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ESR Study of Paramagnetic Nickel Species Obtained by Reduction and Oxidation of Bis(1,3,5-triphenylformazanato)nickel(II)

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Diamagnetic bis(1,3,5-triphenylformazanato)nickel(II) was reduced or oxidized by chemical and electrochemical methods. The paramagnetic Ni(I) and Ni(III) complexes thus obtained were studied by means of ESR spectroscopy. Ni(I) complexes formed by alkali metal reductions showed remarkable changes in their g values, depending on the kinds of alkali metal used. The change of g-values, which related to the ionic radii of the alkali metal ions, was well interpreted by the axial coordination effect due to the alkali metal ions. The electrochemical formation of the Ni(I) complex showed a solvent-dependency; the nickel(II) ion was reduced in DMF solution, but not in acetonitrile. The g-components were 2.030 for $g_{//}$ and 2.001 for $g_{\perp}$. The relation between the two g-components gave a $d_{x^2-y^2}$ ground state for the Ni(I) ion in the complex. Their anisotropy was very small. The Ni(II) ion oxidized by both chemical and electrochemical methods showed a d_{z^2} ground state. The three g-components were 2.056, 2.039, and 2.000 in DMF, which are similar to those obtained from the other oxidation methods.

Formazans, which are essential for the preparation of tetrazolium salts applicable to biological research, are known to form complexes with such transition metal ions as copper, cobalt, and nickel.[1—8] Those complexes were tentatively studied in the field of synthesis because of their dyeing properties.[9] However, there are only a few reports concerning crystallographic, magnetic, and spectroscopic studies of the formazan complexes with transition metal ions.[2,4,6] The authors have studied various kinds of formazan-transition metal complexes by means of magnetic and spectroscopic methods. During our studies, the copper(II)–formazan complexes were divided into three groups on the basis of their stoichiometry and magnetic and spectroscopic behaviors. The structural aspects of each group were made clearer, suggesting several kinds of structural configurations.[10,11] Such variety in the structural configuration was attributed to the flexibility of the ligand formazans. In addition, the correspondence of each group to each of three types of copper(II)-containing proteins was suggested.[12,13] Thus, the flexible copper(II)–formazan complexes comprised a good model system for copper complexes with biological activity.[14—18] With regard to cobalt(II)–formazan complexes, the cobalt(II) ions with approximately planar symmetry are in a low spin state. However, the unpaired electron resides in a different orbital from that of the usual cobalt(II) complexes with similar symmetry.[19,20] The cobalt(II) ions in other formazan complexes are in a high spin state and seem to be in a different structural configuration. Thus, the cobalt(II)–formazan complexes are complicated both in terms of spin state and structural configuration.

Nickel(II) ions having a d^8 electron configuration make complexes with formazans. Magnetic susceptibility data suggested they are diamagnetic.[6] The paramagnetic species obtained by reduction or oxidation of such diamagnetic complexes are interesting, since the nickel(II)–formazan complexes are anticipated to be flexible and to be influenced by the subtle change of the circumstance, the same as the copper(II) complexes are. Considering that reduction or oxidation of the nickel(II) ion gives a d^9 or d^7 configuration, the isoelectron of the copper(II) ion or the cobalt(II) ion, respectively, a study concerning the nickel(II) complex is helpful and useful for a better understanding of the copper(II) and cobalt(II) complexes.

It is chemically important to do a comprehensive study of such nickel complexes with clear nickel oxidation states and various structural configurations. However, most of the paramagnetic species from Ni(II) complexes have been electrochemically obtained and few paramagnetic species have been obtained through other oxidation and reduction methods. On the other hand, several kinds of oxidations and reductions methods have yielded several kinds of paramagnetic species from bis(1,3,5-triphenylformazanato)nickel(II), which showed ESR spectra due to the peculiar structural configurations. This complex has no substituents on the phenyl rings and is representative among the nickel(II)–formazan complexes. Thus, bis(1,3,5-triphenylformazanato)nickel(II) is appropriate for studying the relationship between the structural configuration around the nickel ion and the oxidation states. In this paper, we will present ESR results obtained from several kinds of reduction and oxidation processes. Especially, in the case of alkali metal reductions, weak axial coordination effect on the *g* components will be discussed. For the electrochemical methods, the electron transfer site and *g* parameters will be reported and discussed in relation to the solvation effect.

