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Binuclear Metal Complexes. VII.[1] Preparation and Properties of Binuclear Copper(II) and Nickel(II) Complexes of Hydrogen-bridged Macrocycles[2]

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Two types of binuclear copper(II) and nickel(II) complexes, OK-3(H), 3(H)-M_2 and [OK-m, 3(H)-M_2]ClO_4 ($m=2$ or 3), have been synthesized, where OK-3(H),3(H) is a macrocycle composed of two 2,6-diformyl-4-methylphenol and four hydroxylamine, and OK-m,3(H) is a macrocycle composed of two 2,6-diformyl-4-methylphenol, one diamine (ethylene diamine ($m=2$) or 1,3-diaminopropane ($m=3$)), and two hydroxylamine. It was found that a very strong antiferromagnetic exchange interaction is operating between two copper(II) ions for OK-3(H), 3(H)-Cu_2 and [OK-2,3(H)-Cu_2]ClO_4. The complex [OK-2,3(H)-Ni_2]ClO_4.DMF was found to be a novel-type binuclear nickel(II) complex, in which one nickel(II) ion is diamagnetic and the other is paramagnetic.

In the preceding paper of this series, Okawa and Kida[3] synthesized some binuclear copper(II) and nickel(II) complexes of the macrocycles formulated in Fig. 1. In this paper we report two types of binuclear copper(II) and nickel(II) complexes of new hydrogen-bridged macrocycles (Fig. 2).

The macrocycles were prepared by the combination of 2,6-diformyl-4-methylphenol, hydroxylamine and diamines. The complexes of the macrocycle composed of two 2,6-diformyl-4-methylphenol and four hydroxylamine are abbreviated to OK-3(H), 3(H)-M_2, in which imino nitrogens are connected by two O···H···O bridges. The complexes of the macrocycle composed of two 2,6-diformyl-4-methylphenol, one diamine and two hydroxylamine are abbreviated to [OK-m, 3(H)-M_2]$^+$, where imino nitrogens are connected by one alkylene (ethylene ($m=2$) or 1,3-propylene($m=3$)) chain and one O···H···O bridge.

The structures and properties of the complexes were studied from elemental analyses, infrared and visible spectra, mass spectrum, molar conductivities, and cryomagnetic measurements.

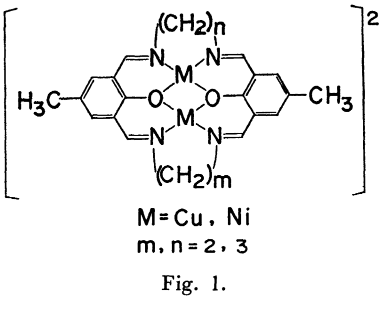
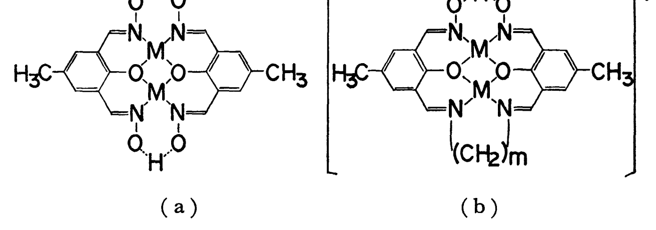


Fig. 1.



(a) (b)

Fig. 2. Structures of (a) OK-3(H),3(H)-M_2 and (b) [OK-m, 3(H)-M_2]$^+$ complexes.

Experimental

Syntheses. *OK-3(H),3(H)-Cu_2*: A solution of 2,6-diformyl-4-methylphenol (330 mg), hydroxylamine hydrochloride (278 mg), and copper(II) acetate monohydrate (400 mg) in 50 % ethanol (100 ml) was neutralized with an aqueous solution of sodium hydroxide (160 mg) to give a dark green precipitate. It was collected and thoroughly washed with hot pyridine.

Found: C, 41.96; H, 3.10; N, 10.49%. Calcd for $C_{18}H_{16}N_4O_6Cu_2$: C, 42.27; H, 3.15; N, 10.95%.

OK-3(H),3(H)-Ni_2·$3H_2O$. To a green solution of 2,6-diformyl-4-methylphenol (330 mg), hydroxylamine hydro-

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[1] Part VI: H. Okawa, T. Tokii, Y. Nonaka, Y. Muto, and S. Kida, This Bulletin, **46**, 1462 (1973).

[2] This work was presented at the 22nd synposium on Coordination Chemistry, Osaka, November 8, 1972.

