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Binuclear Metal Complexes. III.[1] Preparation and Properties of Mononuclear and Binuclear Copper(II) and Nickel(II) Complexes of New Macrocycles and Their Related Ligands[2]

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The syntheses and properties of copper(II) and nickel(II) complexes of *N,N'*-alkylenebis(3-formyl-5-methylsalicylaldimine (alkylene=ethylene, propylene, or trimethylene) are described. By the reaction of these complexes with other alkylenediamines (ethylenediamine or trimethylenediamine), mononuclear copper(II) and nickel(II) complexes of new N_4O_2-type macrocycles have been synthesized. These complexes react with additional copper(II) or nickel(II) ions to form binuclear copper(II) or nickel(II) complexes. The geometries and properties of these new complexes are discussed.

It is known that the syntheses of macrocyclic, polydentate ligands are much facilitated by the template effect of metal ions.[3] In recent years considerable efforts have been directed towards syntheses of new macrocycles and their metal complexes. However, it appears that most of the work in this area dealt with mononuclear complexes of macrocycles, and only a few macrocycles making a binuclear metal complex have been reported.[4–7]

It is known that *N,N'*-ethylenebis(salicyclaldimino)copper(II) reacts with copper(II) and other divalent metal ions to form a binuclear or trinuclear complex.[8] It is also well established that binuclear copper(II) complexes are obtained when copper(II) chloride or bromide is allowed to react with bis-(*N*-R-salicylaldimino)copper(II),[9] where R is an alkyl or a phenyl group attached to the imino nitrogen. Formation of these complexes is based on the fact that a phenolic oxygen atom can form bonds with two metal ions. Binuclear copper(II) complexes of 2,6-diformyl-4-4-methylphenol[10] and its Schiff base derivatives[10,11,12] have also been reported, where the phenolic oxygen acts as a bridge and the two formyl oxygens or imino nitrogens coordinate to copper(II) ions.

We have attempted to prepare new macrocycles which form a nearly planar, binuclear metal complex in such a way that two phenolic oxygens in the macrocyclic moiety bridge two metal ions. We prepared the copper(II) and nickel(II) complexes of *N,N'*-alkylenebis(3-formyl-5-methylsalicylaldimine) (alkylene=ethylene, propylene, or trimethylene) and then the mononuclear copper(II) and nickel(II) complexes of new N_4O_2-type macrocycles, using the above complexes as starting materials. The four macrocycles obtained are: 23,24-dihydroxy-10,21-dimethyl-3,6,14,17-tetraazatricyclo[17,3,1,1$^{8,12)}$]tetracosa-1(23),2,6,8(24),9,11,13,17,19,21-decaene (abbreviated to

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[1] Part I: Ref. 9 and Part II: Ref. 10.

[2] Presented at the 20th Symposium on Coordination Chemistry, Tokyo, Novermber, 1970. A part of this work has been reported by H. Okawa and S. Kida, *Inorg. Nucl. Chem. Lett.*, **7**, 751 (1971).

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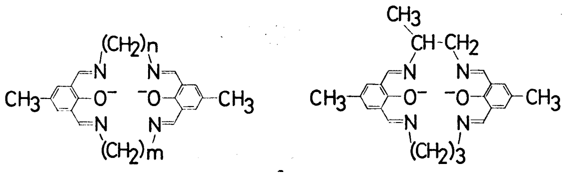
[12] R. Robson, *Inorg. Nucl. Chem. Lett.*, **6**, 125 (1970).

OK-2,2), 24,25-dihydroxy-10,22-dimethyl-3,6,14,18-tetraazatricyclo[18,3,1,$1^{8,12)}$]pentacosa-1(24),2,6,8(25),9,11,13,18,20,22-decaene (OK-2,3), 24,25-dihydroxy-4,10,22-trimethyl-3,6,14,18-tetraazatricyclo[18,3,1,$1^{8,12)}$]pentacosa-1(24),2,6,8(25),9,11,13,18,20,22-decaene (OK-2(pn),3), and 25,26-dihydroxy-11,23-dimethyl-3,7,15,19-tetraazatricyclo[19,3,1,$1^{9,13)}$]hexacosa-1(25),2,7,9(26),10,12,14,19,21,23-decaene (OK-3,3) (Fig. 1).