Nickel ions with various oxidation states are included in some enzymes and play central roles in several kinds of biological activity as sites of electron transfer reactions.[21)] The ligand configuration around the nickel ion also seems to be an important factor in determining the site of the electron transfer reaction and the oxidation state of the nickel ion.[22)] Many kinds of nickel complexes have been studied in relation to the active sites in enzymes containing the nickel ions. They, as model complexes, have been helpful in understanding the ligand configurations and the oxidation states of the nickel ions in biologically active sites.[23)] However, the oxidation states and the structural configurations of the nickel ions in some enzymes have not been exemplified yet and are still a current problem.[24,25)] Some comments concerning this problem will be presented, hopefully so that the results from the present complex will offer helpful information in order to understand the structural aspects and oxidation states of the nickel ions in nickel-containing enzymes.

Experimental

Bis(1, 3, 5-triphenylformazanato)nickel(II), **A** in Fig. 1, was prepared by the reaction of commercially obtained 1,3,5-triphenylformazan with nickel(II) acetate tetrahydrate in lukewarm ethanol.[26)] The acetone solution of **A** precipitated fine black micro crystals of **A** upon the addition of an arbitrary amount of water. Elemental analyses were in good accordance with the calculated values {Found: H, 4.45; C, 69.63; N, 17.14%. Calcd for $C_{38}H_{30}N_8Ni$: H, 4.57; C, 69.44; N, 17.05%.}. Complex **A** showed neither temperature dependence in the magnetic susceptibility measurements nor ESR absorption over the range of 77 K to room temperature, indicating a diamagnetic complex.

Three alkali metals, Li, Na, and K, were used for the reduction of **A** after purification. A cesium metal mirror was obtain by the reaction of cesium chloride with metallic calcium in vacuo and was in contact with **A**. The reduced samples were immediately frozen in liquid nitrogen and used for ESR measurements. If the reduction was not enough for the measurement, the temperature of the sample was raised to near room temperature and the reduction was tried again. The solvents used for the alkali metal reductions were tetrahydrofuran (THF) and 1,2-dimethoxyethane (DME). $NaBH_4$ was also used as a reduction reagent in the solvents CH_3OH and THF. For the oxidation of **A**, oxidation reagents, H_2SO_4 itself and $SbCl_5$ dissolved in dichloromethane, were used. For electrochemical ESR and cyclic voltammetry (CV) measurements, the cell described in the literature was used.[27,28)] Acetonitrile and *N*,*N*-dimethyl formamide (DMF) containing 10^{-1} M tetrabutylammonium tetrafluoroborate ($TBABF_4$) were used for the solvents (1 M=1 mol dm^{-3}). The air in the cell was replaced by dry nitrogen gas by means of the freeze-pump-thaw method.

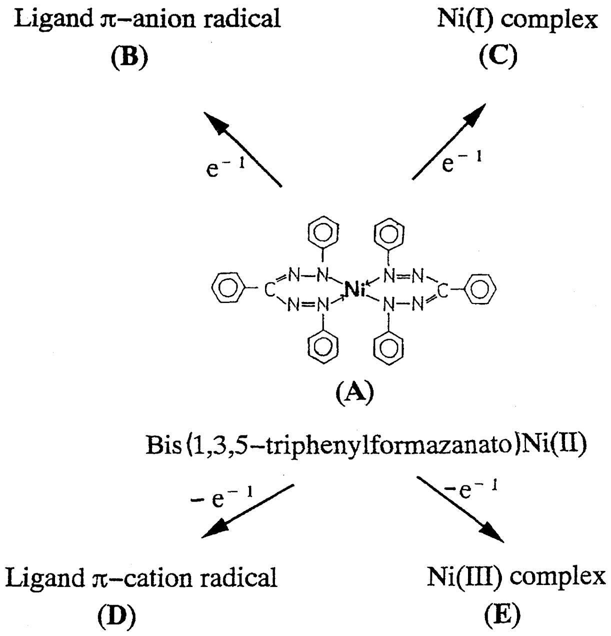

Fig. 1. Reduction and oxidation scheme of bis(1,3,5-triphenylformazanato)nickel(II), **A**.

