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Synthesis, Crystal Structure, and Property of Novel Tetranuclear Nickel(II) Complex with Multidentate Ligand 7-[(3,5-Dichloro-2-pyridyl)azo]-8-hydroxyquinoline-5-sulfonic Acid

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Reaction of nickel(II) perchlorate with the title ligand (Hpahqs) in aqueous solution followed by standing for about six months produces a complex having the formulation $[Ni_4(pahqs)_4(H_2O)_4]\cdot 20H_2O$. A single crystal X-ray analysis revealed that the complex contained the four nickel(II) and four ligand molecules and showed a novel structure of oxygen bridged tetranuclear nickel(II) complex. Crystal data: triclinic, space group $P\bar{1}$, a=17.884(7), b=22.071(8), c=12.819(8) Å, α=100.77(4)°, β=92.55(4)°, γ=71.46(4)°, Z=2. Except one N atom in each azo-group, all the other donor atoms in the ligand were fully used in coordination to nickel(II), forming either *N,N,O*- or *N,O*-chelate rings, simultaneously. The geometry around each of the four nickel(II) was distorted octahedron. The bond lengths of Ni–N(N atoms in *N,N,O*-terdentate moieties) were elongated compared with those of the corresponding complex, and the lengths of Ni–N(N atoms in quinoline rings) were kept almost similar values to those of the Ni(II)-8-hydroxyquinoline complex. The bond lengths of Ni–O were elongated compared with those of the nickel(II) complexes with either *N,N,O*- or *N,O*-chelate rings, resulting in the contraction of the angles of N–Ni–N or N–Ni–O. The angles of Ni–O–Ni around four nickel(II) sites were ca. 140°. The antiferromagnetic exchange interaction was operating between the four nickel(II) via bridging oxygen atoms.

The multidentate ligands of ortho-hydroxyazo system containing more than two groups of potentially chelating donor atoms have become of interest in connection with the coordination selectivity for a variety of metal ions.[1] Previously, we prepared the new multidentate ligands, 7-[(3,5-dihalo-2-pyridyl)azo]-8-hydroxyquinoline-5-sulfonic acid (abbr. as Hpahqs), and investigated their coordination behavior toward metal(II) ions in aqueous solution. As a result, Ni(II), Zn(II), and Cd(II) ions, which are classified as soft or medium acids, coordinated selectively to the *N,N,O*-terdentate moiety containing azo-group to form the 1 : 2 (metal : pahqs) complexes having four five-membered fused chelate rings.[2] On the contrary, VO(IV) (hard acid) bonded selectively to the only *N,O*-skeleton in hydroxyquinoline(HQ) moiety.[3]

The metal complexes of azo system ligands are difficult to isolate as a single crystal. There are only several studies for syntheses and analyses of single crystals of metal(II) complexes with ortho-hydroxyazo ligands, and, in addition, all these complexes have simple mononuclear or dinuclear structures.[4] In the present work,[5] a single crystal of Ni(II) complex with the title ligand having the peculiar composition of Ni(II): pahqs=4 : 4 was isolated and its structure has been characterized by X-ray crystallography. The most striking aspect of the present results was that, in this complex, except one N atom in each azo-group, all the other donor atoms in pahqs were fully used in coordination to Ni(II), and the four Ni(II) were bridged by O atoms in the HQ moieties, showing a first novel structure of tetranuclear Ni(II) complex. The difference in composition of metal to ligand of the species in solution[2] and of the present solid complex can not be explained so clear at this stage. Furthermore, it was found that an antiferromagnetic interaction was operating between the four Ni(II) via bridging oxygen atoms. These results suggest that this multidentate ligand will be expected to form various tetranuclear metal complexes via bridging oxygen atoms with other metal ions, which will be interested in structural and magnetic chemistry.[6,7]

