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ESR Study of ^{63}Cu(II) Doped in Single Crystals of Bis(alkyl 3-alkylidenedithiocarbazato)nickel(II) and -zinc(II). II. Proton Hyperfine Structure and Tetrahedral Distortion

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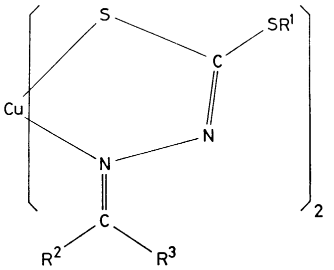
The ESR spectra of ^{63}Cu(II) diluted in several single crystals of the title Ni(II) and Zn(II) complexes are reported. In the substituted benzylidene groups, hyperfine structure(hfs) due to the magnetically equivalent two protons have been observed. The hfs were resolvable only in a limited magnetic direction due to the small anisotropic coupling constants. The coordination around Cu(II) ion has been found to be *cis* in all the Zn(II) complexes and the ESR parameters are more anisotropic than in the Ni(II) complexes. The relationship between the tetrahedral distortion and the ESR parameters has been interpreted using the d-orbital coefficients in the ground state.

There have been a number of theoretical studies on tetrahedral distortion around copper(II) centers and extensive ESR studies on the solid state system.[1-9] The tendency for $g_{\parallel}$ to increase and $|A_{\parallel}|$ to decrease with increasing tetrahedral distortion has been reported for well-characterized complexes of copper(II) with *N*-salicylidenealkylamine,[10,11] bis(pyrazolyl)gallates,[12] and dipyrromethenates.[13] Yokoi and Addision[14] reported the ESR measurements of several bis(*N*-substituted 2-pyrrolylmethyleneaminato)copper(II) complexes in toluene and concluded that the small value of $|A_0|$ is due to the large positive value of $A_{\perp}$ by tetrahedral distortion. Bates explained the small hf coupling constants on the basis of 3d^{8}4p mixing in the 3d^9 configuration.[4]

The ESR parameters of the Cu(II) site which is tetrahedrally distorted from *cis*-CuN$_2$S$_2$ planar symmetry has been discussed in a previous report.[15] The Schiff bases derived from alkyl dithiocarbazate were found to form a series of ligands,[16-19] whose properties were greatly modified by the introduction of organic substituents into the ligand thereby inducing different stereochemistry in the resultant metal complexes. The relationship between the ESR parameters and tetrahedral distortion around the Cu(II) ion site have been investigated by measuring the ESR spectra for ^{63}Cu(II) diluted with Zn(II) complexes in place of the Ni(II) complexes which have a *S*-methyl group, and with the Ni(II) complexes which possess a *S*-benzyl group. In either case the tetrahedral distortion is expected to be larger than in Ni(II) complexes with a *S*-methyl group.

In the first report the ESR spectra of Cu(II)/Ni(bdc)$_2$ exhibited additional hfs. The additional hfs are assignable to two azomethine protons or to noncoordinated nitrogen, in order to establish which was the case the ESR spectra of ^{63}Cu(II) diluted in Zn(II) and in Ni(II) complexes with Schiff bases which have azomethine protons were measured. Figure 1 shows the structures of the host complexes used. The alkyl and alkylidene groups denote methyl and 1-phenylethylidene, methyl and 1-(*p*-tolyl)ethylidene, methyl and *o*-tolylidene, methyl and *m*-tolylidene, methyl and *o*-chlorobenzylidene, benzyl and 1-(2-naphthyl)ethylidene, benzyl and 1-(*p*-tolyl)ethylidene, and benzyl and 1-phenylethylidene, and the corresponding ligands have been abbreviated as pedcH, tedcH, omdcH, mmdcH, ocdcH, bndcH, btdcH, and bpdcH respectively.