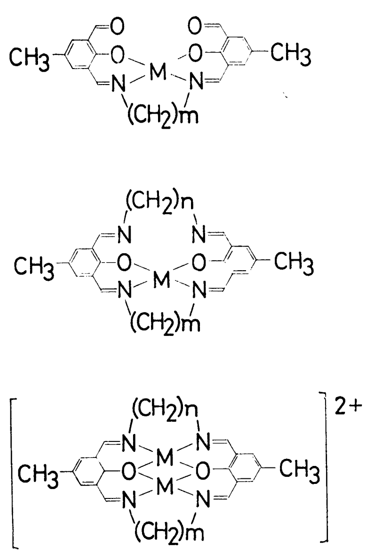


m=2, *n*=2: OK-2,2
m=2, *n*=3: OK-2,3
m=3, *n*=3: OK-3,3

OK-2(pn), 3

Fig. 1. Structures of macrocycles.

Three types of complexes have been prepared. The strucutral formulas are given in Fig. 2. The metal complexes of *N,N'*-alkylenebis(3-formyl-5-methylsalicylaldimine) (type 1) are abbreviated to Fsal-*m*-M, where *m* is 2 or 3 and M stands for copper or nickel. OK-*m*,*n*-M indicates the mononuclear metal complex of the macrocycles, in which *m* and *n* denote the number of methylene groups in the chelate ring and the number of the methylene groups in the bridge combining the two uncoordinated nitrogens, respectively. In the case where *l*-propylenediamine is included in the ligand instead of ethylenediamine, the macrocycle is abbreviated to OK-2-(*l*-pn),3. $[\text{OK-}m,n\text{-M}_2]^{2+}$ represents the binuclear metal complex of the macrocycle.



Type 1
Fsal-*m*-M

Type 2
OK-*m*,*n*-M

Type 3
$[\text{OK-}m,n\text{-M}_2]^{2+}$

Fig. 2. Structures of three types of complexes.

Experimental

Syntheses. *2,6-diformyl-4-methylphenol*: Denton and Suschitzky's method[13] was modified for the preparation of 2,6-diformyl-4-methylphenol. *p*-Cresol (50 g) and hexamethylenetetramine (50 g) were mixed in a mortar. The pulverized mixture was added to polyphosphoric acid (500 g) at 160°C under vigorous stirring. The reaction mixture was cooled and hydrolyzed with water, and the product was isolated by steam distillation. Chameleon chemical grade polyphosphoric acid is suitable for this reaction. The yield was 8—11%, which is superior to that reported in literature.[13]

Fsal-2: 2,6-diformyl-4-methylphenol (9.85 g) and ethylenediamine (1.8 g) were mixed in ethanol. The orange prisms which separated were collected and recrystallized from dioxane to give yellow prisms with a melting point of 190—193°C.

Found: C, 68.05; H, 5.90; N, 8.49%. Calcd for $C_{20}H_{20}N_2O_4$: C, 68.17; H, 5.72; N, 7.95%.

Fsal-3: This compound was prepared by treating 2,6-diformyl-4-methylphenol (9.85 g) with 1,3-diaminopropane (2.22 g) in ethanol. The precipitate was collected and recrystallized from dioxane as yellow prisms. It melts at 144—147°C.

Found: C, 69.10; H, 6.02; N, 7.67%. Calcd for $C_{21}H_{22}N_2O_4$: C, 68.84; H, 6.05; N, 7.65%.

