ESR Study of ^{63}Cu(II) Doped in Single Crystals of Bis(methyl 3-alkylidenedithiocarbazato)nickel(II)

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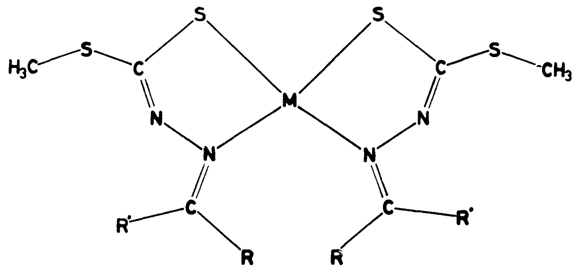
ESR spectra of ^{63}Cu(II) diluted by various single crystals of the title Ni(II) complexes are reported. The alkylidene groups denote 1-(2-naphthyl)ethylidene, 1-(*p*-tolyl)ethylidene, 1-phenylethylidene, benzylidene, 1-(*m*-nitrophenyl)ethylidene, and 1-(*p*-nitrophenyl)ethylidene, and the corresponding Ni(II) complexes are abbreviated as Ni(nedc)$_2$, Ni(tedc)$_2$, Ni(pedc)$_2$, Ni(bdc)$_2$, Ni(mndc)$_2$, and Ni(pndc)$_2$ respectively. Before the analyses of the ESR data, the crystal structures of Ni(nedc)$_2$ and Ni(tedc)$_2$ were determined. In both Ni(II) complexes, the molecules have been found to be of a C$_2$ symmetry, with a tetrahedrally distorted *cis*-NiN$_2$S$_2$ arrangement. The unpaired electrons of the Cu(II) complexes were thus described in terms of C$_2$ symmetry except for the case of Cu(bdc)$_2$. The d-orbital coefficients of the ground-state Kramers doublet were determined from the observed *g* values in such a way that the hyperfine parameters calculated from the coefficients closely reproduce the observed values. In ^{63}Cu(II)/Ni(bdc)$_2$, the *g* values are rhombic, and an additional hyperfine structure due to atoms which do not directly coordinate to Cu(II) ion was observed. The coordination of the Cu(II) ion in Ni(bdc)$_2$ was concluded from the ESR data to be a *trans* arrangement.

The complexes containing Cu–S bonds are interesting for their covalent character. The copper-ligand bindings have been studied by ESR, mainly in complexes with oxygen and nitrogen ligands, and there have been many studies of the square planar, CuS$_4$-type complexes, that is dithiocarbamates,[1,2] dithiophosphate,[3] bis(maleonitriledithiolato)copper(II),[4] and 1,4,8,11-tetrathiacyclotetradecane copper(II) tetrafluoroborate.[5] However relatively few studies have been reported of the CuN$_2$S$_2$-type complexes, that is *trans*-bis(thiosemicarbazide)copper(II) nitrate,[6] α-thiopicolinanilide copper(II),[7] and *N,N'*-ethylene bis(monothioacethylacetoniminato)copper(II).[8]

The evaluation of the bonding parameters from the ESR data requires a knowledge of the assignment of the d-d transition bands in the electronic spectra of Cu(II) complexes. In the electronic spectra of bis(methyl 3-alkylidenedithiocarbazato) copper(II), however, the intense charge-transfer bands mask the d-d transitions. The general method of calculating covalent parameters by the use of d-d energy could not be employed for these complexes.

In this study, the ESR spectra of ^{63}Cu(II) diluted by single crystals of six Ni(II) complexes and the crystal structures of Ni(nedc)$_2$ and Ni(tedc)$_2$ are reported (Fig. 1). The d-orbital coefficients of the ground state are determined from the *g* values with C$_2$ symmetry except for the case of Cu(bdc)$_2$, in which D$_{2h}$ symmetry was used. The method of treating the ESR data follows the general scheme of Swalen *et al.*,[10] extended to C$_2$ symmetry.



	R′	R	
a	-CH$_3$	2-naphthyl	Cu(nedc)$_2$
b	-CH$_3$	*p*-tolyl	Cu(tedc)$_2$
c	-CH$_3$	phenyl	Cu(pedc)$_2$
d	-H	phenyl	Cu(bdc)$_2$
e	-CH$_3$	*m*-nitrophenyl	Cu(mndc)$_2$
f	-CH$_3$	*p*-nitrophenyl	Cu(pndc)$_2$

Fig. 1. Assumed basic structure of bis(methyl 3-alkylidenedithiocarbazato)metal(II), and abbreviations of copper(II) complexes. The coordination around Cu(II) in Ni(bdc)$_2$ was concluded to be *trans* arrangement from ESR.

Experimental

The complexes were prepared according to a modification of the methods of Ref. 11. The single crystals were obtained by the slow evaporation of chloroform–ethanol solutions.

X-Ray Analyses. Three-dimensional intensity data were collected by the 2θ-θ scan technique on a Syntex P$\bar{1}$ four-circle diffractometer using Mo K_α radiation monochromated by a graphite plate. All the reflections with $2\theta \leqq 48°$ were collected. In this way, 3265 independent reflections were measured for Ni(tedc)$_2$, and 2100 for Ni(nedc)$_2$, of which 2642 and 1946 having $I \geqq 2\sigma$ (I) were used in the subsequent analyses. They were corrected for Lorentz and polarization effects, but corrections for absorption were not applied, as the samples were sufficiently small. The calculations were performed on the FACOM 230-75 computer of the Computer Center of Kyushu University, using the UNICS program system.[12] The scattering factors for all the atoms were taken from Ref. 13. The F_o-F_c table is kept at the office of This Bulletin as Document No. 7827.