Magnetic susceptibility measurements were carried out by use of the torsion balance described elsewhere.[29)] The ESR equipment used was a JEOLCO-1XG equipped with 100 kHz field modulation.

Results

The reduction and oxidation scheme is shown in Fig. 1. The reduction of **A** yielded paramagnetic species **B** and **C**, and the oxidation also yielded paramagnetic species **D** and **E**. Species **A**, **B**, **C**, **D**, and **E** are a Ni(II) complex, ligand π-anion radical, Ni(I) complex, ligand π-cation radical, and Ni(III) complex, respectively.

1. Reduction and Oxidation by an Electrochemical Method. Reduction and oxidation potentials were estimated by means of cyclic voltammetry. The cyclic voltammograms of **A** in DMF are shown in Fig. 2. However, reduction and oxidation potentials can not be set because the potential was not compensated between the working and counter electrodes.[27)] In order to carry out the electrolysis in as short a time as possible, a higher potential was set to obtain enough intensity. As soon as the signal appeared, the solution was frozen and the spectrum was recorded.

Over the whole range of the reduction potential, the ligand π-anion radical with an isotropic *g* value of 2.001 was observed in both solutions of CH_3CN and THF.[30)] No other ESR signal due to the Ni(I) complex was observed. In DMF solution, the isotropic ab-

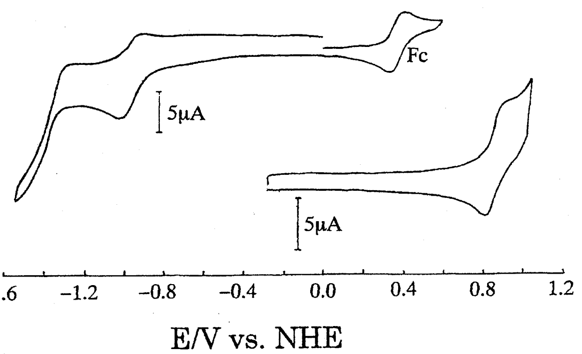

Fig. 2. Cyclic voltammograms of 1.5×10^{-3} M bis(1,3,5-triphenylformazanato)Ni(II) in DMF containing 0.1 M $TBABF_4$ at −31 °C. Ferrocene was added to the solution in order to calibrate the potential with Fc/Fc^+ couple (0.400 V vs. NHE).

sorption with a g-value of 2.001 due to the ligand π-anion radical appeared first and then, at a higher reduction potential, the other isotropic absorption with a g-value of 2.010 appeared at −30 °C (Fig. 3a). On instantly decreasing the temperature to −130 °C, where the DMF solution was already frozen, the absorption showed an anisotropy, $g_{//}=2.030$, $g_2=2.002$, and $g_3=2.000$ (Fig. 3b). Since the Ni(I) complex yielded by the reduction has a d^9 configuration, which is an isoelectron of a Cu(II) ion, it would have a $d_{x^2-y^2}$ ground state, indicating the relation $g_{//}>g_2\cong g_3>g_e$. Therefore, the anisotropic absorption in Fig. 3b was attributable to the Ni(I) complex with a $d_{x^2-y^2}$ ground state.[31] Whereas the anisotropy of the present Ni(I) complex was small and the deviation from g_e was also small, the absorption with the three g-components of 2.030, 2.002, and 2.000 was clearly different from that due to the π-anion radical. Therefore, we assigned it to the Ni(I) species. However, the possibility of a π-anion radical with Ni(I) character can not be discounted.[32] The ligand π-anion radical in solution showed only one absorption line with a line width of about 5 mT. An anisotropic absorption with three g-components of 2.006, 2.001, and 1.994 was observed in the glassy DMF solution. The absorption is clearly distinguishable from the other absorption attributed to the nickel(I) species and is due to the ligand π-anion radical.

