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Equilibrium and kinetics of the dinuclear complex formation between *N*,*N*′-ethylenebis(salicylideneiminato)copper(II) and metal(II,I) ions in acetonitrile

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Abstract

The equilibrium constants and rate constants of the reactions between *N*,*N*′-ethylenebis(salicylideneiminato)copper(II) ([Cu(salen)]) and metal(II,I) ions in acetonitrile have been spectrophotometrically determined. [Cu(salen)] acts as a didentate ligand to form a dinuclear complex. The rate constants for the very labile Mn(II), Fe(II), and Zn(II) ions were directly evaluated using a variable flow-rate instrument that was newly constructed for this study. The rate constants of the dinuclear complex formation for a series of metal(II) ions vary in parallel with those of the acetonitrile solvent exchange on the corresponding metal(II) ions. This finding indicates that the dinuclear complex formation reaction of the metal(II) ions proceeds via almost the same reaction mechanism as for the acetonitrile solvent exchange reaction.

Keywords: Schiff base; [Cu(salen)]; Dinuclear complex; Dissociative-interchange mechanism; Acetonitrile solvent exchange

1. Introduction

Tetradentate Schiff-base metal complexes with an N_2O_2 donor atom set can act as didentate chelating ligands for metal(II,I) cations that produce dinuclear complexes. Thus, they behave like many complexing agents. From this point of view, interest in the chelate adducts is due to the fact that since they have two metal centers with different Lewis acid–base properties, they promote coordination and activation on small molecules [1,2]. Furthermore, the metal complexes with salen-type ligands are important catalysts for oxidation, aziridine formation, epoxide opening and cycloaddition, both in the asymmetric and non-stereoselective versions [3]. Recently, some heteropolynuclear complexes including salen complexes have been synthesized and their magnetic properties investigated [4–6].

Whereas the structure of these adducts with Schiff bases has been thoroughly explored in the solid state [7], very little is known of their formation equilibrium in solution. Alkali and alkaline earth metal ions in acetonitrile solution were found to form the 1:1 adducts with transition metal Schiff-base complexes [8–10]. However, there is no report about the kinetics and mechanism for the dinuclear complex formation reaction between Schiff-base metal complexes with an N_2O_2 donor atom set and metal ions in solution. In this study, the tetradentate Schiff-base copper complex, [Cu(salen)]: *N*,*N*′-ethylenebis(salicylideneiminato)copper(II), has been used as a

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ligand to form the binuclear complexes with various metal ions in acetonitrile (AN) in order to clarify the mechanistic aspects for the dinuclear complex formation reactions. The investigated reaction system can be expressed by Scheme 1.

The reactions of [Cu(salen)] with very labile metal ions such as Mn(II), Fe(II), and Zn(II) ions were too fast to follow the reaction rates by a conventional stopped-flow method. Thus, we constructed a pulsed-accelerated-flow (PAF) apparatus developed by Margerum and co-workers [11–13], which permits measurement of pseudo-first-order rate constants as high as 5×10^5 s^{-1}. The instrument newly constructed in this study has in principle the same mechanicals as the so-called PAF apparatus and is called a "variable flow-rate (VFR)" instrument. We can follow the reactions as fast as $t_{1/2} = \sim 1$ μs (vide infra). Thus, we are the first to measure the fast formation reactions of the dinuclear complexes ($Cu(salen)M^{2+}$) of labile metal(II) ions. We will evaluate the mechanism for the present dinuclear complex formation by comparison with the available solvent exchange rate and mechanism for the metal(II) ions in acetonitrile (AN) [14–18].

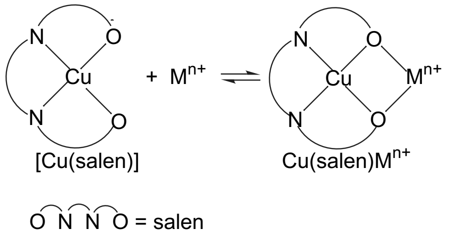
2. Experimental

2.1. Materials and preparation of sample solutions

N,*N*′-Ethylenebis(salicylideneamine), H_2salen, and *N*,*N*′-ethylenebis(salicylideneiminato)copper(II), [Cu(salen)], were prepared and purified according to the method described in the literature [19–21]. *Anal.* Calc. for H_2salen: C, 71.6; H, 6.01; N, 10.4. Found: C, 71.7; H, 5.98; N, 10.4%. *Anal.* Calc. for [Cu(salen)]: C, 58.3; H, 4.28; N, 8.50. Found: C, 58.8; H, 4.15; N, 8.45%.