ESR Measurements. The ESR spectra were recorded every 15° around three mutually perpendicular rotational axes. The most elongated axis was defined as the 2-axis, which is parallel to the crystal b-axis in the case of Ni(nedc)$_2$ or Ni(tedc)$_2$. The 1- and 3-axes were taken at will in the plane perpendicular to the 2-axis. The spectra were taken on a JEOL ME 3X spectrometer at the X band. Mn(II) diluted with MgO and DPPH were used as the *g* marker.

Results

Crystal Structures. The structures were solved by the heavy-atom technique. After block-diagonal least-squares refinement with anisotropic thermal

TABLE 1. FRACTIONAL ATOMIC COORDINATES[a] AND ANISOTROPIC TEMPERATURE FACTORS($\times 10^4$) FOR Ni(nedc)$_2$
The temperature factor is of this form: $\exp[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)]$.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ni	0(0)	289(1)	2500(0)	8(0)	71(1)	52(1)	0(0)	14(1)	0(0)
S (1)	683(1)	2055(2)	3141(1)	12(0)	86(2)	89(1)	8(1)	19(1)	−11(3)
S (2)	1915(1)	1437(2)	4739(1)	12(0)	134(3)	66(1)	−20(1)	12(1)	−21(3)
N (1)	604(2)	−1187(5)	2701(3)	9(1)	83(6)	39(3)	−5(4)	13(3)	4(7)
N (2)	1188(2)	−841(5)	3535(3)	8(1)	105(7)	44(3)	−2(4)	11(3)	−1(7)
C (1)	1242(2)	650(7)	3761(4)	10(1)	108(9)	52(4)	−8(5)	19(3)	−5(9)
C (2)	2386(3)	−297(9)	5186(5)	13(1)	181(12)	79(7)	17(7)	13(4)	28(14)
C (3)	551(2)	−2454(6)	2171(4)	12(1)	84(8)	47(4)	2(5)	24(3)	6(9)
C (4)	1056(3)	−3572(8)	2480(5)	15(1)	129(10)	74(5)	25(6)	27(4)	−12(12)
C (5)	−24(2)	−2776(6)	1190(4)	12(1)	106(8)	42(4)	−2(5)	22(3)	−12(9)
C (6)	−258(3)	−4333(7)	986(5)	18(1)	117(9)	52(4)	−8(6)	29(4)	−27(10)
C (7)	−811(3)	−4609(8)	106(5)	18(1)	145(10)	59(4)	−13(6)	29(4)	−37(11)
C (8)	−1138(2)	−3368(8)	−612(4)	15(1)	157(10)	48(4)	−8(6)	23(4)	−39(11)
C (9)	−1712(3)	−3612(9)	−1524(5)	16(1)	230(14)	60(5)	−5(7)	24(4)	−66(14)
C (10)	−2004(3)	−2391(10)	−2200(5)	19(2)	267(16)	58(5)	19(8)	22(5)	−34(15)
C (11)	−1767(3)	−863(10)	−2031(5)	18(1)	261(15)	56(5)	25(8)	30(4)	26(14)
C (12)	−1208(3)	−570(8)	−1143(5)	17(1)	204(13)	51(4)	21(7)	29(4)	40(12)
C (13)	−891(2)	−1830(7)	−426(4)	13(1)	143(10)	45(4)	3(5)	26(4)	2(10)
C (14)	−325(2)	−1567(7)	497(4)	13(1)	120(9)	44(4)	−1(5)	24(3)	2(9)

a) The numbers in parentheses are the estimated standard deviations in units of the last significant digit.

TABLE 2. FRACTIONAL ATOMIC COORDINATES AND ANISOTROPIC TEMPERATURE FACTORS($\times 10^4$) FOR Ni(tedc)$_2$

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ni	2374(1)	1495(1)	2752(0)	48(1)	84(1)	23(0)	2(1)	26(1)	−14(1)
S (1)	1699(2)	2557(2)	3406(1)	79(2)	124(3)	35(1)	0(3)	55(2)	−43(2)
S (1)′	2724(2)	3627(2)	2388(1)	77(2)	83(2)	37(1)	−1(3)	47(2)	−11(2)
S (2)	760(2)	1055(3)	4284(1)	86(2)	222(4)	29(1)	4(4)	60(2)	−43(3)
S (2)′	3161(2)	3962(2)	1096(1)	90(2)	120(3)	39(1)	12(4)	52(2)	41(2)
N (1)	1693(4)	−304(6)	2822(3)	39(4)	109(8)	20(2)	22(8)	24(4)	1(5)
N (1)′	3273(4)	630(6)	2368(3)	40(4)	88(7)	22(2)	3(8)	19(4)	0(5)
N (2)	1363(4)	−432(7)	3398(3)	52(4)	139(9)	22(2)	10(10)	31(4)	−7(6)
N (2)′	3378(4)	1381(6)	1783(3)	48(4)	101(8)	25(2)	−5(9)	25(4)	1(6)
C (1)	1314(5)	877(8)	3658(3)	44(5)	161(12)	23(2)	17(12)	22(5)	−21(8)
C (1)′	3123(5)	2759(7)	1774(3)	45(5)	109(10)	26(2)	−13(11)	15(5)	−4(7)
C (2)	16(5)	−644(9)	4133(4)	77(7)	177(14)	37(3)	0(15)	60(7)	19(10)
C (2)′	3470(6)	2661(9)	517(4)	85(7)	174(14)	36(3)	15(15)	55(7)	20(10)
C (3)	1445(4)	−1463(7)	2393(3)	35(4)	113(9)	19(2)	8(10)	17(4)	−17(7)
C (3)′	3803(5)	−563(7)	2567(3)	38(5)	92(9)	23(2)	−5(10)	10(5)	−20(7)
C (4)	1048(6)	−2888(8)	2575(4)	69(6)	121(11)	29(2)	−50(12)	39(6)	1(8)
C (4)′	4398(6)	−1225(9)	2160(4)	64(6)	168(13)	33(2)	71(14)	53(6)	9(9)
C (5)	1512(4)	−1286(7)	1688(3)	39(4)	93(9)	18(2)	−22(10)	13(4)	−9(6)
C (5)′	3835(5)	−1311(7)	3229(3)	38(4)	89(9)	25(2)	3(10)	18(5)	−2(7)
C (6)	1803(5)	−2484(7)	1362(3)	38(5)	112(9)	24(2)	−14(10)	23(4)	−17(7)
C (6)′	3933(5)	−412(8)	3827(3)	45(5)	142(11)	26(2)	18(12)	21(5)	−9(8)
C (7)	1817(5)	−2303(7)	682(3)	52(5)	117(10)	21(2)	−24(11)	22(5)	−8(7)
C (7)′	3998(5)	−1136(9)	4461(4)	51(5)	188(14)	28(2)	23(14)	19(5)	16(9)
C (8)	1514(5)	−971(8)	310(3)	45(5)	148(11)	19(2)	−33(12)	17(5)	−3(7)
C (8)′	3973(5)	−2676(9)	4508(4)	40(5)	190(14)	38(3)	20(13)	30(6)	53(10)
C (9)	1185(5)	224(8)	624(3)	46(5)	141(11)	24(2)	−23(12)	15(5)	4(8)
C (9)′	3856(5)	−3561(8)	3907(4)	52(5)	130(11)	37(3)	1(13)	23(6)	29(9)
C (10)	1183(5)	69(8)	1314(3)	38(5)	127(10)	23(2)	−20(11)	10(5)	−1(7)
C (10)′	3807(5)	−2872(8)	3274(4)	46(5)	110(10)	34(2)	7(11)	15(5)	12(8)
C (11)	1515(5)	−781(10)	−441(3)	79(6)	212(15)	19(2)	−35(15)	31(5)	16(9)
C (11)′	4097(5)	−3423(10)	5217(4)	94(7)	250(18)	26(3)	37(18)	38(6)	66(10)