Table 1. Crystal Data, Experimental Conditions, and Refinement Details

Chemical formula	$C_{56}H_{24}N_{16}O_{16}Cl_8S_4Ni_4\cdot 24H_2O$
Formula weight	2255.98
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	17.884(7)
b/Å	22.071(8)
c/Å	12.819(8)
α/deg	100.77(4)
β/deg	92.55(4)
γ/deg	71.46(4)
V/Å^3	4712(4)
Z	2
D_c/g cm^{-3}	1.589
D_m/g cm^{-3}	1.587
μ(Cu $K\alpha$)/mm^{-1}	4.638
Crystal size/mm^3	0.33×0.24×0.16
Scan mode	ω–2θ
Scan range/deg	$0\leqq\theta\leqq50$
Number of reflections measured	10224
Number of unique reflections with $[\lvert F_o\rvert\geqq 2.3\sigma(\lvert F_o\rvert)]$	8224
Number of variables	1190
Maximum residual electron density/eÅ^{-3}	0.91
R	0.105
R_w	0.145

Experimental

Synthesis of Ligand. The ligand was prepared by the method described in our previous paper.[2)]

Preparation of Crystal of $[Ni_4(pahqs)_4(H_2O)_4]\cdot 20H_2O$. To a solution of the ligand (0.205 g, 0.44 mmol) in 250 cm^3 of water was added $Ni(ClO_4)_2\cdot 6H_2O$ (0.195 g, 0.53 mmol) under stirring. The pH of the solution was adjusted to 2.81 by adding a perchloric acid (60%). The solution was stirred

Table 2. Atomic Coordinates(×10^4) and Equivalent Isotropic Temperature Factors with esd Values in Parentheses

