

MO theory and illustrated with some representative examples.

The distinction between *cluster* orbitals and *molecular* orbitals is emphasized. In particular, the highest occupied or the lowest unoccupied molecular orbitals of a cluster may or may not be cluster orbitals. As a result, there are various causes of multiple electron counts, some involving cluster orbitals, others not. For the latter case, simple electron-counting rules are incapable of discerning the nature and/or predicting the consequences of the added or the subtracted electrons.

Finally, while we have restricted our discussions to clusters containing up to 20 vertex atoms, the principles outlined in this

paper can easily be extended to higher clusters.⁴⁵

Acknowledgment. I am indebted to Prof. J. Lauher of SUNY, Stony Brook, for suggesting the alternative interpretation of the parameter *X* as the number of "false" metal-metal bonds in ref 1a, which provided a seed for the present paper. I am also grateful to Kelly Keating for many helpful comments.

- (45) For complications introduced by too much symmetry in electron counting of high-nuclearity clusters, see, for example: (a) Bicerano, J.; Marynick, D. S.; Lipscomb, W. N. *Inorg. Chem.* **1978**, *17*, 3443. (b) Brown, L. D.; Lipscomb, W. N. *Ibid.* **1977**, *16*, 2989.

Contribution from the Department of Chemistry,
Kinki University, Kowakae, Higashi-Osaka 577, Japan

Classification of Solvents Based on Their Coordination Power to Nickel(II) Ion. A New Measure for Solvent Donor Ability

MEGUMU MUNAKATA,* SUSUMU KITAGAWA, and MASAHARU MIYAZIMA

Received June 5, 1984

Coordination power (CP), a new measure for the donor ability of a solvent, was determined by using nickel(II) ion and applying the rule of average environment. The values of CP on the basis of acetonitrile are 2.24 (pyridine), 1.24 (dimethyl sulfoxide), 0.85 (*N,N*-diethylformamide), 0.79 (water), 0.72 (*N,N*-dimethylformamide), 0.11 (methanol), 0.08 (trimethyl phosphate), 0.00 (acetonitrile), -0.07 (*n*-hexanol and *n*-pentanol), -0.12 (ethanol and *n*-butanol), -0.14 (*n*-propanol), -0.15 (propionitrile), -0.37 (benzonitrile), -0.46 (acrylonitrile and isobutyl alcohol), -0.48 (acetone), -0.54 (isopropyl alcohol), -0.68 (*sec*-butyl alcohol), -0.77 (propylene carbonate), and -0.92 (*tert*-butyl alcohol). The stability constants of Mg(II) and Ag(I) complexes with bpy and the Ni(II) complex with 2,9-Me₂phen decrease with the increase of CP. The activation enthalpy for the ligand substitution reaction of nickel(II) ion with bpy increases linearly with the increase of CP in the solvents with the same functional group. The half-wave potentials of the Ni²⁺/Ni⁰ couple in nitrile solvents become more negative with the increase of CP and a good relationship between CP and the ligand field splitting parameter (10Dq) for the nickel(II) solvate ion was found. Thus, CP is concluded to be a good measure for the donor ability of the solvents.

Introduction

Chemical reactions in solutions cannot be essentially understood without clarification of the effect of a solvent. An important and urgent problem in the study on the inorganic reaction in solutions is to obtain a measure representing the strength of the interaction between solvent and metal ion. The effects of solvents on the complexation reactions, electrode reactions, catalytic reactions, and syntheses in which metal ions participate should be divided into the solvation effect and the dilution effect to be discussed. The former especially plays an important role in these reactions. Many attempts have been made to correlate observed changes in the reactivity of metal ions with fundamental bulk properties of the solvents involved, such as their dielectric constants, dipole moments, and polarizabilities. Such attempts have met with only limited success.

Gutmann has proposed the donor number, which is the enthalpy change on the solvation of pentachloroantimony(V), as a measure for the basicity of solvents.^{1,2} The donor number has served as a useful guide for the interpretation of the solvent effects on the chemical shift of CF₃I,³ the stability constants of SbCl₆²⁻ and complexes of univalent cations with solvents,⁴ the half-wave potentials of metal ions,⁵ Mössbauer isomer shifts,⁶ and the electron

binding energies of the 3d_{5/2} orbitals of antimony.⁷ But no donor numbers of alcohols, which are frequently used as solvents and are indispensable in the study of nonaqueous chemistry, were reported by Gutmann. The prediction of the donor number of methanol from the solvent dependence of the dissociation rate and the equilibrium constant of the nickel complex with the thiocyanate,⁸ the activation for dissociation of the nickel(II) complexes with isoquinoline,⁹ and NMR measurement¹⁰ has been attempted. A modified value for it was suggested from a relationship between ESR parameters of bis(2,6-dimethyl-3,5-heptanedionato)copper(II) and the donor numbers of solvents.¹¹ From kinetic studies on the ligand substitution¹² and the solvent-exchange enthalpies^{13a} of nickel(II) ions, it was suggested that the donor numbers did not necessarily apply to such acceptors as nickel(II) ions having covalent bonds.

There is no good measure for the strength of a metal ion-solvent interaction except for the donor number, though we strongly expect to establish a new concept for the classification of a solvent based

- (1) Gutmann, V.; Wychera, E. *Inorg. Nucl. Chem. Lett.* **1966**, *2*, 257.
- (2) Gutmann, V. "Coordination Chemistry in Non-Aqueous Solution"; Springer-Verlag: New York, 1968.
- (3) Spaziante, P.; Gutmann, V. *Inorg. Chim. Acta* **1971**, *5*, 273.
- (4) Izutsu, K.; Nakamura, T.; Iwata, K. *Anal. Chim. Acta* **1980**, *117*, 329.
- (5) (a) Gutmann, V. *Monatsh. Chem.* **1969**, *100*, 2113. (b) Gutmann, V. *Fortschr. Chem. Forsch.* **1972**, *27*, 59.
- (6) Vertes, A.; Burger, K. *J. Inorg. Nucl. Chem.* **1972**, *34*, 3665.