R^1	R^2	R^3	*cis*	*trans*
methyl	−H	*o*-tolyl	Zn(omdc)$_2$	Ni(omdc)$_2$
methyl	−H	*m*-tolyl		Ni(mmdc)$_2$
methyl	−H	*o*-chloro-phenyl	Ni(ocdc)$_2$	
methyl	methyl	phenyl	Zn(pedc)$_2$	
methyl	methyl	*p*-tolyl	Zn(tedc)$_2$	
benzyl	methyl	2-naphthyl	Ni(bndc)$_2$	
benzyl	methyl	*p*-tolyl	Ni(btdc)$_2$	
benzyl	methyl	phenyl	Ni(bpdc)$_2$	

Fig. 1. The structures of the host complexes used; bis(alkyl 3-alkylidenedithiocarbazato)nickel(II) or -zinc(II), and abbreviations which are classified into *cis* or *trans* form around copper(II) ion site.

Experimental

The complexes were prepared according to the methods of cited in the literature.[16,17] The ESR spectra were recorded every 5° or 10° around three mutually perpendicular rotational axes. The most elongated axis was defined as the 2-axis, and the broadest crystal face was defined as the 12-plane. The room temperature ESR spectra were taken on a JEOL ME 1X spectrometer at the X band. A frequency counter, Mn(II) diluted with MgO, and DPPH were used as the g marker. The second order effects of the ESR spectra were calculated by the method of Iwasaki.[20] The forbidden transitions could not be obtained, so that no attempt was made to determine the quadrupole coupling parameters. The calculations were performed on an Olivetti P 652 computer.

Results and Discussion

Proton Hyperfine Structures. The four complexes with the ligands which have azometihne protons were

Table 1. The ESR parameters for Cu(II) complexes containing azomethine protons. The principal elements of $A(^{63}\text{Cu})$ and A^{N} are in units of $10^{-4}\ \text{cm}^{-1}$

Host	Principal values	Direction cosines		
		1	2	3
Ni(omdc)$_2$	$g_x=2.021\,(1)$	0.82	±0.16	−0.56
(*trans*)	$g_y=2.044\,(1)$	0.13	∓0.99	−0.09
	$g_z=2.129\,(1)$	0.56	±0.01	0.83
	$A_x=26\,(3)$	0.82	±0.13	−0.56
	$A_y=37\,(3)$	0.12	∓0.99	−0.06
	$A_z=175\,(1)$	0.57	±0.02	0.83
	$A^{\text{N}}{}_x=19.6\,(5)$	0.82	0.08	−0.56
	$A^{\text{N}}{}_y=A^{\text{N}}{}_z=15.6\,(8)$			
	$A^{\text{H}}{}_{\text{max}}=3$ G			
Ni(mmdc)$_2$	$g_x=2.024\,(1)$	−0.13	0.99	0
(*trans*)	$g_y=2.045\,(1)$	0.02	−0.11	0.99
	$g_z=2.139\,(1)$	0.99	0.13	−0.01
	$A_x=22\,(3)$	−0.13	0.99	0
	$A_y=32\,(3)$	0	0	1
	$A_z=176\,(1)$	0.99	0.13	0
	$A^{\text{N}}{}_x=18.9\,(5)$	−0.09	0.99	0.12
	$A^{\text{N}}{}_y=A^{\text{N}}{}_z=15.0\,(8)$			
	$A^{\text{H}}{}_{\text{max}}=3$ G			
Zn(omdc)$_2$	$g_x=2.030\,(1)$	0.97	0.02	0.26
(*cis*)		−0.39	−0.10	−0.92
	$g_y=2.150\,(1)$	−0.24	−0.31	0.92
		0.88	0.25	−0.40
	$g_z=2.037\,(1)$	−0.10	0.95	0.30
		0.27	−0.96	−0.01
	$A_x=17\,(5)$	0.91	0.34	0.24
		−0.23	−0.40	−0.89
	$A_y=137\,(1)$	−0.15	−0.27	0.95
		0.93	0.20	−0.33
	$A_z=32\,(5)$	−0.39	0.90	0.19
		0.30	−0.90	0.33
	$A^{\text{N}}=7$—9			
	$A^{\text{H}}{}_{\text{max}}=6$ G			
Ni(ocdc)$_2$	$g_x=2.027\,(1)$	0.91	0.32	0.26
(*cis*)	$g_y=2.125\,(1)$	−0.34	0.94	0.04
	$g_z=2.031\,(1)$	−0.23	−0.13	0.96
	$A_x=28\,(4)$	0.93	0.28	0.22
	$A_y=167\,(1)$	−0.29	0.96	0.03
	$A_z=35\,(4)$	−0.20	−0.09	0.97
	$A^{\text{N}}=9.5$—11.6			
	$A^{\text{H}}{}_{\text{max}}=4$ G			

