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Studies of Formation of Some Metal(II) Chloride Complexes in Methanol Using a Chloride Ion Selective Electrode

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The formation of chloride complexes of cobalt(II), nickel(II), and zinc(II) in methanol has been studied at 25 °C by chloride ion measurements with an Ag–AgCl electrode. At the relatively low ionic strength of 0.05 or 0.1 M measurements have been carried out with sodium perchlorate to obtain an approximately constant ionic strength medium. The stepwise stability constants of monochloride and dichloride complexes have been investigated for the most part. The studies at low ionic strength may facilitate the evaluation of thermodynamic stability constants by the Debye–Hückel theory and so forth. The stabilities of cobalt(II) and nickel(II) chloride complexes are somewhat smaller than those of zinc(II) chloride complexes. Copper(II) chloride complexes have been investigated also under the same conditions, but accurate stability constants have not been obtained owing to the poor response of the Ag–AgCl electrode. Clearly, however, the stability of the monochloride complex of copper, $CuCl^+$, is larger than that of zinc, $ZnCl^+$, in methanol.

Introduction

Many studies on metal complex stabilities have been performed in high ionic strength media, but the results show a lack of universality from a theoretical point of view. Reliable thermodynamic parameters are necessary to understand complicated behaviors in electrolytic solutions. Studies in low ionic strength media are difficult on account of restrictions on experimental conditions, e.g., optimum concentration ranges of some species. Especially in nonaqueous solvents, association of a metal ion with the constant ionic strength medium is often observed, so that evaluation of the stability constants of the main complexes is complicated. Therefore, we have attempted to correct our results by both the ionic association constants of metal perchlorates obtained from conductometric experiments and the ion activities estimated by Debye–Hückel theory.

Many studies for various systems using diverse ion-selective electrodes have been reported,[1] and some studies using halide ion sensitive electrodes have been carried out.[2-5] Only a little information on the stabilities of cobalt(II), nickel(II), copper(II), and zinc(II) chloride complexes in methanolic media is available.[6-9]

In a previous paper,[10] zinc(II) chloride complexes in methanol–nitromethane and methanol–water mixtures and in ethylene glycol were investigated, and it has been suggested that the stepwise stability constant of the monochloride complex, K_1, is smaller than that of the dichloride complex, K_2, in the other solvents except ethylene glycol. The present work has been instigated by our interest in comparing the K_1 values of metal chloride complexes in methanol with the K_2 values.

Experimental Section

Materials. Cobalt(II) perchlorate hexahydrate ($Co(ClO_4)_2 \cdot 6H_2O$)[11,12] and nickel(II) perchlorate hexahydrate ($Ni(ClO_4)_2 \cdot 6H_2O$)[13] were prepared from the corresponding nitrates. Copper(II) perchlorate hexahydrate ($Cu(ClO_4)_2 \cdot 6H_2O$) and zinc(II) perchlorate hexahydrate ($Zn(ClO_4)_2 \cdot 6H_2O$) were prepared by neutralizing copper hydroxide and zinc carbonate, respectively, with perchloric acid.[14] These metal perchlorate hexahydrates were purified by triple recrystallization from distilled water. Sodium perchlorate monohydrate ($NaClO_4 \cdot H_2O$, Merck) was used without further purification. Methanol was dried over 3A molecular sieves and distilled fractionally. The electrolytic conductivity of the purified methanol was 1.5×10^{-7} Ω^{-1} cm^{-1}, and the water content was found to be 0.045 wt. % by gas chromatography. All other chemicals were special grade materials (Wako).

The 0.1025 M stock solution of sodium chloride in methanol was prepared by weighing and diluting dried primary standard grade salt (Wako). The methanolic stock solution of sodium perchlorate was prepared by weighing out dried $NaClO_4 \cdot H_2O$. The metal perchlorate hexahydrates were dried on a vacuum line over silica gel for several hours and were used to prepare stock solutions in methanol. The individual stock solutions were standardized by titration with EDTA.

Instrumentation. Electrochemical experiments were carried out with instrumentation described previously.[10] Electrode potential measurements were made with use of a Corning Model 130 digital pH/ion meter. The reference electrode was a Corning C 067 double-junction reference electrode, and the outer solution of the reference electrode was methanolic 0.1 M sodium perchlorate. Since leakage of the outer solution was negligible, reproducibility of potential measurements was within 0.1 mV for sequential measurements, and well within ±1 mV from day to day. Potentials reached equilibrium generally within 5 min.