- (7) Burger, K.; Fluck, E. *Inorg. Nucl. Chem. Lett.* **1974**, *10*, 171.
- (8) Dickert, F.; Hoffmann, H.; Janjic, T. *Ber. Bunsenges. Phys. Chem.* **1974**, *78*, 712.
- (9) Chattopandhyay, P. K.; Kratochvil, B. *Inorg. Chem.* **1976**, *15*, 3104.
- (10) (a) Erlich, R. H.; Roach, E.; Popov, A. I. *J. Am. Chem. Soc.* **1970**, *92*, 4989. (b) Erlich, R. H.; Popov, A. I. *J. Am. Chem. Soc.* **1971**, *93*, 5620. (c) Greenberg, M. S.; Bodner, R. L.; Popov, A. I. *J. Phys. Chem.* **1973**, *77*, 2449.
- (11) Ogata, T.; Fujisawa, T.; Tanaka, N.; Yokoi, H. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 2759.
- (12) Coetzee, J. F.; Karakatsanis, C. G. *Inorg. Chem.* **1976**, *15*, 3112.
- (13) (a) Rusnak, L. L.; Yang, E. S.; Jordan, R. B. *Inorg. Chem.* **1978**, *17*, 1810. (b) Funahashi, S.; Jordan, R. B. *Inorg. Chem.* **1977**, *16*, 1301.

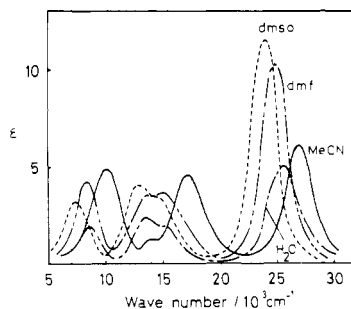


Figure 1. Electronic spectra of nickel(II) solvate ions (dmsO = Me₂SO).

on the donor ability. A new measure for the coordinating ability of a solvent was here determined by using nickel(II) ion and applying the rule of average environment, and the solvent effects on the stability constant and half-wave potential, the activation enthalpy for a ligand substitution reaction, and the splitting energy of d-d orbitals were discussed in terms of the measure.

Experimental Section

Materials. Nickel(II) perchlorate hexahydrates were crystallized twice from aqueous solvent. Ni(ClO₄)₂·2H₂O was obtained on heating the corresponding pure hexahydrates for 1 day at 120 °C under vacuum over P₂O₅. The anhydrous salts were not obtained under these conditions. Hexakis(acetonitrile)nickel(II) perchlorate, [Ni(MeCN)₆](ClO₄)₂, and hexakis(dimethyl sulfoxide)nickel(II) perchlorate, [Ni(Me₂SO)₆](ClO₄)₂, were prepared by the same procedure as described in the literature^{14,15} and identified by comparing their infrared and electronic spectra with those in the literature.^{14,15} Mg(ClO₄)₂ and AgClO₄ (Wako Chemical, Purified Grade) were used without further purification.

Solvents. Propylene carbonate was dried over molecular sieves for 1 day and distilled under 1 mmHg atmosphere. Dimethyl sulfoxide was dried over calcium chloride for 1 day and then distilled under a reduced pressure. *N,N*-Dimethylformamide was dried over P₂O₅ and then distilled under a reduced pressure. Methanol, ethanol, and *n*-propanol were dried by heating under reflux over magnesium turnings and then distilled. Nitriles,¹⁶ isopropyl alcohol, *sec*-butyl alcohol, isobutyl alcohol, *n*-pentanol, *n*-hexanol, *tert*-butyl alcohol, and trimethyl phosphate were dried over calcium hydride for 1 day and then distilled. The water content of the solvents was estimated by the Karl Fischer titration and found to be less than 0.01% by weight.

Electronic Spectral Measurements. The solutions of nickel(II) ions were prepared by direct addition of weighed Ni(ClO₄)₂·2H₂O, [Ni(MeCN)₆](ClO₄)₂, or [Ni(Me₂SO)₆](ClO₄)₂ to the solvents in a glovebox (dry atmosphere). The concentration of the nickel solutions was determined by EDTA titration. The solutions of the nickel solvates were sealed in absorption cells, and the electronic spectra were measured from 250 to 1800 nm on a Hitachi 340 spectrophotometer.

Kinetic Runs. Kinetic measurements were made with a Union Giken Co. Model RA-401 stopped-flow spectrophotometer equipped with an RA-400 kinetic data processor. This instrument is thermostated easily to better than 0.1 °C. Reactions were monitored at the wavelength (308 nm) of maximum absorption of 2,2'-bipyridine coordinating to nickel(II). The kinetics were measured under pseudo-first-order conditions with the total 2,2'-bipyridine (bpy) concentration 2.5 × 10⁻⁵ M and the nickel concentration varied through four or five values, typically from ca. 1 to 4 × 10⁻³ M. Nickel(II) ion was introduced as Ni(ClO₄)₂·2H₂O. The five reaction traces on one system were accumulated and recorded with the kinetic data processor. Reproducibility of second-order rate constants was generally within ±2%.

Polarograms. Polarographic measurements were carried out with a Yanagimoto P8 polarograph. The temperature was maintained to 25 ± 0.1 °C in a water bath. The reference electrode was a saturated calomel electrode (SCE) equipped with a salt bridge consisting of two parts: aqueous agar solution containing saturated NaCl and a solution composed of the desired nonaqueous solvent (7 mL), NaClO₄ (0.88 g), and methyl cellulose (1.2 g).