The aquametal(II) trifluoromethanesulfonate salts of Mn(II), Fe(II), Co(II), Ni(II), Cu(II), and Zn(II) ions were prepared by the following method. Each $MnCO_3$ (Wako Pure Chemical Industries, Japan, Sp. Gr.), iron sponge (Wako, 99.99%), $CoCO_3 \cdot Co(OH)_2 \cdot 4H_2O$ (Wako, Sp. Gr.), $NiCO_3 \cdot Ni(OH)_2 \cdot 4H_2O$ (Wako, Pr. Gr.), CuO (Wako, 99.9%), and zinc metal (Wako, 99.998%) were dissolved in an aqueous solution of trifluoromethanesulfonic acid (triflic acid, Wako, 98%). The residue was removed by filtration and the filtrate was concentrated to obtain the corresponding hydrated crystals. For Fe(II), the procedure was performed under an argon atmosphere. The anhydrous triflate power of Mn(II), Fe(II), Co(II), Cu(II), and Zn(II) was obtained by heating the corresponding hydrates at ca. 200 °C for several hours. For the Ni(II), the hydrate was dissolved in AN and the water in the solution was removed under reflux in a modified Soxhlet extractor with activated 4A molecular sieves [18]. The reflux was repeated several times until complete removal of the water and then the AN solution of Ni(II) was obtained. The available anhydrous Na(I) and Ag(I) triflates were used without further purification after heating for several hours. The crystals of $[Cu(an)_4]ClO_4$ were obtained by the reaction of Cu_2O and $HClO_4$ in AN. All the sample solutions of the metal ions except for the nickel(II) ion were prepared by dissolving weighed amounts of the anhydrous metal salts in AN. The concentration of the metal(II) ions in AN was determined by the EDTA titration in an aqueous solution. Acetonitrile (AN, Wako) was dried over activated 3A molecular sieves for several days and distilled at 110 °C under a nitrogen atmosphere. All the sample AN solutions were prepared by the use of weighed amounts of the samples in a dry box. The water content in the sample solutions was confirmed to be less than 10 $mmol\,kg^{-1}$ by the Karl–Fisher method. The concentration unit of $mol\,kg^{-1}$ was used for the AN solutions.

For the reaction of $[Cu(dmp)_2]^+$ with $[IrCl_6]^{2-}$ in water, the $[Cu(dmp)_2]^+$ and $[IrCl_6]^{2-}$ solutions were prepared as follows. Two equivalent moles of 2,9-dimethyl-1,10-phenanthroline (dmp, Wako, reagent grade) were added to an ethanol solution of $Cu(CF_3SO_3)_2$, and then by the addition of the ascorbic acid aqueous solution, the copper(II) ion was reduced to give $[Cu(dmp)_2]^+$. The resultant solution to which an excess of $NaCF_3SO_3$ salt was added was concentrated to produce the crystals of $[Cu(dmp)_2]CF_3SO_3$. The $[Cu(dmp)_2]^+$ solution was kept to pH 6 with the 0.010 M MES buffer (MES: 2-(*N*-morpholino)ethanesulfonic acid, Wako). The $[IrCl_6]^{2-}$ solution was kept slightly acidic to prevent decomposition of the iridium



acetonitrile-solvated metal ion = $M^{n+} = Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Na^+, Cu^+, Ag^+$

Scheme 1.

complex. The ionic strength of both solutions was adjusted to 0.10 M with K_2SO_4. The concentrations of the $[Cu(dmp)_2]^+$ and $[IrCl_6]^{2-}$ solutions were determined from the absorbance at 454 nm (ε 7950 $M^{-1}\,cm^{-1}$) [22] and at 487 nm (ε 4075 $M^{-1}\,cm^{-1}$) [23], respectively.