Conductometric experiments were carried out with a Yanagimoto Model MY-7 conductivity outfit and a type C cell. All measurements were conducted in closed cells, thermostated at 25.0 ± 0.1 °C by a Sharp TE-12K thermoelectric circulating system. A sketch of the cell used for potentiometric measurements has been given in ref 15.

Procedure of Potentiometry. Solution A, adjusted to a constant ionic strength with metal perchlorate and sodium perchlorate, was made up in a 50-cm^3 measuring flask from stock solutions and transferred into the thermostated cell. The solution A in the cell was gently stirred, and titrated by solution B from a buret. The titrating solution B was prepared by adding the proper quantity of sodium chloride to solution A. The free chloride ion concentrations were measured after each chloride ion addition. Electrode calibration was carried out with solutions A and B containing no metal perchlorate under the same conditions.

Data Treatment and Results

Conductometry. The association of metal(II) and perchlorate ions was investigated with electric conductance measurements, and the Fuoss and Edelson method[16] was used

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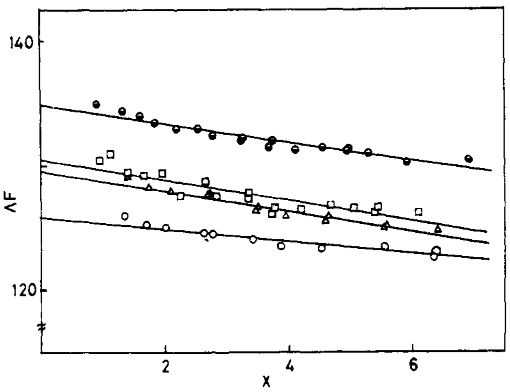

Figure 1. Fuoss and Edelson plots for the metal perchlorate: □, Co(II); ◒, Ni(II); △, Cu(II); ○, Zn(II).

Table I. Summary of the Results of Conductometry

$M(ClO_4)_2$	Λ_0/Ω^{-1} cm^2 mol^{-1}	K_{1A}/M^{-1}
$Co(ClO_4)_2$	130.6 ± 0.4	109.6 ± 13.6
$Ni(ClO_4)_2$	134.9 ± 0.2	100.8 ± 8.2
$Cu(ClO_4)_2$	129.6 ± 0.3	106.8 ± 3.0
$Zn(ClO_4)_2$	125.8 ± 0.2	60.4 ± 6.3

for evaluation of the present results. The method involves the assumption that only the first-step association

$$M^{2+} + ClO_4^- \rightleftarrows MClO_4^+ \quad (K_{1A}) \tag{1}$$

takes place, and the equation is expressed as

$$\Lambda F = \Lambda_0 - XK_{1A}/\Lambda_0 \tag{2}$$

where

$$X = cy_{2+}\Lambda F(\Lambda F - \Lambda_0/2)$$

where F is the Fuoss and Edelson function, Λ and Λ_0 are the equivalent conductance and the limiting equivalent conductance, respectively, y_{2+} is the activity coefficient of the divalent metal ion, and c is the concentration of the anion, ClO_4^-. The equation was solved for the two unknown parameters K_{1A} and Λ_0 by an iterative procedure. The value of y_{2+} was estimated by the Debye–Hückel second approximation (eq 3). As the

$$\log y = -A|z_i|^2 I^{1/2}/(1 + BaI^{1/2}) \tag{3}$$

values of the ion size parameter, a, in methanol are similar in magnitude to those in water,[17,18] the value of 6 Å is assumed to be a reasonable value for each metal(II) ion.[19] In methanol systems, the values of the dielectric constant, ϵ, the viscosity, η, and the limiting equivalent conductance of ClO_4^-, $\lambda^0_{ClO_4^-}$, are 32.63, 5.45×10^{-3} P,[20] and 70.1 Ω^{-1} cm^2 mol^{-1},[21] respectively.