Results

10Dq Value of Nickel(II) Solvate Ion. Figure 1 shows the electronic spectra of four nickel(II) solvate ions. The spectra are

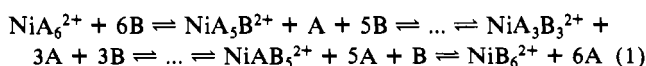
Table I. Ligand Field Splitting Energies of Nickel(II) Solvate Ions, Ni(solvent)₆²⁺

solvent	10Dq/10 ³ cm ⁻¹		
	³ A _{2g} → ³ T _{2g} transition	Tanabe-Sugano diagram	
pyridine (py)	10.26	10.00	10.00 ^a
dimethyl sulfoxide (Me ₂ SO)	7.81	7.85	7.81 ^b
water (H ₂ O)	8.55	8.64	8.60 ^{a,c}
<i>N,N</i> -dimethylformamide (dmf)	8.40	8.44	8.50 ^{a,c}
<i>N,N</i> -diethylformamide (def)	8.58	8.59	8.40 ^c
acetonitrile (MeCN)	10.31	10.09	10.26 ^a
propionitrile (PrCN)	10.18	10.10	
benzotrile (PhCN)	10.03	10.00	9.70 ^a
acrylonitrile (AN)	9.98	9.95	
trimethyl phosphate (tmp)	7.14	7.29	7.96 ^d
methanol (MeOH)	8.51	8.55	8.50 ^a
ethanol (EtOH)	8.62	8.64	
<i>n</i> -propanol (<i>n</i> -PrOH)	8.70	8.72	
<i>n</i> -butanol (<i>n</i> -BuOH)	8.73	8.74	
isobutyl alcohol (<i>i</i> -BuOH)	8.70	8.78	
isopropyl alcohol (<i>i</i> -PrOH)	8.77	8.79	
<i>sec</i> -butyl alcohol (<i>s</i> -BuOH)	8.64	8.74	
<i>tert</i> -butyl alcohol (<i>t</i> -BuOH)	8.44	8.73	
<i>n</i> -pentanol (<i>n</i> -PeOH)	8.66	8.67	
<i>n</i> -hexanol (<i>n</i> -HxOH)	8.61	8.62	
acetone (Me ₂ CO)	8.55	8.59	
propylene carbonate (pc)	8.92	8.93	

^a Waddington, T. C. "Non-aqueous Solvents"; Nelson: 1965; 5. ^b Schlafer, H. L.; Opitz, H. D. *Z. Elektrochem.* 1961, 65, 372. ^c Drago, R. S.; Meek, D. W.; Joestem, M. D.; LaRoche, L. *Inorg. Chem.* 1963, 2, 124. ^d Gutmann, V.; Bardy, J. *Monatsh. Chem.* 1968, 99, 763.

typical of nickel(II) having a six-coordinated octahedron.¹⁷ The peaks at the lowest, middle, and the highest frequencies are assigned to the ³A_{2g} → ³T_{2g}, ³A_{2g} → ³T_{1g}(F), and ³A_{2g} → ³T_{1g}(P) transitions, respectively, as are well-known.¹⁷ The ligand field splitting energies, 10Dq, of the nickel(II) solvate ions calculated directly from the ³A_{2g} → ³T_{2g} transition energies are shown in Table I. The 10Dq value calculated by using Tanabe-Sugano diagrams are also summarized in the third column of Table I. The former was used here in the estimation of 10Dq values of mixed solvatonickel(II) ions. The solutions of [Ni(H₂O)₆]²⁺, [Ni(MeCN)₆]²⁺, and [Ni(Me₂SO)₆]²⁺ were prepared by addition of [Ni(H₂O)₆](ClO₄)₂, [Ni(MeCN)₆](ClO₄)₂, and [Ni(Me₂SO)₆](ClO₄)₂ to the corresponding solvents. The solutions of other nickel(II) ions were prepared by addition of Ni(ClO₄)₂·2H₂O to the desired solvent. The 10Dq values of nickel(II) solvate ions of H₂O, dmf, alcohols, and pc are almost the same. It is noted that the 10Dq values of [Ni(MeCN)₆]²⁺ and [Ni(py)₆]²⁺ are larger than those of the other nickel(II) solvate ions, whereas those of [Ni(Me₂SO)₆]²⁺ and [Ni(tmp)₆]²⁺ are the smallest. These nickel(II) solvate ions are convenient in the determination of the coordination ability with the 10Dq values because the replacement of MeCN or Me₂SO, which coordinates to the nickel(II) ion, by other solvents gives a sensitive change in the 10Dq value of the resulting nickel(II) solvate ion as described below.

Coordination Ability and Coordination Power. Nickel(II) ions having six-coordination in the mixed solvent of A and B are represented by eq 1. When the mole ratio of A to B in the mixed



solvent is equal to the reciprocal of the ratio of the coordination ability (CA_A) of A to that (CA_B) of B

$$[\text{A}]/[\text{B}] = \text{CA}_\text{B}/\text{CA}_\text{A} \quad (2)$$

(14) Wickenden, A. E.; Krause, R. A. *Inorg. Chem.* 1965, 4, 404.

(15) Langford, C. H.; Tsiang, H. G. *Inorg. Chem.* 1970, 9, 2346.

(16) Riddick, J. A.; Bunger, W. B. "Organic Solvents", 3rd ed.; New York, 1969.

(17) Strictly speaking, the activity coefficients of the solvents should be considered. However, we have insufficient data on them in the mixed solvents.

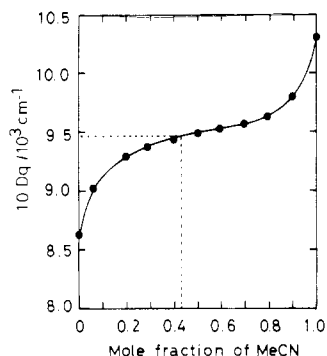


Figure 2. Plot of the $10Dq$ values of nickel(II) solvate ions against the mole fraction of acetonitrile in ethanol-acetonitrile mixed solvent.

Table II. Relative Coordination Ability and Coordination Power of Solvents

solvent ^a	CA _{MeCN} ^b	CA _{Me₂SO} ^b	CP ^c
py		10.1	2.24
Me ₂ SO		1.00	1.24
def		0.41	0.85
H ₂ O	6.1	0.35	0.79
dmf		0.30	0.72
MeOH	1.30	0.075	0.11
tmp	1.20		0.08
MeCN	1.00		0.00
<i>n</i> -HxOH	0.86		-0.07
<i>n</i> -PeOH	0.85		-0.07
EtOH	0.75		-0.12
<i>n</i> -BuOH	0.75		-0.12
<i>n</i> -PrOH	0.73		-0.14
PrCN	0.70		-0.15
PhCN	0.43		-0.37
AN	0.35		-0.46
<i>i</i> -BuOH	0.35		-0.46
Me ₂ CO	0.33		-0.48
<i>i</i> -PrOH	0.29		-0.54
<i>s</i> -BuOH	0.21		-0.68
pc	0.17		-0.77
<i>t</i> -BuOH	0.12		-0.92