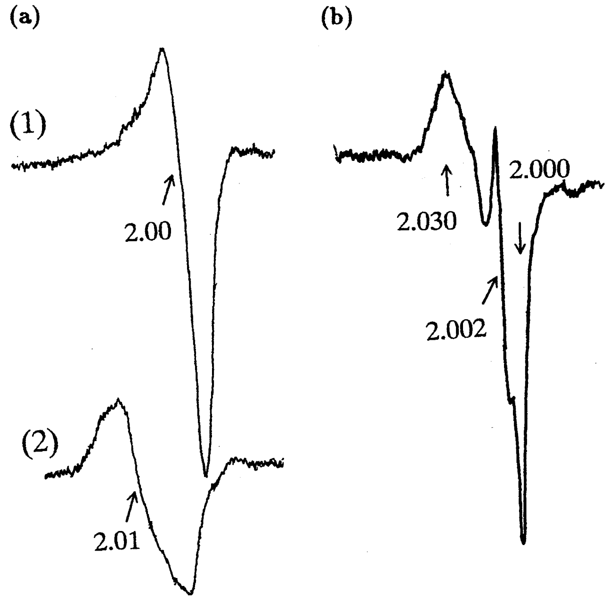

Fig. 3. ESR spectra obtained by the reduction of **A** in DMF. (a) recorded at −30 °C by the reduction at lower potential (1) and at higher potential (2), (b) recorded at −130 °C.

On oxidation, Ni(III) complex was observed both in CH_3CN and DMF. The g_{iso} values of the Ni(III) complex were 2.030 and 2.038 in CH_3CN and DMF, respectively. On freezing the CH_3CN solution at −70 °C, it changed to an anisotropic absorption with g-components of 2.051, 2.040, and 2.000 for g_1, g_2, and g_3, respectively. The average of these three values, g_{avg}, was 2.030. In DMF at −130 °C, however, they were 2.056, 2.039, and 2.000 giving a g_{avg} of 2.032. The isotropic g-values in CH_3CN and DMF were consistent with g_{avg} in each of the two glassy solvents, respectively. These g components indicate a d_{z^2} ground state. The anisotropy was small and the g-values were similar in both solvents. In contrast to these aspects, the ESR spectrum was very sharp in CH_3CN and broad in DMF. The reason could be attributable to different solvations. The spectrum in CH_3CN is presented in Fig. 4.

2. Reduction and Oxidation by Chemical Methods; ***Alkali Metal Reduction.*** The reduction of bis(1,3,5-triphenylformazanato)nickel(II) by the use of such alkali metals as Li, Na, K, and Cs produced the ligand π-anion radical and the nickel(I) complex at the same time. A representative ESR spectrum obtained by lithium metal reduction is shown in Fig. 5. The ESR spectrum is composed of two kinds of absorption; one, with a $g_{//}$ of 2.285 and a $g_{\perp}$ of 2.093, is due to the Ni(I) complex, while the other, with a g_{iso} of 2.002, is due to the ligand π-anion radical. The spectral pattern indicated that a one-electron reduction in either the ligand or the Ni(II) ion

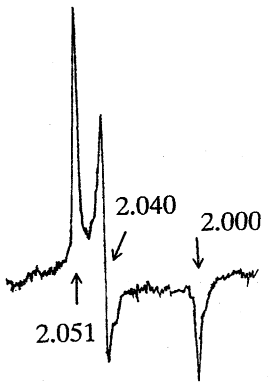

Fig. 4. ESR spectrum obtained by electrochemical oxidation of **A** in CH_3CN at −70 °C.

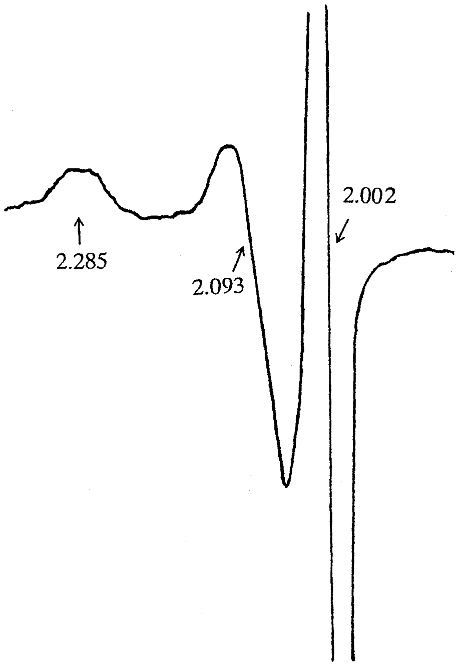

Fig. 5. ESR spectrum at 77 K obtained by Li metal reduction of **A**.

