*Inorg. Chem.* **1987**, *26*, 2244–2247

Contribution from the Department of Chemistry, Faculty of Science,
Osaka City University, Sumiyoshi-Ku, Osaka 558, Japan

# Potentiometric Study of Cadmium(II) Halide and Thiocyanate Complexes in Methanol

Hidekazu Doe,* Kenichi Wakamiya, Chie Yoshida, Hiroe Ozaki, Khin Nwe Soe,
and Toyokichi Kitagawa

*Received April 25, 1986*

The formation of $\mathrm{Cd^{II}X_n^{2-n}}$ ($\mathrm{X^-}$ = $\mathrm{Cl^-}$, $\mathrm{Br^-}$, $\mathrm{I^-}$, $\mathrm{NCS^-}$) complexes in methanol has been studied by $\mathrm{X^-}$ ion measurements with Ag–AgX and $\mathrm{NCS^-}$ ion selective electrodes. The ionic strength of measured solutions has been adjusted to 0.05 M (M = mol/dm$^3$) with sodium and cadmium perchlorates, and all measurements have been made in a closed cell thermostated at 25.0 ± 0.1 °C. In this study, the data treatment is improved, considering variations both in the concentration of $\mathrm{CdX_2}$ and in ionic strength. Stepwise thermodynamic stability constants, $K_1$ and $K_2$, have been determined; $K_1$ and $K_2$ are $(1.83 \pm 0.01) \times 10^6$ and $(9.4 \pm 3.4) \times 10^2$ for the chloride, $(3.5 \pm 0.2) \times 10^6$ and $(4.4 \pm 0.7) \times 10^3$ for the bromide, $(7.8 \pm 0.2) \times 10^6$ and $(2.5 \pm 0.2) \times 10^4$ for the iodide, and $(7.2 \pm 0.1) \times 10^5$ and $(1.7 \pm 0.1) \times 10^3$ for the thiocyanate, respectively. The results have been compared with those of zinc(II) complexes. The tendencies of $K_1$ and $K_2$ are different from those for the zinc complexes; for example, their magnitudes are on the order of $K_1 > K_2$ for the cadmium complexes whereas the order is $K_1 < K_2$ for the zinc halides, and both orders of $K_1$ and $K_2$ are $\mathrm{Cl^-} < \mathrm{Br^-} < \mathrm{I^-}$ for the cadmium complexes whereas they are $\mathrm{Cl^-} > \mathrm{Br^-} > \mathrm{I^-}$ for the zinc complexes.

## Introduction

We have been taking an interest in structural changes of metal complexes occurring at some complexation step in a solution and have scrutinized the stability constants of metal complexes though it is not a direct way to understand the structural changes. In order to discuss these changes effectively, it is most desirous to compare the stability constants by using thermodynamic stability constants. The determination of reliable thermodynamic stability constants primarily needs data obtained by measurements at a low ionic strength, but there are some difficult problems in the measurements. Using a potentiometric technique, therefore, we have made some attempts to determine reliable thermodynamic stability constants of some $\mathrm{M^{II}X_n^{2-n}}$ complexes ($\mathrm{X^-}$ = $\mathrm{Cl^-}$, $\mathrm{Br^-}$, $\mathrm{I^-}$, $\mathrm{NCS^-}$).[1-4]

In the present study of Cd(II)–$\mathrm{X^-}$ in methanol, an improved equation was applied to calculate the stability constants. If $K_1 \gg K_2$ such as for Cd(II)–$\mathrm{X^-}$ in methanol, it is very difficult to determine the reliable $K_2$ by the previous method in which measurements are carried out at a very low $\mathrm{X^-}$ concentration, $[\mathrm{X^-}]$.[1,2] Therefore, the present study was made at a high $[\mathrm{X^-}]$ to such an extent that the initial ionic strength of $5.00 \times 10^{-2}$ M does not vary considerably, though this variation was taken into account to correct ion activity coefficients by the Debye–Hückel second approximation. The other improvement of the data treatment is the consideration of $[\mathrm{MX_2}]$ in the calcuation of $[\mathrm{M^{2+}}]$ and the ionic strength etc. In the previous studies, the consideration of $[\mathrm{MX_2}]$ was unnecessary because the total concentration of NaX was much smaller than that of $\mathrm{M(ClO_4)_2}$.