[3] H. Okawa and S. Kida, This Bulletin, **45**, 1759 (1972).

chloride (278 mg) and nickel(II) chloride hexahydrate (475 mg) in 50% ethanol (100 ml), a 10% aqueous solution of sodium hydroxide was added until the solution was neutralized. Soon yellow crystalline powder separated out. It was collected and washed with water.

Found: C, 39.11; H, 3.68; N, 10.13%. Calcd for $C_{18}H_{22}N_4O_9Ni_2$: C, 38.90; H, 3.99; N, 10.01%.

[OK-2,3(H)-Cu₂]ClO₄. *N,N'*-Ethylenebis(3-formyl-5-methylsalicylaldimino)copper(II)[3] (828 mg), hydroxylamine hydrochloride (278 mg), and copper(II) perchlorate hexahydrate (741 mg) were dissolved in methanol (100 ml). To the clean solution was added dropwise an aqueous solution of sodium hydroxide (160 mg) to give brown prisms. They were collected and washed with ethanol.

Found: C, 39.97; H, 3.46; N, 9.50; Cu, 20.76%. Calcd for $C_{20}H_{19}N_4O_8ClCu_2$: C, 39.65; H, 3.16; N, 9.25; Cu, 20.97%.

[OK-3,3(H)-Cu₂]ClO₄·H₂O. *N,N'-1,3*-Propylenebis(3-formyl-5-methylsalicylaldimino)copper(II)[3] (214 mg), hydroxylamine hydrochloride (70 mg), and copper(II) perchlorate hexahydrate (182 mg) were dissolved in 70% methanol, and were stirred at 50 °C for 3 hr. When the reaction mixture was cooled, dark green prisms separated out. They were collected and recrystallized from methanol.

Found: C, 39.17; H, 4.11; N, 9.22%. Calcd for $C_{21}H_{23}N_4O_9ClCu_2$: C, 39.54; H, 3.63; N, 8.78%.

[OK-2,3(H)-Ni₂]ClO₄·DMF. *N,N'*-Ethylenebis(3-formyl-5-methylsalicylaldimino)nickel(II)[3] (705 mg), hydroxylamine hydrochloride, (208.5 mg), and nickel(II) perchlorate hexahydrate (384 mg) were dissolved in *N,N*-dimethylformamide (200 ml). To this solution an aqueous solution of sodium hydroxide (180 mg) was added. The reaction mixture was refluxed for 4 hr and concentrated to 30 ml to give orange prisms.

Found: C, 41.70; H, 3.91; N, 10.27%. Calcd for $C_{23}H_{26}N_5O_9ClNi_2$: C, 41.27; H, 3.92; N, 10.46%.

Measurements. Infrared spectra were measured with a Hitachi 215 grating spectrophotometer on a KBr disk. Electronic spectra were measured with a Hitachi EPS-3T recording spectrophotometer. Magnetic susceptibilities were determined by the Gouy method over the range from liquid nitrogen to room temperature. Effective magnetic moments were calculated from the equation

$$\mu_{\mathrm{eff}} = 2.83\sqrt{(\chi_A - N\alpha)T}\ ,$$

where Pascal's constants were used for correction of diamagnetism. The temperature independent paramagnetism, $N\alpha$, for a nickel(II) ion was estimated to be 193×10^{-6} c.g.s./mol.[4] Molar conductivities were measured in absolute methanol solution (*ca.* 10^{-3} mol) at 25 °C.

Results and Discussion

OK-3(H),3(H)-M₂ complexes. Some main infrared absorption bands, ligand field bands and magnetic moments at room temperature of OK-3(H), 3(H)-Cu_2 and OK-3(H),3(H)-$Ni_2\cdot3H_2O$ are given in Table 1.

The band at 1610 cm^{-1} can be assigned to the C=N stretching vibration. The broad band observed in the region 1750—1740 cm^{-1} appears to be similar in its origin to the bands found for $Ni(DMG)_2$[5] and $[Co(DMG)_2XY]^{-1}$ (X, Y=Cl^-, Br^-, NO_2^- or H_2O)[6] (DMG=dimethylglyoximate anion), where each of the band was assigned to a strongly hydrogen-bonded OH-vibration. The mass spectrum of OK-3(H),3(H)-Cu_2 showed two signals at m/e=510 and 512; these are well corresponding to the molecular ion (mol wt= 511.43). Recently we also found two peaks due to the molecular ion for a binuclear copper(II) complexes.[1] The appearance of two (or three) molecular ion peaks, therefore, characteristic of a binuclear copper(II) complex, since naturally occurring copper is composed of ^{63}Cu(69.09%) and ^{65}Cu(30.91%). Judging from these facts we concluded that the complexes possess a binuclear structure constructed with the macrocycle containing hydrogen-bridges shown in Fig. 2a.

