Structure and Characterization of Copper(II) and Nickel(II) Complexes with 3-Acetyl-5,6-dimethylpyridazine Hydrazone, the Condensation Product of Biacetyl and Hydrazine

Hisashi OKAWA, Naohide MATSUMOTO, and Sigeo KIDA

Department of Chemistry, Faculty of Science, Kyushu University 33, Hakozaki, Higashi-ku, Fukuoka 812

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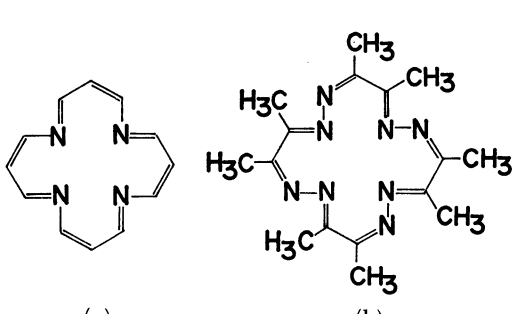
Copper(II) and nickel(II) complexes, $MLX_2 \cdot nH_2O$ ($L=C_{16}H_{24}N_8$; $X=Cl^-$, Br^-, NO_3^-, ClO_4^-, BF_4^-; $n=0, 2$), were obtained by reacting diacetyl with hydrazine in the presence of a metal ion and characterized. The condensation product L was found to be 3-acetyl-5,6-dimethylpyridazine hydrazone. The molecular structure of $NiL(ClO_4)_2 \cdot 2H_2O$ has been determined, the configuration around the nickel(II) ion being a distorted octahedron.

Metal complexes of 1,5,9,13-tetraaza[16]annulene (Fig. 1, a), which is the inner-ring system of porphyrins, are of interest in connection with the study on metalloenzymes such as peroxidases and cytochromes. Busch *et al.*[1-4] obtained tetrabenzo[*b,f,j,n*][1,5,9,13]tetraaza[16]annulene complexes by condensing 2-aminobenzaldehyde in the presence of a metal ion. Step-wise oxidation of metal complexes with tetraazamacrocycles of lower unsaturation seems a promising method for synthesizing tetraazaannulene metal complexes. By this method 5,7,12,14-tetramethyl-1,4,8,11-tetraaza[14]annulene has been prepared.[5] Tang and Holm[6] oxidized 15- and 16-membered tetraazamacrocyclic complexes and synthesized corrin-like macrocyclic complexes. However, 1,5,9,13-tetraaza[16]annulene and its homologues with simple substituents are not known.

In order to prepare 3,4,7,8,11,12,15,16-octamethyl-1,2,5,6,9,10,13,14-octaaza[16]annulene complexes (Fig. 1, b), we treated biacetyl and hydrazine in the presence of copper(II) or nickel(II) ion and obtained metal complexes of the type $MLX_2 \cdot nH_2O$ (M=Cu(II), Ni(II): $X=Cl^-$, Br^-, NO_3^-, ClO_4^-, BF_4^-; $n=0, 2$) where L denotes the condensation product with the composition $C_{16}H_{24}N_8$. The composition is the same as that of the desired compound 3,4,7,8,11,12,15,16-octamethyl-1,2,5,6,9,10,13,14-octaaza[16]annulene. However, L can not be the annulene, since the infrared spectrum of each complex clearly indicates the presence of an amino group. The purpose of this study is to characterize the condensation product and the metal complexes.

Experimental

Syntheses. *$CuL(ClO_4)_2$*: A methanol solution (50 ml) of biacetyl (4.3 g) and hydrazinium chloride (3.5 g) was refluxed for 10 min. To this was added copper(II) acetate monohydrate (2.5 g) and the mixture was heated under reflux for 3 h. A yellow precipitate formed was separated from the solution by filtration, and an aqueous solution of sodium perchlorate was added to the filtrate to give yellow-brown prisms. These were recrystallized from water. The yield was 0.7 g.



(a) (b)

Fig. 1.

Found: C, 32.43; H, 3.98; N, 19.03; Cu, 10.85%. Calcd for $C_{16}H_{24}N_8O_8Cl_2Cu$: C, 32.52; H, 4.09; N, 18.96; Cu, 10.75%.