Atom	x	y	z	B_{eq}/Å^2 a)	Atom	x	y	z	B_{eq}/Å^2 a)
Ni(1)	663(1)	2577(1)	−2488(2)	4.51(6)			Ligand C		
Ni(2)	2202(1)	2848(1)	−206(1)	4.12(5)	C(2C)	1409(7)	4261(6)	−505(10)	3.42(39)
Ni(3)	2475(1)	1037(1)	248(1)	4.11(5)	C(3C)	1360(7)	4789(5)	−950(11)	3.67(40)
Ni(4)	1750(1)	689(1)	−2688(1)	4.24(5)	C(4C)	1923(8)	4764(6)	−1681(12)	4.30(45)
		Ligand A			C(5C)	2515(7)	4187(6)	−1932(11)	3.68(42)
C(2A)	−609(7)	3970(6)	−2251(10)	3.74(40)	C(6C)	2582(6)	3659(5)	−1453(9)	2.52(34)
C(3A)	−873(7)	4592(6)	−2422(11)	3.81(39)	C(9C)	3630(6)	2046(5)	−1298(9)	2.56(34)
C(4A)	−416(9)	4820(7)	−2965(12)	4.80(48)	C(10C)	4405(6)	1846(5)	−1752(10)	2.80(35)
C(5A)	307(8)	4422(6)	−3286(10)	3.69(41)	C(11C)	4874(6)	1229(6)	−1775(9)	2.82(36)
C(6A)	600(7)	3787(6)	−3060(10)	3.25(38)	C(12C)	4592(6)	746(5)	−1432(9)	2.41(34)
C(9A)	2176(6)	2326(5)	−3429(9)	2.42(34)	C(13C)	5019(7)	80(6)	−1546(10)	3.46(40)
C(10A)	2832(7)	2367(6)	−4003(10)	3.46(40)	C(14C)	4660(8)	−327(6)	−1222(12)	4.34(45)
C(11A)	3481(6)	1837(6)	−4242(10)	2.94(37)	C(15C)	3898(7)	−71(5)	−766(10)	2.96(36)
C(12A)	3538(6)	1219(6)	−3968(9)	2.57(35)	C(17C)	3845(6)	967(5)	−947(9)	2.33(33)
C(13A)	4204(7)	662(6)	−4135(10)	3.31(38)	C(18C)	3355(6)	1631(5)	−811(9)	2.40(33)
C(14A)	4166(7)	98(6)	−3885(10)	3.66(41)	N(1C)	2006(5)	3715(4)	−731(7)	2.56(28)
C(15A)	3462(7)	91(6)	−3392(10)	3.20(38)	N(7C)	3195(5)	3082(4)	−1674(7)	2.83(30)
C(17A)	2876(7)	1181(5)	−3447(9)	2.70(35)	N(8C)	3086(5)	2651(4)	−1230(7)	2.27(27)
C(18A)	2180(6)	1731(5)	−3199(10)	2.94(36)	N(16C)	3515(5)	556(4)	−607(7)	2.40(27)
N(1A)	132(6)	3568(5)	−2543(8)	3.30(32)	O(22C)	5999(5)	1586(4)	−2366(8)	4.47(31)
N(7A)	1369(6)	3377(4)	−3388(8)	3.03(30)	O(23C)	5984(5)	488(4)	−3125(8)	5.07(32)
N(8A)	1489(5)	2806(4)	−3193(7)	2.37(27)	O(24C)	6304(5)	750(5)	−1311(9)	5.33(35)
N(16A)	2850(5)	615(4)	−3212(7)	2.49(28)	O(25C)	2684(4)	1836(3)	−286(6)	2.73(23)
O(22A)	3988(6)	2544(5)	−5227(9)	6.14(38)	S(21C)	5881(2)	989(2)	−2201(3)	3.72(10)
O(23A)	4944(6)	1752(6)	−4420(9)	6.56(43)	Cl(19C)	581(2)	5494(2)	−606(4)	5.94(13)
O(24A)	4302(5)	1404(5)	−5963(7)	4.92(33)	Cl(20C)	3224(2)	4098(2)	−2881(4)	5.99(14)
O(25A)	1572(4)	1665(3)	−2764(5)	2.36(22)			Ligand D		
S(21A)	4246(2)	1897(2)	−5021(3)	3.85(11)	C(2D)	1612(9)	363(7)	−5119(10)	4.14(45)
Cl(19A)	−1819(2)	5059(2)	−2017(4)	6.45(14)	C(3D)	1152(9)	342(7)	−6033(10)	4.34(47)
Cl(20A)	911(2)	4693(2)	−4000(3)	5.70(13)	C(4D)	328(8)	552(6)	−5991(11)	4.13(46)
		Ligand B			C(5D)	2(7)	742(6)	−4986(11)	3.42(40)
C(2B)	3574(8)	3175(6)	1104(12)	4.14(45)	C(6D)	461(7)	708(5)	−4101(10)	2.89(36)
C(3B)	3873(7)	3400(7)	2091(13)	4.82(48)	C(9D)	418(6)	937(5)	−1327(9)	2.37(33)
C(4B)	3463(8)	3554(7)	3015(12)	4.97(49)	C(10D)	−313(7)	907(6)	−961(9)	2.99(37)
C(5B)	2724(8)	3475(7)	2955(11)	4.32(45)	C(11D)	−438(7)	1047(5)	99(11)	3.23(38)
C(6B)	2438(8)	3254(6)	1992(10)	3.74(41)	C(12D)	103(7)	1264(5)	868(10)	3.01(37)
C(9B)	717(7)	3026(5)	803(9)	2.68(35)	C(13D)	−60(7)	1501(5)	1942(10)	3.28(38)
C(10B)	120(7)	3147(6)	1582(10)	3.23(38)	C(14D)	508(8)	1710(6)	2538(10)	3.69(41)
C(11B)	−600(7)	3080(6)	1270(11)	3.53(40)	C(15D)	1251(8)	1653(6)	2059(10)	3.39(39)
C(12B)	−719(7)	2824(6)	208(11)	3.24(38)	C(17D)	835(6)	1237(5)	434(10)	2.59(34)
C(13B)	−1424(7)	2688(7)	−162(12)	4.23(46)	C(18D)	1021(6)	1034(5)	−672(9)	2.31(32)
C(14B)	−1473(8)	2459(7)	−1217(13)	4.75(50)	N(1D)	1257(6)	537(5)	−4194(7)	3.07(31)
C(15B)	−873(7)	2372(6)	−1935(12)	3.93(44)	N(7D)	108(5)	830(5)	−3094(8)	2.92(30)
C(17B)	−145(6)	2723(5)	−571(10)	2.75(35)	N(8D)	608(5)	846(4)	−2368(8)	2.54(28)
C(18B)	605(7)	2827(5)	−264(11)	3.34(39)	N(16D)	1388(5)	1424(4)	1057(7)	2.72(29)
N(1B)	2851(5)	3119(4)	1101(8)	2.77(29)	O(22D)	−1847(5)	1551(5)	935(10)	5.98(37)
N(7B)	1655(6)	3221(5)	1970(8)	3.56(33)	O(23D)	−1018(7)	588(6)	1477(11)	7.55(47)
N(8B)	1469(5)	3059(4)	998(8)	2.71(28)	O(24D)	−1527(8)	531(8)	−248(10)	10.71(65)
N(16B)	−213(5)	2500(4)	−1620(8)	2.97(30)	O(25D)	1722(4)	950(3)	−1019(6)	2.45(22)
O(22B)	−1592(7)	2782(5)	2325(10)	7.27(44)	S(21D)	−1299(2)	930(2)	591(3)	4.37(11)
O(23B)	−1955(6)	3843(5)	1937(11)	7.66(45)	Cl(19D)	1626(3)	54(2)	−7253(3)	6.26(15)
O(24B)	−1003(8)	3585(8)	3215(10)	9.96(62)	Cl(20D)	−1016(2)	1015(2)	−4850(3)	5.25(12)
O(25B)	1130(4)	2738(3)	−992(6)	2.60(22)			Oxygen atom in coordinated water		
S(21B)	−1344(2)	3336(2)	2280(3)	4.79(12)	OW(1)	187(6)	2310(5)	−3946(8)	5.29(34)
Cl(19B)	4801(3)	3488(3)	2058(4)	7.43(17)	OW(2)	2476(4)	180(4)	656(7)	3.36(25)
Cl(20B)	2168(3)	3652(3)	4105(3)	7.27(17)	OW(3)	3069(5)	1239(4)	1579(7)	4.16(30)
					OW(4)	2058(5)	−262(4)	−2522(7)	3.83(27)