^a For abbreviations, see Table I. ^b CA_{MeCN} and CA_{Me₂SO} are relative coordination abilities on the basis of acetonitrile and Me₂SO, respectively. ^c CP is the logarithmic value of coordination ability on the basis of acetonitrile.

it is assumed that NiA₃B₃²⁺ is the major species and the following equations hold for the minor species

$$[\text{NiA}_6^{2+}] = [\text{NiB}_6^{2+}] \quad (3a)$$

$$[\text{NiA}_5\text{B}^{2+}] = [\text{NiAB}_5^{2+}] \quad (3b)$$

$$[\text{NiA}_4\text{B}_2^{2+}] = [\text{NiA}_2\text{B}_4^{2+}] \quad (3c)$$

In other words, the relative coordination ability of A to B can be determined from the mole ratio¹⁷ where NiA₃B₃²⁺ is maximally formed in the mixed solvent A and B. The question is how to determine the mole ratio. The ratio was here determined by using nickel(II) ion and by applying the rule of average environment,¹⁸ because the ligand field splitting energy, $10Dq_{av}$, for [NiA₃B₃]²⁺ is given by eq 4, where $10Dq_A$ and $10Dq_B$ are the ligand field

$$10Dq_{av} = (10Dq_A + 10Dq_B)/2 \quad (4)$$

splitting energies of [NiA₆]²⁺ and [NiB₆]²⁺, respectively.^{19,20} Figure 2 shows a plot of $10Dq$ value observed against the mole fraction of MeCN in EtOH-MeCN mixed solvents. The mole fraction of MeCN is 0.43 at the value $10Dq_{av}$ (9.470 cm^{-1}) for

(18) Figgis, B. N. "Introduction to Ligand Fields"; Wiley: New York, 1969.

(19) Krishnamurthy, R.; Schaap, W. B. *J. Chem. Educ.* **1969**, *46*, 799.

(20) This rule applies to the *fac*-[MA₃B₃] systems and would not seem to apply to *mer*-[MA₃B₃].¹⁹ Thus, the *mer/fac* ratio must be taken into account. The purpose, however, is to obtain experimentally "relative" coordination ability, but not "absolute" coordination ability.

Table III. Stability Constants ($K/\text{mol}^{-1} \text{ L}$) of the Mono Complexes of Magnesium(II) and Silver(I) Ions with 2,2'-Bipyridine and Nickel(II) with 2,9-Dimethyl-1,10-phenanthroline at 25 °C

solvent ^a	log $K_{\text{Mg}(\text{bpy})}$	log $K_{\text{Ni}(\text{dmp})}$	log $K_{\text{Ag}(\text{bpy})}$
Me ₂ SO	-0.39	2.8	2.4
H ₂ O	0.5 ^b	2.6-2.8 ^c	3.7 ^d
dmf	-0.26	3.8	3.4
MeOH	0.93	3.8	4.3
tmp		5.4	
MeCN	4.8	4.5	3.6
EtOH	3.2	5.0	4.6
<i>n</i> -BuOH	2.8		
<i>i</i> -BuOH	3.5		
Me ₂ CO			
<i>i</i> -PrOH	3.9	5.8	
<i>s</i> -BuOH	3.8	6.1	
pc	4.2		
<i>t</i> -BuOH	4.8		

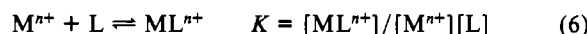
^a For abbreviations, see Table I. ^b Reference 45. ^c Reference 46. ^d Reference 47.

[Ni(EtOH)₃(MeCN)₃]²⁺ calculated from eq 4. The ratio of the coordination ability of EtOH to that of MeCN is therefore 0.75 (eq 2). The values of the coordination abilities for solvents obtained on the basis of MeCN (CA_{MeCN} = 1.00) and Me₂SO (CA_{Me₂SO} = 1.00) were obtained in this manner and are shown in Table II. The ratio of the coordination ability of water based on MeCN (6.1) to that of Me₂SO (0.35) is 17. From the values of methanol based on MeCN (1.3) and Me₂SO (0.075), the ratio becomes 17. The good agreement between the former and the latter strongly suggests that the coordination abilities obtained in this work are relatively correct. The logarithmic values of the coordination abilities on the basis of MeCN are termed "coordination power" and are summarized in the last column of Table II:

$$\text{coordination power (CP)} = \log (\text{CA}/\text{CA}_{\text{MeCN}}) \quad (5)$$

$$\text{CA}_{\text{MeCN}} \equiv 1.00$$

Stability Constant. The stability constants of the Mg(II)-2,2'-bipyridine (bpy) 1:1 complex, the Ag(I)-bpy 1:1 complex, and the Ni(II)-2,9-dimethyl-1,10-phenanthroline (dmp) 1:1 complex were measured spectrophotometrically at 306, 300, and 302 nm, respectively.

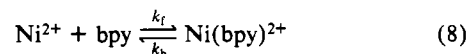


Generally a set of five to eight complex solutions were prepared in each solvent for the measurements. In each set of solutions the ligand concentration was kept constant, usually $2.5 \times 10^{-5} \text{ M}$, and the metal ion concentration varied from about 2.5×10^{-5} to 0.1 M (for Ag⁺, Mg²⁺) or $5 \times 10^{-3} \text{ M}$ (for Ni²⁺). The stability constants for the 1:1 complexes are given by eq 7, where M_0 and

$$K = \frac{E - E_L}{M_0(E_C - E_L) + L_0(E_L - E)} \frac{E_C - E_L}{(E_C - E)} \quad (7)$$

L_0 represent the total concentrations of metal ion and ligand, respectively, E_C and E_L are the absorptions of the complex and ligand, respectively, and E is the absorbance of the solution. The value of E_C was determined by minimizing the standard deviation of K . The stability constants obtained are summarized in Table III.