$CuLBr_2$: Biacetyl (4.3 g) and hydrazinium bromide (5.7 g) were dissolved in methanol (70 ml) and the mixture was refluxed for 10 min. To this was added copper(II) acetate monohydrate (2.5 g) and the mixture was heated under reflux for 3 h. The reaction mixture was filtered while it was hot and the filtrate wes allowed to stand overnight to give greenish brown prisms. The yield was 0.2 g.

Found: C, 34.70; H, 4.35; N, 20.22; Cu, 11.79%. Calcd for $C_{16}H_{24}N_8Br_2Cu$: C, 34.83; H, 4.38; N, 20.31; Cu, 11.52%.

$NiL(ClO_4)_2 \cdot 2H_2O$: This complex was obtained in the same way as that for $CuL(ClO_4)_2$ from biacetyl (4.3 g), hydrazine hydrochloride (3.5 g) and nickel(II) chloride hexahydrate (3.0 g). A yellow precipitate formed was separated from the reaction mixture. To the filtrate was added an aqueous solution of sodium perchlorate (3.0 g) to give yellow prisms. A small amount of the product was recovered from the solid part of the reaction mixture by extraction with hot water and treatment with an aqueous solution of sodium perchlorate. The product was recrystallized from water to give yellow brown prisms (3.9 g).

Found: C, 30.76; H, 4.71; N, 17.84%. Calcd for $C_{16}H_{28}N_8N_8O_{10}Cl_2Ni$: C, 30.89; H, 4.54; N, 18.01%.

$NiL(BF_4)_2 \cdot 2H_2O$: The complex was obtained as golden yellow needle by addition of an aqueous solution of sodium tetrafluoroborate to an aqueous solution of $NiL(ClO_4)_2 \cdot 2H_2O$.

Found: C, 32.13; H, 4.73; N, 18.50%. Calcd for $C_{16}H_{28}N_8O_2B_2F_8Ni$: C, 32.20; H, 4.73; N, 18.78%.

$NiLCl_2$: The complex was obtained as red-orange prisms, when an aqueous solution of excess sodium chloride was added to an aqueous solution of $NiL(ClO_4)_2 \cdot 2H_2O$.

Found: C, 41.44; H, 5.32; N, 24.33%. Calcd for $C_{16}H_{24}N_8Cl_2Ni$: C, 41.96; H, 5.28; N, 24.46%.

$NiL(NO_3)_2$: The complex was obtained as yellow-brown prisms by mixing an aqueous solution of $NiL(ClO_4)_2 \cdot 2H_2O$ and an aqueous solution of excess sodium nitrate.

Found: C, 37.36; H, 4.77; N, 27.41%. Calcd for $C_{16}H_{24}N_{10}O_6Ni$: C, 37.60; H, 4.73; N, 27.40%.

Isolation of the Condensation Product. To an aqueous solution (200 ml) containing $Na_2H_2edta \cdot 2H_2O$ (4.0 g) and NaOH (4.0 g) was added $NiL(ClO_4)_2 \cdot 2H_2O$ (3.0 g), and the mixture was heated under reflux for 5 h. Pale yellow needles which separated were collected and recrystallized from metha-

nol. The yield was 1.3 g; mp 185 °C.

Found: C, 64.81; H, 6.75; N, 28.53%; MS: *m/e*, 296 and 297. Calcd for $C_{16}H_{20}N_6$: C, 64.86; H, 6.80; N, 28.38%; mol wt, 296.38.

Measurements. Infrared spectra were measured with a Hitachi Infrared Spectrophotometer Model 215 on a KBr disk, electronic spectra with a Shimadzu Multipurpose Spectrophotometer Model MSP-5000, and NMR spectra with a Hitachi NMR Spectrophotometer Model R-20B in CD_3CN using tetramethylsilane as the internal standard.