Application of this method requires reliable data for the very lowest concentrations. Therefore, measurements have been conducted in the concentration range 1×10^{-4} M $< c < 2 \times 10^{-3}$ M. Data on each metal perchlorate are plotted in Figure 1 according to eq 2. The values of Λ_0 and K_{1A} obtained from the slopes and the intercepts are given in Table I. The errors indicated in Table I are the standard deviations.

Potentiometry. Generally, only four chloride complexes of the metals, from monochloride to tetrachloride, even at high chloride ion concentrations, exist in the solution, and NaCl and $NaClO_4$ in methanol dissociate almost perfectly into ions.[22,23] In recent papers,[24,25] the association constant of NaCl in methanol has been estimated to be ca. 17 M^{-1}. However, the magnitude of this association must be negligible in our systems. Thus, the following equilibria and the equilibrium of eq 1 are considered.

$$MCl_{n-1}^{3-n} + Cl^- \rightleftarrows MCl_n^{2-n} \quad (K_n,\ n = 1\text{–}4) \tag{4}$$

$$MCl^+ + ClO_4^- \rightleftarrows MCl{\cdot}ClO_4 \quad (K_{mA}) \tag{5}$$

So that the relationships between the stepwise constants of thermodynamic stabilities, K_n, n = 1–4, and those of concentration stabilities, y_nK_n, might be interpreted, eq 6 and 7 are indicated, which use, for an example, the stability constant of monochloride complex

$$K_1 = \frac{y_{MCl}[MCl^+]}{y_{2+}[M^{2+}]y_{Cl}[Cl^-]} \tag{6}$$

where y is the ion activity coefficient. On the assumption that $y_{MCl} = y_{Cl}$, the concentration stability constant, y_1K_1, is given by

$$y_1K_1 = y_{2+}K_1 = \frac{[MCl^+]}{[M^{2+}][Cl^-]} \tag{7}$$

In a similar manner, the other constants have the relationships of $y_2K_2 = y_\pm^2K_2$, $y_3K_3 = K_3$, and $y_4K_4 = (y_\pm^2/y_{2+})K_4$. These equations are based on the bold assumption that the y values of ions of identical charge, $|z_i|$, are equal.

In the previous paper,[10] we indicated that the amount of $ZnCl{\cdot}ClO_4$ relative to $ZnCl^+$ was always very low at the ClO_4^- concentrations used in our studies. Then, the ionic association constant evaluated by Fuoss' theory[26] is ca. 10 M^{-1} for 1:1 electrolytes in methanol at a = 6 Å. This magnitude of the association must be negligible in our system. Therefore, the concentration of $MCl{\cdot}ClO_4$ may also be negligibly small at $[ClO_4^-] < 0.1$ M.

Thus the usual mass balance equations are applied as shown in eq 8–10, where C^0_M, C^0_{Cl}, and C^0_I represent the initial

$$C^0_M = \sum_{n=0}^{4}[MCl_n^{2-n}] + [MClO_4^+] \tag{8}$$

$$C^0_{Cl} = [Cl^-] + \sum_{n=1}^{4} n[MCl_n^{2-n}] \tag{9}$$

$$C^0_{ClO_4} = C^0_I + 2C^0_M = [ClO_4^-] + [MClO_4^+] \tag{10}$$

concentrations of $M(ClO_4)_2$, NaCl, and $NaClO_4$, respectively. On combination of eq 8 and 9, a function, $\bar{n}$, defined as the average number of ligands, Cl^-, attached to the metal, M, is given by

$$\bar{n} = \Delta_{Cl}/C^0_M = \frac{\sum\limits_{n=1}^{4} n(\prod\limits_{i=1}^{n} y_iK_i)[Cl^-]^n}{(1 + y_{2+}K_{1A}[ClO_4^-]) + \sum\limits_{n=1}^{4}(\prod\limits_{i=1}^{n} y_iK_i)[Cl^-]^n} \tag{11}$$

where

$$\Delta_{Cl} = C^0_{Cl} - [Cl^-]$$

Complexes with low coordination numbers of chloride ion are favored by high metal-to-chloride concentration ratios. Under these conditions, eq 9 is rearranged as

$$Y = \Delta_{Cl}/([M^{2+}][Cl^-]) = y_{2+}K_1 + 2y_{2+}y_\pm^2K_1K_2[Cl^-] \tag{12}$$