obtained. Table 1 shows the obtained ESR parameters and direction cosines against 1, 2, and 3 axes. In all the complexes, additional hfs were observed. Figure 2 shows well resolved extra hfs which consist of three lines with an intensity ratio of 1:2:1. It was concluded, that the extra hfs are due to two azomethine protons. The proton hfs were anisotropic and small, and well resolved only in the limited magnetic direction. Table 1 shows, therefore, only the maximum coupling constants(G). The proton hfs were observed in the cases of bis(salicylideneaminato)copper(II),[21] *N*,*N*-bis(2-pyrrolylmethylene)ethylenediaminatocopper(II),[22] Cu(II) doped in L-alanine,[23] and measured in great detail by ENDOR in the case of bis(salicylaldehyde oximato)copper(II).[24] In the present work the proton hfs are observable even if the proton is binded to a carbon atom which is not in the chelate ring.

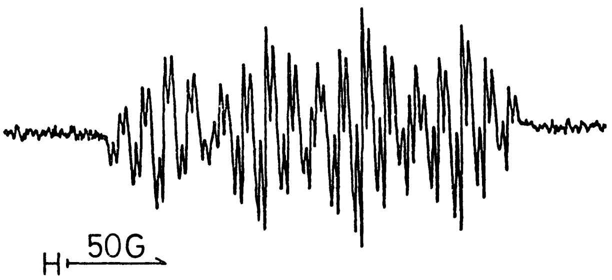


Fig. 2. The well resolved single crystal ESR spectra of ^{63}Cu(II)/Ni(ocdc)$_2$. The proton hfs is well resolved at high field with the intensity ratio of 1:2:1, $(\theta, \varphi)=(15°,0°)$, where θ and φ is the angles in the spherical 123 coordinate.

A methanolic solution of omdcH and copper acetate is deep-green at low temperature, but in a short time, the solution changes in color from deep-green to reddish-brown. Only reddish-brown crystals of Cu(omdc)$_2$ were obtained and readily doped in Ni(omdc)$_2$. Cu(omdc)$_2$, synthesized in the presence of zinc acetate at low temperature, enables the deep-green Cu(omdc)$_2$ to be doped in Zn(omdc)$_2$. In a series of copper(II) complexes, the color is deep-green in the *cis* coordination and reddish-brown in the *trans* coordination. The ESR spectra of deep-green ^{63}Cu(II)/Zn(omdc)$_2$ shows the presence of two magnetically non-equivalent nitrogen hfs in the limited magnetic direction, and small nitrogen hf coupling constants. These results suggest that the coordination around the Cu(II) ion in Zn(omdc)$_2$ is of a *cis* configuration.[15] Cu(bdc)$_2$ and Cu(mmdc)$_2$ are also deep-green in the preparation at low temperature, but the deep-green Cu(II) doped Zn(II) complexes were not obtained due to the inability of achieving single crystals of the Zn(II) complexes at low temperature.

Tetrahedral Distortion. Table 2 shows the ESR parameters of ^{63}Cu(II) in Zn(II) complexes and in the Ni(II) complexes with *S*-benzyl groups. In all the complexes of Table 2, the coordination around the Cu(II) ion was found to be of a *cis* configuration from the same reasoning as described in the case of ^{63}Cu(II)/Zn(omdc)$_2$. The nitrogen hf coupling constants could not be determined accurately for the *cis* coordination since the magnetically non-equivalent nitrogen hfs were well resolved only in the limited magnetic direction along one of the Cu–N axes.

The ESR parameters are more rhombic in the *cis* complexes than in the *S*-methyl containing Ni(II) complexes.[15] The anisotropies of the ESR parameters are probably due to the tetrahedral distortion of the host complexes.

