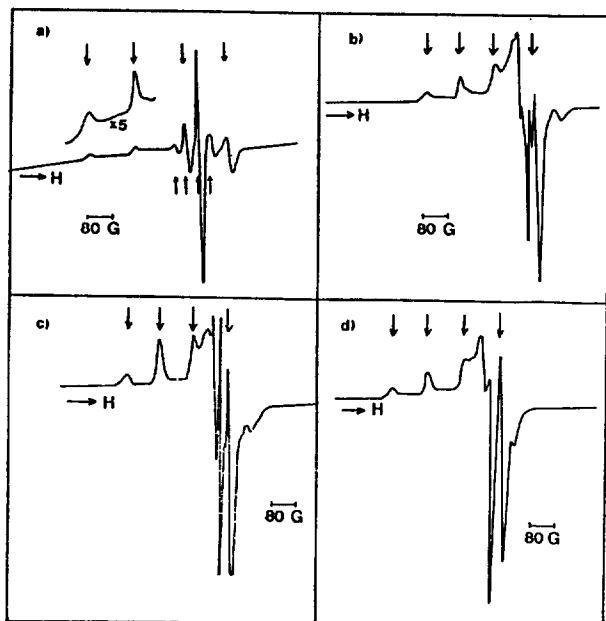
Figure 1. EPR Spectrum of $Cu(N-CH_3$ acdc$)_2$ doped into the corresponding diamagnetic nickel(II)(a), zinc(II)(b), cadmium(II)(c), mercury(II)(d) (% Cu; 1.00%). The arrows pointing downward indicate the parallel absorption and the arrows pointing upwards indicate the perpendicular absorption.

doped into the corresponding diamagnetic nickel(II) complex are shown in Figures 1.

The solution ESR spectra of $Cu(N-CH_3$ acdc$)_2$ exhibited the expected four line patterns. Since the ligand yields a diamagnetic nickel(II) complex, nitrogen suporhyporfine splitting in the ESR spectrum of the doped Cu(II) complex might be anticipated if the amino group is involved in metal-binding. However, no nitrogen superhyperfine splitting was observed in the ESR spectrum. It was also noted that the Cu $(N-CH_3$ acdc$)_2$ complex exhibited narrow linewidths characteristic of CuS$_4$ compounds. The axial spin-Hamiltonian:

$$\hat{H}=g_{\shortparallel}\beta H_z\hat{S}_z+g_\perp\beta\,(H_x\hat{S}_x+H_y\hat{S}_y)+A_{\shortparallel}\hat{I}_z\hat{S}_z$$
$$+A_\perp\,(\hat{I}_x\hat{S}_x+\hat{I}_y\hat{S}_y) \tag{1}$$

where the symbols have their usual meanings, was employed in the analysis of anisotropic spectra of $Cu(N-CH_3$ acdc$)_2$ (d^9 system) complex.

In the absence of crystal structure data for the complexes,

single crystal studies were not attempted and it was assumed that the g and A tensors share the same principal axis system. Tables 1 and 2 collect the spin–Hamiltonian parameters for $Cu(N-CH_3$ acdc$)_2$. From the anisotropic spectra,

$<g>=\frac{1}{3}\,(g_{\shortparallel}+2g_\perp)$ and $<A>=\frac{1}{3}\,(A_{\shortparallel}+2A_\perp)$ were calculated and compared with g_o and A_o obtained from the solution spectra. The parameters $<g>$ and $<A>$ were very close to g_o and A_o values for both complexes in acetone and dimethylsulfoxide. Due to the limited solubility of these compounds in various solvents, solvent effects were not further explored.

It is well-known that metal-sulfur bonding is more covalent than metal-oxygen or metal-nitrogen bounding[7-10]. Kivelson and Neiman[11] pointed out that g_{11} values for Cu(II) complexes are a moderately sensitive function of metal-ligand covalency. For ionic environments g_{11} is normally 2.3 or larger and for more covalent environments it is less than 2.3. Theoretical work by D.W. Smith[12] seems to confirm this view. The g_{11} value of 2.088 for Cu(acdc)$_2$ is decidedly indicative of a strongly covalent environment.