a) $B_{eq}=(4/3)\sum_i\sum_j \beta_{ij}(\boldsymbol{a}_i\cdot\boldsymbol{a}_j)$, where β_{ij} is the anisotropic temperature factor, and $\boldsymbol{a}_i$ and $\boldsymbol{a}_j$ are lattice parameters.

for ca. 12 h and then allowed to stand for about six months. The violet prismatic crystals (65.4 mg, yield: 28%) were obtained. Found: C, 30.04; H, 2.81; N, 10.00%. Calcd for $C_{56}H_{24}N_{16}O_{16}Cl_8S_4Ni_4\cdot 24H_2O$: C, 29.82; H, 2.86; N, 9.93%. Thermogravimetric analysis of the complex indicates a weight loss of 18.98% in the region 292—480 K (heating rate 3 K min^{-1}). This is in good agreement with the calculated weight loss (19.17%) for twenty-four water molecules from the complex. All the other chemicals used were of an analytical or equivalent grade and were used as received.

Physical Measurements. Infrared spectra of KBr pellets were recorded on a JASCO-A102 spectrometer. Polarograms were recorded on a Yanaco Polarographic Analyzer P-1100 in an aqueous solution. A three-electrode system comprising a dropping mercury working electrode (DME), a Pt-wire auxiliary electrode, and a saturated calomel reference electrode (SCE) was used for measurements. TG-DTA analyses were performed using Rigakudenki PTC-10A Differential Thermogravimetric Analyzer. Magnetic susceptibilities (χ_A) were measured by the Faraday method in the temperature range from 80 to 300 K. The apparatus was calibrated by the use of $[Ni(en)_3]S_2O_3$.[8] All the susceptibilities were corrected for a diamagnetism of the constituting atoms by the use of Pascal's constants.[9] The effective magnetic moments were calculated by the equation, $\mu_{eff}=2.828[(\chi_A-N_\alpha)T]^{1/2}$. In which, the temperature-independent paramagnetic contribution (N_α) was taken as 230×10^{-6}emu mol^{-1} (1 emu=$4\pi\times10^{-6}$ m^3).

Crystallographic Data Collection and Refinement of the Structure. Three dimensional X-ray diffraction data were collected on an Enraf-Nonius CAD4F-11 diffractometer with graphite monochromated Cu-*Kα* radiation using an ω-2θ scan mode. The data reduction was carried out using the Enraf-Nonius structure determining package.[10] The structure was solved by direction method using MALTAN11/82 program.[11] The positional and thermal parameters of all non-hydrogen atoms were determined and refined by successive block-diagonal least-squares method using BDLS program (UNICS III).[12] The atomic scattering factors for all atoms and the anomalous dispersion corrections for non-hydrogen atoms were taken from Ref. 13. Comparatively large *R* value (ca. 10%) may be due to the disordered waters of crystallization in the crystal.