Calculation of d-Orbital Mixing. The electronic spectra of the Cu(II) complexes consist of very strong charge transfer bands, the single d-d transition band being detected in the region 500—650 nm. This band has been tentatively assigned to the $d_{zx}\rightarrow d_{z^2}$ or $d_{zx}\rightarrow d_{x^2-y^2}$ transition for *cis* complexes. The ESR param-

TABLE 2. THE ESR PARAMETERS FOR Cu(II) COMPLEXES WHICH DO NOT CONTAIN AZOMETHINE PROTONS

Host	Principal values	Direction cosines		
		1	2	3
$Ni(bpdc)_2$ (*cis*)	$g_x=2.032(1)$	0.92	0.34	−0.17
	$g_y=2.148(1)$	0.18	0.01	0.98
	$g_z=2.033(1)$	−0.34	0.94	0.05
	$A_x=21(4)$	0.79	0.58	−0.20
	$A_y=152(1)$	0.25	0.01	0.97
	$A_z=27(4)$	−0.56	0.82	0.15
	$A^N=9.3$—11.8			
$Ni(btdc)_2$ (*cis*)	$g_x=2.030(1)$	0.21	0.93	−0.30
	$g_y=2.141(1)$	0.01	0.31	0.95
	$g_z=2.032(1)$	0.98	−0.20	0.06
	$A_x=24(4)$	0.23	0.89	−0.39
	$A_y=143(1)$	0.01	0.41	0.91
	$A_z=25(4)$	0.97	−0.21	0.10
	$A^N=7.0$—9.1			
$Ni(bndc)_2$ (*cis*)	$g_x=2.029(1)$	−0.25	−0.01	0.97
	$g_y=2.140(1)$	0.96	0.13	0.25
	$g_z=2.032(1)$	−0.13	0.99	−0.03
	$A_x=23(4)$	−0.28	−0.19	0.94
	$A_y=159(1)$	0.95	0.10	0.31
	$A_z=31(4)$	−0.16	0.98	0.15
	$A^N=9.5$—11.7			
$Zn(tedc)_2$ (*cis*)	$g_x=2.031(1)$	0.91	−0.31	−0.29
		0.70	0.30	−0.65
	$g_y=2.153(1)$	0.25	−0.15	0.96
		−0.71	0.17	0.68
	$g_z=2.037(1)$	0.34	0.94	0.06
		0.09	−0.94	−0.34
	$A_x=19(4)$	0.92	−0.16	−0.36
		0.62	0.66	−0.41
	$A_y=140(1)$	0.35	−0.12	0.93
		−0.64	0.13	−0.75
	$A_z=26(4)$	0.19	0.98	0.06
		0.45	−0.74	−0.51
	$A^N=7.7$—9.8			
$Zn(pedc)_2$ (*cis*)	$g_x=2.032(1)$	0.74	0.38	0.55
		−0.72	−0.46	0.52
	$g_y=2.154(1)$	0.54	0.14	−0.83
		0.66	−0.19	0.73
	$g_z=2.037(1)$	−0.40	0.91	−0.10
		0.24	−0.87	−0.44
	$A_x=17(4)$	0.52	0.68	0.51
		−0.66	−0.45	0.60
	$A_y=138(1)$	0.63	0.10	−0.77
		0.73	−0.16	0.67
	$A_z=24(4)$	−0.58	0.72	−0.38
		0.21	−0.88	−0.44
	$A^N=7.8$—9.8			

eters could not be completely determined from only this band. The d-orbital coefficients of the ground-state were then determined from the observed ESR parameters.[25] The ground state function for *trans* coordination is given by,[15]

$$\Phi^\alpha = a|x^2-y^2\rangle^\alpha + b|z^2\rangle^\alpha + ic|xy\rangle^\alpha - id|yz\rangle^\beta + e|zx\rangle^\beta, \tag{1}$$

and for *cis* coordination by,

$$\Phi^\alpha = a|zx\rangle^\alpha + ib|yz\rangle^\alpha + c|z^2\rangle^\beta - d|x^2-y^2\rangle^\beta - ie|xy\rangle^\beta. \tag{2}$$

Table 3 shows the coefficients obtained from Eqs. 1 or 2. Changing the x and z directions produces a larger value of d than c. It is uncertain from only the ESR data whether the axis should be assigned as x or z.