The ESR parameters for Cu(acdc)$_2$ are similar to those reported by Weeks and Frackler[13] for bis(diethyldithiocarbamato) copper(II). ESR parameters characteristic of CuS$_4$, CuN$_2$S$_2$ and CuN$_4$ chromophores[2,10,13-27], are compared with those for $Cu(N-CH_3$ acdc$)_2$ in Table 3. The data for $Cu(N-CH_3$ acdc$)_2$ give strong support for the CuS$_4$ chromophore-structure(II) for the complex.

Lattice Effects. Table 1, summarizes the EPR parameters evaluated from the spectra of polycrystalline samples of $Cu(N-CH_3$ acac$)_2$ doped into the diamagnetic $Ni(N-CH_3$ acdc$)_2$, $Zn(N-CH_3$ acdc$)_2$, $Cd(N-CH_3$ acdc$)_2$, and $Hg(N-CH_3$ acdc$)_2$ lattices. Figure 1 shows typical data. The EPR spectra of $Cu(N-CH_3$ acdc$)_2$ in the host lattices could be fit to the axial spin–Hamiltonian (equation 1).

Upon variation of the host lattice the EPR parameters change, g_{11} and A_{11} values being the most affected. The $<g>$ and $<A>$ values for $Cu(N-CH_3$ acdc$)_2$ in $Ni(N-CH_3$ acdc$)_2$, which has a D_{2h} local planar symmetry about the metal ion, are very close to the isotropic g_o and A_o values (Table 2) obtained from solution spectra. This indicates that copper substitutes into the nickel lattice with minimal lattice distortion of the copper compound. Doping the $Cu(N-CH_3$ acdc$)_2$ compound into the zinc, cadmium, and mercury host lattice give rise to marked differences in $<g>$ and $<A>$ values (Table 2) from the isotropic data as expected for compounds with structures reasonably anticipated to have pseudo-tetrahedral coordination geometries about the metal

Table 1. Spin-Hamiltonian Parameters for $Cu(N-CH_3-acdc)_2$ (all A values $\times$ 10^{-4}cm^{-1})

host lattice	% Cu doping	g_{11}	g_1	A_{11}	A
$Ni(N-CH_3-acdc)_2$	1	$2.085(\pm 0.001)$	$2.018(\pm 0.001)$	156	$36(\pm 2)$
	5	$2.090(\pm 0.001)$	$2.021(\pm 0.001)$	156	$36(\pm 2)$
$Zn(N-CH_3-acdc)_2$	3	$2.116(\pm 0.001)$	$112(\pm 1)$	$36(\pm 2)$	
	5	$2.114(\pm 0.001)$	$2.026(\pm 0.001)$	$110(\pm 1)$	$36(\pm 2)$
$Cd(N-CH_3-acdc)_2$	1	$2.114(\pm 0.001)$	$2.024(\pm 0.002)$	$111(\pm 1)$	$28(\pm 1)$
	3	$2.112(\pm 0.001)$	$2.028(\pm 0.002)$	$108(\pm 1)$	$23(\pm)$
$Hg(N-CH_3-acdc)_2$	1	$2.219(\pm 0.002)$	$2.038(\pm 0.005)$	$113(\pm 1)$	$36(\pm 3)$
	3	$2.126(\pm 0.002)$	$2.038(\pm 0.005)$	$114(\pm 1)$	$33(\pm 3)$
	5	$2.117(\pm 0.002)$	$2.023(\pm 0.005)$	$116(\pm 1)$	$39(\pm 3)$