Details of the crystal data, intensity measurements, and refinements are given in Table 1, final atomic fractional coordinates in Table 2, and selected bond distances and angles in Table 3, respectively.

Tables of structure factors, anisotropic thermal parameters, mean square displacement tensor of atoms, coordinates of atoms, and complete bond lengths and angles are deposited as Document No. 8954 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Results and Discussion

The structure consists of discrete $[Ni_4(pahqs)_4(H_2O)_4]$ molecule. The position of twenty water molecules of crystallization could not be definitely determined. The molecular and chemical structures of the complex are given in Figs. 1 and 2, respectively. The four ligands were differentiated as A, B, C, and D. The atom-numberings for the ligands and nickel(II) sites are shown in Fig. 2. The O atoms in the coordinated water molecules are represented by OW(*i*) (*i*=1—4).

Coordination Geometry around Nickel Atoms. Figure 3 shows the coordination environments of the four

Table 3. Selected Bond Distances (Å) and Angles (°) with esd Values in Parentheses

Distance of Ni–X			
Ni(1)–N(1A)	2.103(10)	Ni(1)–N(8A)	2.004(11)
Ni(1)–N(16B)	2.030(11)	Ni(1)–OW(1)	2.081(10)
Ni(1)–O(25A)	2.127(7)	Ni(1)–O(25B)	2.188(8)
Ni(2)–N(1B)	2.099(10)	Ni(2)–N(8B)	1.960(10)
Ni(2)–N(1C)	2.067(10)	Ni(2)–N(8C)	1.986(9)
Ni(2)–O(25B)	2.188(8)	Ni(2)–O(25C)	2.107(7)
Ni(3)–N(16C)	2.067(8)	Ni(3)–N(16D)	2.093(9)
Ni(3)–OW(2)	2.054(9)	Ni(3)–OW(3)	2.023(9)
Ni(3)–O(25C)	2.147(9)	Ni(3)–O(25D)	2.083(7)
Ni(4)–N(1D)	2.101(10)	Ni(4)–N(8D)	2.008(9)
Ni(4)–N(16A)	2.054(10)	Ni(4)–OW(4)	2.042(9)
Ni(4)–O(25D)	2.107(8)	Ni(4)–O(25A)	2.096(8)
Distance of Ni–Ni			
Ni(1)···Ni(2)	4.021(3)	Ni(2)···Ni(3)	4.020(3)
Ni(3)···Ni(4)	3.943(3)	Ni(4)···Ni(1)	3.963(3)
Angle of X–Ni–Y			
O(25A)–Ni(1)–N(8A)	79.2(3)	N(8A)–Ni(1)–N(1A)	76.5(4)
N(16B)–Ni(1)–O(25B)	81.5(4)	O(25B)–Ni(2)–N(8B)	78.0(4)
N(8B)–Ni(2)–N(1B)	76.4(4)	N(1C)–Ni(2)–N(8C)	76.7(4)
N(8C)–Ni(2)–O(25C)	80.0(4)	O(25C)–Ni(3)–N(16C)	79.8(3)
N(16D)–Ni(3)–O(25D)	80.2(3)	O(25D)–Ni(4)–N(8D)	78.9(3)
N(8D)–Ni(4)–N(1D)	76.2(4)	N(16A)–Ni(4)–O(25A)	80.4(3)
Angle of O–Ni–O			
O(25A)–Ni(1)–O(25B)	87.0(3)	O(25B)–Ni(2)–O(25C)	91.3(3)
O(25C)–Ni(3)–O(25D)	90.1(3)	O(25D)–Ni(4)–O(25A)	88.2(3)
Angle of Ni–O–Ni			
Ni(1)–O(25B)–Ni(2)	141.5(4)	Ni(2)–O(25C)–Ni(3)	141.8(4)
Ni(3)–O(25D)–Ni(4)	140.5(5)	Ni(4)–O(25A)–Ni(1)	139.6(4)