followed and that the two paramagnetic species were merely mixing without interaction, since no exchange interaction between the two was observed. The g-components of the Ni(I) complex showed a $d_{x^2-y^2}$ ground state, the same as that in the case of the electrochemical reduction.[33] However, the anisotropy in this case was larger than that in the electrochemical reduction. The other absorption was isotropic even at 77 K with a line width of about 5 mT. The whole absorption width was in accordance with that of the π-neutral radical obtained from 2,3,5-triphenyltetrazolium chloride.[34] Resolution of this absorption remained unchanged through the solvent-dilution. This could be because the isotropic broad line contains splittings due to the four nitrogens of the ligand formazan similar to the case of tetrazolium chloride. The reduction by the other alkali metals showed similar aspects, but the g-values were different. The site of the electron transfer, either the nickel(II) ion of **A** or the ligand formazan, seems to depend upon the energy of the vacant orbital of the nickel(II) ion or the ligand π-system. This finding indicates that both energies are not very much different. In the present report, the ESR absorption due to the nickel(I) complex will be focused on and adopted for discussion.

The perpendicular component of the g-value decreased in the order Li, Na, K, and Cs, while the parallel component seemed not to show any specific tendency to these alkali metals. In order to estimate the efficiency of the change of the distance between the alkali metal ion and the nickel(I) ion, 18-Crown (which has a cage to take in a sodium ion), was added to the THF solution. The $g_\perp$-value became smaller than that measured with no 18-Crown. For sodium reduction, both solvents, DME and THF, gave quite similar g-values. The g-values for different alkali metals and different solvents are presented in Table 1.

NaBH$_4$ Reduction. The reduction by $NaBH_4$ was accomplished in a protic solvent such as methanol, but not in such aprotic solvents as THF and DME. Even in THF and DME, the addition of a slight amount of methanol or water promoted the reduction. As soon as the reduction was carried out, the sample was frozen at 77 K. The ESR spectrum in methanol is mainly due to the absorption of the nickel(I) complex with a $g_{//}$ of 2.248 and a $g_\perp$ of 2.118 (Fig. 6).[35] The values indicate that the unpaired electron resides in a $d_{x^2-y^2}$ orbital, the same as in the other reduction methods. The absorption intensity caused by the ligand π-anion radical was not as strong as that of the nickel(I) complex. The relative intensity of two kinds of absorptions contrasted with the

Table 1. The g-Values of Ni(I) Complexes Obtained by Chemical Reductions

Metal–Solvent	$g_{//}$	$g_\perp$	Ionic radius/Å
Li–THF	2.285	2.097	0.6
Na–THF	2.285	2.093	0.95
Na–DME	2.284	2.096	
Na–THF–18-Crown	2.277	2.083	
K–THF	2.269	2.070	1.33
Cs–THF	2.289	2.066	1.69
$NaBH_4$–CH_3OH	2.248	2.118	0.3[a]

a) Atomic radius of hydrogen atom.

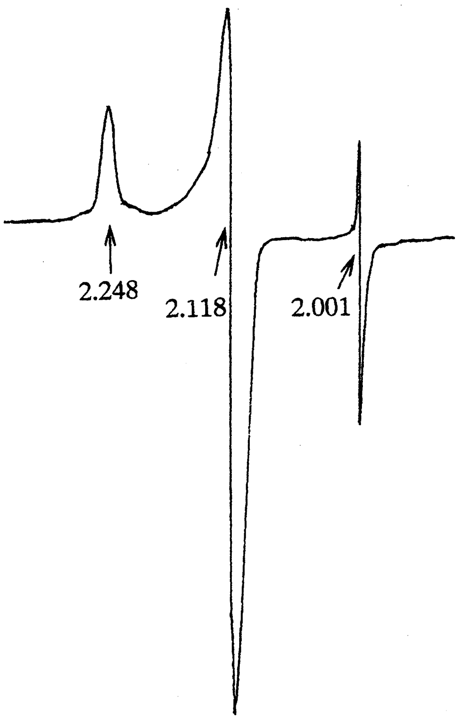

Fig. 6. ESR spectrum at 77 K obtained by $NaBH_4$ reduction of **A**.