Table 2. EPR and Covalency Parameters for $Cu(N-CH_3-acdc)_2$

Host lattice	$<g>^a$	$<g_0>^b$	$<A>^d$	A_0	α^2	f^2
$Ni(N-CH_3-acdc)_2$	2.043	—	76	—	0.483	1.000
$Zn(N-CH_3-acdc)_2$	2.056	—	61	—	0.366	0.758
$Cd(N-CH_3-acdc)_2$	2.055	—	54	—	0.393	0.814
$Hg(N-CH_3-acdc)_2$	2.063	—	62	—	0.384	0.795
dimethyl sulfoxide	—	2.042	—	75	—	—
acetone	—	2.044	—	74	—	—

$^a<g>$ values were obtained from the expressions $<g> = \frac{1}{3}(g_{11} + 2g_\perp)$. $<g> = \frac{1}{3}<g_x + g_y + g_z>$. $<A>$ values were obtained similarly. $^b g_0$ isotropic g-value from solution spectrum. ^{c} For the calculation of a^2 for the mercury and cadmium host lattices, g_1 was taken as the average of g_x and g_y. ^{d} The $<g>$, $<A>$, a^2, and f^2 for each host lattice are average values for the various dopant concentrations (A-values $\times 10^{-4}$ cm^{-1}).

ion.

The pseudo-tetrahedral site symmetry around metal ions of host compounds will presumably distort the planar coordination geometry about Cu(II) of $Cu(N-CH_3-acdc)_2$ when Cu(II) is doped into these host compounds.

Although crystal structures are not available for compounds containing the $N-CH_3$ acdc anion, these complexes must have structures similar to the corresponding metal dithiocarbamates. The crystal structures of nickel(II)[27], copper (II)[29], zinc(II)[30], cadmium[31], and mercury(II)[32] diethyldithiocarbamate (dtc) have been described. In $Zn(dtc)_2$ and $Cd(dtc)_2$ the geometry of the sulfur atoms about the metal ions is such that it may be considered as distorted trigonal bipyramidal or distorted square pyramidal due to the proximity of molecules in the solid state. $Cu(dtc)_2$ has a similar structure but the geometry more closely approaches a planar four-coordinate structure. $Ni(dtc)_2$ shows rigorously planar four coordination with no apparent interaction of the nickel ion with sulfur atoms in neighboring molecules; the local symmetry about the metal ion is nearly D_{2h}. $Hg(dtc)_2$ has a helical quasi-polymeric structure with four sulfur atoms nearly coplanar with the mercury atoms. From the structural information cited above and assuming the structure are similar it was anticipated that the EPR spectra of $Cu(N-CH_3$ acdc$)_2$ would exhibit the most pronounced effects in the zinc and cadmium hosts. This is what was observed,

In D_{2h} symmetry the ground state of $Cu(N-CH_3$ acdc$)_2$ can be written[33,34]

$$|xy> = ad_{xy} + \frac{1}{2}a' \text{ (ligand orbital terms}\cdots) \quad (2)$$

where a is the metal d orbital coefficient and a' the ligand group orbital coefficient for the ground state. Complete expressions for the g- and hyperfine coupling constants are available in the literature[33,34]. The evaluation of the molecular orbital coefficients using the complete treatment is not feasible due to the uncertainties involving the assignments of the electronic spectra as well as the marked distortion from D_{2h} symmetry afforted by the zinc and cadmium host lattices. The parameter a can be evaluated using the expression[35]

$$a^2 = \frac{-A_{11}}{P} + (g_{11} - 2.0023) + \frac{3}{7}(g_{11} - 2.0023) + 0.04) \quad (3)$$

where P is the free ion dipolar term proportional to $<^1 1/r^3>$ and is taken to have the value 0.036 cm^{-1}. A value of a^2 which reflects the covalency of metal-ligand bonding can thus be obtained without knowledge of "$d-d$" excitation energies. Kuska and Rogers[36] have indicated that the expression

$$a^2 = \frac{7}{4}|\frac{|A_{11}|}{P} - \frac{|A_0|}{P} + \frac{2}{3}g_{11} - \frac{5}{21}g_+ - \frac{6}{7} \quad (4)$$