The copper hf coupling constants for the *trans* coordination have the same sign which are in reasonable agreement with the ESR spectra of chloroform solutions (83—86 G). The situation around the Cu(II) ion in chloroform solution is not the same as in the Zn(II) complexes. The ESR spectra of chloroform solutions supports the finding that the copper hf coupling constants are the same sign in *cis* Ni(II) complexes (64—72 G). It is reasonable to assume that the copper hf coupling constants are also the same sign in the Zn(II) complexes.

Figure 3 shows the variations of copper hf coupling constants against the values of c/d. The d-orbital coefficients satisfy the observed g values in all regions of c/d values. The acceptable region which satisfies the copper hf coupling constants is in the narrow range of c/d values. McGregor and Hatfield[26] measured the ESR spectra of bis(2,2′-bipyridyl)thioureacopper(II) perchlorate and determined the d-orbital coefficients only from the g values. The copper hf coupling constants could not be obtained from the single crystal. The method of Swalen *et al.*[25] cannot be applied when the copper hf coupling constants are not obtained, if there is no strong evidence for a relationship between the d-orbital coefficients.

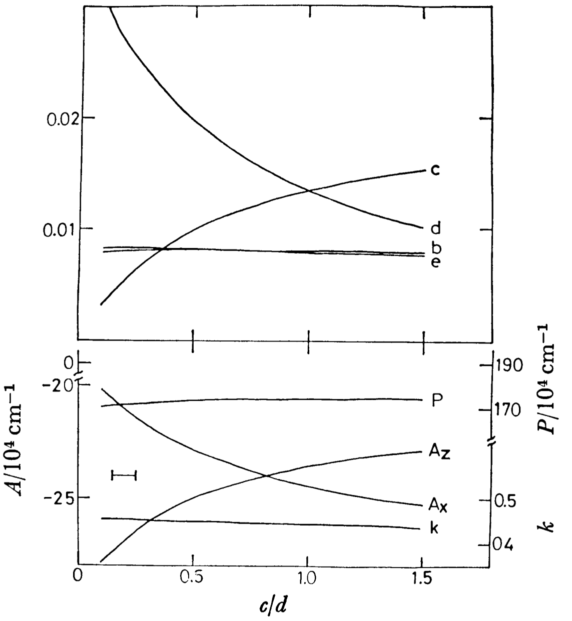


Fig. 3. The example of calculations for $^{63}Cu(II)/Ni(bpdc)_2$; the coefficients of the Kramers doublet (top) and the hf parameters(bottom) *vs.* c/d; the value of A_y is fixed to -152×10^{-4} cm^{-1}, and the value of a is almost constant at 0.99975 in all the c/d values; the acceptable regions are indicated.

Table 3. The best values for the d-orbital coefficients and calculated hyperfine coupling constants (10^{-4} cm^{-1})

Host		*a*	*b*	*c*	*d*	*e*	*k*	*P*	A_x	A_y	A_z
Ni(omdc)$_2$	(*trans*)	0.9991	−0.0379	0.0159	0.0055	0.0099	0.471	194	−26	−37	−175
Ni(mmdc)$_2$	(*trans*)	0.9990	−0.0391	0.0173	0.0061	0.0104	0.445	204	−22	−32	−176
Zn(omdc)$_2$	(*cis*)	0.9992	0.0095	0.0010	0.0362	0.0087	0.450	160	−17	−137	−26
Ni(ocdc)$_2$	(*cis*)	0.9996	0.0076	0.0026	0.0263	0.0071	0.482	182	−28	−167	−35
Ni(bpdc)$_2$	(*cis*)	0.9996	0.0079	0.0072	0.0241	0.0082	0.447	177	−21	−152	−27
Ni(btdc)$_2$	(*cis*)	0.9998	0.0077	0.0125	0.0132	0.0074	0.462	162	−24	−143	−25
Ni(bndc)$_2$	(*cis*)	0.9995	0.0079	0.0029	0.0295	0.0078	0.461	181	−23	−159	−31
Zn(tedc)$_2$	(*cis*)	0.9994	0.0093	0.0032	0.0324	0.0086	0.454	163	−19	−140	−26
Ni(tedc)$_2$[a]	(*cis*)	0.9997	0.0081	0.0097	0.0162	0.0076	0.505	163	−32	−155	−33
Zn(pedc)$_2$	(*cis*)	0.9995	0.0091	0.0045	0.0303	0.0086	0.439	164	−17	−138	−24
Ni(pedc)$_2$[a]	(*cis*)	0.9998	0.0081	0.0096	0.0160	0.0078	0.507	167	−33	−159	−34

a) From Ref. 15.

