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ENDOR SPECTRA OF Cu(SALEN) IN Ni(SALEN) SINGLE CRYSTALS

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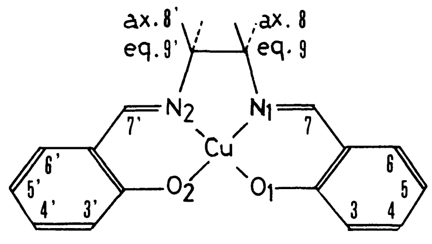
It is shown from the observation of the ligand hf interaction that the Cu-N bond in N,N'-ethylenebis(salicylideneiminato)copper(II) may have stronger covalency than that of bis(salicylaldoximato)copper(II) and bis(N-methylsalicylaldiminato)copper(II) which have the trans N-Cu-N configuration, while the Cu-O in the former complex may have weaker covalency than that in the latter complexes. The presence of correlation between the orbital population on the coordinating atoms and spin distribution in the ligands is also suggested.

N,N'-Ethylenebis(salicylideneiminato)copper(II), Cu(salen), in a single crystal form doped in N,N'-ethylenebis(salicylideneiminato)nickel(II), Ni(salen), has been examined by the ENDOR spectroscopy. The single crystal of Ni(salen) containing approximately 0.5 % Cu(salen) was used for ENDOR measurements. The Ni(salen) crystal is orthorhombic with the space group Pbca, containing eight molecules per unit cell and centrosymmetric dimers form the structure.[1)] The ENDOR spectra and its angular dependence were measured at 10 ~ 20K. The angular dependence was analyzed by the equations:[2)]



Cu(salen)

$$h\nu^{N}(M_S,M_I-M_{I-1}) = \left| K^{N}M_S + \frac{3}{2}(\hat{\mathbf{k}}^{N}\cdot\mathbf{Q}\cdot\mathbf{k}^{N})(2M_I-1) - g_N\beta_N H(\hat{\mathbf{k}}^{N}\cdot h)\right|$$

for nitrogen nuclei and

$$h\nu^{H}(M_S) = K^{H}(M_S) - \frac{\det \mathbf{A}^{H}}{4g\beta HK^{H}(M_S)}[M_S-g_H\beta_n H(\tilde{\mathbf{h}}\cdot\tilde{\mathbf{g}}\cdot(\mathbf{A}^{H})^{-1}\cdot\mathbf{h})/g] + \frac{1}{2g\beta H}P^{H,Cu}M_S M_I{}^{Cu}$$

for proton, where

$$g^2 = \tilde{\mathbf{h}}\cdot\tilde{\mathbf{g}}\cdot\mathbf{g}\cdot\mathbf{h},\quad \mathbf{k}^N = \mathbf{A}^N\cdot\mathbf{g}\cdot\mathbf{h}/gK^N,\quad g^2(K^N)^2 = \tilde{\mathbf{h}}\cdot\tilde{\mathbf{g}}\cdot\tilde{\mathbf{A}}^N\cdot\mathbf{A}^N\cdot\mathbf{g}\cdot\mathbf{h},\quad g^2(K^{Cu})^2 = \tilde{\mathbf{h}}\cdot\tilde{\mathbf{g}}\cdot\tilde{\mathbf{A}}^{Cu}\cdot\mathbf{A}^{Cu}\cdot\mathbf{g}\cdot\mathbf{h},$$

$$(K^H(M_S))^2 = \tilde{\mathbf{K}}^H(M_S)\cdot\mathbf{K}^H(M_S) = \tilde{\mathbf{h}}\cdot[(\tilde{\mathbf{g}}\cdot\mathbf{A}^H/g)M_S - g_H\beta_n H\mathbf{E}]\cdot[(\mathbf{A}^H\cdot\mathbf{g}/g)M_S - g_H\beta_n H\mathbf{E}]\cdot\mathbf{h}$$

$$gK^{Cu}K^H(M_S)P^{H,Cu} = \tilde{\mathbf{h}}\cdot\tilde{\mathbf{g}}\cdot(\tilde{\mathbf{A}}^{Cu}\cdot\tilde{\mathbf{A}}^{Cu}\cdot\tilde{\mathbf{g}}^{-1}\cdot\tilde{\mathbf{K}}^H(M_S)\cdot\tilde{\mathbf{A}}^H + g^{-1}\cdot\mathbf{K}^H(M_S)\cdot\mathbf{A}^H\cdot\mathbf{A}^{Cu}\cdot\mathbf{A}^{Cu})\cdot\mathbf{g}\cdot\mathbf{h}$$
$$- 2(K^{Cu})^2(\tilde{\mathbf{h}}\cdot\tilde{\mathbf{K}}^H(M_S)\cdot\mathbf{A}^H\cdot\mathbf{g}\cdot\mathbf{h}).$$

In the equation for $h\nu^H$, the second order correction is included by taking into account the fact that the copper nuclei couples more strongly with the unpaired electron than the other nuclei in the ligand. For nitrogen the second order correction was not included because precise evaluation of the effects beyond experimental errors was difficult in the present system.