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Table II. Results of Calculations Based on Eq 12 for the Zinc Chloride System, $I = 5.0 \times 10^{-2}$ M

$10^2C^0_M$/M	$10^2C^0_I$/M	$10^2 \times [ClO_4^-]$/M	$10^{-6} \times (2y_{2+}y_{\pm}^2K_1K_2)$/$M^{-2}$	$y_{2+}K_1$/M^{-1}	$-r$
1.87_7	0	3.44_3	7.39_9	$787._9$	0.9994
1.69_8	0.50	3.60_4	6.90_0	$746._4$	0.9998
1.51_6	1.00	3.76_3	6.48_3	$763._1$	0.9996
1.33_3	1.50	3.92_3	6.54_7	$741._3$	0.9998
1.14_8	2.00	4.08_0	7.14_4	$757._8$	0.9997
0.96_1	2.50	4.23_6	6.54_9	$746._8$	0.9995

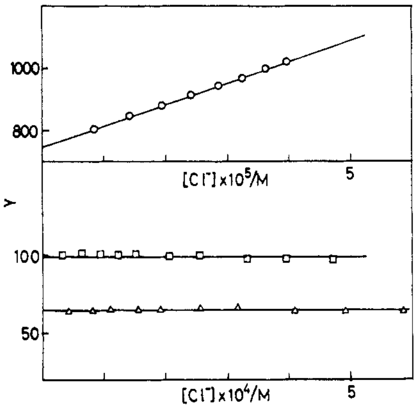

Figure 2. Y vs. $[Cl^-]$ plots according to eq 12, $I = 5.0 \times 10^{-2}$ M: □, Co(II), $C^0_M = 2.03_8 \times 10^{-2}$ M, $C^0_I = 0$ M; △, Ni(II), $C^0_M = 2.01_0 \times 10^{-2}$ M, $C^0_I = 0$ M; ○, Zn(II), $C^0_M = 1.69_8 \times 10^{-2}$ M, $C^0_I = 0.50 \times 10^{-2}$ M.

So eq 12 is not employed for data treatment unless the M^{2+} concentration is known. Under the conditions of $C^0_M >> C^0_{Cl}$, we can calculate the M^{2+} concentration, approximately.

If the amounts of MCl_3^- and MCl_4^{2-} are neglected and eq 8 and 9 are used, the relationship

$$C^0_M - \Delta_{Cl} = [M^{2+}] + [MClO_4^+] - [MCl_2] \simeq [M^{2+}] + y_{2+}K_{1A}[M^{2+}][ClO_4^-] \quad (13)$$

is obtained. From the appproximation $[MCl^+] = \Delta_{Cl} - 2[MCl_2]$, eq 14 is obtained by combining the charge and mass balance equations:

$$[ClO_4^-] = C^0_I + C^0_M + [M^{2+}] + \Delta_{Cl} \quad (14)$$

If eq 14 is substituted into eq 13, the equation on rearrangement gives

$$y_{2+}K_{1A}[M^{2+}]^2 + \{y_{2+}K_{1A}(C^0_I + C^0_M + \Delta_{Cl}) + 1\}[M^{2+}] - (C^0_M - \Delta_{Cl}) = 0 \quad (15)$$

Now we can calculate the M^{2+} concentration from eq 15 and the available parameters.

The adjustment of C^0_M and C^0_I for constant ionic strength was made by both eq 15 (with neglect of the Δ_{Cl} term) and eq 16. For the zinc chloride system, the results of calculations

$$I = 2[M^{2+}] + C^0_M + C^0_I \quad (16)$$

based on eq 12 are summarized in Table II. The results for cobalt and nickel chlorides are indicated in Figure 2. Under the condition of low Cl^- concentration, the calibration graph for determining free chloride ion concentrations at ionic strength $I = 5.0 \times 10^{-2}$ M has been found to be strictly linear with a slope of 58.6 mV/decade. As the values of coefficients of correlation, r, in Table II and Figure 2 indicate, there are remarkably linear relationships found for each plot. If the existence of $MCl{\cdot}ClO_4$ is taken into account, the intercepts of the plots are equal to $y_{2+}K_1(1 + y_{\pm}^2K_{mA}[ClO_4^-])$. Properly speaking, we can obtain the value of K_{mA} from the relationship between the intercept and the ClO_4^- concentration. However, it is difficult to adjust the concentration range of ClO_4^- to such an extent that it is possible to determine the relatively small K_{mA} value accurately in our system. In fact, no relation between the intercept and ClO_4^- concentration has been observed in Table II. A representative result for zinc chloride is illustrated in Figure 2.