Kinetics and Activation Enthalpy. The rate constants of the ligand substitution reactions of nickel(II) ion with bpy in water and nonaqueous solvents (eq 8) were measured with use of the



stopped-flow method. Under the pseudo-first-order rate conditions when $[\text{Ni}^{2+}] \gg [2,2'\text{-bipyridine}]$, the observed pseudo-first-order rate constant, k_{obsd} , is given by

$$k_{\text{obsd}} = k_f[\text{Ni}^{2+}] + k_b \quad (9)$$

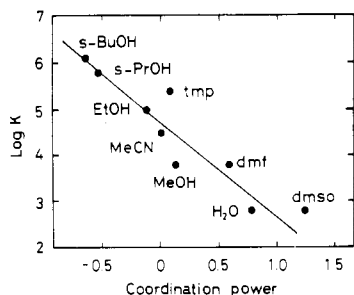


Figure 3. Dependence of the stability constant of the nickel(II) complex with 2,9-dimethyl-1,10-phenanthroline at 25 °C upon the coordination power of solvents. For abbreviations, see Table I. (dmsO and *s*-PrOH represent Me₂SO and *i*-PrOH, respectively.)

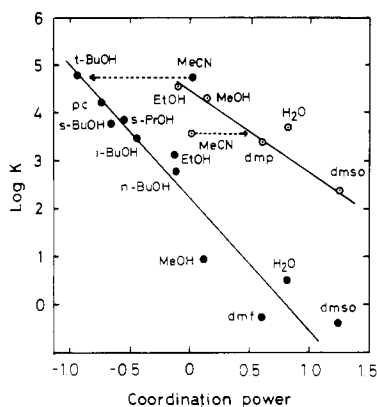


Figure 4. Dependence of the stability constants of magnesium(II) (●) and silver(I) (○) complexes with 2,2'-bipyridine at 25 °C upon the coordination power. For abbreviations, see Table I. (dmsO and *s*-PrOH represent Me₂SO and *i*-PrOH, respectively.)

where k_f and k_b are the forward and reverse rate constants for the ligand substitution reaction, respectively. k_f is obtained from the slope in the plot of k_{obsd} vs. $[\text{Ni}^{2+}]$. The forward rate constants and the activation enthalpies for the ligand substitution reactions of nickel(II) solvate ions with 2,2'-bipyridine are summarized in Table III. The values at 25 °C are in agreement with the values in the literature.¹¹

Discussion

Stability Constant and Coordination Power. The stability constants of metal complexes (eq 7) are expected to be inversely proportional to the coordination power of the solvents because of the competition between ligand and solvent. Those of mixed iodide and thiocyanate nickel(II) complexes of the two macrocyclic systems follow the coordination power with the exception of water²¹ (Table S-I, supplementary material). With the increase of the coordination power, the stability constant of the Ni(II)-dmp 1:1 complex also linearly decreases as shown in Figure 3, which reveals its reliability. It is noteworthy that those of the Mg(II)-bpy 1:1 complex and Ag(I)-bpy 1:1 complex also decrease with the increase of the coordination power of the solvents except MeCN (Figure 4), indicating that the coordination power series holds for Mg²⁺ (hard metal ion) and Ag⁺ (soft metal ion) as well as Ni²⁺ (borderline metal ion). Hard metal ions prefer to coordinate to hard solvents, and soft metal ions prefer to coordinate soft bases such as MeCN.²² The bonding in the former solvates is largely ionic, and in the latter solvates covalent bonding contributes substantially to the bonding,²³ so the covalent bonding in the metal-MeCN bonds is enhanced in the order Mg²⁺ < Ni²⁺ < Ag⁺. The value of the coordination power of MeCN obtained for Ni²⁺ is overestimated for Mg²⁺, whereas the value is underestimated

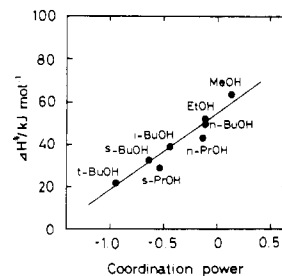


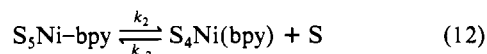
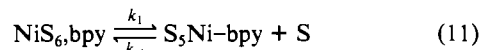
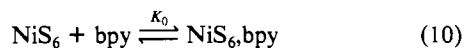
Figure 5. Dependence of the activation enthalpy for the ligand substitution reaction of nickel(II) ion with 2,2'-bipyridine in alcohols and nitriles upon their coordination power. For abbreviations, see Table I. (*s*-PrOH represents *i*-PrOH.)

for Ag⁺. In MeCN, the positive deviation of the stability constant of the Mg(II)-bpy complex and the negative deviation of that of the Ag(I)-bpy complex can be accounted for by the overestimation and the underestimation, respectively. The large medium effect of MeCN on the Gibbs free energy for the transfer of silver ions from water to the solvent²⁴ is also interpreted in terms of the covalent bonding.

Schneider and Gudlin have reported that the aluminum(III) solvate ion $[\text{Al}(\text{Me}_2\text{SO})_3(\text{dmf})_3]^{3+}$, is formed at about 0.2 mole fraction of Me₂SO in Me₂SO-dmf mixed solvents.²⁵ Therefore, the difference in the coordination power between Me₂SO and dmf is 0.6. This value is near the difference, 0.54, obtained in this work, though the aluminum(III) ion is a hard acid and the ionic radius is smaller than that of nickel(II). This again indicates that the values of the coordination power are reliable and the coordination power series holds for hard metal ions.

Kinetics and Coordination Power. Extensive investigations have indicated that the rate-determining step in the ligand substitution reaction of hydrated metal ions involves the loss of a water molecule from the inner coordination sphere of metal ion in aqueous solution.²⁶ Kinetic studies on the ligand substitution reaction of nickel(II) ion in nonaqueous solvent carried out in the past decade reach the general conclusion that the same mechanism is applicable to those solvent systems as well.^{12,27-30} However, the effects of solvents on the ligand substitution reactions^{8,9,12,13,31,32} are complicated.

In the case of the fully solvated nickel(II) ions ($[\text{NiS}_6]^{2+}$) and a normal bidentate ligand, 2,2'-bipyridine, the ligand substitution reaction is written as^{27,33-35}



where K_0 is the ion-pair formation constant and can be estimated

(24) Matsuura, N.; Umamoto, K. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 1334.

(25) (a) Gudlin, D.; Schneider, H. *J. Magn. Reson.* **1974**, *16*, 362. (b) Schneider, H. *Electrochim. Acta* **1976**, *21*, 711.