Fsal-m-M type Complexes: Copper(II) and nickel(II) complexes of Fsal-2 and Fsal-3 were synthesized. Methods of preparation for these complexes are the same in principle. A typical procedure is as follows. An aqueous solution of a slight excess of copper(II) acetate monohydrate was added to a solution of Fsal-2 in warm ethanol. Soon brown needles separated. They were collected and washed with ethanol.

The complexes can be prepared by treating stoichiometric amounts of 2,6-diformyl-4-methylphenol, diamine, and metal acetate in ethanol. Fsal-2(*l*-pn)-Cu was synthesized by this method.

Fsal-2-Cu and Fsal-2(*l*-pn)-Cu form greenish brown needles and Fsal-3-Cu green needles. The nickel(II) complexes form orange needles. Elemental analyses of the complexes are given in Table 1.

TABLE 1. ANALYSES OF Fsal-*m*-M TYPE COMPLEXES

	Found(%)			Calcd(%)		
Fsal-*m*-M[a]	C	H	N	C	H	N
Fsal-2-Cu	57.79	4.50	6.86	58.04	4.38	6.77
Fsal-2(*l*-pn)-Cu	58.81	4.78	6.39	58.94	4.71	6.55
Fsal-3-Cu	58.56	4.61	6.10	58.94	4.71	6.55
Fsal-2-Ni·1/2H_2O	57.18	4.53	6.60	57.46	4.58	6.70
Fsal-3-Ni	59.42	4.78	6.41	59.61	4.76	6.62

a) Fsal-2=$C_{20}H_{18}N_2O_4$; Fsal-2(*l*-pn) and Fsal-3=$C_{21}H_{20}N_2O_4$.

OK-m,n-M type Complexes: These were synthesized by the reaction of Fsal-*m*-M and ethylenediamine or 1,3-diaminopropane in *N,N*-dimethylformamide. The general synthetic method for macrocyclic complexes is given for OK-2,2-Cu as an example. Ethylenediamine (120 mg) was added to a vigorously stirred, hot solution of Fsal-2-Cu (828 mg) in *N,N*-dimethylformamide (800 m*l*) for thirty seconds. Stirring was continued for ten minutes and the reaction mixture was allowed to stand overnight. The brown prisms which separated were collected and washed with ethanol.

OK-2,3-Cu and OK-3,3-Cu form greenish brown and green prisms, respectively. OK-2,2-Ni and OK-2,3-Ni form orange prisms. The elemental analyses of the complexes are given in Table 2.

$[OK\text{-}m,n\text{-}M_2]^{2+}$ *type Complexes*: These were synthesized when an equimolar quantity of OK-*m*,*n*-M and M(II) salt

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[13] A. Denton and H. Suschitzky. *J. Chem. Soc.*, **1963**, 4741.

Table 2. Yields and analyses of OK-*m*, *n*-M type complexes

OK-*m*,*n*-M[a)]	Yield %	Analysis					
		Found (%)			Calcd (%)		
		C	H	N	C	H	N
OK-2,2-Cu·H_2O	91	57.90	5.21	11.94	57.95	5.31	12.29
OK-2(*l*-pn), 3-Cu·H_2O	70	59.39	5.87	11.64	59.55	5.83	11.57
OK-2,3-Cu·H_2O	73	58.68	5.76	11.95	58.77	5.58	11.93
OK-3,3-Cu	97	61.56	5.62	11.73	61.58	5.62	12.02
OK-2,2-Ni·1/2H_2O	95	59.70	5.11	12.38	59.78	5.24	12.67
OK-2,3-Ni	75	61.65	5.50	12.29	61.68	5.41	13.53

a) OK-2,2=$C_{22}H_{22}N_4O_2$; OK-2,3=$C_{23}H_{24}N_4O_2$; OK-2(*l*-pn),3 and OK-3,3=$C_{24}H_{26}N_4O_2$.