TABLE 3. IMPORTANT INTERATOMIC DISTANCES AND ANGLES FOR Ni(nedc)$_2$

Distances (Å)			
Ni-S (1)	2.147(2)	Ni-N (1)	1.926(5)
N (1)-N (2)	1.423(7)	S (1)-C (1)	1.741(7)
N (2)-C (1)	1.283(8)	C (1)-S (2)	1.740(7)
N (1)-C (3)	1.276(8)	C (3)-C (4)	1.502(10)
C (3)-C (5)	1.483(8)		
Angles (deg.)			
S (1)-Ni-S (1)	92.5(1)	N (1)-Ni-N (1)	99.4(3)
S (1)-Ni-N (1)	86.1(2)	Ni-S (1)-C (1)	93.2(3)
Ni-N (1)-N (2)	116.9(3)	N (1)-N (2)-C (1)	110.2(5)
N (2)-C (1)-S (1)	125.2(5)	N (2)-C (1)-S (2)	120.8(5)
S (1)-C (1)-S (2)	114.0(4)	Ni-N (1)-C (3)	128.5(4)
N (2)-N (1)-C (3)	114.6(5)		

TABLE 4. IMPORTANT INTERATOMIC DISTANCES AND ANGLES FOR Ni(tedc)$_2$

Distances (Å)			
Ni-S (1)	2.142(3)	Ni-S (1)'	2.151(3)
Ni-N (1)	1.914(6)	Ni-N (1)'	1.921(6)
N (1)-N (2)	1.425(8)	N (1)'-N (2)'	1.418(8)
S (1)-C (1)	1.731(8)	S (1)'-C (1)'	1.736(8)
N (2)-C (1)	1.284(10)	N (2)'-C (1)'	1.273(9)
C (1)-S (2)	1.751(8)	C (1)'-S (2)'	1.757(8)
N (1)-C (3)	1.310(9)	N (1)'-C (3)'	1.291(9)
Angles (deg.)			
S (1)-Ni-S (1)'	93.0(2)	N (1)-Ni-N (1)'	99.1(2)
S (1)-Ni-N (1)	86.9(2)	S (1)'-Ni-N (1)'	85.7(2)
Ni-S (1)-C (1)	94.8(5)	Ni-S (1)'-C (1)'	92.5(5)
Ni-N (1)-N (2)	118.1(4)	Ni-N (1)'-N (2)'	116.8(4)
N (1)-N (2)-C (1)	110.6(6)	N (1)'-N (2)'-C (1)'	109.8(6)
N (2)-C (1)-S (1)	125.3(6)	N (2)'-C (1)'-S (1)'	126.0(6)
Ni-N (1)-C (3)	129.1(5)	Ni-N (1)'-C (3)'	129.0(5)
N (2)-N (1)-C (3)	112.8(5)	N (2)'-N (1)'-C (3)'	114.2(6)

parameters for non-hydrogen atoms, the final R values became 0.058 in both crystals. The parameters obtained are given in Tables 1—4.

Ni(nedc)$_2$: $NiS_4N_4C_{28}H_{26}$, formula weight 605.48, monoclinic, space group C2/c, a=26.518(8), b=8.399(1), c=14.546(3) Å, β=121.05(2)°, V=2775.6 Å^3, Z=4, D_m=1.423 g·cm^{-3} (by floatation), D_x=1.449 g·cm^{-3}.

The Ni atoms lie on the crystallographic two-fold axes. Each of the ligands is bonded to the Ni atom through the thiol S atom and one of the hydrazine N atoms, yielding a 5-membered chelate ring, and the Ni atom has a *cis*-planar coordination by two S and two N atoms. The molecule has a crystallographically imposed two-fold axis which bisects the S–Ni–S bond angle and which is parallel to the b-axis. The four ligator atoms are somewhat tetrahedrally disposed around the Ni atom. The interplanar angle between N–Ni–S planes is 22°. The packing of the complexes is illustrated in Fig. 2.