2.2. Equilibrium and kinetic measurements

The stability constants (K) and the molar absorption coefficients ($\varepsilon_{Cu(salen)M}$) of the dinuclear complex, Cu(salen)M^+, for the M(I) ions have been determined by UV–Vis absorption spectrometry. The spectra of a constant concentration solution of [Cu(salen)] with increasing concentrations of the metal(I) triflate were recorded with a spectrophotometer (JASCO V-570) between 300 and 500 nm. The reaction vessel and the cell compartment of the spectrophotometer were thermostated at 25.0 ± 0.1 °C. Absorbance data as a function of the total concentrations of the M(I) ion were computer-fitted to the appropriate equation using a nonlinear least-squares program to obtain their molar absorption coefficients at the selected wavelengths and the equilibrium constants.

The spectral change for the reaction of [Cu(salen)] with the Co(II) and Ni(II) ions in AN was measured by a stopped-flow rapid detection system (RSP-801, Unisoku, Japan) in the wavelength range from 300 to 550 nm. The temperature of all the measurements was maintained at 25.0 ± 0.1 °C using circulating thermostated water. The reaction traces under the pseudo-first-order conditions of a large excess of the metal ion relative to [Cu(salen)] were expressed by the exact exponential function and then the conditional first-order rate constants k_{obs} were determined by the non-linear least-squares method. For the very labile Mn(II), Fe(II), and Zn(II) ions, the pseudo-first-order rate constants were determined using the VFR instrument (vide infra).

3. Results and discussion

3.1. Calibration reaction

The following oxidation–reduction Reaction (1) was used as a calibration reaction for the newly constructed VFR instrument.

$$[Cu(dmp)_2]^+ + [IrCl_6]^{2-} \rightarrow [Cu(dmp)_2]^{2+} + [IrCl_6]^{3-} \tag{1}$$

In order to confirm the accurate performance of the newly constructed VFR instrument, the oxidation–reduction Reaction (1) between $[Cu(dmp)_2]^+$ and $[IrCl_6]^{2-}$ was followed at 450 nm under the second-order equal concentration conditions at 25 °C. The second-order rate constants for three runs under the conditions of the reactant concentrations of 0.884, 2.24, and 1.98×10^{-6} M were determined to be (1.80 ± 0.01), (2.48 ± 0.04), and $(2.07 \pm 0.04) \times 10^9\ M^{-1}\,s^{-1}$ at 25 °C, respectively. Thus, the second-order rate constant was determined to be $(2.1 \pm 0.3) \times 10^9\ M^{-1}\,s^{-1}$ at 25 °C and $I = 0.1$ M, which is in good agreement with the value of $(1.8 \pm 0.2) \times 10^9\ M^{-1}\,s^{-1}$ previously obtained by Margerum and co-workers [12] using a PAF apparatus. It has been confirmed that the newly constructed VFR instrument works well and is useful for reactions as fast as $t_{1/2} = \sim 1$ μs.

3.2. Equilibrium and kinetics

The conditional first-order rate constants k_{obs} at 25 °C for various concentrations of the Mn(II), Fe(II), Co(II), Ni(II), and Zn(II) ions were determined under the pseudo-first-order conditions where the metal concentration (C_M) is in large excess relative to the concentration of [Cu(salen)]. The linear relationship between k_{obs} and the metal concentration C_M with an intercept is shown in Fig. 1 which indicates the following relation: $k_{obs} = k_f C_M + k_b$, where k_f and k_b are the second-order rate constant for the forward reaction and the first-order rate constant for the backward reaction, respectively. The equilibrium constant, K/mol^{-1} kg, is thus given by k_f/k_b. The obtained rate constants and equilibrium constants are tabulated in Table 1 together with the bond distances between the metal and nitrogen atom of the coordinating acetonitrile in AN-solvated metal ions [24–28] and the rate constants for the solvent exchange reaction on the AN-solvated metal(II) ions [14–16].

In addition, for the Cu(II) ion, we observed the consecutive three phase processes for the reaction of [Cu(salen)] with the Cu(II) ion. The first step is completed within 1 ms, the second step with half-lives of several tens of ms is affected by the triflate anion concentration, while the third step, which proceeds for several seconds, partly depends on the Cu(II) ion concentration. [1]

The absorption spectra for the reaction between [Cu(salen)] and the monovalent metal(I) ions such as Na(I), Cu(I), and Ag(I) ions were measured as a function of the concentration of the M(I) ion (see Fig. 2 for the Na(I) ion). The equilibrium constants were evaluated for the Na(I) and Ag(I) ions, but the equilibrium constant for the Cu(I) ion was not obtained due to its low value.