Table. 3. Analyses of [OK-*m*,*n*-M_2]$^{2+}$ type complexes

[OK-*m*,*n*-M_2]$^{2+}$	Found (%)			Calcd (%)		
	C	H	N	C	H	N
[OK-2,2-Cu_2]Cl_2·C_2H_5OH·2H_2O	44.15	4.36	8.60	44.04	4.93	8.56
[OK-2,3-Cu_2]Cl_2·2H_2O	44.76	4.42	8.71	44.38	4.53	9.00
[OK-3,3-Cu_2]Cl_2·H_2O	46.61	4.54	9.11	46.61	4.56	9.06
[OK-3,3-Cu_2]SO_4·2H_2O	43.61	4.82	8.20	43.56	4.57	8.47
[OK-2,2-Ni_2]Cl_2·3H_2O	43.02	4.33	8.93	42.84	4.58	9.03
[OK-2,3-Ni_2]Cl_2·2H_2O	45.33	4.44	9.09	45.08	4.61	9.14

were treated in methanol. A typical procedure is given for [OK-3,3-Cu_2]Cl_2·H_2O. Copper(II) chloride dihydrate (35 mg) was added to a suspension of OK-3,3-Cu (120 mg) in methanol (20 m*l*), and the mixture was heated on a water bath. A clean solution was filtered, concentrated to 5 m*l* and diluted with ethanol (5 m*l*) to give green needles. They were collected and washed with a small amount of ethanol.

The results of elemental analyses of binuclear complexes of macrocycles are given in Table 3.

Measurements. Electronic spectra were determined in solution and in solid with a Hitachi EPS-3T recording spectrophotometer. A reflectance attachment was used for the measurements on the solid samples. Infrared spectra were measured with a Hitachi EPI-S2 spectrophotometer in the region from 4000 to 650 cm^{-1}, using the KBr disk method. Magnetic susceptibilities were measured by the Gouy method at room temperature, where Pascal's constants were used for diamagnetic correction. Circular dichroism spectra were recorded with a JASCO ORD/SP optical rotatary dispersion recorder.

Results and Discussion

Fsal-m-M type Complexes. Condensation of two molecules of 2,6-diformyl-4-methylphenol with one molecule of ethylenediamine or 1,3-diaminopropane affords the monomeric Schiff base, Fsal-2 or Fsal-3, in quantitative yield with no formation of polymer. Copper(II) and nickel(II) complexes of Fsal-2 and Fsal-3 were synthesized. Their IR and visible spectral bands and magnetic moments are given in Table 4.

In the IR spectra, the bands around 1670 and 1635—1628 cm^{-1} can be assigned to the C=O and C=N stretching vibrations, respectively. A new band appeared around 1545 cm^{-1} upon complex formation. The band can be assigned to the skeletal vibration of the aromatic ring.[15)]

The ligand field bands of Fsal-2-Cu and Fsal-3-Cu were observed at 17.5 and 16.6 kK, respectively. The *d-d* band for Fsal-3-Cu was found at a lower energy region than that for Fsal-2-Cu, which is thought to be a typical square-planarr copper(II) complex.[21–23)] Since it is well established that the red shift in the d-d band takes place when the configuration around the copper(II) ion is distorted from planarity,[17,24–26)] Fsal-3-Cu is assumed to possess a slightly distorted structure. The distortion of the configuration around the copper(II) ion in Fsal-3-Cu may also be demonstrated by its large magnetic moment of 2.01 B.M.

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14) This band had previously been assigned to $\nu_{\mathrm{C=N}}$[15)], but it is known from N^{15} data that the band due to $\nu_{\mathrm{C=N}}$ is located at a higher frequency.[16)] Now the band around 1545 cm^{-1} is attributed to the phenolic C–O vibration[17)] or the C–C vibration of the aromatic ring.[4)] However, the former assignment is inconsistent with the assignment of the band near 1340 cm^{-1} to the phenolic C–O vibration.[4,18,19)] Recently it has been reported that anilato complexes also show a similar band around 1530 cm^{-1}.[20)] From this fact it seems reasonable to assign this new band to the skeletal vibration of the aromatic ring.

