Coordination of 2,5-Dihydroxy-*p*-benzoquinone to Nickel(II) Ion

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2,5-Dihydroxy-*p*-benzoquinonatonickel(II) [dhqNi(II)] coordination polymer was carefully prepared from 2,5-dihydroxy-*p*-benzoquinone (L) and anhydrous nickel(II) chloride. The elemental and thermal analyses indicate two coordinated and one additive water molecules in the dhqNi(II) complex. A strong peak in IR spectrum at 3330 cm^{-1} and a shoulder at 1660 cm^{-1} attributed to O–H stretching vibration were detected. The paramagnetic moment of the complex, $\mu_{eff} = 2.94\ \mu_B$, was calculated from the observed susceptibility. Consequently, dhqNi(II) coordination polymer seemed to be D_{4h} structure, where Ni was coordinated by two ligand water molecules and four oxygen atoms from two ligand (dhq^{2-}) molecules.

Preparation of coordination polymers from organic ligands and metal ions has been attempted for the last three decades.[1—5] Recently, Fox and Chandler reported the photoconductivity of nickel-phosphine coordination polymer,[5] prepared from 1,2,4,5-tetrakis(dimethylphosphino)benzene and $NiCl_2 \cdot 6H_2O$. Kanda and Saito had reported that 2,5-dihydroxy-*p*-benzoquinone and its halogen derivatives coordinated to Ni^{2+} ion and Cu^{2+} ion to form coordination polymers.[1] 2,5-Dihydroxy-*p*-benzoquinonatocopper(II) [dhqCu(II)] was investigated as to its electric conductivity,[2] magnetic susceptibilities,[3] and the shape of the dispersed particles.[1] Control of molecular weight of the copper coordination polymer was attempted, but the result was not satisfactory. In 1989 Rao et al. reported the crystal structure of dhqCu(II) was the tetragonal system from its X-ray diffraction pattern.[4] However, 2,5-dihydroxy-*p*-benzoquinonatonickel(II) [dhqNi(II)] had not been fully investigated, so far.

In this study, the coordination of 2,5-dihydroxy-*p*-benzoquinone to Ni(II) ion was investigated from its components and the thermal, magnetic and IR spectroscopic properties.

Experimental

2,5-Dihydroxy-*p*-benzoquinone ($dhqH_2$) was synthesized as previously reported[3] and it was recrystallized from ethanol. All of the water molecules in $NiCl_2 \cdot 6H_2O$ were released by heating at 383 K for 2 h in vacuo. As turbidity accompanied by the formation of dhqNi(II) appears very slowly, the following preparation methods were tried to check the possible variation in degree of polymerization : 1) An ethanol solution of $dhqH_2$ (5 mM) (Wako Pure Chemical Co. analytical grade) and the equimolar amount of $NiCl_2$ ethanol solution were slowly mixed in a reaction vessel so as to keep the same concentration in every instance (abbr. L →← Ni). 2) The equimolar amount of anhydrous $NiCl_2$ ethanol solution was dropped to the ehanol solution of $dhqH_2$(Ni → L). 3) The equimolar of $dhqH_2$ ethanol solution was poured to the ethanol solution of anhydrous $NiCl_2$ (L → Ni). In these methods, the mixed solution became turbid gradually, and settled as a gelatinous brown precipitate after standing over night. After the mother liquor was removed from the suspensions, ethanol was added to the gelatinous precipitate, and centrifugation at 5000 rpm for 10 min was repeated several times for purification. Brown powders were obtained. The C and H were analyzed on the specimens equilibrated with saturated water vapor at ca. 293 K. Ni content in the complex was obtained by the EDTA titration method. Using the same specimen, the differential thermal analysis (DTA) and the thermogravimetric analysis (TGA) of dhqNi(II) powder were performed on a thermoanalyzer (Shimadzu, DA-30, TG-30). The susceptibility of the hydrated specimen was measured on a magnetic balance (Shimadzu, MB-11) under N_2 atmosphere (ca. 10 Torr, 1 Torr = 133.322 Pa) between 77 and 268 K.

Results and Discussion

IR spectra of $dhqH_2$ and dhqNi(II) are shown in Figs. 1a and 1b. Each IR spectrum of the complexes prepared in above three methods agreed with that in Fig. 1b. The absorption peaks at 1311, 1200, and 1112 cm^{-1} attributed to C–O–H in-plane bending vibration and a 691 cm^{-1} peak for $dhqH_2$ disappeared, and the peak for C=O stretching vibration in $dhqH_2$ at 1610 cm^{-1} shifted to a lower wavenumber at 1520 cm^{-1} in the complex. Thus we concluded that OH group and CO group in $dhqH_2$ took part in coordination bonds to Ni^{2+}. The enhanced peak at 3330 cm^{-1} due to O–H stretching vibration and the shoulder at around 1660 cm^{-1} are attributable to the coordinated water molecules. The peak at 531 cm^{-1} for dhqNi seems to be due to Ni–O vibration, because of absence of the corresponding peak in $dhqH_2$ and because of the appearance of a metal-sensitive band attributed to M–O stretching mode[6] in this low frequency region.