Ni(tedc)$_2$: $NiS_4N_4C_{22}H_{26}$, formula weight 533.41, monoclinic, space group P2$_1$/c, a=14.793(5), b=8.835(3), c=20.309(5) Å, β=110.77(2)°, V=2481.8 Å^3, Z=4, D_m=1.419 g·cm^{-3}, D_x=1.427 g·cm^{-3}.

The Ni atom has a coordination similar to that of Ni(nedc)$_2$. The molecule has a fictitious two-fold axis which is inclined from the b-axis. The interplanar angle between N–Ni–S planes is 24°. The packing is illustrated in Fig. 3.

ESR Spectra. *^{63}Cu(II)/Ni(nedc)$_2$*: There are four molecules in the unit cell. It was found, however, that there is only one copper quartet in all the crystal orientations. All the sites for copper ions were, therefore, magnetically indistinguishable. Figure 4 shows some representative spectra. The crystal b-axis is along the 2-axis. When the magnetic field($\boldsymbol{H}_0$) is in the 31-plane, the two Cu–N bondings are magnetically equivalent and the equally spaced nitrogen hyperfine structure(hfs) with an intensity ratio of 1:2:3:2:1 was well defined. The crystal c-axis is parallel to the 1-axis and nearly bisects the N–Cu–N angle, and the two Cu–N bondings are equivalent. The 23-plane is nearly parallel to the molecular plane. When the $\boldsymbol{H}_0$ is within 15° of one Cu–N bond direction, a nonequivalent nitrogen hfs is obtained (see b in Fig. 4). The g_z direction is parallel to the crystal b-axis, which is the molecular two-fold axis. The forbidden spectra corresponding to $\Delta m=\pm 1$ and ± 2 were not clearly

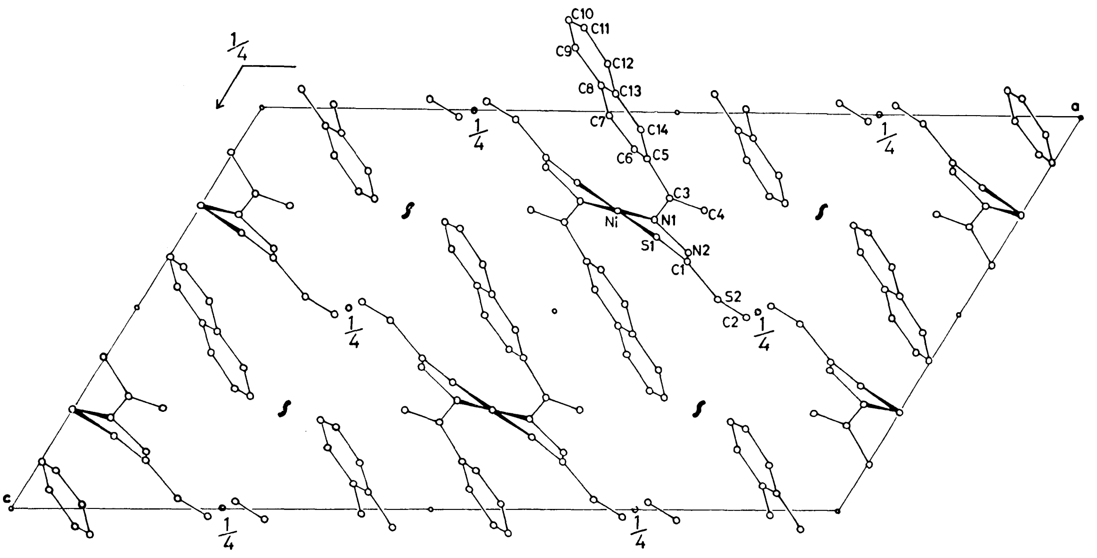


Fig. 2. Projection of the crystal structure along the b-axis of Ni(nedc)$_2$.

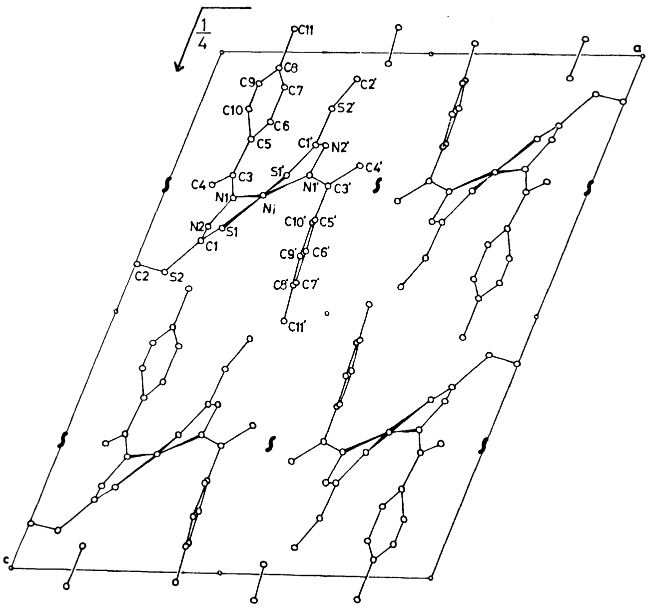


Fig. 3. Projection of the crystal structure along the b-axis of Ni(tedc)$_2$.