Table 4. The bonding parameters obtained from Eqs. 3 and 4 and *P* values (10^{-4} cm^{-1})

Host		$N\alpha_1^2$	$N\alpha_2^2$	$N\alpha_4^2$ or $N\alpha_3^2$	*P*
Ni(omdc)$_2$	(*trans*)	0.061	0.157	0.306	194
Ni(mmdc)$_2$	(*trans*)	0.059	0.153	0.310	204
Zn(omdc)$_2$	(*cis*)	0.028	0.078	0.672	150
Ni(ocdc)$_2$	(*cis*)	0.037	0.082	0.678	182
Ni(bpdc)$_2$	(*cis*)	0.037	0.098	0.680	177
Ni(btdc)$_2$	(*cis*)	0.028	0.082	0.684	162
Ni(bndc)$_2$	(*cis*)	0.037	0.086	0.687	181
Zn(tedc)$_2$	(*cis*)	0.030	0.082	0.681	163
Zn(pedc)$_2$	(*cis*)	0.031	0.078	0.671	164

In the *cis*-CuN_2S_2 planar symmetry, the d_{zx} orbital is in the ground state, and the coefficient *b* is a function of the spin orbital coupling and pure $d_{zx} \rightarrow d_{yz}$ energy separation.

In the case of a small tetrahedral distortion, a mixture of the d_{zx} and d_{yz} orbitals become the ground state, and the excited d_{xy}, $d_{x^2-y^2}$, and d_{z^2} orbitals are mixed in the same manner. A spin orbit interaction also occurs between the d_{yz} and other d orbitals, and the ESR parameters cannot be determined solely from one d-d transition. Assuming the $d_{zx} \rightarrow d_{yz}$ energy separation does not vary from complex to complex, the value of $(b/a)^2$ gives a measure of the degree of tetrahedral distortion since the value of $|b|$ increases with increasing tetrahedral distortion. The increase of $|b|$ values is observed in the case of Zn(II) complexes as may be seen from Table 3.

The copper hf coupling constants in Zn(II) complexes are smaller than in other complexes a result in agreement with that found by Yokoi and Addison.[14] The values of A_x and A_z, however, are negative since the distortion is not so large.

The molecular orbital of an unpaired electron in the *cis* coordination is given by,

$$\begin{aligned}|zx\rangle = N^{1/2}[&d_{zx}-(\alpha_1/\sqrt{2})(s^1-s^2)-(\alpha_2/2)\\ &\times(-p_x^1-p_x^2-p_z^1+p_z^2)-(\alpha_3/\sqrt{2})\\ &\times(-s^3+s^4)-(\alpha_4/2)(p_x^3+p_x^4-p_z^3+p_z^4)],\end{aligned} \tag{3}$$

and in the *trans* coordination by,

$$\begin{aligned}|A_{1g}\rangle = N^{1/2}[&d_{x^2-y^2}+(b/a)d_{z^2}-(\alpha_1/\sqrt{2})(s^1+s^2)\\ &-(\alpha_2/\sqrt{2})(-p_x^1+p_x^2)-(\alpha_3/\sqrt{2})(p_y^3-p_y^4)].\end{aligned} \tag{4}$$

The bonding parameters of $N\alpha_1^2$, $N\alpha_2^2$, and $N\alpha_4^2$ in Eq. 3, and of $N\alpha_1^2$, $N\alpha_2^2$, and $N\alpha_3^2$ in Eq. 4 were obtained as in the first report and are shown in Table 4. The normalization constants *N* have been assumed to be 0.7 in either case. The small A^N values and large $N\alpha_4^2$ values in the *cis* coordination are explainable as follows. In *cis* coordination, the Cu–N bond length is longer than in *trans* coordination because of steric repulsion by the large phenyl group. The Cu–S bond length on the other hand is shorter than in a *trans* coordination since there is no such repulsion. A similar situation occurs in the case of bis(thiosemicarbazide)nickel sulfate.[27]

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