The calculated values of the components are given in Table 1, assuming that the number of polymerization is ∞ and some water molecules per Ni unit are contained. The number

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Table 1. Results of Elementary Analysis for dhqNi(II) Powder

	Elementary analysis / %			Mole ratio	Subtracted
	Ni	C	H	H_2O/Ni^{2+}	O%
Obsd	22.0±0.9	28.5±0.4	3.21±0.09	$(3.5\pm0.2)^{b)}$	46±1
Calcd[a)]	23.4	28.7	3.21	3.0	44.7

a) The calculated values were determined by trial-and-error method so as to coincide the calculated H% with the observed one, assuming that the number of polymerization is ∞ and some water molecules per Ni^{2+} ion are contained. b) This was obtained as supplemental calculation: $\{100-(22+28.5+3.21+28.5\times16/12\times4/6)\}/16/(22/58.71)$.

of water molecules n were determined by a trial-and-error method so as to make the calculated H% coincide with the observed one. About three water molecules were estimated in the dhqNi(II) complex. Each component of the above three types of preparation resulted in inherent errors of elemental analyses as indicated.

The thermal properties of water molecules need to be analyzed. Figure 2 shows curves of DTA (dashed line) and TGA (solid line). The same curves were obtained for all samples prepared by any of the three methods. As shown in Fig. 2, the downward peak below the base line in DTA curve indicates endothermic reactions, and at the same temperature ranges TGA curve shows weight losses in two steps. Therefore, these endothermic reactions were most probably dehydrations. Assuming that dhq : Ni = 1 : 1 and $p=\infty$, the losses of water molecules per Ni^{2+} for each step I (lower temperature), II (higher temperature), and total in dhqNi specimens were 1.1±0.2(I), 1.81±0.04(II) and total by 2.9±0.2, respectively. From room temperature to ca. 400 K (step I) about one molecule of crystalline water and thereafter to 523 K (step II) about two coordinated water molecules were lost. Consequently, the structure of dhqNi(II) was estimated as follows: bridging molecules of 2,5-dihydroxy-*p*-benzoquinone quadruply coordinate to Ni^{2+} ions in an equatorial plane, and two water molecules also coordinate to each Ni^{2+} ion vertically; that is, an octahedral coordination is proposed.

Figure 3 shows the temperature dependence of molar sus-

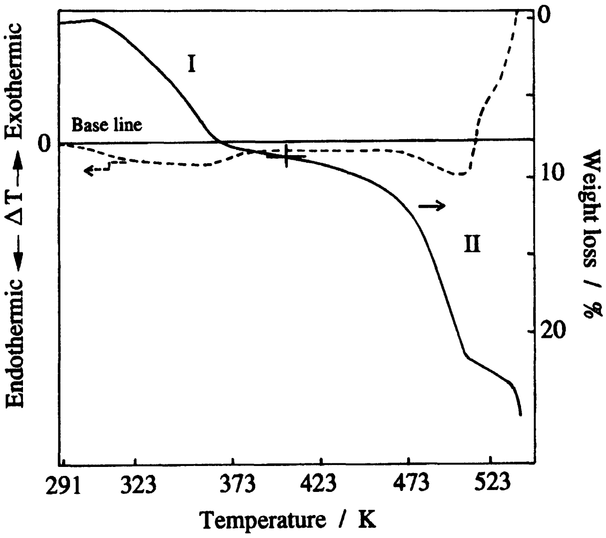

Fig. 2. DTA (- - -) and TGA (——) curves of dhqNi(II) powder (L →← Ni) against the temperature of the specimen in the air.

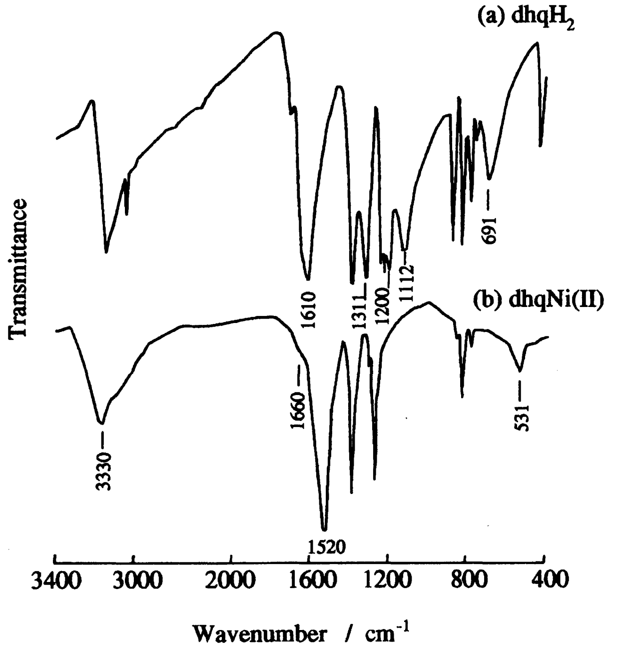

Fig. 1. IR spectra of $dhqH_2$ (a) and dhqNi(II) (b) at room temperature.