The complex OK-3(H),3(H)-Cu_2 is practically insoluble even in the solvents of high donar-ability such as pyridine and *N,N*-dimethylformamide. The complex is stable in cold concentrated hydrochloric acid, sulfuric acid, and sodium hydroxide solution. The magnetic moment of the complex at room temperature is subnormal (0.59 B.M.). Its magnetic susceptibility was measured over a temperature range 77—300 K (Fig. 3). Although a deviation was found below 120 K owing to a small amount of paramagnetic impurity, the experimental data are well explained on the basis of the Bleaney-Bowers equation[7]

TABLE 1. PROPERTIES OF OK-3(H), 3(H)-M_2, AND [OK-m, 3(H)-M_2]$^+$ COMPLEXES

	IR (cm^{-1})				Λ[a]	d-d bands (kK)		μ_{eff} (B.M.)
	O···H···O	C=N	C=O	ClO_4^-		solid	methanol	
OK-3(H), 3(H)-Cu_2	1750	1610				14.9	—[b]	0.59
OK-3(H), 3(H)-$Ni_2\cdot3H_2O$	1740	1610				—[c]	—[b]	2.87
[OK-2,3(H)-Cu_2]ClO_4	1760	1635 1628		1110—1080	—[b]	20—15.4	—[b]	0.59
[OK-3,3(H)-Cu_2]$ClO_4\cdot H_2O$	1770	1637 1629		1110—1080	109	15.6	16.4(110) 14.3 (93)	0.61
[OK-2,3(H)-Ni_2]ClO_4·DMF	1780	1680 1622	1635	1110—1060	95	—[c]	20—16.7	2.25 (3.31)[d]

a) Molar conductivity ($\Omega^{-1}cm^2mol^{-1}$). b) Hardly soluble in methanol. c) Given in Fig. 4. d) This moment is obtained by assuming that one nickel(II) ion is diamagnetic.

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[4] Ballhousen, "Introduction to Ligand Field Theory," McGraw-Hill Book Company, Inc. (1962), p. 142.

[5] R. E. Rundle and M. Parasol, *J. Chem. Phys.*, **20**, 1487 (1952).

[6] J. Fujita, A. Nakahara, and R. Tsuchida, *ibid.*, **23**, 1541 (1955).

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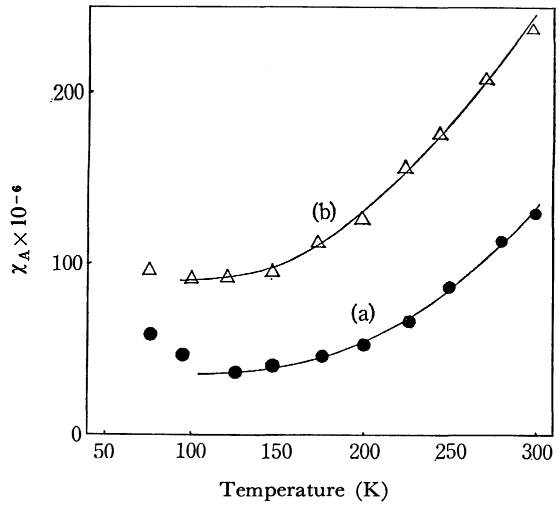

Fig. 3. Variation of molar susceptibility with temperature of (a) OK-3(H), 3(H)-Cu_2, and (b) [OK-2, 3(H)-Cu_2]ClO_4.

$$\chi_A = \frac{Ng^2\beta^2}{3kT}\left[1+\frac{1}{3}\exp(-2J/kT)\right]^{-1} + N\alpha,$$

in which each simbol means the general meaning. By the best fit of the experimental χ_A values to the equation, $-2J$, g, and $N\alpha$ were evaluated to be 870 cm^{-1}, 2.20, and 36×10^{-6} e.s.u./mol respectively. This large $-2J$ value indicates a very strong antiferromagnetic exchange interaction between the copper(II) ions. Generally the more planar the geometry around the copper(II) ion is, the larger the spin-exchange interaction between the copper(II) ions becomes.[8-10]

The reflectance spectrum of OK-3(H),3(H)-Ni_2·$3H_2O$ in Fig. 4 clearly indicates that the geometry around the nickel(II) ion is practically octahedral. The magnetic moment at room temperature is 2.84 B. M., that is slightly lower value compared with most octahedral nickel(II) complexes. The magnetic susceptibility of the complex obeys the Curie-Weiss law (Fig. 5a). The Weiss constant was determined to be −77 K, indicating an antiferromagnetic exchange interaction between a pair of nickel(II) ions.