case of the alkali metal reductions. It may be speculated that the H^- ion produced from $NaBH_4$ in the course of the reduction process prefers the reduction of the nickel(II) ion to that of the electron-enrich π-ligand system of formazan in the complex. After giving the electron to the nickel(II) ion, the proton would remain in a closer neighborhood of the nickel ion than the alkali metals do. This proton could have effectively modified the d-energy levels, giving a larger $g_\perp$ value.

Oxidation by H_2SO_4 and $SbCl_5$. Complex **A** was oxidized with the oxidation reagents H_2SO_4 and $SbCl_5$.

As soon as H_2SO_4 was added to **A** in a sample tube, the complex was oxidized to turn blue in color. This sample was frozen at 77 K immediately. Absorptions due to three kinds of paramagnetic species were observed; (1) the π-cation radical with a g_{iso} of 2.001, (2) the Ni(III) species with the perpendicular components of the g-value, g_1 and g_2, of 2.056 and 2.039, and (3) an other kind of Ni(III) species with $g_\perp$ and $g_{//}$ of 2.321 and 2.227. Since the g-values of (2) are consistent with those obtained by the electrochemical method in CH_3CN and DMF, this was assigned to the absorption due to the Ni(III) complex, and the parallel component with a g-value of 2.00 would overlap with the absorption (1).

As soon as $SbCl_5$ dissolved in dichloromethane was added to **A**, the solution also turned blue in color and then was frozen at 77 K. The ESR spectrum (Fig. 7) consisted of, (1) an absorption with g_1 and g_2 of 2.040 and 2.026 and the parallel component, g_3, of 2.002, and (2) a broader absorption with a $g_\perp$ of 2.242 and a $g_{//}$ of 2.142. The former is also assigned to the absorption due to the Ni(III) complex and the latter also to an other kind of Ni(III) species such as an inorganic Ni(III) species.[36] The ESR spectra of the Ni(III) complex obtained by using two kinds of oxidation reagents were generally similar. The g_1 and g_2 values were slightly smaller.

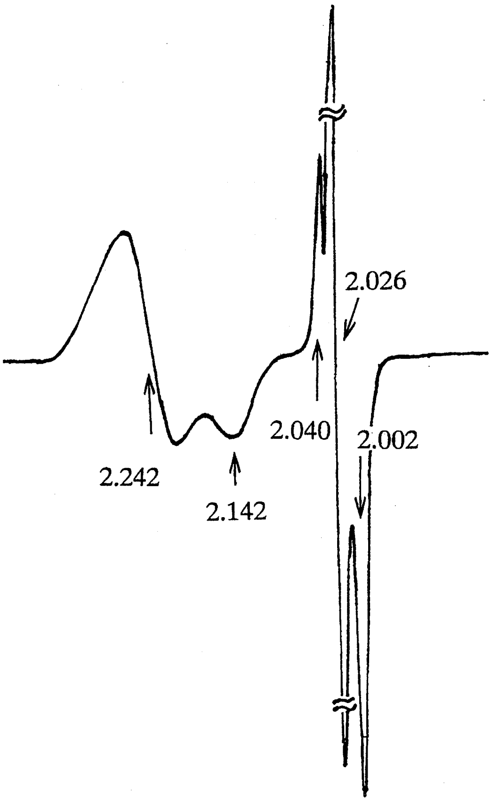

Fig. 7. ESR spectrum at 77 K obtained by $SbCl_5$ oxidation of **A** in CH_2Cl_2.