Table 1. Crystal data

$NiCl_2O_{10}N_8C_{16}H_{28}$, Mol wt=622.07
Monoclinic, $P2_1/c$
$a=7.095(2)$Å
$b=11.578(3)$
$c=16.515(7)$
$\beta=102.7(3)°$
$V=1323.6$Å^3
μ(Mo$K\alpha$)=18.58 cm^{-1}
$D_m=1.56$ g cm^{-3}, $D=1.56$ g cm^{-3} (for $Z=2$)

Structure Determination of $NiL(ClO_4)_2\cdot 2H_2O$. The crystal is yellow-brown rhombic prisms elongated along the c-axis. Unit cell dimensions were determined by the least-squares method from high-angle fifteen reflections measured on a Syntex $P\bar{1}$ four-cycle automatic diffractometer. The crystal data are givin in Table 1. Three-dimensional intensity data were collected by the 2θ-θ scan technique on a Syntex $P\bar{1}$ diffractometer using Mo$K\alpha$ radiation made monochromatic by means of graphite plate. Of 2345 independent reflections collected in $2\theta \lesssim 48°$, 1636 reflections greater than $2.33\sigma(F)$ were used in the analysis. They were corrected for the Lorentz and polarization effects, no corrections being made for absorption.

Solution and Refinement of the Structure

The structure was solved by the heavy atom method. For two molecules in a unit cell of space group $P2_1/c$, the nickel atom is required to be in a special position. The chlorine atom was easily deduced from the three dimensional Patterson synthesis and the minimum function. All the remaining non-hydrogen atoms were revealed by the Fourier syntheses. The positional and anisotropic thermal parameters were refined by the block diagonal least-squares method, the final disagreement factor being 11.2% for the observed reflections. The final positional and thermal parameters and their standard deviations are given in Table 2. In the least-squares procedure, weight ω is taken to be equal to unity for $|F_0| \geqq 5.0$ reflections and zero for $|F_0| < 5.0$ reflections. The F_o-F_c table is kept at the office of the Chem. Soc. Japan (Document No. 7712). The scattering factors for all the atoms were taken from the International Table for X-ray Crystallography.[7] All calculations were carried out by the UNICS program system using a Facom 230-75 Computer in the Computer Center of Kyushu University.

Description of the Structure

The molecule has a center of symmetry, the nickel atom being required to be in its position. Two molecules of 3-acetyl-5,6-dimethylpyridazine hydrazone are coordinated to nickel(II) ion with two water molecules in apical positions. The molecular structure of $NiL(ClO_4)_2\cdot 2H_2O$ with the numbering systems utilized for description of the molecule is shown in Fig. 2. Bond distances and bond angles with their standard deviations are given in Table 3. Two organic moieties and nickel(II) ion are almost coplanar. The deviation of each atom from the least-squares plane formed by N2, N3, and Ni atoms is given in Table 4.

Discussion

As is seen in Fig. 2, the organic moiety is demonstrated

Table 2. The final positional and thermal parameters with their standard deviations ($\times 10^4$)
The anisotoropic thermal parameters are in the form of $\exp[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)]$.