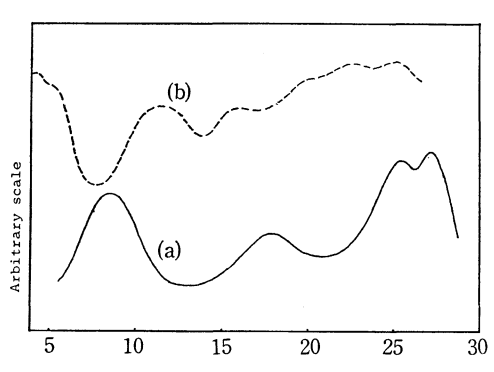

Fig. 4. Reflectance spectra of (a) OK-3(H), 3(H)-Ni_2·$3H_2O$, and (b) [OK-2, 3(H)-Ni_2]ClO_4·DMF.

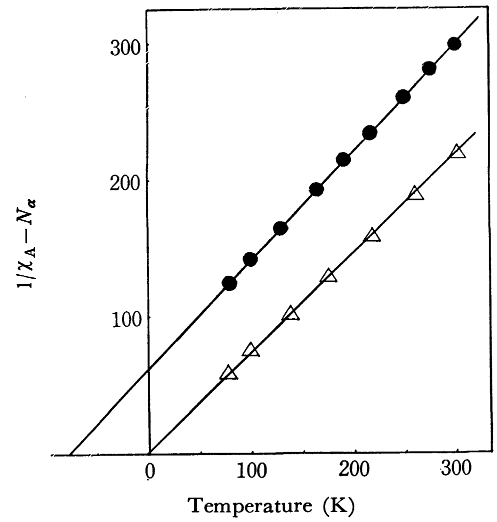

Fig. 5. Plots of the inverse susceptibilities of (a) OK-3(H), 3(H)-Ni_2·$3H_2O$, and (b) [OK-2, 3(H)-Ni_2]ClO_4·DMF per nickel atom as a function of temperature. In the latter case one nickel(II) ion is assumed to be diamagnetic.

Pilkington and Robson[11] reported that the μ_{eff} value for $LCu_2(ClO_4)_2$·$2H_2O$ (=[OK-3,3-Cu_2]$(ClO_4)_2$·$2H_2O$) was 0.58 B.M. at room temperature and the Weiss constant for LNi_2Cl_2·$2H_2O$ (=[OK-3,3-Ni_2]-Cl_2·$2H_2O$) was −125 K.

[OK-m,3(H)-M_2]$^+$ Complexes. The properties of [OK-m,3(H)-M_2]$^+$ complexes are given in Table 1. Since in the infrared spectra a band due to the O···H···O bond was observed in the region 1780—1760 cm^{-1}, the complexes were assumed to have a binuclear structure of the macrocycle formulated in Fig. 2b. Two bands in the region 1640—1620 cm^{-1} were attributed to the C=N stretching vibrations. This is consistent with the fact that there are two non-equivalent azomethine groups in [OK-m,3(H)-M_2]$^+$ complexes. The broad, strong band near 1110—1070 cm^{-1} was assigned to perchlorate ion.[12] In [OK-2,3(H)-Ni_2]ClO_4·DMF a shoulder was observed at 1635 cm^{-1}, which might be assigned to the $\nu_{C=O}$ mode of coordinated *N,N*-dimethylformamide.

The molar conductivities for [OK-3,3(H)-Cu_2]-ClO_4·H_2O and [OK-2,3(H)-Ni_2]ClO_4·DMF in absolute methanol at 25 °C clearly indicate that they are 1 : 1 electrolytes.

The reflectance spectrum of [OK-2,3(H)-Cu_2]ClO_4 possesses a very broad band around 20—15.5 kK. Similar spectrum was found for [OK-2,3-Cu_2]Cl_2.[3] The broadening of the band will be caused by the superposition of the d–d transition bands of the copper(II) ions, whose geometries are different from each other. The electronic spectrum of [OK-3,3(H)-Cu_2]-ClO_4·H_2O is similar to that of [OK-3,3-Cu_2]Cl_2·H_2O.[3] The splitting of the d–d band (16.4 and 14.3 kK) in methanol has been attributed to the fact[11] that the solvent molecule coordinates to the copper(II) ion to

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[8] H. Okawa, M. Honda, and S. Kida, *Chem. Lett.*, **1972**, 1027.