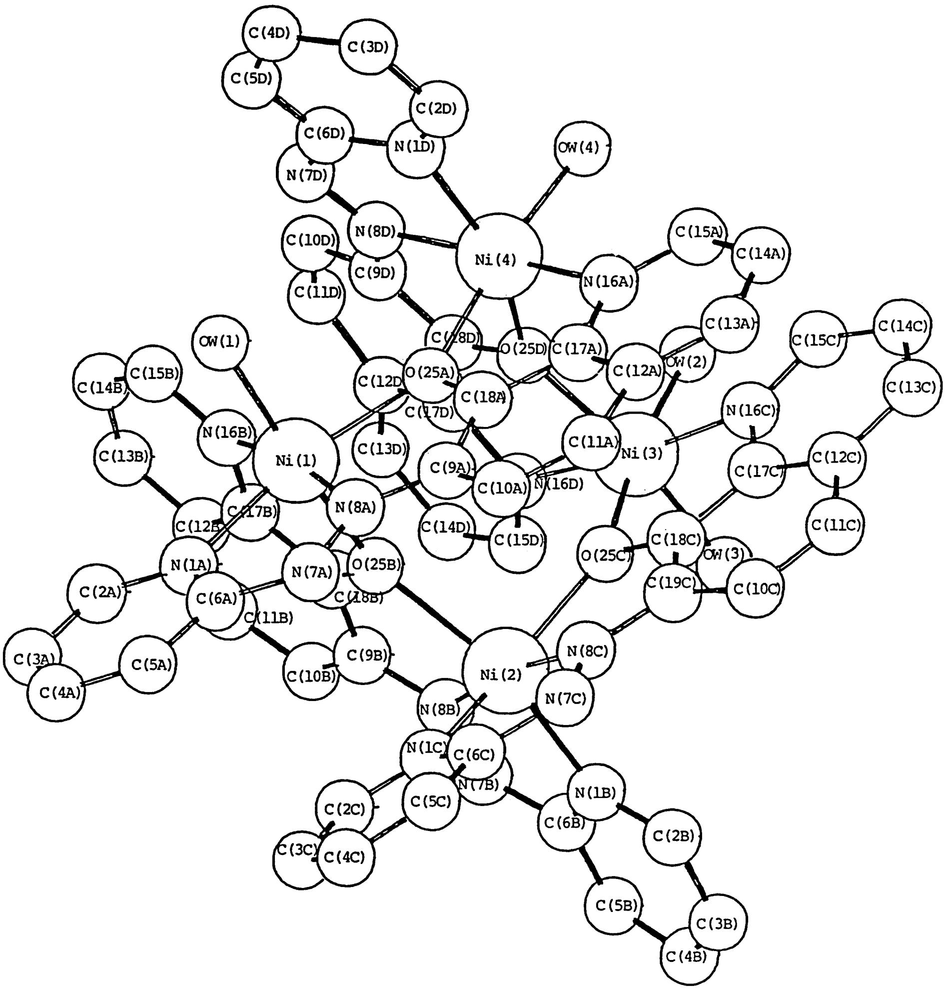

Fig. 1. Perspective view and atomic numbering for the complex. Substituent groups in aromatic rings are omitted for simplicity.

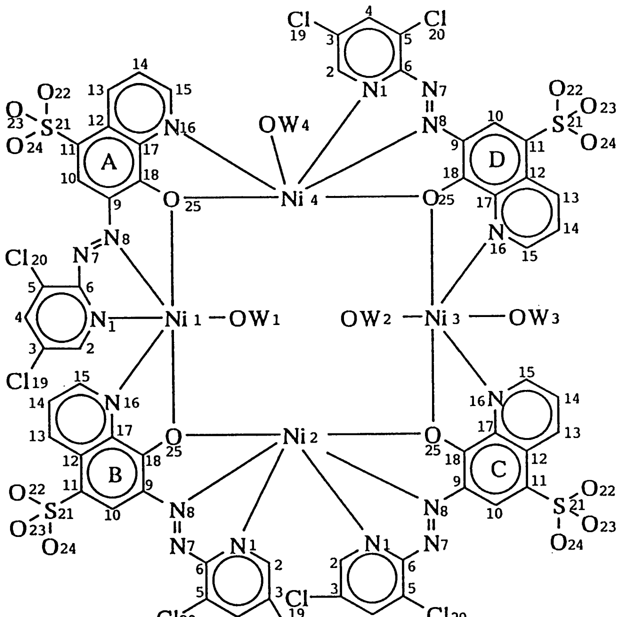

Fig. 2. Chemical structure of Ni(II) complex with pahqs. OW denotes coordinated water molecules.