The eight proton hf couplings within the molecule and the five proton couplings due to the neighbor molecules were determined. As the principal axes of the proton hf couplings are considered to orient to the Cu-H directions, assignment of the observed proton hf couplings was made by comparison of their direction cosines with those of the Cu-H vectors calculated from the crystallographic data.$^{1)}$ The Cu-H distances calculated from the observed anisotropic dipolar couplings are in well agreement with the crystallographic data. The hf coupling data on the intramolecular protons are listed in Table 1, together with the hf coupling parameters for nitrogen nuclei.

The nitrogen hf couplings arise from three sources, i.e., the isotropic coupling, and the anisotropic coupling due to the interaction with the unpaired electron on the copper(II) ion and the nitrogen

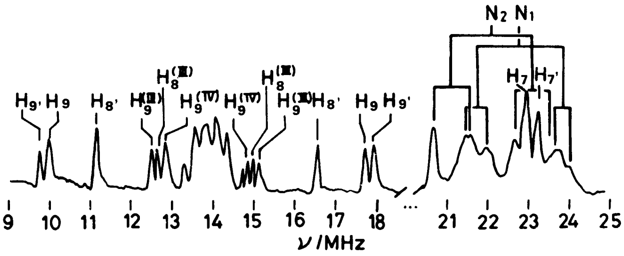


Fig. 1. ENDOR spectrum obtained with the magnetic field parallel to the *a* axis. The signals due to the extramolecular protons are indicated by the symbol with number in a parenthesis.

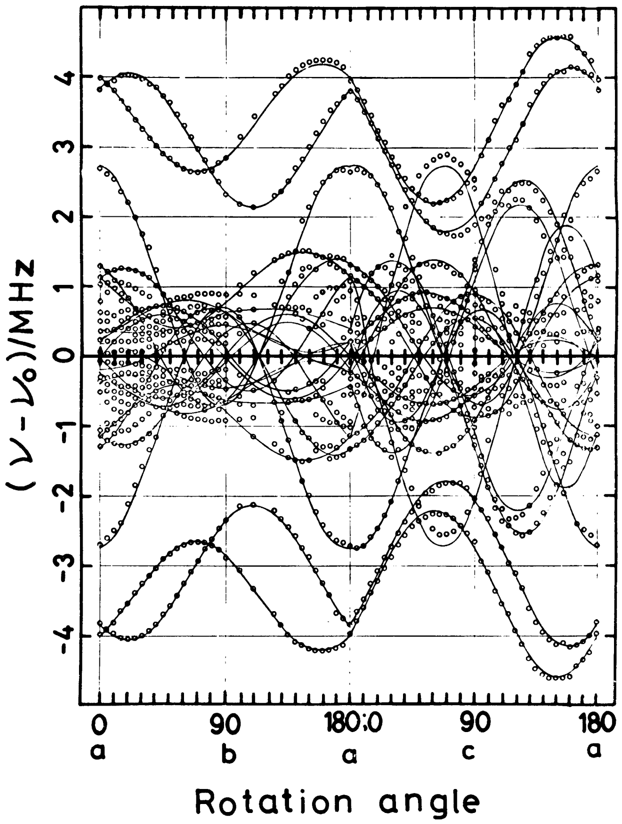


Fig. 2. Angular dependence of the proton ENDOR signals which appeared near the free proton frequency region.

Table 1. Hf Coupling Parameters of Intramolecular Protons and Nitrogen Nuclei

	Positions	Principal values(MHz)			a_{iso}	Direction cosines of A_1			Direction cosines of Cu-H or Cu-N *1			r(Å)	
		A_1	A_2	A_3	(MHz)	1a	1b	1c	1a	1b	1c	(ENDOR)	(cryst.data)
A^H	7	22.80	19.35	18.43	20.22	0.372	0.890	-0.264	0.465	0.817	-0.341	3.97	3.78
	7'	23.62	19.45	18.64	20.57	0.397	-0.877	-0.272	0.489	-0.827	-0.279	3.76	3.73
	3	1.77	-1.34	-1.87	-0.48	-0.639	0.614	0.464	-0.640	0.655	0.402	4.16	4.43
	3'	1.84	-1.26	-1.39	-0.27	-0.648	-0.633	0.423	-0.637	-0.650	0.414	4.25	4.42
	8	5.13	-0.90	-3.47	0.76	0.582	0.002	-0.813	0.655	0.171	-0.736	3.37	3.36
	9	8.74	4.29	3.56	5.53	0.890	0.316	-0.330	0.873	0.340	-0.349	3.71	3.69
	8'	9.57	5.32	4.40	6.43	0.833	-0.304	-0.463	0.840	-0.364	-0.402	3.74	3.67
	9'	5.54	-1.41	-1.43	0.90	0.996	-0.055	0.075	0.980	-0.190	0.024	3.30	3.19
A^{N*2}	1	49.9	37.2	38.7	41.9	0.729	0.583	-0.359	0.637	0.664	-0.393		
	2	51.5	37.0	39.1	42.5	0.706	-0.600	-0.377	0.674	-0.681	-0.288		

*1: Crystallographic data. *2: The direction of 1 is nearly directed to the copper ion and 2 is nearly normal to the molecular plane.