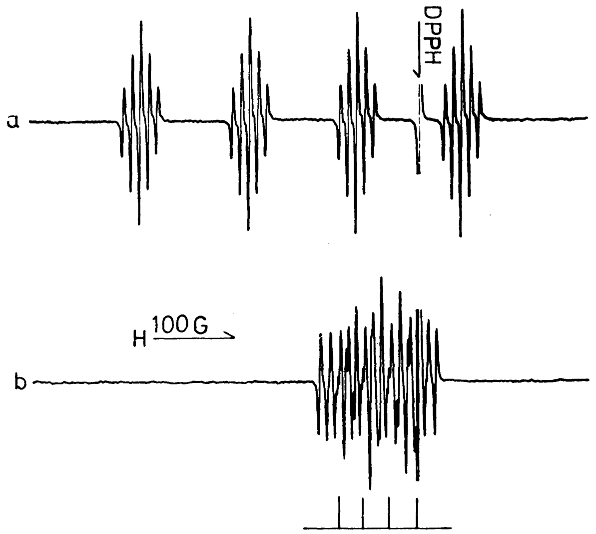


Fig. 4. Single crystal ESR spectra of ^{63}Cu(II)/Ni(nedc)$_2$. a: $(\theta,\varphi)=(120°,0°)$, b: $(60°,90°)$.

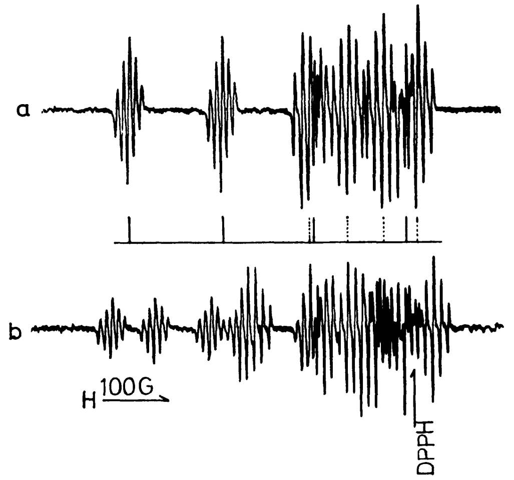


Fig. 5. Single crystal ESR spectra of ^{63}Cu(II)/Ni(pndc)$_2$. a: (90°,15°), b: (165°,0°).

identified, hence, no attempt was made to determine quadrupole coupling parameters. The g values and hf coupling constants were determined by a method similar to that of Fujimoto *et al.*[14]

^{63}Cu(II)/Ni(mndc)$_2$ and Ni(pedc)$_2$: The spectra in both complexes were very similar to those of ^{63}Cu(II)/Ni(nedc)$_2$ except for the difference in the laboratory coordinate systems.

^{63}Cu(II)/Ni(tedc)$_2$: The crystal b- and a-axes are parallel to the 2- and 1-axes respectively. One set of absorption is obtained when $\boldsymbol{H}_0$ is in the 31-plane or along the 2-axis, while two sets are observed when $\boldsymbol{H}_0$ is in the 12- or 23-plane. The deviation of the g_z direction from the crystal b-axis is 24°.

^{63}Cu(II)/Ni(pndc)$_2$: Four sets of absorptions are observed when $\boldsymbol{H}_0$ is in the 31-plane. The four resonances merge into two more intense lines when $\boldsymbol{H}_0$

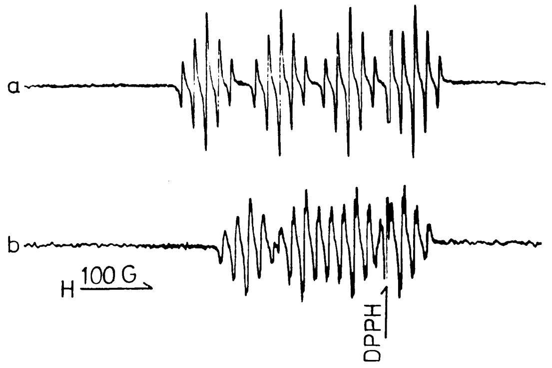


Fig. 6. Single crystal ESR spectra of ^{63}Cu(II)/Ni(bdc)$_2$. a: (90°,0°), b: (15°,0°).

is along the 3- or 1-axis and when $\theta=45$ or 135°. When $\boldsymbol{H}_0$ is in the 12- or 23-plane, two sets are obtained, and these spectra are exactly identical in both planes.

^{63}Cu(II)/Ni(bdc)$_2$: When $\boldsymbol{H}_0$ is in the 31-plane or along the 2-axis, a single spectrum is observed, while two spectra are observed when $\boldsymbol{H}_0$ is in the 12- or 23-plane. The g and A^{Cu} values are rhombic. The nitrogen hfs is very large compared with those of the other samples, and the maximum direction of the nitrogen hfs agrees roughly with the g_x direction. The intensity ratio is 1:2:3:2:1 in all the crystal orientations. These results indicate that the Cu(II) ion in Ni(bdc)$_2$ is in a *trans* arrangement. The ESR parameters and the principal directions are very similar to those of *trans*-bis(thiosemicarbazide)copper(II) nitrate.[6]

When $\boldsymbol{H}_0$ is within 30° from the 3-axis, the additional hfs was observed (see b in Fig. 6). In the other orientations, the line width was very sharp but no additional hfs could be detected at room temperature. As far as the details of measurements around the 3-axis, it was found that the spectra consist of 3 lines with an intensity ratio of about 1:4:1. It is uncertain whether this hfs should be assigned to azomethine hydrogen or to two nitrogens in which one of the hfs is very small. The details are now under investigation.

Discussion

The molecule in Ni(nedc)$_2$ or Ni(tedc)$_2$ has the C$_2$ or the fictitious C$_2$ symmetry. The ESR results shall, therefore, be analyzed in terms of the C$_2$ symmetry except in the case of Cu(bdc)$_2$.

The ESR data of Cu(II) ions generally have been analyzed by the method of Abragam and Pryce,[15,16] which was adapted by Maki and McGarvey[17] to the ligand-field concept.[9,18] There is, however, difficulty caused by the increased number of parameters to be determined in the C$_2$ symmetry, since some coefficients in the linear combination of the Kramers doublet are complex.