(26) Eigen, M.; Wilkins, R. G. "Mechanism of Inorganic Reactions"; American Chemical Society: Washington, DC, 1965; Adv. Chem. Ser. No. 49.

(27) (a) Chattopadhyay, P. K.; Coetzee, J. F. *Inorg. Chem.* **1973**, *12*, 113. (b) Coetzee, J. F.; Umamoto, K. *Inorg. Chem.* **1976**, *15*, 3109.

(28) (a) Bennetto, H. P.; Caldin, E. F. *J. Chem. Soc. A* **1971**, 2198. (b) Bennetto, H. P.; Caldin, E. F. *J. Chem. Soc. A* **1971**, 2191.

(29) (a) Mackellar, W. J.; Rorabacher, D. B. *J. Am. Chem. Soc.* **1971**, *93*, 4379. (b) Shu, F. R.; Rorabacher, D. B. *Inorg. Chem.* **1972**, *11*, 1496.

(30) Williams, J.; Petrucci, S.; Sesta, B.; Battistini, M. *Inorg. Chem.* **1974**, *13*, 1968.

(31) (a) Benton, D. J.; Moore, P. *J. Chem. Soc., Dalton Trans.* **1973**, 399. (b) Moore, P.; Buck, D. M. W. *J. Chem. Soc., Dalton Trans.* **1973**, 1062. (c) Buck, D. M. W.; Moore, P. *J. Chem. Soc., Dalton Trans.* **1974**, 2082.

(32) Tanaka, M. *Inorg. Chem.* **1976**, *15*, 2325.

(33) Pasternack, R. F.; Sigel, H. *J. Am. Chem. Soc.* **1970**, *92*, 6146.

(34) Munakata, M.; Yamada, K. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 3500.

(35) Langford, C. H.; Tong, J. P. K.; Merbach, A. *Can. J. Chem.* **1975**, *53*, 702.

(21) Burger, K. "Solvation, Ionic and Complex Formation Reactions in Non-Aqueous Solvent"; Elsevier: Amsterdam, 1983; pp 57-58.

(22) (a) Pearson, R. G. *J. Chem. Educ.* **1968**, *46*, 581. (b) Pearson, R. G. *J. Chem. Educ.* **1968**, *45*, 643.

(23) Klopman, G. *J. Am. Chem. Soc.* **1968**, *90*, 223.

Table IV. Forward Rate Constants and Activation Enthalpies for the Ligand Substitution Reactions of Nickel(II) Solvate Ions with 2,2'-Bipyridine

solvent ^a	log k_f /mol ⁻¹ s ⁻¹									$\Delta H^*/$ kJ mol ⁻¹
	10 °C	15 °C	20 °C	25 °C	30 °C	35 °C	40 °C	45 °C		
Me ₂ SO		1.1		1.8 (1.8) ^b		2.1		2.3	50 (53) ^c	
H ₂ O		2.8		3.1 (3.4) ^b		3.5		3.8	59 (53) ^c	
dmf	1.9		2.4	2.5 (2.7) ^b	2.7		3.2		69 (53) ^c	
tmp		3.0		3.2		3.4		3.6	35	
pc	5.4		5.5	5.6 (5.4) ^b	5.7		5.8		24	
MeCN	3.7	3.8	3.9	4.0 (3.6) ^b					30 (28) ^c	
PrCN		3.8		4.0	4.0		4.2		28	
PhCN		3.9		4.1	4.1		4.3		25	
AN		4.4		4.5	4.6		4.7		20	
MeOH			1.8	2.0 (2.0) ^b	2.2		2.6		64 (71) ^c	
<i>n</i> -HxOH				3.6						
<i>n</i> -PeOH				3.8						
EtOH	3.1		3.6	3.9 (3.8) ^b	4.0		4.3		53	
<i>n</i> -BuOH		3.6		3.9		4.2		4.5	51	
<i>n</i> -PrOH		3.9		4.2 (4.0) ^b		4.5		4.7	44	
<i>i</i> -BuOH	4.2		4.5	4.6	4.7		5.0		39	
<i>i</i> -PrOH	5.2		5.1	5.2 (5.2) ^b	5.3		5.4		29	
<i>s</i> -BuOH	5.0		5.2	5.4	5.5				33	
<i>t</i> -BuOH	6.0		6.1	6.2					22	

^a For abbreviations, see Table I. ^b Reference 12. ^c Reference 28b.

from the Fuoss equation.³⁶ If the rate-determining step is the loss of the first solvent,³⁷ the forward rate constant, k_f , is then

$$k_f = K_0 k_1 \quad (13)$$

where k_1 is the rate constant for the loss of the first solvent (eq 11).

Figure 5 shows a plot of the activation enthalpy (ΔH^*) for the ligand substitution reactions of nickel(II) ion with 2,2'-bipyridine in alcohols against their coordination power. The same trends are found in the nitrile solvent series (Table IV). It is especially noted that the activation enthalpy is correlated linearly with the coordination power of the solvents having the same functional group.

$$\Delta H^* \propto \text{coordination power} \quad (14)$$

This evidently indicates that the ligand substitution depends on the coordination power, and the coordination power of the solvent having the same functional group is a measure for the strength of the metal-solvent interaction. The ligand substitution at room temperature decreases with the increase of the coordination power (Table IV), and the same tendency has been found for the ligand substitution reaction of nickel(II) ion with 4-phenylpyridine in alcohols:¹¹ *i*-PrOH (log k_f = 5.2), *n*-PrOH (4.2), EtOH (3.0), and MeOH (2.1). On the other hand, the dissociation of a metal complex might be expected to increase with the increase of the coordination power. In fact, the dissociation of the nickel(II) complex with isoquinoline⁹ roughly correlates with the coordination power (Figure S-1, supplementary material).