Judging from K on the order of 10^3–10^4 mol^{-1} kg for the M(II) ions and of 10^2 mol^{-1} kg for the M(I) ions (see Table 1), the two donor oxygen atoms in the essentially planar [Cu(salen)] should bind to the AN-solvated metal ions. The fact that the K values of the d^5 Mn(II) and d^{10}

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[1] The reaction for the Cu(II) ion is very complex involving the oxidation–reduction reaction to produce the mixed valent copper complexes such as $Cu^{III}(salen)Cu^I$ and $Cu^{III}(salen)Cu^{II}$. The results will be reported elsewhere.

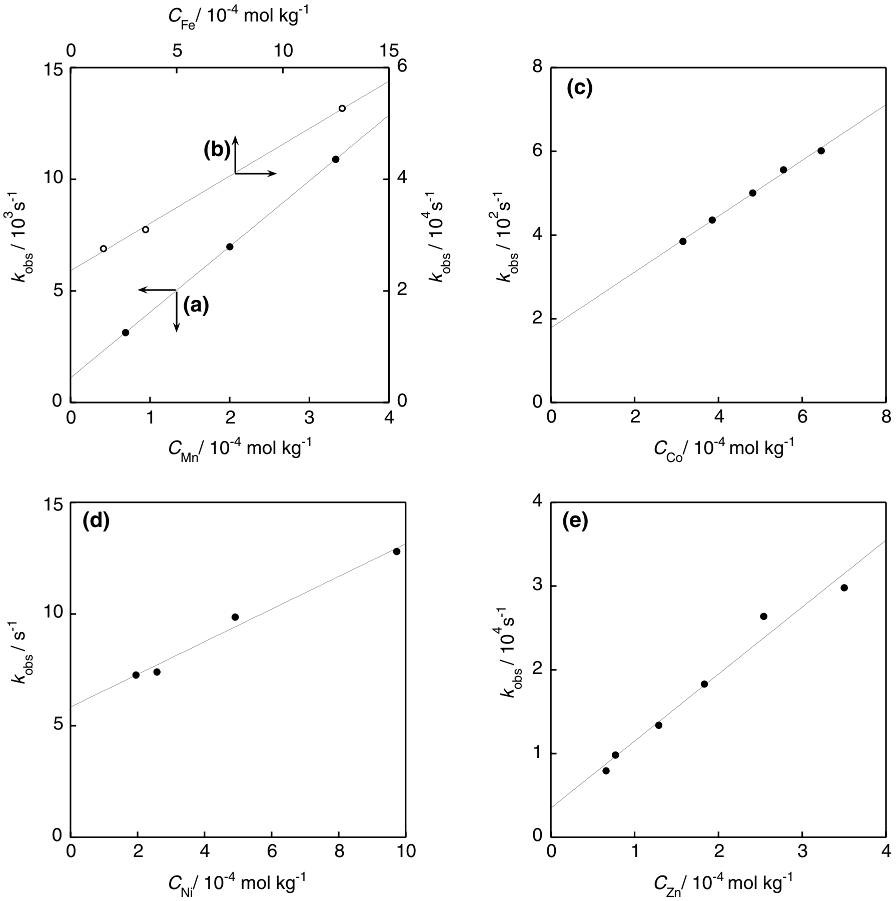

Fig. 1. Dependence of the conditional first-order rate constants k_{obs} (25 °C) on the metal(II) ion concentration C_M for the formation of the dinuclear complexes Cu(salen)M^{2+}: (a) for Mn(II); (b) for Fe(II); (c) for Co(II); (d) for Ni(II); (e) for Zn(II). Each point in Fig. 1 refers to the average value for several runs, which has the standard deviation of about 5%.