Discussion

For the d^9 electron configuration, a relation with g_z greater than g_x and g_y indicates that the unpaired electron occupies the $d_{x^2-y^2}$ orbital. In the case of Ni(I) ion, the geometry around the Ni(I) ion is considered approximately planer with a small tetragonal distortion.[33] The g-components for such an electron configuration are as follows.[37]

$$g_{//} = g_e + 8\lambda/\Delta_1, \quad \Delta_1 = d_{x^2-y^2} - d_{xy} \tag{1}$$

$$g_\perp = g_e + 2\lambda/\Delta_2, \quad \Delta_2 = d_{x^2-y^2} - d_{yz,zx} \tag{2}$$

Here, g_e is the free electron g-value and λ, the sign of which is positive for more than half the d-electrons, is an eigenvalue of the spin-orbit coupling. Now, the energy differences between the d-orbitals are estimated from the g-components as follows.

$$\Delta_1/\lambda = 8/(g_{//} - g_e) \tag{3}$$

$$\Delta_2/\lambda = 2/(g_\perp - g_e) \tag{4}$$

Since the optical absorption due to the Ni(I) complex was difficult to observe in this system, the Δ_1 and Δ_2 values were not estimated definitely. Therefore Δ_1/λ and Δ_2/λ in Eqs. 3 and 4, respectively, were derived from the g-value anisotropy. The energy differences containing λ as a denominator were plotted versus the ionic radius of the alkali metal ions (Fig. 8). The graph indicates that the Δ_2 value changed much more than Δ_1 and that Δ_2 increased in the order Li^+, Na^+, K^+, and Cs^+; the energy difference between $d_{x^2-y^2}$ and d_{xy} changed less and that between $d_{x^2-y^2}$ and d_{yz} or d_{zx} decreased, as the ionic radius was small.

The result can be interpreted as supposing that the alkali metal ions reside closer to the Ni(I) ion as the ionic radius becomes smaller and influence some d orbitals.[38] In the case of approximately planar symmetry, the alkali metal ions, assuming that they approach from the z-direction, would raise the energy levels of the d_{z^2}, d_{yz}, and d_{zx} orbitals. However, the influence of raising d_{z^2} would not have explicitly appeared, since the $d_{x^2-y^2}$ orbital, the unpaired electron orbital, has no matrix element with the d_{z^2} orbital through the spin-orbit coupling. The effect of raising the d_{yz} and d_{zx} orbitals has decreased Δ_2 and the result was noticeably observed in the increase of the $g_\perp$ value. The small change of the energy difference between $d_{x^2-y^2}$ and d_{xy} would not have influenced the value of Δ_1. Therefore, the $g_\perp$ change vs. the ionic radius was evident. A similar interpretation could be applied to the result of the Na–THF–18-Crown system as shown in Table 1; the Na^+ located in the hole of 18-Crown would be a longer distance from the nickel(I) ion to give less perturbation; the raising of the d_{yz} and d_{zx} energy levels would be smaller than that in the Na–THF system. As a result, in the Na–THF–18-Crown system, Δ_2 became larger than that in the Na–THF system and a larger $g_\perp$ value was observed in the former than in the latter. Thus, the effect from the axial direction to the Ni(I) ion, the effect which modifies d-energy levels, may be regarded as a kind of coordination.

In the case of the $NaBH_4$ reduction of **A**, the hydrogen atom produced from the H^- ion would be an axial coordinate. The g value was plotted versus the atomic radius of the H atom. As depicted in Fig. 8, the trend observed in the alkali metal reduction was similarly applied. The result also supports the appropriateness of the above-mentioned relation between the axial coordination and the energy level.

It was reported that tetragonal distortion from square planar symmetry increases the $g_{//}$ component of the copper complex with a d^9 electron configuration.[16] It is characteristic in the present result that in the complex with the same electron configuration, the change of the $g_\perp$ component has dominantly been recognized and has been consistently interpreted by the axial coordination effect.

In the case of the electrochemical reduction of **A**, the influence of the axial perturbation seems to have appeared as a solvation effect. It is well-known that stronger solvation stabilizes the d-energy level of nickel(II) complexes and as a result, the electron transfer site is on the nickel(II) ion. Since the DMF molecule is known to solvate stronger than CH_3CN does, the nickel(II) ion would have been stabilized in DMF and reduced. As a result, the absorption with a different g_{iso} from g_e was observed at a higher potential and at −10 °C. On freezing the DMF solution, absorption with g-anisotropy appeared, indicating a $d_{x^2-y^2}$ ground state. In contrast to the result in DMF, the π-anion radical alone was observed in acetonitrile over the entire range of the reduced potential. The stronger solvation of DMF stabilized the d-energy level to make the Ni(I) complex observable.[39] In the case of oxidation however, the Ni(II) ion was the site of the electron transfer and was oxidized to the Ni(III) ion in both DMF and CH_3CN solvents.[40] The g-values were similar in both solvents. Concluding the electrochemical reactions, the observation of the Ni(I) species depended upon the degree of solvation. However, the generation of the Ni(III) species did not depend upon the solvents.