TABLE 5. THE g VALUES AND HYPERFINE COUPLING CONSTANTS(10^{-4} cm^{-1}) FOR ^{63}Cu(II) IN BIS(METHYL 3-ALKYLIDENEDITHIOCARBAZATO)NICKEL(II) AT ROOM TEMPERATURE

Host	g	$A(^{63}\mathrm{Cu})$	A^{N}	Principal direction
Ni(nedc)$_2$	$g_x=2.032(1)$	$A_x=31(4)$	$A_\perp=9.1(5)$	(0.25, 0, −0.97)
	$g_y=2.130(1)$	$A_y=163(1)$	$A_\parallel=12.1(5)$	(0.97, 0, 0.25)
	$g_z=2.033(1)$	$A_z=33(4)$		(0, 1, 0)
Ni(mndc)$_2$	$g_x=2.032(1)$	$A_x=36(4)$	$A_\perp=9.5(5)$	(0, 0.62, −0.78)
	$g_y=2.129(1)$	$A_y=168(1)$	$A_\parallel=13.2(5)$	(0, 0.78, 0.62)
	$g_z=2.033(1)$	$A_z=33(5)$		(1, 0, 0)
Ni(pedc)$_2$	$g_x=2.032(1)$	$A_x=33(4)$	$A_\perp=9.2(5)$	(0.76, 0, −0.65)
	$g_y=2.132(1)$	$A_y=159(1)$	$A_\parallel=11.0(5)$	(0.65, 0, 0.76)
	$g_z=2.034(1)$	$A_z=34(4)$		(0, 1, 0)
Ni(tedc)$_2$	$g_x=2.031(1)$	$A_x=32(4)$	$A_\perp=8.5(5)$	(0.82, ±0.38, 0.43)
	$g_y=2.134(1)$	$A_y=155(1)$	$A_\parallel=11.1(5)$	(0.52, ∓0.15, −0.84)
	$g_z=2.034(1)$	$A_z=33(4)$		(0.25, ∓0.91, 0.32)
Ni(pndc)$_2$	$g_x=2.036(1)$	$A_x=31(4)$	$A_\perp=8.7(5)$	(0.23, 0, ±0.97) (0.97, 0, ∓0.23)
	$g_y=2.130(1)$	$A_y=155(1)$	$A_\parallel=11.6(5)$	(0.97, 0, ∓0.23) (0.23, 0, ±0.97)
	$g_z=2.038(1)$	$A_z=29(4)$		(0, 1, 0)
Ni(bdc)$_2$	$g_x=2.029(1)$	$A_x=30(4)$	$A_\perp=15.0(5)$	(0.53, ∓0.05, −0.85)
	$g_y=2.048(1)$	$A_y=41(4)$	$A_\parallel=19.1(5)$	(0.71, ∓0.51, 0.48)
	$g_z=2.138(1)$	$A_z=180(1)$		(0.46, ±0.86, 0.24)

The iteration method introduced by Swalen *et al.*10) can determine the coefficients of the atomic d-orbitals from only the experimental g values and the normalization condition. The copper hfs is used only for a consistency check. The same procedure is followed in this work, and the hole description is adopted throughout in the formulation.

In the C_2 symmetry, $3d_{zx}$- and $3d_{yz}$-type orbitals belong to the same irreducible representation and form a linear combination:

$$\psi = a|\mathrm{zx}> + ib|\mathrm{yz}>. \tag{1}$$

In this case, the symmetry axis is parallel to the z-axis, and the $3d_{xy}$, $3d_{z^2}$, and $3d_{x^2-y^2}$ orbitals are then admixed *via* spinorbit coupling, $\xi \boldsymbol{l}\cdot\boldsymbol{s}$, to give the general expression for the Kramers doublet:

$$\begin{aligned}\psi^\alpha = a|\mathrm{zx}>^\alpha + ib|\mathrm{yz}>^\alpha + c|\mathrm{z}^2>^\beta \\ - d|\mathrm{x}^2 - \mathrm{y}^2>^\beta - ie|\mathrm{xy}>^\beta,\end{aligned} \tag{2-1}$$

$$\begin{aligned}\psi^\beta = i\{a|\mathrm{zx}>^\beta - ib|\mathrm{yz}>^\beta - c|\mathrm{z}^2>^\alpha \\ + d|\mathrm{x}^2 - \mathrm{y}^2>^\alpha - ie|\mathrm{xy}>^\alpha\},\end{aligned} \tag{2-2}$$

where the superscripts α and β designate the spin functions.

The expressions for the g values are obtained as the matrix elements of the Zeeman term, $\boldsymbol{H}=\beta(\boldsymbol{l}+g_e\boldsymbol{s})\cdot\boldsymbol{H}_0$:19)

$$g_x = (1-2b^2-2c^2-2d^2)g_e + 4ae - 4bd + 4\sqrt{3}\,bc, \tag{3-1}$$

$$g_y = (1-2b^2-2e^2)g_e - 4be + 4ad + 4\sqrt{3}\,ac, \tag{3-2}$$

$$g_z = (1-2c^2-2d^2-2e^2)g_e + 8de + 4ab, \tag{3-3}$$

where g_e represents the g value of the free electron.