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21) S. M. Crawford, *Spectrochim. Acta*, **19**, 255 (1963).

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23) K. S. Patel and J. C. Bailar, Jr., *J. Inorg. Nucl. Chem.*, **33**, 1399 (1971).

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25) R. L. Belford and T. S. Piper, *Mol. Phys.*, **5**, 251 (1962).

26) L. Sacconi, and M. Ciampolini, *J. Chem. Soc.*, **1964**, 276.

TABLE 4. PROPERTIES OF Fsal-*m* AND Fsal-*m*-M TYPE COMPLEXES

	IR bands (cm^{-1})			*d-d* band (kK)		μ_{eff} (B.M.)
	C=O	C=N	Skeletal	in DMF	Powder	
Fsal-2	1688	1645				
Fsal-2-Cu	1670	1635	1540	17.5	17.5	1.80
Fsal-2-Ni·1/2H_2O	1670	1630	1545	18.2	18.2	diamag.
Fsal-3	1685	1645				
Fsal-3-Cu	1670	1631	1548	16.6	16.5	2.01
Fsal-3-Ni	1667	1629	1549	16.7	16.3	diamag.

TABLE 5. PROPERTIES OF OK-*m*,*n*-M TYPE COMPLEXES

<table>
<tr><th rowspan="2"></th><th colspan="3">IR bands (cm^{-1})</th><th rowspan="2"><i>d-d</i> band (powder) (kK)</th><th rowspan="2">μ_{eff} (B.M.)</th></tr>
<tr><th>C=N</th><th>C=N→M</th><th>Skeletal</th></tr>
<tr><td>OK-2,2-Cu·H_2O</td><td>1645</td><td>1635</td><td>1540</td><td>17.5</td><td>1.80</td></tr>
<tr><td>OK-2,3-Cu·H_2O</td><td colspan="2">1632</td><td>1543</td><td>17.3</td><td>1.81</td></tr>
<tr><td>OK-2(<i>l</i>-pn),3-Cu·H_2O</td><td colspan="2">1635</td><td>1545</td><td>17.3</td><td>1.82</td></tr>
<tr><td>OK-3,3-Cu</td><td>1630</td><td>1625</td><td>1545</td><td>16.9</td><td>1.92</td></tr>
<tr><td>OK-2,2-Ni·1/2H_2O</td><td>1645</td><td>1627</td><td>1547</td><td>18.2</td><td>diamag.</td></tr>
<tr><td>OK-2,3-Ni</td><td colspan="2">1628</td><td>1547</td><td>18.1</td><td>diamag.</td></tr>
</table>

as compared with 1.81 B.M. for Fsal-2-Cu, since it is well known that the distortion from planar towards tetrahedral configuration gives rise to an increase in μ_{eff} value.[17] The large magnetic moment of 2.01 B.M. for Fsal-3-Cu as compared with 1.90 B.M. for *N*,*N*′-1,3-propylenebis(salicylaldimino)copper(II)[17] can be attributed to the greater distortion caused by the steric repulsion between its formyl groups, which are in the ortho-position relative to phenol oxygen.

Fsal-2-Ni and Fsal-3-Ni are diamagnetic and have only one ligand field band at 18.2 and 16.7 kK, respectively (in DMF). Thus it is evident that these complexes have a planar configuration. This agrees with the fact that Ni-salen families (salen=*N*,*N*′-ethylenebis(salicylaldimine)) retain the planar structure even if the number of methylene groups is increased to 3, 4, or 5.[28,29] However, it appears that the configuration around the nickel(II) ion in Fsal-3-Ni is slightly distorted judging from the position of its d-d band which is lower in energy than that of Fsal-2-Ni.