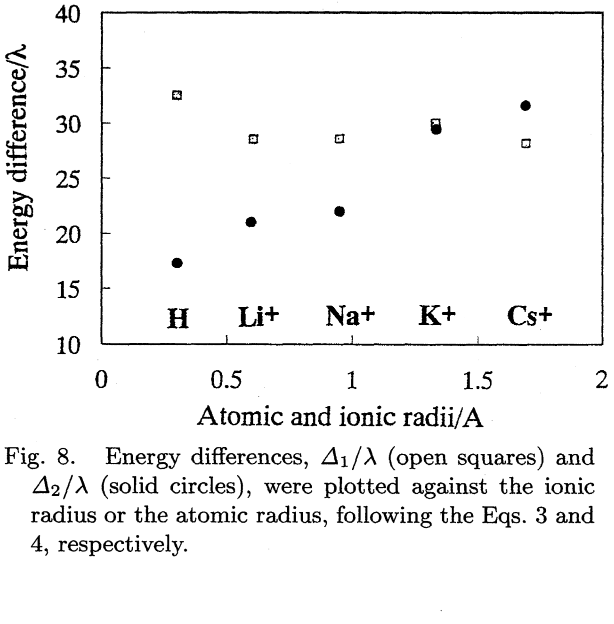

Fig. 8. Energy differences, Δ_1/λ (open squares) and Δ_2/λ (solid circles), were plotted against the ionic radius or the atomic radius, following the Eqs. 3 and 4, respectively.

Comments for Nickel-Containing Enzymes. Some nickel complexes have been studied attempting to elucidate the coordination and oxidation state of the nickel ions in enzymes.[40b,41] Since the present nickel(II) complex **A** enabled us to observe various kinds of reduction and oxidation processes, the authors would like to comment on the relation of the present paramagnetic nickel complexes to some nickel-containing enzymes.

In cofactor F430, the reduction of Ni(II)–F430 results in Ni(I)–F430 having a $d_{x^2-y^2}$ ground state with planar four-coordination symmetry, showing an ESR absorption with approximate $g_{//}$ and $g_\perp$ values of 2.25 and 2.06—2.07, respectively.[42] The ESR spectra obtained by K or Cs reduction of **A** gave 2.27—2.28 and 2.06—2.07 for the $g_{//}$ and $g_\perp$ values, respectively, which are quite similar to those of Ni(I)–F430. Accordingly, the Ni(I) species obtained by means of K and Cs reductions of **A** correspond to Ni(I)–F430 in their structural configurations. On the other hand, the Li and Na reductions of **A** gave larger $g_\perp$ values which deviated from those of Ni(I)–F430.

The g-values of the present Ni(III) complexes indicated a d_{z^2} ground state. The two perpendicular components, 2.056 and 2.040, in DMF were small, indicating quite large energy differences between the d orbitals. Such small g-values have been found in a few complexes with four-nitrogen coordination.[39,43] They are also interesting in a biological sense because of their similarity to the g-values of acetyl coenzyme A synthase, having g-components of 2.062, 2.047, and 2.028 in Signal(II).[44] The oxidation state of the nickel ion in this enzyme, however, has not been exemplified yet.[45] The similar g-values of the present Ni(III) complex to those of acetyl coenzyme A synthase suggest the possibility of a trivalent Ni(III) in the enzyme. In reduction, the Ni(I) ion showed very small g-values also similar to those of acetyl coenzyme A synthase, although the relation between $g_{//}$ and $g_\perp$ were opposed to the case of the nickel(III) species. The present results could provide a better understanding of the oxidation state of acetyl coenzyme A synthase.

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