Table 1

Rate constants and equilibrium constants for the dinuclear complex formation reaction between [Cu(salen)] and metal(II,I) ions in acetonitrile at 25 °C

M^{n+}	k_f/mol^{-1} kg s^{-1}	k_b/s^{-1}	K/mol^{-1} kg	Bond distance[a]/pm	k_{ex}[b]/s^{-1}
Mn^{2+}	$(2.95 \pm 0.02) \times 10^7$	$(1.09 \pm 0.05) \times 10^3$	$(2.71 \pm 0.13) \times 10^4$	222 (6)	1.2×10^7[c]
Fe^{2+}	$(2.27 \pm 0.09) \times 10^7$	$(2.36 \pm 0.07) \times 10^4$	$(9.62 \pm 0.29) \times 10^2$	214 (6)	6.6×10^5[c]
Co^{2+}	$(6.67 \pm 0.23) \times 10^5$	$(1.78 \pm 0.11) \times 10^2$	$(3.75 \pm 0.27) \times 10^3$	211 (6)	3.5×10^5[d]
Ni^{2+}	$(7.28 \pm 0.63) \times 10^3$	5.86 ± 0.36	$(1.05 \pm 0.12) \times 10^3$	207 (6)	6.2×10^3[e]
Zn^{2+}	$(8.00 \pm 0.66) \times 10^7$	$(3.50 \pm 1.34) \times 10^3$	$(2.29 \pm 1.76) \times 10^4$	213 (6)	3×10^7[f]
Na^+			$(1.80 \pm 0.27) \times 10^2$		
Cu^+			$<10^2$	200 (4)	
Ag^+			$(5.42 \pm 1.13) \times 10^2$	233 (4)	

[a] The bond distance between metal and nitrogen atom of the coordinating acetonitrile in the acetonitrile-solvated metal ion [24–28]. Figure in parentheses is a coordination number.

[b] The rate constant at 25 °C for the solvent exchange reaction on the acetonitrile-solvated metal ion [14–16].

[c] Ref. [14].

[d] Ref. [15].

[e] Ref. [16].

[f] The rate constant for the water exchange on the Zn(II) ion in water [38].

Zn(II) ions are slightly greater than those of the Fe(II), Co(II), and Ni(II) ions indicates that the binding angle of [Cu(salen)] as a didentate chelate ligand is restrictively strained due to the four-membered ring chelate formation [29]. Interestingly, for the tetrahedrally solvated d^{10} Cu(I) and Ag(I) ions [27,28], a larger Ag(I) ion

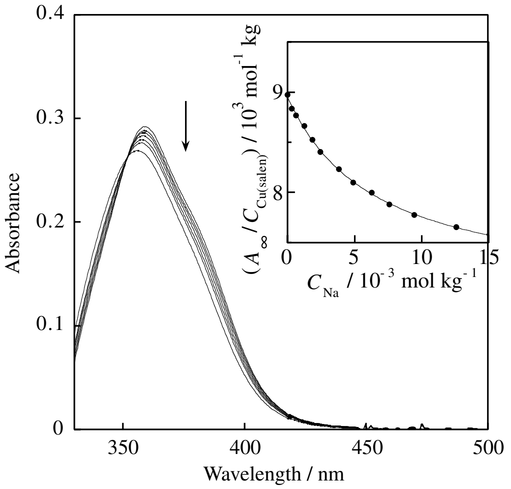

Fig. 2. Absorption spectra for the reaction between [Cu(salen)] and Na(I) ion at 25 °C. Conditions: $C_{\mathrm{Cu(salen)}} = (3.34 \pm 0.04) \times 10^{-5}$ mol kg^{-1}; from top: $C_{\mathrm{Na}} = 0$, 0.621×10^{-3}, 1.86×10^{-3}, 3.81×10^{-3}, 7.61×10^{-3}, 12.6×10^{-3} mol kg^{-1}. The curve in the inset is depicted using the obtained values: $K = 180$ mol^{-1} kg, $\varepsilon_{\mathrm{Cu(salen)}} = 8.65 \times 10^3$ mol^{-1} kg cm^{-1}, and $\varepsilon_{\mathrm{Cu(salen)Na}} = 6.96 \times 10^{-3}$ mol^{-1} kg cm^{-1} at 360 nm.

may form the dinuclear complex, but a smaller Cu(I) ion does not form. This should come from the fit of the bond lengths (see the bond distances in Table 1).