Atom	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ni	0	0	0	130(3)	397(1)	57(1)	41(4)	−60(3)	−22(2)
Cl	1569(4)	1518(3)	3405(2)	195(7)	66(2)	91(2)	−20(7)	38(6)	−38(4)
O	−778(9)	−387(6)	1126(6)	209(20)	63(6)	79(5)	69(19)	−14(17)	−34(10)
N1	−3908(10)	1061(8)	−724(7)	136(20)	73(9)	82(7)	58(23)	−107(20)	−26(13)
N2	−2129(10)	1260(6)	−231(6)	147(19)	45(6)	56(5)	44(19)	−52(17)	−9(10)
N3	1415(10)	1422(6)	596(6)	143(19)	41(6)	55(5)	35(19)	−28(17)	−12(10)
N4	3239(10)	1397(7)	981(6)	139(19)	49(7)	60(5)	15(20)	−62(17)	−8(10)
C1	−2945(12)	3311(9)	−137(7)	198(27)	45(8)	67(7)	101(26)	−65(23)	−1(13)
C2	−1658(12)	2278(9)	58(7)	149(24)	48(8)	55(6)	45(23)	−26(20)	−2(12)
C3	311(11)	2369(9)	557(7)	134(22)	42(7)	55(6)	41(22)	−57(20)	−14(12)
C4	1032(12)	3363(9)	985(7)	188(25)	40(7)	43(6)	15(24)	−23(20)	−13(11)
C5	2928(12)	3346(9)	1424(7)	195(26)	45(8)	46(6)	−27(24)	−14(20)	−2(12)
C6	3997(12)	2340(9)	1410(7)	160(23)	46(8)	43(6)	−3(23)	−16(19)	4(11)
C7	6076(12)	2212(9)	1861(8)	144(24)	70(10)	64(7)	−22(27)	−47(22)	0(14)
C8	3799(13)	4371(10)	1948(8)	301(36)	48(9)	71(8)	−63(31)	−75(29)	−36(14)
O1	930(17)	722(14)	2770(10)	712(60)	232(20)	125(10)	−45(56)	41(39)	−136(23)
O2	3040(14)	2195(13)	3281(9)	407(39)	222(19)	133(11)	−186(45)	−66(33)	124(24)
O3	−162(16)	1947(13)	3345(9)	313(33)	269(22)	145(11)	134(46)	18(32)	−135(28)
O4	2047(14)	697(13)	3965(10)	667(57)	196(18)	110(9)	−147(51)	−21(37)	128(22)

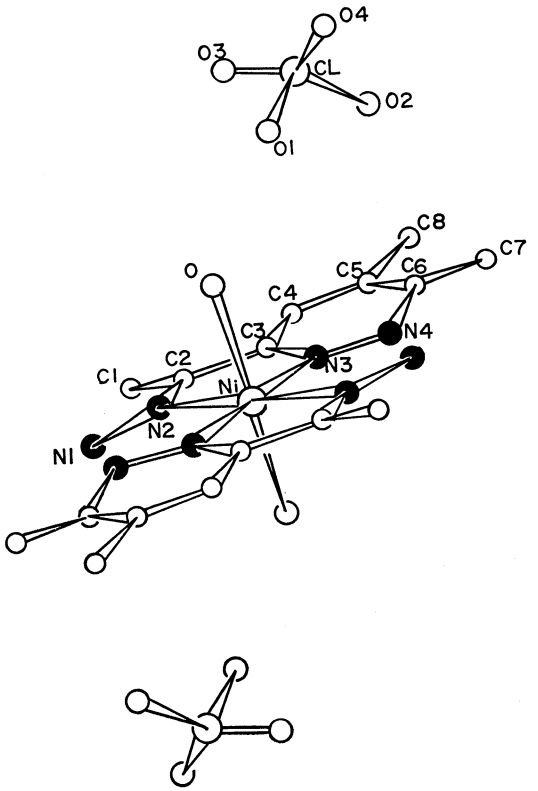


Fig. 2. Molecular structure of $NiL(ClO_4)_2 \cdot 2H_2O$.

Table 3. Bond distances and bond angles

Bond distances (Å) with their standard deviations.			
Ni–O	2.102(10)	C4–C5	1.382(18)
Ni–N2	2.075(11)	C3–C4	1.389(18)
Ni–N3	2.047(10)	C1–C2	1.496(20)
N1–N2	1.363(17)	C5–C8	1.518(20)
N2–C2	1.288(17)	C6–C7	1.507(19)
C2–C3	1.462(19)	C1–C1	1.372(20)
C3–N3	1.345(17)	C1–O2	1.380(19)
N3–N4	1.323(15)	C1–O3	1.343(20)
N4–C6	1.347(17)	C1–O4	1.339(20)
C5–C6	1.393(18)		
N2···N3′	3.215(17)	N1···N4′	2.93 (17)