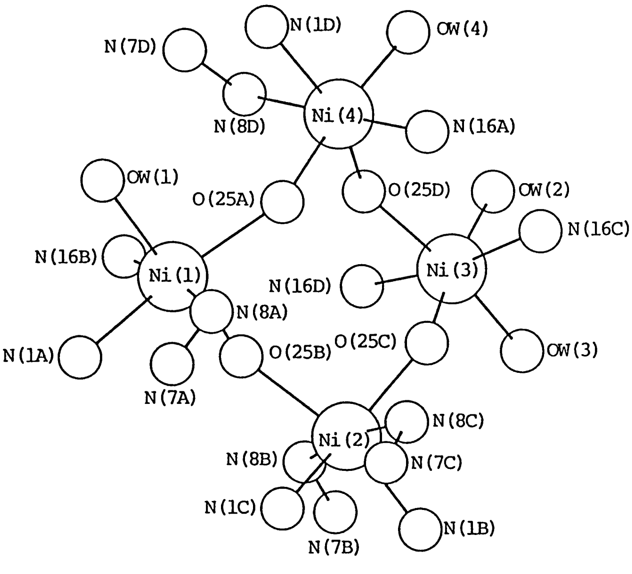

Fig. 3. Coordination environments of four Ni(II) sites.

nickel(II) sites. Each of the ligands bonded to two nickel(II) by N atom in the pyridine ring, N atom in the azo-group adjacent to the HQ moiety, O atoms of the hydroxyquinolinate and N atom in the quinoline ring to form three five-membered chelate rings (two *N,N,O*- and one *N,O*-chelate rings), where all the nickel(II) were bridged by O atom of the hydroxyquinolinate. In other words, in this complex, except one N atom in each azo-group, all the other donor atoms in pahqs were fully used in coordination to nickel(II), forming either *N,N,O*- or *N,O*-chelate rings, simultaneously. A part of the chelate ring was the same as that expected for Ni(II)-αPAN (2-(2-pyridylazo)-1-naphthol), Ni(II)-βPAN (1-(2-pyridylazo)-2-naphthol), and Ni(II)-HQ complexes in aqueous solution[2,14] and that observed for Cu(II)-βPAN and Ni(II)-HQ complexes by single crystal X-ray analyses.[4b,4c,15,16] The geometry around each of the four nickel(II) was distorted octahedron. As can be seen from Fig. 3, the complex contained three types of nickel(II) sites with respect to their coordination groups: 1) two *N,N,O*-terdentate moieties of the ligands coordinate to nickel(II) with *mer*-configuration (Ni(2) site); 2) two *N,O*-bidentate moieties of the ligands and two water molecules coordinate to nickel(II) with *cis-cis-cis* configuration (Ni(3) site); 3) one *N,N,O*-terdentate moiety and one *N,O*-bidentate moiety of the ligands and one water molecule coordinate to nickel(II) with formation of a mixed chelate system (Ni(1) and Ni(4) sites).