2p orbitals. The second one was obtained by calculation using the following equations and assuming the unpaired electron population of 0.8 on the copper(II) ion.

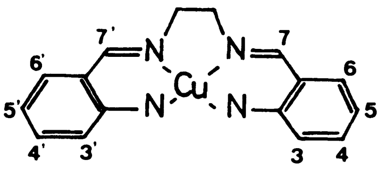
$$A^N_{d,1} = (2P/a^3)[1 + 6/7(\langle r^2\rangle/a^2)], \qquad A^N_{d,2} = -(P/a^3)[1 + 3/7(\langle r^2\rangle/a^2)],$$

$$A^N_{d,3} = -(P/a^3)[1 + 9/7(\langle r^2\rangle/a^2)], \qquad P = g\beta g_N\beta_n h^{-1},$$

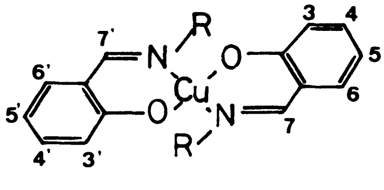
From the isotropic and anisotropic couplings with the delocalized unpaired electron on the nitrogen, the unpaired electron population on the nitrogen orbitals was determined. The results are listed in Table 2, together with those for N,N'-ethylenebis(*o*-aminobenzylideneiminato)copper(II), Cu(amben),[3] bis(N-methylsalicylaldiminato) copper(II), Cu(Nmesal)$_2$,[4] and bis(salicylaldoximato)copper(II), Cu(saloxm)$_2$,[5] obtained in the similar manner. It is seen that the unpaired electron population, f_s and $f_{p,1}$, on the nitrogen 2s and 2p orbitals as well as the s/p ratios vary appreci-

Table 2. Unpaired Electron Population on the Nitrogen Orbitals

Complexes	f_s	$f_{p,1}$	$f_{p,2}$	$f_{p,3}$	$f_s/f_{p,1}$		$f_s + f_{p,1}$	$a_{iso}(H_7)$
					(ENDOR or ESR)	(cryst.data)		(MHz)
Cu(salen)	0.027	0.075	0.0	0.012	0.36	0.41	0.102	20.22
	0.028	0.081	0.0	0.014	0.34	0.31	0.109	20.57
Cu(amben)	0.031	0.078	—	—	0.40	—	0.109	17
Cu(Nmesal)$_2$	0.025	0.06	—	—	0.42	—	0.085	14
Cu(saloxm)$_2$	0.031	0.051	0.0	0.012	0.60	0.66	0.082	10.17



Cu(amben),



R = Me:Cu(Nmesal)$_2$
R = OH:Cu(saloxm)$_2$

ably with the complexes.

These s/p ratios well coincide with the s/p ratios of the nitrogen lone-pair orbital calculated based on the crystallographic data (Table 2). Interestingly, both these observed s/p ratios and the spin densities on the nitrogen 2p orbital, $f_{p,1}$, have well correlation with the isotropic proton coupling constants at 7 and 7' positions in the copper complexes, i.e., the smaller $f_s/f_{p,1}$ is the larger $a_{iso}(H_7)$ is, and the larger $f_{p,1}$ is the larger $a_{iso}(H_7)$ is.

It is valuable to note further that the arrangement of the coordinating nitrogen and oxygen atoms affects appreciably the spin distribution in the ligands. It is seen from Table 2 that the in-plane σ orbitals of the nitrogen atoms in Cu(salen) have larger spin densities than those of $Cu(Nmesal)_2$ and $Cu(saloxm)_2$ which have trans N-Cu-N configuration. The protons at 7 position in $Cu(Nmesal)_2$ and $Cu(saloxm)_2$ have smaller isotropic coupling constants than the protons at 7 and 7' positions in Cu(salen), while the protons at 3 position in $Cu(saloxm)_2$ have a larger isotropic coupling constant, -0.59MHz,⁵⁾ than those at the corresponding 3 and 3' positions, in Cu(salen) (in absolute values). These results suggest that the unpaired electron of copper(II) may delocalize more onto the nitrogen atoms in the complexes with the cis N-Cu-N configruation than the trans configuration, while the unpaired electron may less delocalize onto the oxygen atoms in the cis configuration than the trans, causing more spin polarization at the nitrogen side protons and less polarization at the oxygen side in the complexes with the cis N-Cu-N configuration compared to that in the complexes with the trans configuration. To confirm this estimation, the MO calculation based on the INDO approximation was tried for simple model complexes. The calculated result shows that the spin density on the nitrogen atom increases but that on the oxygen atom decreases by taking the cis N-Cu-N configuration.

We have showed some of the information about the metal-ligand bonding in Cu(salen) obtained by the ENDOR spectroscopy. More details of ENDOR of Cu(salen) will be presented elsewhere.

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