We compared the rates and mechanisms for the present reaction system to those for the AN solvent exchange reaction for a series of M(II) ions. The activation parameters for the AN solvent exchange on the Mn(II), Fe(II), Co(II), and Ni(II) ions are available. These rate constants are given in Table 1 [14–16]. The findings that the corresponding activation volumes ($\Delta V^\ddagger$) are −7.0 (Mn(II)), +3.0 (Fe(II)), +8.1 (Co(II)), and +9.6 cm^3 mol^{-1} (Ni(II)) indicate a mechanistic changeover from an associative-interchange to a dissociative-interchange as pointed out by Merbach and coworkers [30]. This changeover is explained by the decrease in the ionic radius and the increase in the number of 3d electrons. Recently, the mechanistic crossover for the water exchange on the first-row transition metal ions was theoretically confirmed [31–35]. The bond distances between metal and nitrogen atom of the coordinating acetonitrile in the AN-solvated metal ion are given in Table 1, which were determined by the EXAFS technique [24–28]. On the other hand, the activation mode for the solvent exchange of the Mn(II) ion in bulkier solvents such as DMF (*N*,*N*-dimethylformamide) and CH_3COOH relative to small solvents such as CH_3CN, CH_3OH, and H_2O becomes less associative, and in fact, the $\Delta V^\ddagger$ values are +1.6 in DMF [36] and +0.4 cm^3 mol^{-1} in CH_3COOH [37]. Thus, we can expect that in the case of the present dinuclear complex formation of the Mn(II) ion, the activation mode will become dissociative due to the bulkiness around the first donor oxygen atom of [Cu(salen)] as an incoming ligand. Although the rate constant is not available for the AN solvent exchange on the Zn(II) ion, the rate constant in water is reported to be 3×10^7 [38]. Recently, the rate constant is theoretically evaluated to be 4.1×10^8 and its mechanism is clarified to be dissociative [39]. Furthermore, it has been theoretically indicated that the solvent exchange on the Zn(II) ion in HCN and CH_3CN may proceed via a dissociative mode of activation [40].

Accepting the Eigen–Wilkins mechanism for the forward reaction [41], k_f is given by $K_{\mathrm{os}}k$, where K_{os} is the equilibrium constant for formation of the outer-sphere complex between [Cu(salen)] and M^{2+} and k is the rate constant for the interchange between an acetonitrile molecule in the inner sphere of M^{2+} and a donor oxygen atom of [Cu(salen)]. We can expect K_{os} of ca. 1 mol kg^{-1} for all the metal ions in AN because of the neutral [Cu(salen)]. As apparent from the values in Table 1, the rate constants (k_f) for the forward reaction are comparable to the available rate constants (k_{ex}) for the solvent exchange reaction in AN, thus the rate-determining step of the forward reaction in the present system is the bond rupture between the M(II) ion and a bound AN molecule, simultaneously accompanying the bond formation between the M(II) ion and the first donor oxygen of [Cu(salen)]. The subsequent chelate ring closure to form the dinuclear complex, in which [Cu(salen)] is bound to M^{2+} as a didentate ligand, must be faster than the rate-determining interchange. Therefore, the ring opening of the four-membered chelate for the backward reaction is not rate determining.

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References

[1] G. Fachinetti, C. Floriani, P.F. Zanazzi, J. Am. Chem. Soc. 100 (1978) 7405.
[2] R.D. Jones, D.A. Summerville, F. Basolo, Chem. Rev. 79 (1979) 139.
[3] E.N. Jacobsen, Acc. Chem. Res. 33 (2000) 421.
[4] I. Ramade, O. Kahn, Y. Jeannin, F. Robert, Inorg. Chem. 36 (1997) 930.
[5] S. Koner, S. Saha, K. Okamoto, J.-P. Tuchagues, Inorg. Chem. 42 (2003) 4668.
[6] S. Osa, Y. Sunatsuki, Y. Yamamoto, M. Nakamura, T. Shimamoto, N. Matsumoto, N. Re, Inorg. Chem. 42 (2003) 5507.
[7] D.A. Atwood, M.J. Harvey, Chem. Rev. 101 (2001) 37.

[8] A. Giacomelli, T. Rotunno, L. Senatore, Inorg. Chem. 24 (1985) 1303.