OK-m,n-M type Complexes. In the case of Fsal-*m-M* type complexes, the two uncoordinated formyl groups are sufficiently close to each other to allow an intramolecular cyclization by treatment with other molecules such as ethylenediamine or 1,3-diaminopropane (kinetic template reaction). The complexes employed as starting matetials for the syntheses of OK-m,n-M were Fsal-2-Cu, Fsal-3-Cu and Fsal-2-Ni. Fsal-3-Ni was not used because of its limited amount. Since OK-*m*,*n*-M type complexes are sparingly soluble in any solvent, their molecular weight could not be determined. The yields of the macrocyclic complexes were nearly quantitative. Their IR and electronic specta and magnetic moments are given in Table 5.

The IR spectra show two bands in the region from 1645 to 1625 cm^{-1} in the case of the same methylene chain (*i.e.* $n=m$), and no band due to the $\nu_{C=O}$ mode. The bands can be attributed to the coordinated and uncoordinated azomethine groups, respectively. On the other hand, in the case of OK-2,3-Cu and OK-2,3-Ni the bands due to the coordinated and uncoordinated azomethine groups do not appear as well-resolved bands. No appreciable shift of the skeletal vibration of the aromatic ring was observed by clcyization.

The powder reflectance spectra of OK-2,2-Cu, OK-2,3-Cu and OK-3,3-Cu possess *d-d* bands at 17.5, 17.3 and 16.9 kK, respectively. The magnetic moments of OK-2,2-Cu, OK-2,3-Cu and OK-3,3-Cu are 1.92, 1.81, and 1.80 B.M., respectively. The sequences of these *d-d* bands and magnetic moments are compatible with each other and agreee in the order of distortion from a square planar configuration, which is effected by the increase in numbers, *n*(and *m*), of methylene groups. A similar trend in the *d-d* bands is found in the copper(II), nickel(II) and cobalt(II) complexes of N_4-macrocycles.[30]

OK-2,2-Ni and OK-2,3-Ni are undoubtedly planar complexes, since they are diamagnetic and have only one *d-d* band around 18.1—18.2 kK. They are insoluble in polar solvents such as pyridine. This implies that coordination bonds in the tetragonal plane are strong enough to exclude the fifth and sixth coordination of the solvent molecules in the axial position. A similar behavior has been observed in Ni-salen,[31] in Ni-amben series[32] (amben=*N*,*N*′-ethylenebis(*o*-aminobenzylideneimine) and in nickel-

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[27] G. E. Batley and D. P. Graddon, *Aust. J. Chem.*, **21**, 1473 (1968).

[28] R. H. Holm, *J. Amer. Chem. Soc.*, **82**, 5632 (1960).

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[32] M. Green and P. A. Tasker, *ibid.*, *A*, **1970**, 2531.

(II) complexes of N_4-macrocycles.[30]

In order to obtain „OK-3,2,-Cu" with 6-6-6 condensed ring system, Fsal-3-Cu and ethylenediamine were allowed to react in *N*,*N*-dimethylformamide. The product obtained, however, showed identical IR and visivle spectra and the same magnetic moment as OK-2,3-Cu. Thus it can be concluded that „OK-3,2-Cu" and OK-2,3-Cu are the same compound. It seems that the copper(II) ion migrates during the cyclization process to form a stable 6-5-6 condensed ring system. For the sake of confirmation, Fsal-2-(*l*-pn)-Cu, OK-2(*l*-pn),3-Cu and „OK-3,2(*l*-pn)-Cu" were prepared by using *l*-propylenediamine instead of ethylenediamine, and their CD spectra were compared (Fig. 3). The CD spectra of OK-2(*l*-pn),3-Cu and „OK-3,2(*l*-pn)-Cu" were found to be practically the same and very similar to that of Fsal-2(*l*-pn)-Cu in intensity as well as in sign. This indicates that they all possess the 6-5-6 condensed ring system, which is more stable than the 6-6-6 condensed ring system. Our results are consistent with the conclusion of Nakahara *et al.*[33] that *N*,*N'*-ethylenebis(salicylaldimino)-copper(II) is more stable than *N*,*N'*-1,3-propylenebis-(salicylaldimino)copper(II). It seems that the reaction carried out in hot N,N-dimethylformamide causes copper(II) ion migration.