Table III. Summary of the Results of Potentiometry, $I = 5.0 \times 10^{-2}$ M

systems	y_1K_1/M^{-1}	y_2K_2/M^{-1}	y_3K_3/M^{-1}	y_4K_4/M^{-1}
Co–Cl	99.2 ± 1.5	$1.9^{a,b}$		
Ni–Cl	64.8 ± 0.9	$44^{a,b}$		
Cu–Cl	1.2×10^4	$6.5 \times 10^{2\,a}$	$1.7 \times 10^{3\,a}$	
Zn–Cl	$(7.57 \pm 0.17) \times 10^2$	$(4.52 \pm 0.27) \times 10^3$	$4.0 \times 10^{2\,a}$	70^a

[a] Results of calculations based on eq 11. [b] $I = 0.10$ M.

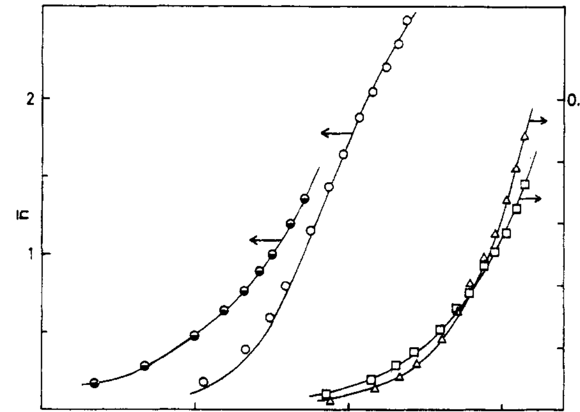

Figure 3. Average coordination numbers, $\bar{n}$, as a function of log $[Cl^-]$: □, Co(II), $C^0_M = 3.58_0 \times 10^{-3}$ M, $C^0_I = 0.10$ M; △, Ni(II), $C^0_M = 3.12_4 \times 10^{-3}$ M, $C^0_I = 0.10$ M; ●, Cu(II), $C^0_M = 1.27_7 \times 10^{-4}$ M, $C^0_I = 0.050$ M; ○, Zn(II), $C^0_M = 2.73_2 \times 10^{-4}$ M, $C^0_I = 0.050$ M.

The results obtained from the plots according to eq 12 are summarized in Table III. The errors in the table are the standard deviations. As Figure 2 shows, the K_2 values for cobalt and nickel chlorides are too small to estimate from the slopes. So when eq 11 was used with the results of calculations based on eq 12, the stability constants of highly coordinated complexes were obtained. The data are plotted in Figure 3. The figure involves calculated curves with stability constants that were adjusted to obtain the best fit between observed and calculated values. The results are shown in Table III, without estimates of the errors. At the relatively high Cl^- concentration required in cobalt and nickel chloride systems, the calibration curves for chloride ion were always linear with a slope of 60.2 mV/decade. The measurements of these systems were conducted at $I = 0.10$ M.

The results of copper chloride in Table III are not very accurate owing to the anomalous behavior of the Ag–AgCl electrode in copper chloride solution. This abnormality has been observed not only for a AgS–AgCl membrane electrode, which has been reported in ref 3, but also for the Ag–AgCl electrode.

The thermodynamic stability constants have been estimated by the Debye–Hückel equation (3), and the values are summarized in Table IV. Values of 6 and 4 Å for a have been used to calculate y_{2+} and $y_{\pm}$, respectively.