[9] A. Giacomelli, T. Rotunno, L. Senatore, R. Settambolo, Inorg. Chem. 28 (1989) 3552.

[10] L. Carbonaro, M. Isola, P.L. Pegna, L. Senatore, F. Marchetti, Inorg. Chem. 38 (1999) 5519.

[11] G.D. Owens, R.W. Taylor, T.Y. Ridley, D.W. Margerum, Anal. Chem. 52 (1980) 130.

[12] M.T. Nemeth, K.D. Fogelman, T.Y. Ridley, D.W. Margerum, Anal. Chem. 59 (1987) 283.

[13] R.H. Becker, W.P. Bartlett, E.T. Urbansky, D.W. Margerum, J. Chem. Soc., Dalton Trans. (2002) 695.

[14] M.J. Sisley, Y. Yano, T.W. Swaddle, Inorg. Chem. 21 (1982) 1141.

[15] A. Monnerat, P. Moore, K.E. Newman, A.E. Merbach, Inorg. Chim. Acta 47 (1981) 139.

[16] F.K. Meyer, K.E. Newman, A.E. Merbach, Inorg. Chem. 18 (1979) 2142.

[17] F.A. Dunand, L. Helm, A.E. Merbach, Adv. Inorg. Chem. 54 (2003) 1.

[18] S. Funahashi, Y. Inada, Bull. Chem. Soc. Jpn. 75 (2002) 1901.

[19] R.H. Bailes, M. Caovin, J. Am. Chem. Soc. 69 (1947) 1886.

[20] T.N. Waters, D. Hall, J. Chem. Soc. (1959) 1200.

[21] D. Hall, T.N. Waters, J. Chem. Soc. (1960) 2644.

[22] J.R. Kirchhoff, R.E. Gamache, M.W. Blaskie, A.A. DelPaggio, R.K. Lengel, D.R. McMillin, Inorg. Chem. 22 (1983) 2380.

[23] C.K. Jorgenson, Mol. Phys. 2 (1959) 309.

[24] S. Funahashi, Y. Inada, Trends Inorg. Chem. 5 (1998) 15.

[25] Y. Inada, K. Sugimoto, K. Ozutsumi, S. Funahashi, Inorg. Chem. 37 (1998) 1886.

[26] Y. Inada, S. Funahashi, Anal. Sci. 13 (1997) 373.

[27] Y. Inada, Y. Tsutsui, H. Wasada, S. Funahashi, Z. Naturforsch. 54b (1999) 193.

[28] Y. Tsutsui, K. Sugimoto, H. Wasada, Y. Inada, S. Funahashi, J. Phys. Chem. 101 (1997) 2900.

[29] K.A. Leslie, R.S. Drago, G.D. Stucky, D.J. Kitko, J.A. Breese, Response Inorg. Chem. 18 (1979) 1885.

[30] Y. Ducommun, K.E. Newman, A.E. Merbach, Inorg. Chem. 19 (1980) 3696.

[31] F.P. Rotzinger, J. Am. Chem. Soc. 118 (1996) 6760.

[32] F.P. Rotzinger, J. Am. Chem. Soc. 119 (1997) 5230.

[33] Y. Tsutsui, H. Wasada, S. Funahashi, Bull. Chem. Soc. Jpn. 70 (1997) 1813.

[34] Y. Tsutsui, H. Wasada, S. Funahashi, Bull. Chem. Soc. Jpn. 71 (1998) 73.

[35] Y. Tsutsui, H. Wasada, S. Funahashi, Bull. Chem. Soc. Jpn. 71 (1998) 1771.

[36] M. Ishii, S. Funahashi, M. Tanaka, Chem. Lett. (1987) 871.

[37] M. Ishii, S. Funahashi, M. Tanaka, Inorg. Chem. 27 (1988) 3192.

[38] M. Eigen, Pure Appl. Chem. 6 (1963) 97.

[39] Y. Inada, A.M. Mohammed, H.H. Loeffler, S. Funahashi, Helv. Chim. Acta (in press).

[40] Y. Wasada-Tsutsui, H. Wasada, S. Funahashi, Bull. Chem. Soc. Jpn. 76 (2003) 1713.

[41] R.B. Jordan, Reaction Mechanisms of Inorganic and Organometallic Systems, Oxford University Press, New York, 1998.