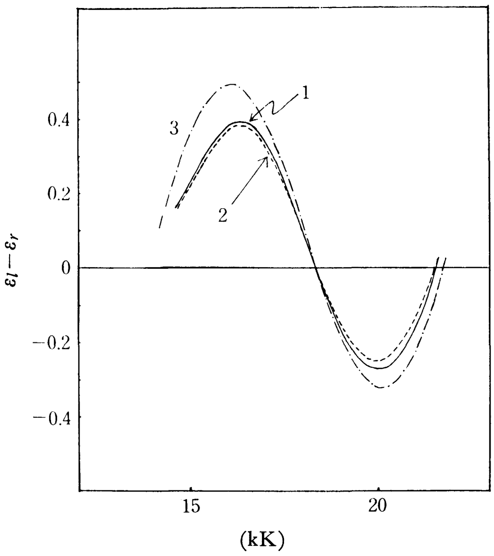

Fig. 3. CD spectra of OK-2(*l*-pn), 3-Cu(1), „OK-3,2(*l*-pn)-Cu"(2) and Fsal-2(*l*-pn)-Cu(3)(in *N*,*N*-dimethylformamide).

[OK-m,n-M_2]$^{2+}$ type Complexes. The ligand field bands and some IR bands of complexes of this type are given in Table 6. Their magnetic moments were not measured because of limited amounts.

Infrared spectra show only one band for the C=N stretching vibration. The marked difference in IR spectra between OK-*m*,*n*-M and [OK-*m*,*n*-M_2]$^{2+}$ is seen in the frequencies of the skeletal vibration of the benzene ring; 1540 cm^{-1} for the former and 1560—1565 cm^{-1} for the latter with the exception of [OK-2,2-Cu_2]$Cl_2 \cdot C_2H_5OH \cdot 2H_2O$. A similar behavior was found in a complex where a phenolic oxygen atom bridges two copper(II) ion.[34,35] Thus such a behavior in the skeletal vibration appears to be characteristic of this type of binuclear structure. However, [OK-2,2-Cu_2]$Cl_2 \cdot C_2H_5OH \cdot 2H_2O$ shows a band due to a skeletal vibration of the aromatic ring at 1540 cm^{-1}, which is difficult to explain at present.

The reflectance and absorption spectra of [OK-2,2-Cu_2]$Cl_2 \cdot C_2H_5OH \cdot 2H_2O$ show one ligand field band at 18.1 and 17.4 kK, respectively, which are higher in energy than that of OK-2,2-Cu. In both the solid and solution spectra of [OK-2,3-Cu_2]$Cl_2 \cdot$-$2H_2O$ a very broad band was observed in the range from 15 to 18 kK. This may be due to the presence of two copper(II) ions with enivornments of different steric geometry. The reflectance spectra of [OK-3,3-Cu_2]$Cl_2 \cdot H_2O$ and [OK-3,3-Cu_2]$SO_4 \cdot 2H_2O$ show one ligand field band at 15.3 and 15.6 kK, respectively, while their solution spectra show a main peak at 16.5 kK and a discernible shoulder at the longer wavelength side of the main absorption band. Recently Pilkington and Robson[3] prepared $LCu_2Cl_2 \cdot 6H_2O$ and $LCu_2SO_4 \cdot 2H_2O$ (L is their abbreviation for OK-3,3) by another method. $LCu_2SO_4 \cdot 2H_2O$ and our