Bond angles (°). Each of the standard deviations is blow 1.1°.			
O–Ni–N2	90.5	N2–C2–C3	114.3
O–Ni–N3	87.9	C1–C2–C3	121.7
N2–Ni–N3	77.4	N3–C3–C2	115.5
N2–Ni–N3′	102.5	N3–C3–C4	121.3
Ni–N2–N1	122.1	C2–C3–C4	123.1
Ni–N2–C2	117.1	C3–C4–C5	117.5
N1–N2–C2	120.4	C4–C5–C6	118.2
Ni–N3–N4	122.9	C4–C5–C8	121.0
Ni–N3–C3	115.0	C6–C5–C8	120.6
N4–N3–C3	121.7	N4–C6–C5	122.0
N3–N4–C6	118.9	N4–C6–C7	114.5
N2–C2–C1	123.7	C5–C6–C7	123.4

to be 3-acetyl-5,6-dimethylpyridazine hydrazone. This acts as a bidentate chelating agent, in which the ring nitrogen adjacent to the acetyl and the imino-nitrogen of hydrazone coordinate to nickel(II) ion to form a five-membered chelate ring. Two 3-acetyl-5,6-dimethylpyridazine hydrazone and nickel(II) ion are almost coplanar, although C8 (methyl carbon at the 6-position of pyridazine) slightly deviates from the least-squares plane formed by N2, N3, and Ni atoms. The distance between the nickel(II) ion and the water oxygen is 2.102 Å, the direction being nearly at right angles to the least-squares plane. Thus, the molecule has a twofold axis, the symmetry around the nickel(II) ion being approximately D_{2h}.

Table 4. Deviation of atoms from the least squeares plane (Å)

N1	−0.10	C4	0.21
N4	0.03	C5	0.26
C1	−0.10	C6	0.17
C2	0.00	C7	0.20
C3	0.08	C8	0.48

The least squares plane is defined by Ni, N2, and N3.

One of the characteristics of this molecule is a distorted configuration around the metal ion. Equatorial nitrogens form a rectangle; the distance between N2 and N3 is 2.58 Å, while the distance between N2 and N3′ is 3.215 Å. Thus, the N2–Ni–N3 angle is only 77.4°, while the N2–Ni–N3′ angle is 102.5°. These interatomic distances and bond angles are comparable with those in the nickel(II) complex with 2-pyridinecarboxamide anion.[8] The marked distortion around the metal ion can be attributed to the strain inherent in the ligand, which forms a five-membered chelate ring with conjugated double bonds.

In general, hydrazines condense with carbonyl compounds to form heterocyclic compounds.[9] However, the condensation between hydrazine and biacetyl has not yet been fully elucidated. Biacetyl hydrazone, the initial condensation product between diacetyl and hydrazine, has an active methyl group in addition to amino and carbonyl groups. Accordingly, under acidic and alkaline conditions the Aldol type condensation reaction as well as Schiff base formation are possible It is likely that 3-acetyl-5,6-dimethylpyridazine hydrazone was formed by the scheme shown in Fig. 3.

In order to separate and characterize the hydrazone, $NiL(ClO_4)_2 \cdot 2H_2O$ was decomposed with ethylenediaminetetraacetic acid in an alkaline solution. The isolated product, however, differs in composition from that of 3-acetyl-5,6-dimethylpyridazine hydrazone.

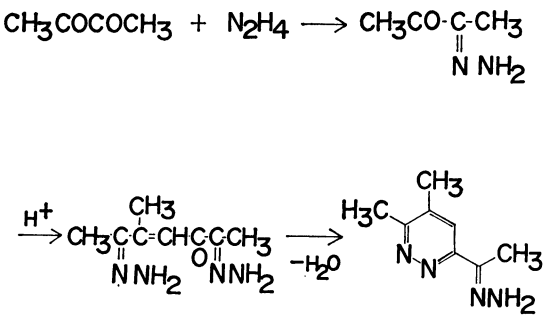


Fig. 3. The possible reaction scheme for 3-acetyl-5,6-dimethylpyridazine hydrazone formation.

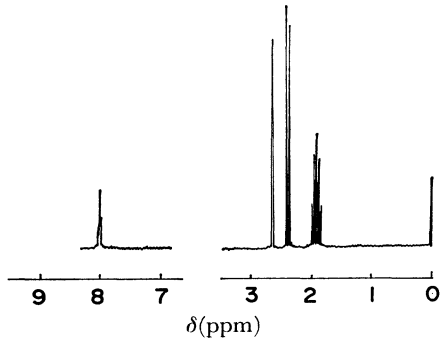


Fig. 4. NMR spectrum of 3-acetyl-5,6-dimethylpyridazine azine.