The expressions for the hyperfine coupling constants are derived as follows:20)

$$\begin{aligned}A_x = P[4ae-4bd+4\sqrt{3}\,bc-k(1-2b^2-2c^2-2d^2) \\ +(2/7)(1+b^2-2d^2-3ab-\sqrt{3}\,ac+3ad-3be \\ -2\sqrt{3}\,cd-2\sqrt{3}\,ce)],\end{aligned} \tag{4-1}$$

$$\begin{aligned}A_y = P[-4be+4ad+4\sqrt{3}\,ac-k(1-2b^2-2e^2) \\ +(2/7)(-1-a^2+2d^2+3ab-\sqrt{3}\,bc-3bd \\ +3ae-2\sqrt{3}\,cd-2\sqrt{3}\,ce)],\end{aligned} \tag{4-2}$$

$$\begin{aligned}A_z = P[8de+4ab-k(1-2c^2-2d^2-2e^2) \\ +(2/7)(1-3c^2+d^2+e^2+\sqrt{3}\,ac-3ad \\ -3ae-\sqrt{3}\,bc-3bd-3be)],\end{aligned} \tag{4-3}$$

where $P=g_eg_N\beta_e\beta_N\langle r^{-3}\rangle_{3d}$, and where k is the contact term.

The 3 equations and the normalization condition form a set of nonlinear simultaneous equations for a, b, c, d, and e, an iteration procedure similar to that of Swalen *et al.*8) being used. The solutions were made with a value of $r(=c/d)$ between 0.5 and 2.0 by the use of an Olivetti P652 computer. The calculated values are given in Table 6.

Nitrogen hfs. From Table 6, the contributions of the upper states may be found to be very small. We shall thus ignore these admixtures in our calculation of the nitrogen hfs. We obtain the following antibonding molecular orbital of the unpaired electron:

$$\begin{aligned}|\mathrm{zx}> = N^{1/2}[\mathrm{d_{zx}}-(\alpha_1/\sqrt{2})(\mathrm{s}^1-\mathrm{s}^2)-(\alpha_2/2) \\ \times(-\mathrm{p}_x^1-\mathrm{p}_z^2-\mathrm{p}_x^1+\mathrm{p}_z^2)-(\alpha_3/\sqrt{2}) \\ \times(-\mathrm{s}^3+\mathrm{s}^4)-(\alpha_4/2)(\mathrm{p}_x^3+\mathrm{p}_x^4-\mathrm{p}_z^3+\mathrm{p}_z^4)],\end{aligned} \tag{5}$$

where the z axis is along the two-fold axis, and 1,2 and 3,4 represent, respectively, the ligand nitrogen and sulfur atoms. The normalization of this orbital gives

$$\begin{aligned}N(1+\alpha_1^2+\alpha_2^2+\alpha_3^2+\alpha_4^2-2\sqrt{2}\,\alpha_1S_1-4\alpha_2S_2 \\ -2\sqrt{2}\,\alpha_3S_3-4\alpha_4S_4) = 1,\end{aligned} \tag{6}$$

where $S_1=\langle \mathrm{d_{zx}}|\mathrm{s}^1\rangle$, $S_2=\langle \mathrm{d_{zx}}|-\mathrm{p}_x^1\rangle$, $S_3=\langle \mathrm{d_{zx}}|-\mathrm{s}^3\rangle$, and $S_4=\langle \mathrm{d_{zx}}|\mathrm{p}_x^3\rangle$.

The components of the nitrogen hfs are

$$A_\parallel^N = A_s + 2A_p, \tag{7-1}$$

$$A_\perp^N = A_s - A_p, \tag{7-2}$$

where the isotropic part, A_s, and anisotropic part, A_p, are

$$A_s = (8\pi/3)g_eg_N\beta_e\beta_N\times(1/2)N\alpha_1^2\times|\psi_{2s}(0)|^2, \tag{8-1}$$

$$A_p = (4/5)g_eg_N\beta_e\beta_N\times(1/4)N\alpha_2^2\times\langle r^{-3}\rangle_{2p}. \tag{8-2}$$

The values of $32.4\times10^{24}\,\mathrm{cm}^{-3}$ for $|\psi_{2s}(0)|^2$ and $20.9\times10^{24}\,\mathrm{cm}^{-3}$ for $\langle r^{-3}\rangle_{2p}$ of a nitrogen atom are obtained from the analytical SCF wave functions.21) Table 7 gives the values of $N\alpha_1^2$, $N\alpha_2^2$, and $N\alpha_4^2$, the $N\alpha_4^2$ values have been calculated on the following bases: (1) the overlap integrals, S_1=0.085, S_2=0.097,

TABLE 6. THE BEST VALUES FOR THE COEFFICIENTS OF KRAMERS DOUBLET AND CALCULATED HYPERFINE COUPLING CONSTANTS (10^{-4} cm^{-1})

Host	Ni(nedc)$_2$	Ni(mndc)$_2$	Ni(pedc)$_2$	Ni(tedc)$_2$	Ni(pndc)$_2$	Ni(bdc)$_2$$^{a)}$
r	0.60	1.50	0.60	0.60	1.30	0.688
a	0.9998	0.9998	0.9998	0.9997	0.9998	0.9990
b	0.0078	0.0079	0.0081	0.0081	0.0091	−0.0392
c	0.0094	0.0133	0.0096	0.0097	0.0129	0.0171
d	0.0157	0.0089	0.0160	0.0162	0.0099	0.0075
e	0.0078	0.0077	0.0078	0.0076	0.0086	0.0109
P	174	178	167	163	167	197
k	0.490	0.498	0.507	0.505	0.488	0.495
A_x	−31	−36	−33	−32	−31	−30
A_y	−163	−168	−159	−155	−155	−41
A_z	−33	−33	−34	−33	−29	−180

a) Calculated from Eqs. 10 and 11.