The bond lengths of Ni(1,2,4)-N(N atoms in pyridine rings, 2.067(10)—2.103(10) Å; N atoms in azo-groups, 1.960(10)—2.008(9)Å), and Ni(1,2,4)-O(2.107(7)—2.188(8) Å, O atoms in *N,N,O*-terdentate moietites) were slightly longer than those of Ni-N (1.93(5) Å, N atom in azo-group) , Ni-N (1.97(4) Å, N atom in thiazole ring) , Ni-O (1.98(4) Å of an analogous nickel(II) complex with thiazolylazo dye.[4a] And the angles of N-Ni-N (76.2(4)—76.7(4)°) and N-Ni-O (78.0(4)—80.0(4)°) were smaller than those of N-Ni-N (78(2)°) and N-Ni-O (80(2)°) of the analogous complex, in which a ligand also acted as *N,N,O*-terdentate one.[4a] On the other hand, the bond lengths of Ni(1,3,4)-N (N atoms in quinolinolate, 2.030(11)—2.093(9) Å) were almost similar to that of Ni-N (2.043(2)—2.082(2)°) in Ni(II)-HQ complex,[17] and Ni(1,3,4)-O (O atoms in *N,O*-bidentate moieties, 2.083(7)—2.188(8) Å) were significantly longer than those of Ni-O (2.054(1)—2.058 (1) Å) of the nickel (II) complex with HQ.[17] The average angles of N-Ni-O (80.5(3)°, *N,O*-bidentate moieties) were smaller than those of N-Ni-O (86.50(6)° [17]) of the nickel(II) complex with HQ. In any event, the bond lengths of Ni-N (N atoms in *N,N,O*-terdentate moieties) were elongated compared with those of the corresponding complex,[4a] and the bond lengths of Ni-N (N atoms in quinoline rings) were kept similar values to those of Ni(II)-HQ complex,[17] this may be associated with the electron-rich N atoms in the quinoline rings.[17] The bond lengths of Ni-O were elongated compared with those of the corresponding nickel(II) complexes with either *N,N,O*- or *N,O*-chelate rings, resulting in the contractions of the angles of N-Ni-N or N-Ni-O, since O atoms acted as bridging donor atoms between nickel(II) sites.

Properties of the Complex. The complex exhibits characteristic IR spectra due to ligand vibration modes. The most significant difference of the IR bands between the present complex and those of the pahqs itself was that the $\nu_{(N=N)}/cm^{-1}$ (1367, 1324) in the complex was shifted to lower frequencies compared with that of the free ligand ($\nu_{(N=N)}$, 1375 cm^{-1}), and was split into two bands. This may be resulted from a delocalization of the negative charge on the azo-group by the complexation with nickel(II) which lead to a reduction of the N=N bond order.[18]

The half wave potential of the azo-group in the aqueous solution of the complex (−0.405 V vs. SCE at pH=6.9) at the same pH values was markedly shifted toward the negative side compared with that of the ligand itself (−0.272 V vs. SCE at pH=6.9), showing that the very stable *N,N,O*-chelate rings of the complex were present even in the solution state.[2,19]

The variation of the magnetic susceptibility (χ_A) and effective magnetic moment (μ_{eff}) with temperature for the complex is illustrated in Fig. 4. It can be seen in this fugure that the effective magnetic moment per nickel(II) ion, μ_{eff}/Ni, was 2.95 BM at 296.3 K and gradually decreased with the lowering of temperature. This indicates that antiferromagnetic exchange interaction is operating between the four nickel(II) via bridging oxygen atoms. It is reasonable to suggest that the angles of Ni-O-Ni (ca. 140°) may lead to the antiferromagnetic interaction.[7]

Further study on the magnetic exchange mechanism among the four nickel(II) sites is continuing.

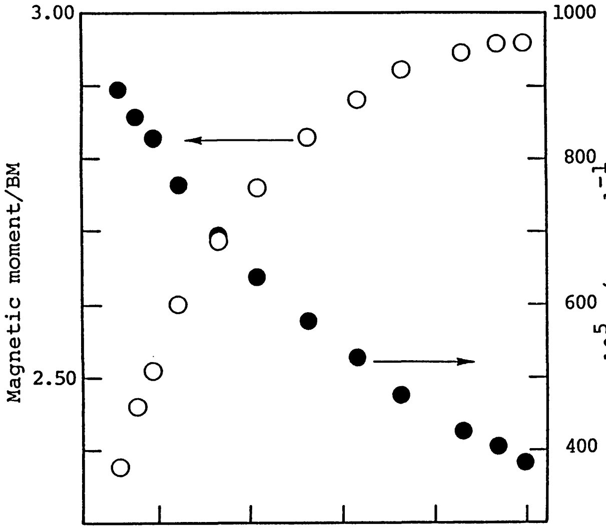

Fig. 4. Temperature dependence of magnetic moments (μ_{eff}/Ni) and magnetic susceptibilities (χ_A).

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