Judging from elemental analyses and the molecular weight determined from mass spectroscopy (m/e=296 and 297), the compound is likely to be 3-acetyl-5,6-dimethylpyridazine azine. This is supported by its NMR spectrum (Fig. 4) in which only four singlet signals are observed at 2.36, 2.42, 2.64, and 8.01 ppm with the intensity of 3, 3, 3, and 1 in ratio, respectively. The quintet around 1.9 ppm is due to CHD_2CN. The signals at 2.65 and 8.01 ppm are assigned to the α-methyl and the hydrogen on the ring, respectively. The signals at 2.36 and 2.42 ppm are ascribed to the methyl on the pyridazine ring. Infrared spectrum of 3-acetyl-5,6-dimethylpyridazine azine displays the C=N stretching vibration at 1670 cm^{-1} and the skeletal vibrations at 1595 and 1445 cm^{-1}. Thus, it is evident that 3-acetyl-5,6-dimethylpyridazine hydrazone in the complex was transformed into to 3-acetyl-5,6-dimethypyridazine azine by demetallation. Since azines are more stable than hydrazones, it is likely that a relatively severe reaction conditions (reflux around 100 °C in an alkaline solution) caused the azine formation.

Selected infrared absorption bands, molar conductivities and magnetic moments of the complexes are given in Table 5. Antisymmetric and symmetric N–H stretching vibrations of the amino group were found around ≈3340 and ≈3180 cm^{-1}, respectively. The C=N stretching vibration and the skeletal vibrations in the complexes were observed at 1640 cm^{-1} and at ≈1580 and ≈1440 cm^{-1}, respectively. Each band is lower in frequency as compared with that in the free ligand. The skeletal vibrations for 3-acetyl-5,6-dimethylpyridazine hydrazone should be practically the same in frequency as 3-acetyl-5,6-dimethylpyridazine azine because of the similarity in structure, while the C=N band in the hydrazone may be slightly higher than that in the azine because of the lower conjugation in the former. This is attributable to the coordination of the hydrazone nitrogen and the pyridazine nitrogen to the metal ion. Effective magnetic moment of each complex is comparable to the value for common copper(II) or high-spin nickel(II) complexes.

Electronic spectra of the complexes are given in Figs. 5 and 6. Reflectance spectra of $CuL(ClO_4)_2$ and $CuBr_2$ differ a great deal from each other, indicating the different structures in solid state. However, their solution spectra in methanol are nearly the same. Since the powder spectrum of $CuL(ClO_4)_2$ is similar to the solution spectrum, the configuration around the metal is nearly the same in solid and in solution. The fact

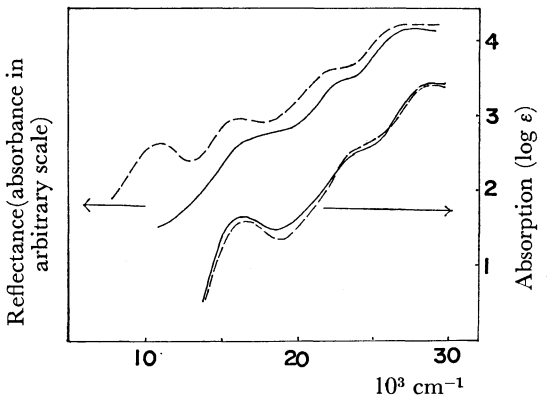


Fig. 5. Electronic spectra of $CuL(ClO_4)_2$ (——) and $CuLBr_2$ (– – –).

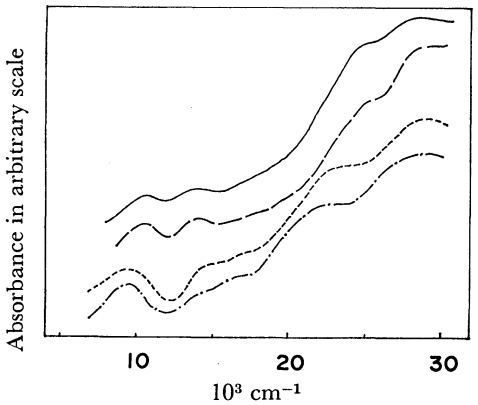


Fig. 6. Reflectance spectra of $NiL(ClO_4)_2 \cdot 2H_2O$ (——), $NiL(BF_4)_2 \cdot 2H_2O$ (– – –), $NiLCl_2$ (------), and $NiL(NO_3)_2$ (-·-·-).