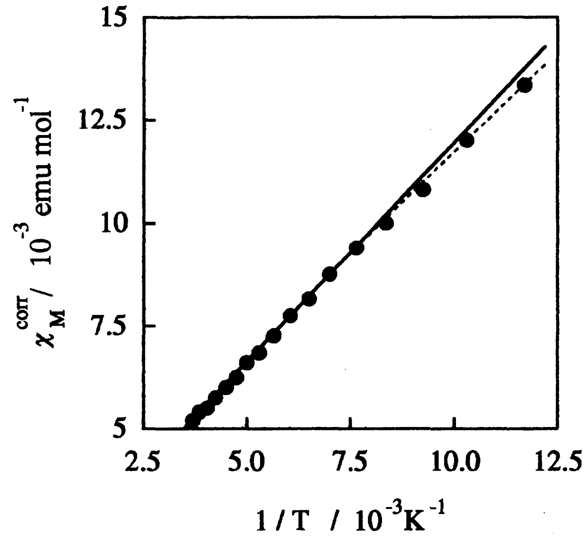

Fig. 3. Molar magnetic susceptibility χ_{Ni}^{corr} of dhqNi(II) vs. T^{-1}.

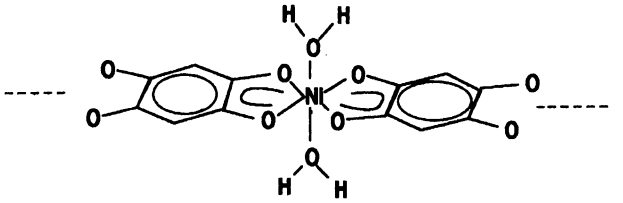

Fig. 4. Assumed chemical structure of dhqNi(II) coordination polymer.

ceptibility ($\chi_{\mathrm{Ni}}^{\mathrm{corr}}$) for dhqNi(II) (L →Ni). As shown the line slope was different at 7.64×10^{-3} K^{-1}. $\chi_{\mathrm{Ni}}^{\mathrm{corr}}$–$T^{-1}$ plot was approximated by a straight line and its line slope was calculated by the least square method, following this equation[7]

$$\chi_{\mathrm{Ni}}^{\mathrm{corr}}=\frac{N\beta^2\mu_{\mathrm{eff}}^2}{3kT},$$

where $\chi_{\mathrm{Ni}}^{\mathrm{corr}}$ is molar magnetic susceptibility corrected by the ligand diamagnetism ($\chi_{\mathrm{M}}^{\mathrm{dia}}=-51.29\times10^{-6}$ emu mol^{-1}), μ_{eff} was effective magnetic moment for Ni^{2+} obtained using Avogadro's number N, Bohr magneton β, and Boltzmann's constant k as usual. The obtained μ_{eff} was 2.94 μ_{B} in a range 3.7×10^{-3}—7.64×10^{-3} K^{-1}, and 2.81 μ_{B} in a range 7.64×10^{-3}—11.7×10^{-3} K^{-1}. The obtained $\mu_{\mathrm{eff}}=2.94$ μ_{B} agreed with the generally accepted value for Ni^{2+} 2.9—3.4 μ_{B}.[7] The slight decrease to 2.81 μ_{B} would indicate the contribution of the antiferromagnitic coupling[3a] through dhq^{2-} at lower temperature range. Therefore, dhqNi(II) was estimated as a high spin complex with two 3d electrons, unlike the plain quadruply coordinated diamagnetic Ni. Figure 4 shows the assumed chemical structure of dhqNi(II) coordination polymer.

Consequently, dhqNi seems to be a local D_{4h} structure where Ni^{2+} is coordinated by two molecules of water and four oxygen atoms from two dhq^{2-}. The coordination polymer is totally constructed by the conjugated double bond system, consisting of benzene rings and Ni–O–C–C–O five menbered rings.

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References

1) a) S. Kanda and Y. Saito, *Bull. Chem. Soc. Jpn.*, **30**, 192 (1957); b) S. Kanda, *Nippon Kagaku Zasshi*, **81**, 1347 (1960).

2) a) S. Kanda and S. Kawaguchi, *J. Chem. Phys.*, **34**, 1070 (1961); b) S. Kanda, *Kogyo Kagaku Zasshi*, **66**, 641 (1963).

3) a) H. Kobayashi, T. Haseda, E. Kanda, and S. Kanda, *J. Phys. Soc. Jpn.*, **18**, 349 (1963); b) S. Kanda, *Nippon Kagaku Zasshi*, **83**, 282 (1962).

4) T. R. Rao, P. Lingaiah, L. Sirdeshmukh, and S. Mehdi, *J. Indian Chem. Soc.*, **66**, 826 (1989).

5) M. A. Fox and D. A. Chandler, *Adv. Mater.*, **3**, 381 (1991).

6) K. Nakamoto and P. J. McCarthy, "Spectroscopy and Structure of Metal Chelates Compounds," John Willey & Sons, New York (1968), p. 272.

7) P. W. Selwood, "Magnetochemistry," 2nd ed, Interscience, New York (1964), pp. 158—159.