Discussion

Although the K_{1A} value for zinc perchlorate is somewhat smaller, the similarity of those values for the other metal perchlorates is plain in Table I. It seems that this similarity is caused by the equality of charges of the metal ions and that specific properties concerned with the orbital electrons of the metals do not greatly effect the values. This means that the

Table IV. Values of the Stepwise Thermodynamic Stability Constants

systems	K_1/M^{-1}	K_2/M^{-1}	K_3/M^{-1}	K_4/M^{-1}
Co–Cl	$(1.02 \pm 0.02) \times 10^3$	10		
Ni–Cl	$(6.64 \pm 0.10) \times 10^2$	1.7×10^2		
Cu–Cl	1.2×10^5	2.5×10^3	1.7×10^3	
Zn–Cl	$(7.76 \pm 0.18) \times 10^3$	$(1.74 \pm 0.10) \times 10^4$	4.0×10^2	26

metal perchlorate ions, $MClO_4^+$, are merely ion pairs. The value of the association constant for an ion pair of $M^{2+} \cdot X^-$ type is calculated from Fuoss' theory[26] to be 180 M^{-1} in methanol at $a = 6$ Å. The present study gives slightly different values for both K_{1A} and Λ_0 of zinc perchlorate from the previous values in methanol,[10] $K_{1A} = 53$ M^{-1} and $\Lambda_0 = 133$ cm^2 Ω^{-1} M^{-1}. This discrepancy may be caused by a slight amount of conductive impurities in the zinc perchlorate salt.

In the previous work,[10] the K_1 and K_2 values of zinc chloride in methanol were also evaluated at constant ionic strength, $I = 0.135$ M: $K_1 = 7.1 \times 10^3$ M^{-1} and $K_2 = 1.4 \times 10^4$ M^{-1}. In spite of the considerably different ionic strength, the previous value of K_1 is in good agreement with the value in Table IV. The K_2 value is somewhat smaller than the value in Table IV. This results because the calculations of Zn^{2+} concentrations in the previous work used an approximate equation; eq 6 in the previous paper is the same as the present eq 15 but with the Δ_{Cl} term neglected.

So that the influence of the neglect of the amount of $MCl \cdot ClO_4$ on the K_1 values might be discussed, the K_{mA} value has been estimated to be 10 M^{-1} by Fuoss' theory.[26] As mentioned in the Data Treatment and Results section, we can find no relation between ClO_4^- concentration and the intercept of the linear plot according to eq 12. However, a variation of only 2% of the intercept is calculated from the concentration range of ClO_4^- in Table II at $K_{mA} = 10$ M^{-1}. Similarly it is calculated from the data in Table II that the proportion of the term containing K_{mA} to the intercept is smaller than 10%; that is to say, we may be overestimating the values of K_1 to the extent of several percent.

Figure 4 is arranged to make relationships between the stabilities of the metal chloride complexes clear. The magnitude of K_1 has been found to increase in the order Ni ≃ Co < Zn < Cu and that of K_2 in the order Co < Ni < Cu < Zn. The K_2 value increases upon changing the metal from Co to Zn, but the K_1 value does not. Though the K_3 values for Co and Ni cannot be obtained, it is presumed that the K_3 value varies with the metal in a manner similar to that of the K_1 value. On the other hand, the K_4 value for Cu is expexted to be small from the plot in Figure 3.

The values of K_1 are larger than those of K_2 for all the metals except for zinc. It is necessary to discuss the stability constants with the following equilibria containing coordinated solvent molecules, S, in general:

$$MS_n^{2+} + L^- \rightleftarrows MLS_{n-1}^+ + S \quad (K_1)$$

$$MLS_{n-1}^+ + L^- \rightleftarrows ML_2S_{n-2} + S \quad (K_2)$$

If MS_n^{2+}, MLS_{n-1}^+, and ML_2S_{n-2} are complexes with the same structure, K_1 must be generally larger than K_2 owing to the difference in charge density between the central metals of MS_n^{2+} and MLS_{n-1}^+ and to the entropy effect from the decrease of the number of S substituted by L^-; thus, ordinary discussions on the peculiar phenomenon that $K_1 < K_2$ in the zinc system are associated with a change of coordination.