Table 5. Selected IR bands (cm^{-1}), molar conductivity Λ (Ω^{-1} cm^2 mol^{-1}), and effective magnetic moment μ_{eff} (Bohr magneton) of complexes

	IR									Λ	μ_{eff}
	N–H		C=N	Skeletal		X⁻					
$CuL(ClO_4)_2$	3350	3150	1640	1580	1445	1105	1050			182 (MeOH)	1.75
$CuBr_2$	3280	3125	1640	1580	1440					171 (MeOH)	1.76
$NiL(ClO_4)_2 \cdot 2H_2O$	3340	3180	1640	1585	1440	1120—1080				165 (MeOH)	2.96
$NiL(BF_4)_2 \cdot 2H_2O$	3330	3180	1640	1583	1440	1080—1020				178 (MeOH)	3.00
$NiLCl_2$	3340	3190	1640	1585	1440					257 (H_2O)	3.06
$NiL(NO_3)_2$	3350	3190	1640	1587	1440	1420	1305	825		235 (H_2O)	3.04

that the infrared spectral band due to perchlorate ion splits considerably (1105 and 1050 cm^{-1}) implies that perchlorate oxygen coordinates weakly to the copper(II) ion at the apical positions.[10]

The d-d band of $CuLBr_2$ in solid state splits into two bands, the lower band being very low in frequency (11100 cm^{-1}). The splitting of the ligand field bands in the low energy region is generally caused by the fifth coordination to copper(II) ion.[11] Since the spectrum of $CuLBr_2$ resembles spectra[12] of [Cu(trien)SCN]SCN, $[Cu(NH_3)_5](BF_4)_2$, and $[Cu(en)_2NH_3]X_2$ whose configuration is supposed to be tetragonal-pyramidal, it is likely that $CuLBr_2$ has a distorted five-coordinate structure with a bromide ion at the apical position. Molar conductivity of the copper(II) complexes indicates that they are 2: 1 electrolyte in methanol.

The nickel(II) complexes are also 2: 1 electrolyte in methanol or water. Because of relatively low solubility in most solvents the electronic spectra of the nickel(II) complexes were measured on a solid sample. The spectra of $NiL(ClO_4)_2 \cdot 2H_2O$ and $NiL(BF_4)_2 \cdot 2H_2O$ are similar to each other, where there are some d-d bands in the region 16000—22000 cm^{-1} in addition to the well resolved bands at $\approx$10500 and $\approx$14000 cm^{-1}. Since the symmetry around the metal in $NiL(ClO_4)_2 \cdot 2H_2O$ is approximately D_{2h} (or lower symmetry), the transitions $^3T_{2g} \leftarrow {}^3A_{2g}$ and $^3T_{1g} \leftarrow {}^3A_{2g}$ for nickel(II) under O_h-symmetry split into two (or three) components respectively in $NiL(ClO_4)_2 \cdot 2H_2O$ and $NiL(BF_4)_2 \cdot 2H_2O$, hence producing a complicated spectrum.

Spectra of $NiLCl_2$ and $NiL(NO_3)_2$ are similar to each other, but differ from those of $NiL(ClO_4)_2 \cdot 2H_2O$ and $NiL(BF_4)_2 \cdot 2H_2O$. Since these spectra also show complicated d-d bands in the region 14000—23000 cm^{-1}, the configuration around the metal may be a distorted octahedron, where it is presumed the apical ligands are chloride or nitrate ion. In fact the infrared spectrum of $NiL(NO_3)_2$ indicates characteristic bands of nitrate ion at 1420, 1305, and 825 cm^{-1} indicating that the nitrate ion acts as a unidentate ligand.[13]

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