where A_0 is the isotropic nuclear hyperfine coupling constant, gives a better measure of metal-ligand covalency. This latter expression was employed in evaluating the a^2 parameters listed in Table 2. It is noted that the a^2 values in Table 2 cannot be used as a direct measure of metal-ligand covalency since the symmetry of the CuS_4 chromophore in each of the lattices is slightly different. The a^2 values are primarily influenced by two factors, $3d-4s$, and $3d-4p$ orbital mixing and change in the group orbital overlap. S. Bates et al.[37] performed a theoretical study of the Cu(II) ion in a tetrahedral ligand field and suggested admixture of the $4p_z$ level into the $3d$ ground state. In order to explain the reverse order of covalency for a series of copper(II) m-diketonates found by physical methods other than EPR spectroscopy, Kuska et al.[38] proposed $4s$ mixing into the $3d$ ground state. Weeks and Fackler[39] proposed $4s$ mixing into the ground state to account for lattice effects on the EPR spectrum of $Cu(dtc)_2$. Distortion of the CuS_4 chromophore to symmetries lower than D_{2h} brings about an A_1 or A ground state containing both metal d- and s-orbitals, i.e., direct participation of the metal $4s$ orbital in the ground state. If it is assumed that changes in a^2 values are caused by $3d-4s$ mixing the preceding equation can be written

$$a^2 f^2 = \frac{7}{4}|\frac{A_{11}}{P} - \frac{|A_0|}{P} + \frac{2}{3}g_{11} - \frac{5}{21}g_+ - \frac{6}{7}| \quad (5)$$

where f^2 is the fraction of $3d$ character in the ground state. Assuming $f^2 = 1$ for the $Ni(acdc)_2$ host lattice, f^2 values for the other host lattices were evaluated (Table 2) and found to follow the same sequence Zn Hg Cd Ni as the a^2 values. On the basis of ionic radii[40] (Ni(II) = 0.68 Å, Cu(II) = 0.72 Å, Zn(II) = 0.74 Å, Cd(II) = 0.97 Å, and Hg(II) = 1.10 Å) the group overlap contribution to the metal-ligand covalency might crudely be expected to follow the sequence Hg<Cd< Zn<Ni when the copper compound is accommodated into the respective lattices.

Structural data cited above suggest the importance of orbital mixing of EPR parameters for $Cu(N-CH_3$ acdc$)_2$. However, no quantitative assessment of the relative contributions of orbital mixing and group overlap to EPR parameters is possible at the present time. The orbital mixing brought about by distortion of a complex in a host lattice may be counterbalanced by bond covalency effects[41]. In the absence of detailed single crystal studies it is pointless to try to discuss the relative importance of s- or p-orbital mixing into the ground state.

Although the results of the present study do not yield startling revelations, they do emphasize the genuine need for further studies of lattice effects on EPR spectra of molecular solids. It can be anticipated that investigations of this type will be of great importance to biochemical problems since rather subtle changes in molecular geometry can have enor-

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Table 3. ESR Data for $Cu(N-CH_3 \ acdc)_2$ and $CuN_{(4-n)}Sn$ Chromophores[a]

Parameter	CuS_4	$Cu(N-CH_3 \ acdc)$[b]	CuN_2S_2	CuN_4
g_o	2.042~2.045	2.043	2.040~2.061	2.090~2.108
$A_o \times 10^{-4} cm^{-1}$	75~82	76	90	84~102
g_{11}	2.082~2.087	2.088	2.160~2.129	2.169~2.177
g	2.023~2.035	2.020	2.020~2.060	2.054~2.067
$A_{11} \times 10^{-4} cm^{-1}$	145~165	156	187~193	202~218
$A \times 10^{-4} cm^{-1}$	37~51	36	45	14~16

[a]Data for CuS_4, CuN_2S_2 and CuN_4 chromorhare were collecteal from the references cited in the text. [b]Copper(II) ion was doped into Ni(N-CH3 acdc)2.

mous effects on biological functions of compounds.

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