d-d Splitting and Coordination Power. The energies of d-d splitting in an octahedral field of the transition metal reflect the strength of the interaction between the metal ion and the ligand. The value of $10Dq$ may, therefore, be regarded as a measure of the donor strength of the solvent. The systematic characterization has been unsuccessful so far because it can be employed for the comparison only of those solvents that form solvates with analogous compositions, symmetries, and bonding natures.³⁸ It should be emphasized that the values of $10Dq$ of hexakis(nitrile)nickel(II) ion, $[\text{Ni}(\text{RCN})_6]^{2+}$, increase with the increase of the coordination power of the nitriles, AN (9.980 cm⁻¹) \leq PhCN (10.030 cm⁻¹) $<$ PrCN (10.180 cm⁻¹) $<$ MeCN (10.310 cm⁻¹), and subsequently, the coordination power of the nitrile solvents reflects well their

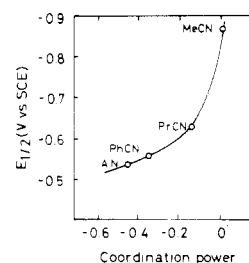


Figure 6. Dependence of half-wave potentials of the Ni(II)/Ni(0) couple upon the coordination power of nitriles. For abbreviations, see Table I.

donor strengths. The values of nickel(II) ions in butanols also increase with the increase of the coordination power: *t*-BuOH (8.440 cm⁻¹) $<$ *s*-BuOH (8.640 cm⁻¹) $<$ *i*-BuOH (8.700 cm⁻¹) \leq *n*-BuOH (8.730 cm⁻¹). The trend was not, however, found for other alcohols.

Redox Potential and Coordination Power. There is an outstanding question to establish a scale of redox potentials relative to the standard hydrogen electrode in a nonaqueous solvent. However, it is difficult to relate such a scale to the scale of standard electrode potentials in aqueous solution. A number of redox potentials determined for metal ion couples in nonaqueous solvent exist.³⁹⁻⁴³ Gutmann has reported that polarographic half-wave potentials for metal ions, $E_{1/2}$, are roughly correlated with solvent donor numbers.⁵

Half-wave potentials⁴³ for Cd²⁺, Zn²⁺, and Co²⁺ also show a trend to become more negative with the increase of the coordination power of the solvent, though there are a few scatters (Table S-II, supplementary material). Moreover, the variation in $E_{1/2}$ of the Ni²⁺/Ni⁰ couple, especially with nitrile solvents, is successfully correlated with the coordination power as shown in Figure 6, where $E_{1/2}$ values (vs. SCE) in MeCN, PrCN, PhCN, and AN are -0.87, -0.63, -0.56, and -0.54 V, respectively. The half-wave potential of Ni²⁺/Ni⁰ in def (-0.98 V vs. SCE) is more negative than that in dmf (-0.90 V vs. SCE), and $E_{1/2}$ values³⁹ for Li⁺/Li⁰ (-3.10, -3.04 V), Na⁺/Na⁰ (-2.73, -2.66 V), and Tl⁺/Tl⁰ (-0.38, -0.34 V) have been found at more negative potentials in methanol

(36) Fuoss, R. M. *J. Am. Chem. Soc.* **1958**, *80*, 5059.

(37) The chelate ring closure (eq 12) of bpy in Me₂SO is the rate-determining step.³¹ This may be attributable to the large CP value, namely the difficulty of the second dissociation of Me₂SO as well as the first.

(38) Burger, K. "Solvation, Ionic and Complex Formation Reactions in Non-Aqueous Solvents"; Elsevier: Amsterdam, 1978; pp 43-44.

(39) Strehlow, H. "The Chemistry of Nonaqueous Solvents"; Vol. 1, Lagowski, J. J., Ed.; Academic Press: New York, 1964; Vol. 1, Chapter 4.

(40) Constanninescu, E. *Rev. Roum. Chim.* **1972**, *17*, 1819.

(41) (a) Kolthoff, I. M.; Coetzee, F. *J. Am. Chem. Soc.* **1957**, *79*, 870, 1852.

(b) Coetzee, J. F.; Simon, J. M. *Anal. Chem.* **1972**, *4*, 1129.

(42) Sunschek, O.; Gutmann, V. *Monatsh. Chem.* **1973**, *104*, 1359.

(43) Burgess, J. "Metal Ions in Solution"; Wiley: New York, 1978; Chapter 8.

(the first value in parentheses) than in ethanol (the second value in parentheses). These findings indicate that the half-wave potentials in the solvents having the same functional group correspond well to the coordination powers of the solvents. The comparison of half-wave potentials measured in different solvents is accompanied by extreme difficulties. In this sense, the above facts should be noted.

Gibbs free energies of transfer of copper(II) ion from water to other solvents also correlate with the coordination power: The energies for dmf, MeOH, MeCN, EtOH, *n*-PrOH, *i*-PrOH, and pc are -11.6, -4.3, +6.2, +14.2, +11.0, +10.3, +15.9, and +17.9 kcal mol⁻¹, respectively.⁴⁴

Conclusion

The values of the coordination power obtained in this work give a theoretically approximate representation, since the considerations of activity of a solvent and the *mer/fac* ratio of nickel solvate ions in the mixed solvents are ignored. Nevertheless, the coordination power successfully explains the solvent effects on the stability constants of metal complexes, the redox potentials, ligand substitutions, and d-d splitting of metal solvate ions. The coordination power series reflects well the strength of the metal ion-solvent interaction, especially for the solvents having the same functional group, and holds for hard, borderline, and soft metal ions with

the exception of soft bases such as MeCN. These facts strongly support that the concept of the coordination power is experimentally reliable and highly useful as a measure for the solvent donor ability, because we have no such measure except the donor number.

Acknowledgment. Thanks are given to S. Niina, T. Tateshita, T. Aboshi, T. Imai, and Y. Kushibe for their assistance in the experimental work. This work was supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education (No. 36202).