In the works of Ahrland and his co-workers on zinc halide complexes in dimethyl sulfoxide, Me_2SO, they have obtained a result similar to ours, that $K_1 < K_2$ for zinc chloride, and discussed it carefully.[27,28] Considering an octahedron for the structure of $Zn(Me_2SO)_6^{2+}$, they have predicted tetrahedrally transformed $ZnCl(Me_2SO)_3^+$ in Me_2SO. However, we have considered that the transformation from octahedral to tetrahedral coordination at the second complex-formation step is responsible for $K_1 < K_2$; that is, a small K_1 suggests that the lesser stability of octahedral $ZnClS_5^+$ is caused by a steric effect between the ligands. Therefore, the coordination of the second Cl^- ion produces tetrahedrally coordinated $ZnCl_2S_2$, which relaxes the steric hindrance and which becomes stable by increasing the strength of bonds between the zinc atom and ligands. From our point of view, the data of Ahrland and co-workers[27,28] can also be interpreted. For example, the large values of $\Delta H_1°$ and $\Delta S_1°$ are caused by a decrease in the strength of coordination bonds of $ZnClS_5^+$, the decrease of coordination number at the second step results in the large $\Delta S_2°$, and then the small $\Delta H_2°$ means that the increase of $\Delta H°$ with the decrease in coordination number is counteracted by the increase of bond force between zinc atom and ligands. Hoffmann has also reported the result of $K_1 < K_2$ for the zinc chloride–methanol system by kinetic measurements.[8]

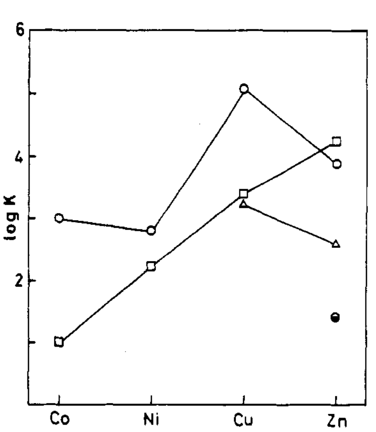

Figure 4. Stepwise thermodynamic stability constants of the metal chloride: ○, K_1; □, K_2; △, K_3; ●, K_4.

Figure 4 also shows the closeness between the K_2 and the K_3 values for the Cu(II) system and that between the K_1 and the K_2 values for the Ni(II) system. We do not know whether these results can be discussed from the same points of view as for the Zn(II) system or not. However, it is expected that the zinc(II) chloride system is a straightforward example of the transformation phenomena and that a similar state of affairs also exists in Co(II) and Ni(II) systems. That Zn(II) with a d^{10} electron configuration has no crystal field stabilization energy has prompted the argument for transformation caused by steric effects in the zinc chloride system apart from those in the other metal chloride systems, which are complicated by the difference of the stabilization energies between octahedral and tetrahedral configurations. Some discussions on octahedral–tetrahedral equilibria in other systems have been reported by Katzin.[29,30]

Although experimental conditions are fairly restricted, the X-ray diffraction method for solutions is a very powerful technique in structural analysis. Some information from X-ray diffraction studies is available for our discussion on structure. It is reported that the first-row transition metal ions from Mn(II) to Zn(II) in aqueous solutions exist as hexahydrates of regular octahedral structure except for the distorted octahedron of Cu(II).[31-34] Wertz et al. have indicated that the

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$CoCl_4^{2-}$ complex in methanolic 4 M cobalt chloride solution exists in a regular tetrahedral coordination[35] and that the $ZnCl_4^{2-}$ complex in aqueous solution also exists in a regular tetrahedral structure.[36] They have also investigated the structure of aqueous copper chloride at high concentrations.[37,38] In a recent paper, Friedman et al. have discussed the complicated structure of aqueous nickel chloride solution in the high concentration range.[39]

As no data on structures of these metal ions in methanol are available, the configurations of the solvated methanol molecules around the ions are not clear. However, if octahedrally coordinated $M(CH_3OH)_6^{2+}$ is assumed, it is possible that a change of coordination, from octahedral to tetrahedral structure, may occur in the course of the complex formation of both cobalt chloride and zinc chloride in methanol. In methanolic solution, $ZnCl_4^{2-}$ must be tetrahedral as in aqueous solutions. For a more conclusive interpretation, further intensive studies on both thermodynamic parameters and structural analyses are necessary for various systems.

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Registry No. $Co(ClO_4)_2$, 13455-31-7; $Ni(ClO_4)_2$, 13637-71-3; $Cu(ClO_4)_2$, 13770-18-8; $Zn(ClO_4)_2$, 13637-61-1; Zn, 7440-66-6; Co, 7440-48-4; Ni, 7440-02-0; Cu, 7440-50-8.