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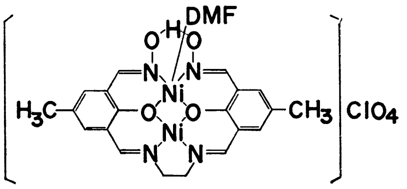

Fig. 6. The probable structure of [OK-2,3(H)-Ni_2]ClO_4·DMF.

form five- or six-coordinate complex.

The magnetic moment for [OK-2,3(H)-Cu_2]ClO_4 at room temperature was very low (0.59 B.M.). Its magnetic susceptibility was measured at various temperatures (Fig. 3b). The χ_A values obeyed the Bleaney-Bower's equation and the magnetic parameters obtained are $-2J=725\ cm^{-1}$, $g=2.10$, and $N\alpha=90\times10^{-6}$ c.g.s./mol.

The reflectance spectrum of [OK-2,3(H)-Ni_2]ClO_4·DMF given in Fig. 4b is markedly complicated; it differs from any of the spectra for octahedral,[13,14] planar,[13,14] and tetrahedral[15] nickel(II) complexes. Since it is evident from infrared spectral data that the strong intramolecular hydrogen-bond is present and that *N*,*N*-dimethylformamide coordinates to the nickel(II) ion, a tetragonal-pyramidal, five-coordinate structure is naturally assigned to the present complex. Recently many spectroscopic investigations of five-coordinate nickel(II) complexes have been reported,[14,16,17] and it is now well known that most low-spin tetragonal-pyramidal nickel(II) complexes have d-d bands in the region 10—20 kK.[16–18] On the other hand, high-spin, tetragonal-pyramidal nickel(II) complexes show d-d bands in the region 25—5 kK.[16,17] Judging from these facts at least one of the two nickel(II) ions in the complex seems to keep a high-spin, tetragonal-pyramidal geometry. In fact its magnetic moment at room temperature was 2.25 B.M. per nickel atom, indicating the presence of a paramagnetic nickel(II) ion. The relatively small magnetic moment of the complex will be explained in terms of (i) antiferromagnetic exchange interaction between a pair of paramagnetic nickel(II) ions or (ii) a binuclear system composed of one paramagnetic and one diamagnetic nickel(II) ions.

In order to clarify this magnetic phenomenon the magnetic susceptibility was measured at various temperatures (Fig. 5b). Since this complex obeys the Curie-Weiss law and its Weiss constant is very small ($\theta=-2$ K), it is evident that the relatively low magnetic moment is attributed to the novel binuclear system containing one high-spin and one low-spin nickel(II) ions. There are only few reports upon the complexes composed of paramagnetic and diamagnetic nickel(II) ions.[19] The reflectance spectrum given in Fig. 4b, therefore, can be interpreted as the superposition of the spectra of low-spin planar and high-spin tetragonal-pyramidal nickel(II) ions. The solution spectrum in methanol, however, was very simplified and showed a broad band around 15—20 kK. This spectrum resembles that of [OK-2,3-Ni_2]Cl_2.[3] This fact indicates that in methanol solution the complex is coordinated with neither *N*,*N*-dimethylformamide nor methanol molecule, and keeps the planar structure.

It is known that *N*,*N*′-ethylenebis(salicylaldimino)nickel(II) retains the planar structure in polar solvents such as pyridine.[20] In addition to this Okawa and Kida[3] reported that *N*,*N*′-ethylenebis(3-formyl-5-methylsalicylaldimino)nickel(II) and OK-2,3-Ni did not add pyridine and *N*,*N*-dimethylformamide. Therefore, in the present case, it is evident that *N*,*N*-dimethylformamide molecule coordinates to the nickel(II) ion in the 6–6–6 condensed ring system involving hydrogen-bridge, but not to the nickel(II) ion in the rigid 6–5–6 condensed ring system. Here, it is to be noted that no apical coordination takes place in any polar solvents in the case of [OK-2,3-Ni_2]Cl_2,[3] which has the same ring-system as [OK-2,3(H)-Ni_2]ClO_4·DMF, except that two imino nitrogens are connected with 1,3-propylene bridge instead of -O···H···O- bridge.

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