Registry No. Ni(py)₆²⁺, 20037-72-3; Ni(Me₂SO)₆²⁺, 26745-60-8; Ni(H₂O)₆²⁺, 15365-79-4; Ni(dmf)₆²⁺, 33789-00-3; Ni(def)₆²⁺, 45318-23-8; Ni(MeCN)₆²⁺, 15554-59-3; Ni(PrCN)₆²⁺, 95725-15-8; Ni(PhCN)₆²⁺, 47873-95-0; Ni(AN)₆²⁺, 67486-29-7; Ni(tmp)₆²⁺, 45320-88-5; Ni(MeOH)₆²⁺, 18443-63-5; Ni(EtOH)₆²⁺, 25286-14-0; Ni(*n*-PrOH)₆²⁺, 42493-31-2; Ni(*n*-BuOH)₆²⁺, 63872-29-7; Ni(*i*-BuOH)₆²⁺, 45303-58-0; Ni(*i*-PrOH)₆²⁺, 45283-62-3; Ni(*s*-BuOH)₆²⁺, 63872-30-0; Ni(*t*-BuOH)₆²⁺, 63872-31-1; Ni(*n*-PeOH)₆²⁺, 63911-14-8; Ni(*n*-HxOH)₆²⁺, 95725-16-9; Ni(Me₂CO)₆²⁺, 25139-60-0; Ni(pc)₆²⁺, 72794-87-7; py, 110-86-1; dmf, 68-12-2; def, 617-84-5; AN, 107-13-1; tmp, 512-56-1; pc, 108-32-7; bpy, 366-18-7; Me₂SO, 67-68-5; H₂O, 7732-18-5; PrCN, 107-12-0; PhCN, 100-47-0; MeCN, 75-05-8; MeOH, 67-56-1; EtOH, 64-17-5; *n*-PrOH, 71-23-8; *n*-BuOH, 71-36-3; *i*-BuOH, 78-83-1; *i*-PrOH, 67-63-0; *s*-BuOH, 78-92-2; *t*-BuOH, 75-65-0; *n*-PeOH, 71-41-0; *n*-HxOH, 111-27-3; Me₂CO, 67-64-1; Ni, 7440-02-0.

Supplementary Material Available: Listings of stability constants and half-wave potentials and a plot of the dissociation rate constant vs. coordination power (3 pages). Ordering information is given on any current masthead page.

- (44) Coetzee, J. F.; Istone, W. K. *Anal. Chem.* **1980**, *52*, 53.
 (45) Sone, K.; Kato, M. *Naturwissenschaften* **1958**, *45*, 10.
 (46) Irving, H.; Mellor, D. H. *J. Chem. Soc.* **1962**, 5237.
 (47) Canani, S.; Scrocco, E. *J. Inorg. Nucl. Chem.* **1958**, *8*, 332.

Contribution from the Department of Chemistry, Purdue University, West Lafayette, Indiana 47907, and Molecular Structure Center, Indiana University, Bloomington, Indiana 47401

Dinuclear Aryloxide Chemistry. 3.¹ Synthesis, Structure, and Fluxional Behavior of 1,2-Bis(2-*tert*-butyl-6-methylphenoxy)tetrakis(dimethylamido)dimolybdenum and -ditungsten (M≡M)

TIMOTHY W. COFFINDAFFER,[†] IAN P. ROTHWELL,*[†] and JOHN C. HUFFMANN[‡]

Received May 17, 1984

Addition of 2-*tert*-butyl-6-methylphenol (HOAr) to the dinuclear compounds M₂(NMe₂)₆ (M = Mo, W) results in the formation of the complexes 1,2-M₂(OAr)₂(NMe₂)₄ [M = Mo (**1**), W (**2**)] as yellow crystalline solids. Spectra are consistent with the presence in solution of the gauche rotamer for these complexes, and variable-temperature studies allow the activation energy for restricted rotation about the M-NMe₂ bonds to be estimated. A single-crystal X-ray diffraction study of **1** shows that in the solid state the gauche rotamer is maintained for the unbridged Mo₂O₂N₄ skeleton. Crystal data at -160 °C were *a* = 13.532 (4) Å, *b* = 16.634 (6) Å, *c* = 14.696 (10) Å, *Z* = 4, and *d*_{calcd} = 1.369 g cm⁻³ for space group P2₁2₁. The metal-metal distance of 2.2198 (14) Å is consistent with the retention of a Mo-Mo triple bond while the Mo-NMe₂ distances of 1.925-1.97 Å indicate the presence of considerable nitrogen p to metal d π bonding.

Introduction

Our discovery of the ability of some mononuclear early-transition-metal systems to activate (cyclometalate) the aliphatic bonds in the sterically bulky ligand 2,6-di-*tert*-butylphenoxide²⁻⁴ has prompted us to investigate other situations where metalation of the alkyl side chains of aryloxide ligands may take place. In particular, we have been exploring the possibility of cyclometalation of such ligands at di-metal centers.¹ Recent results by Cotton and Walton have shown that it is possible to activate the aromatic CH bonds in the ligand 2-(diphenylphosphino)pyridine on a Re₂⁴⁺ core.⁵ Earlier work by Andersen and Wilkinson showed that the γ-hydrogen of alkyl ligands could also be activated across an Mo₂⁴⁺ core.⁶ This rationale has led us to survey the reactivity of sterically demanding 2,6-dialkylphen-

oxides coordinated to both Mo₂⁶⁺ and W₂⁶⁺ (M≡M) cores.^{1,7-9} In a number of reactions we have found reactivity both novel and complimentary compared to the previously well-documented

- (1) Part 2. Coffindaffer, T. W.; Rothwell, I. P.; Huffman, J. C., *Inorg. Chem.* **1984**, *23*, 1433.
 (2) Chamberlain, L.; Rothwell, I. P.; Huffman, J. C. *Organometallics* **1982**, *1*, 1538.
 (3) Chamberlain, L.; Rothwell, I. P.; Huffman, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 7338.
 (4) Chamberlain, L.; Rothwell, I. P. *J. Am. Chem. Soc.* **1983**, *105*, 1665.
 (5) Barder, T. J.; Cotton, F. A.; Powell, G. L.; Tetrick, S. M.; Walton, R. A. *J. Am. Chem. Soc.* **1984**, *106*, 1323.
 (6) Andersen, R. A.; Jones, R. A.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1978**, 446.
 (7) Coffindaffer, T. W.; Rothwell, I. P.; Huffman, J. C. *Inorg. Chem.* **1983**, *22*, 2906.
 (8) Coffindaffer, T. W.; Rothwell, I. P.; Huffman, J. C. *Inorg. Chem.* **1983**, *22*, 2906.
 (9) Coffindaffer, T. W.; Rothwell, I. P.; Huffman, J. C. *J. Chem. Soc., Chem. Commun.* **1983**, 1269.

[†]Purdue University.
[‡]Indiana University.