Table 7. Covalent parameters in bis(methyl 3-alkylidenedithiocarbazato)copper(II)

Host	Ni(nedc)$_2$	Ni(mndc)$_2$	Ni(pedc)$_2$	Ni(tedc)$_2$	Ni(pndc)$_2$	Ni(bdc)$_2$[a]
$N\alpha_1^2$	0.037	0.039	0.035	0.034	0.035	0.059
$N\alpha_2^2$	0.117	0.145	0.070	0.102	0.113	0.158
$N\alpha_4^2$ (N=0.70)	0.186	0.181	0.192	0.188	0.187	
(N=0.75)	0.222	0.216	0.231	0.226	0.224	

a) Calculated from Eq. 13.

and $S_4=0.065$, are assumed for the Cu–N and Cu–S distances of 1.92Å and 2.15Å; (2) $\alpha_3=0$, and (3) the value of N is assumed to be 0.7 or 0.75, either of which is a reasonable value for CuN_2S_2 complexes.[6)]

^{63}Cu(II)/Ni(bdc)$_2$. In a *trans* arrangement, $d_{x^2-y^2}$ and d_{z^2} belong to the same irreducible representation and the spin-orbitals of the ground state are

$$\begin{aligned}\psi^\alpha &= a|x^2-y^2>^\alpha+b|z^2>^\alpha+ic|xy>^\alpha\\ &\quad -id|yz>^\beta+e|zx>^\beta, \end{aligned}\tag{9-1}$$

$$\begin{aligned}\psi^\beta &= i\{a|x^2-y^2>^\beta+b|z^2>^\beta-ic|xy>^\beta\\ &\quad -id|yz>^\alpha-e|zx>^\alpha\}, \end{aligned}\tag{9-2}$$

x and y being the Cu–N and Cu–S bond directions respectively. By analogy with the case of C_2, the g and A^{Cu} values are calculated as follows:

$$g_x = (1-2c^2-2e^2)g_e + 4\sqrt{3}bd + 4ce + 4ad, \tag{10-1}$$

$$g_y = (1-2c^2-2d^2)g_e - 4\sqrt{3}be + 4ae + 4cd, \tag{10-2}$$

$$g_z = (1-2d^2-2e^2)g_e + 8ac - 4de, \tag{10-3}$$

$$\begin{aligned}A_x &= P[4\sqrt{3}bd+4ce+4ad-k(1-2c^2-2e^2)\\ &\quad +(2/7)\{-1+2a^2-d^2-2\sqrt{3}ab\\ &\quad -\sqrt{3}b(e-2c)-3cd-3ae+3de\}], \end{aligned}\tag{11-1}$$

$$\begin{aligned}A_y &= P[-4\sqrt{3}be+4ae+4cd-k(1-2c^2-2d^2)\\ &\quad +(2/7)\{-1+2a^2-e^2+2\sqrt{3}ab\\ &\quad +\sqrt{3}b(d-2c)-3ce-3ad+3de\}], \end{aligned}\tag{11-2}$$

$$\begin{aligned}A_z &= P[8ac-4de-k(1-2d^2-2e^2)\\ &\quad +(2/7)\{-1-a^2+3b^2-c^2-\sqrt{3}b(d-e)\\ &\quad -3(d+e)(c-a)\}]. \end{aligned}\tag{11-3}$$

The molecular orbitals which contribute to the A^N values are

$$\begin{aligned}|A_{1g}> &= N_1{}^{1/2}[d_{x^2-y^2}+(b/a)d_{z^2}-(\alpha_1/\sqrt{2})(s^1+s^2)\\ &\quad -(\alpha_2/\sqrt{2})(-p_x^1+p_x^2)-(\alpha_3/\sqrt{2})(p_y^3-p_y^4)], \end{aligned}\tag{12-1}$$

$$|zx> = N_2{}^{1/2}[d_{zx}-(\beta/\sqrt{2})(p_z^1-p_z^2)]. \tag{12-2}$$

The components of the A^N are

$$A_x^N = A_s + 2A_\sigma + A_\pi , \tag{13-1}$$

$$A_y^N = A_s - A_\sigma , \tag{13-2}$$

$$A_z^N = A_s - A_\sigma - A_\pi , \tag{13-3}$$

where A_s, A_σ, and A_π are

$$A_s = (8\pi/3)g_e g_N \beta_e \beta_N \times (1/2)a^2 N_1 \alpha_1^2 |\psi_{2s}(0)|^2, \tag{14-1}$$

$$A_\sigma = (4/5)g_e g_N \beta_e \beta_N \times (1/4)a^2 N_1 \alpha_2^2 \langle r^{-3}\rangle_{2p}, \tag{14-2}$$

$$A_\pi = (4/5)g_e g_N \beta_e \beta_N \times (3/4)ae(N_1 N_2)^{1/2}\alpha_2 \beta \langle r^{-3}\rangle_{2p}. \tag{14-3}$$

The calculation was performed with $r(=d/e)$ value from 0.5 to 1.0. The calculated values are given in Tables 6 and 7. The β value could not be determined because of the experimental error between A_z^N and A_y^N values.

In *cis*-planar copper(II) complexes, the g values have an axial symmetry. When tetrahedral distortion occurs, this is not true. The g_z and g_x values are no longer equal, as may be seen in Eq. 3. Even if the distortion occurs, the g values sometimes chance to have an axial symmetry. In *cis* bis(methyl 3-alkylidenedithiocarbazato)copper(II), however, the tetrahedral distortion of about 20° does not break the axial symmetry of the g values.

The values of g are rhombic in a *trans* arrangement.[6,14,22)] It was concluded from this fact that Cu(II) in Ni(bdc)$_2$ is in a *trans* arrangement.

The ESR spectra in chloroform solutions of copper(II) complexes at room temperature have A^{Cu} values between 66 and 72×10^{-4} cm^{-1} for the *cis* complexes and of 82×10^{-4} cm^{-1} for Cu(bdc)$_2$. These values are in reasonable agreement with the attributions of negative signs to all the A^{Cu} components.

The A^N values are smaller in the *cis* complexes than in Cu(bdc)$_2$. It is expected that in the *cis* complexes, the Cu–N bond length is longer than in the *trans* arrangement because of steric repulsion by the large phenyl groups.

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