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Comparative Chemistry of Bipyrazyl and Bipyridyl Metal Complexes: Spectroscopy, Electrochemistry, and Photoanation

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The photoanation of the bipyrazyl complex $Ru(bpz)_3(PF_6)_2$, in acetonitrile containing chloride ion, leads to the formation of *cis*-$Ru(bpz)_2(CH_3CN)Cl^+$ (maximum quantum yield 0.37), *cis*-$Ru(bpz)_2Cl_2$ (maximum quantum yield 0.001), and an unidentified mono(bipyrazyl)ruthenium(II) derivative. The mechanism of this reaction is discussed. Reaction of $M(CO)_6$ (M = W, Mo) with bipyrazyl yields $M(CO)_4bpz$. The electronic, vibrational, and ^1H NMR spectra and electrochemistry of these products were compared with those of their bipyridyl analogues. It is concluded that bipyrazyl is no better a π acceptor than bipyridyl because of weaker σ bonding leaving the metal ion more positvely charged.

Introduction

We have recently reported[1] the photochemical properties of a new photocatalyst, the ruthenium(II) tris(bipyrazyl) dication, $Ru(bpz)_3^{2+}$ (I). The charge-transfer excited state of this species has a redox couple (II*/I), estimated to be ca. +1.3 V, thermodynamically sufficient to oxidize water at pH 7. We are currently directing our efforts into developing $Ru(bpz)_3^{2+}$ for use as a photosensitizer in solar energy conversion schemes. In view of the importance of the tris(bipyridyl)ruthenium(II) cation, $Ru(bpy)_3^{2+}$, as an energy conversion catalyst,[2] we have investigated some of the comparative chemistry of bipyridyl and bipyrazyl with a view to a greater understanding of both, but especially of the latter. We report, for the first time, the synthesis and characterization of $[Ru(bpz)_2(CH_3CN)Cl]^+[PF_6]^-$ (II) and $Ru(bpz)_2Cl_2$ (III), both prepared by photoanation of the $Ru(bpz)_3^{2+}$ cation in acetonitrile, and $Mo(CO)_4bpz$ (IV) and $W(CO)_4bpz$ (V) and compare their electrochemical and spectroscopic properties with those of their bipyridyl analogues.

Experimental Section

Bis(2-pyrazinecarboxylato)copper(II) was prepared by reaction of $Cu(CO_3)$ with 2-pyrazinecarboxylic acid (purchased from Fisher and Aldrich, respectively), in aqueous solution. The copper complex was used without further purification in the preparation of 2,2′-bipyrazine. $Ru(Me_2SO)_4Cl_2$[3] and $M(CO)_4bpy$, (M = Mo or W)[4] were prepared with use of literature methods. $RuCl_3\cdot(1-3)H_2O$, $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ were all purchased from Alfa. Tetraethylammonium chloride monohydrate $[(TEA)Cl\cdot H_2O]$ was purchased from Aldrich. All solvents used were reagent grade unless otherwise specified. The light source consisted of a focused 500-W tungsten halogen lamp. Light was passed through IR and 350-nm cutoff filters. Electronic and infrared spectra were recorded with a Perkin-Elmer Hitachi Model 340 microprocessor spectrometer and a Beckman IR 12 spectrometer, respectively. Conductivity data were obtained with a Wayne-Kerr conductivity bridge. All analyses were performed by Canadian Microanalytical Services Ltd. and agreed with the proposed formulations.

Preparation of 2,2′-Bipyrazine. This procedure is a much simplified version of an earlier preparation,[5] which significantly improves the yield without reducing the purity of the product.

Bis(2-pyrazinecarboxylato)copper(II) (14 g) in a Pyrex boat was placed into a 1.2 m long Pyrex tube. The boat was heated under nitrogen atmosphere with a Meker burner, causing pyrolysis of the copper complex. Bipyrazine and pyrazine sublimed onto the sides of the Pyrex tube during pyrolysis, which was completed when the copper residue appeared reddish. After cooling, the boat was removed and air passed through the Pyrex tube to remove most of the pyrazine impurity. Bipyrazine was then washed out of the Pyrex tube with chloroform. The entire procedure was repeated several times to yield,

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