TABLE 6. IR AND *d-d* BANDS OF [OK-*m*,*n*-M_2]$^{2+}$ TYPE COMPLEXES

	IR bands (cm^{-1})		*d-d* bands (kK)		
			Solutions		Powder
	C=N	Skeletal	MeOH	Py	
[OK-2,2-Cu_2]$Cl_2 \cdot C_2H_5OH \cdot 2H_2O$	1630	1540	18.1		17.4
[OK-2,3-Cu_2]$Cl_2 \cdot 2H_2O$	1641	1560	15—18		15—17.5
[OK-3,3-Cu_2]$Cl_2 \cdot H_2O$	1635	1565	16.5 (14.5)		15.3
[OK-3,3-Cu_2]$SO_4 \cdot 2H_2O$	1633	1563	16.5 (14.5)		15.6
[OK-2,2-Ni_2]$Cl_2 \cdot 3H_2O$	1633	1565	18.2	18.2	18.3
[OK-2,3-Ni_2]$Cl_2 \cdot 2H_2O$	1632	1563	18.0	18.1	18.2

Bands in parenthesis appear as a shoulder.

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[33] A. Nakahara, H. Yamamoto, and H. Matsumoto, This Bulletin, **37**, 1137 (1964).

[34] C. M. Harris, J. M. James, P. J. Milham, and E. Sinn, *Inorg. Chim. Acta*, **3**, 81 (1969).

[35] B. Coles, C. M. Harris, and E. Sinn, *Inorg. Chem.*, **8**, 2607 (1969).

[OK-3,3-Cu_2]SO_4·$2H_2O$ are undoubtedly the same complex, since they have the same composition and show very similar IR and visible spectra. Furthermore, LCu_2Cl_2·$6H_2O$ and [OK-3,3-Cu_2]Cl_2·H_2O are the same complex except for water of crystallization, because their IR and visible absorption peaks are practically the same. Pilkington and Robson[3] suggested on the basis of X-ray analysis that LCu_2Cl_2·$6H_2O$ has a square-pyramidal structure with a chlorine or a water molecule in apical positions. According to Ciampolini,[36] the copper(II) ion in a square pyramidal environment shows two distinguishable *d-d* bands, their main peak appearing on the shorter wave-length side with a shoulder on the longer wave-length side, but in the case of trigonal bipyramidal copper(II) complexes the band on the longer wave-length side is the main peak. Thus, [OK-3,3-Cu_2]Cl_2·H_2O and [OK-3,3-Cu_2]SO_4·$2H_2O$ probably keep a square-pyramidal, five-coordinate configuration in methanol solution.

[OK-2,2-Ni_2]Cl_2·$3H_2O$ and [OK-2,3-Ni_2]Cl_2·$2H_2O$ form orange prisms. Their visible spectra possess only one d-d band in the region from 18.3 to 18.0 kK. No absorption is found up to 2000 mμ. Thus it is expected that they are low-spin, square-planare binuclear complexes. It might be concluded that both complexes retain the planar geometry in a polar solvent such as pyridine, since there is no significant difference in electronic spectra between solid state, methanol solution and pyridine solution (Table 6). On the other hand, they differ from LNi_2Cl_2·$2H_2O$ (corresponding to „[OK-3,3-Ni_2]Cl_2·$2H_2O$") prepared by Pilkington and Robson,[3] in that the latter is dark-green and para-magnetic. Thus it can be concluded that nickel(II) ions in [OK-2,2,-Ni_2]Cl_2·$3H_2O$ and [OK-2,3-Ni_2]Cl_2·$2H_2O$ keep the square-planar configuration even in pyridine owing to the sufficiently strong ligand field, but that in LNi_2Cl_2·$2H_2O$ (=[OK-3,3-Ni_2]Cl_2·$2H_2O$) a chloride ion or water molecule can coordinate to apical positions, consistent with the decrease in the ligand field caused by an increase in the number of methylene groups.

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[36] M. Ciampolini, *Structure and Bonding*, **6**, 52 (1969).