Resembling a $\mathrm{Zn^{2+}}$ ion, a $\mathrm{Cd^{2+}}$ ion is octahedrally solvated by six solvent molecules in aqueous solutions[5,6] and also in dimethylsulfoxide ($\mathrm{Me_2SO}$) solutions.[7] According to the studies of $\mathrm{CdI_n^{2-n}}$ complexes, the structure of a tetraiodide complex is a regular tetrahedron both in aqueous[5] and in $\mathrm{Me_2SO}$[8] solutions, as is a zinc complex. These facts indicate that the structural change from a octahedron to a tetrahedron occurs at some complexation step of $\mathrm{CdI_n^{2-n}}$ in aqueous and in $\mathrm{Me_2SO}$ solutions. It is very presumable that the same also occurs at a complexation step of the other cadmium halides,[9] and then we think that this phenomenon similarly occurs in methanol solutions.

The structural features of $\mathrm{Cd(NCS)_n^{2-n}}$ are different from those of $\mathrm{Zn(NCS)_n^{2-n}}$. For example, $\mathrm{Cd(NCS)_3^-}$ has an octahedral configuration in $\mathrm{Me_2SO}$,[10] and $\mathrm{Cd(NCS)_4^{2-}}$ may have the same because the central cadmium of crystalline $\mathrm{Cd(SCN)_2}$ is octahedrally surrounded by four sulfur and by two trans-nitrogen atoms with a slightly distorted geometry.[11,12] On the other hand, $\mathrm{Zn(NCS)_4^{2-}}$ has a regular tetrahedral configuration in $\mathrm{Me_2SO}$[10] similar to zinc halide complexes, and in crystalline $\mathrm{Zn(NCS)_2}$, a zinc atom is tetrahedrally coordinated either by four nitrogen or by four sulfur atoms.[13] An atom through which $\mathrm{NCS^-}$ is coordinated is the N (N-coordination) for Zn(II) in water,[14] in $\mathrm{Me_2SO}$,[10] aned probably in methanol, the S (S-coordination) for Cd(II) in $\mathrm{Me_2SO}$,[10] and the N or the S for Cd(II) in water.[10,14,15]

In the present study, the previous data for zinc complexes were recalculated by the improved equation to be well comparable with the results of cadmium complexes. At the same time, the recalculation was made by using our new ionic association constant of $\mathrm{Zn^{2+}}$–$\mathrm{ClO_4^-}$, $K_{1A}$, which was determined by conductometric measurements.[16] In our data treatment of potentiometry, the ion-pair formation of $\mathrm{M^{II}ClO_4^+}$ is considered to decrease a systematic error caused by ion-pairing of a metal ion with an ionic medium ($\mathrm{ClO_4^-}$ in our studies). Recently, we have improved a conductance equation[16] and reanalyzed our previous conductance data to determine the new values of $K_{1A}$ of $\mathrm{M^{II}ClO_4^+}$.[17]

## Experimental Section

**Materials.** Cadmium(II) perchlorate hexahydrate was prepared by neutralizing cadmium carbonate (Nakarai, Guaranteed Grade) with perchloric acid.[18] This hexahydrate salt was purified by triple recrystallization from distilled water and then was dried on a vacuum line over diphosphorus pentaoxide for 3 days to obtain a dihydrate salt. The preparations of other reagents were described in previous papers.[1,2]

**Instrumentation.** The outline of instrumentation and the procedure of measurments were described previously.[1,2] In the present study, the sensor for $\mathrm{I^-}$ was a Horiba iodide ion selective electrode, 8005-06T. All measurements were carried out in a closed cell thermostated at 25.0 ± 0.1 °C. The cell contained 40 cm$^3$ of sample solution before titration.

---

(1) Doe, H.; Shibagaki, A.; Kitagawa, T. *Inorg. Chem.* **1983**, *22*, 1639.
(2) Doe, H.; Kitagawa, T. *Inorg. Chem.* **1982**, *21*, 2272.
(3) Doe, H.; Matsuda, A.; Kitagawa, T. *Bunseki* Kagaku, **1984**, *33*, E511.
(4) Doe, H.; Matsui, M.; Shigematsu, T. *Bull. Inst. Chem. Res., Kyoto Univ.* **1980**, *58*, 154.
(5) Ohtaki, H.; Maeda, M.; Ito, S. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 2217.
(6) Bol, W.; Gerrits, G. J. A.; van Panthaleon van Eck, C. L. *J. Appl. Crystallogr.* **1970**, *3*, 486.
(7) Sandström, M.; Persson, I.; Ahrland, S. *Acta Chem. Scand., Ser. A* **1978**, *A32*, 607.
(8) Pocev, S.; Triolo, R.; Johansson, G. *Acta Chem. Scand., Ser. A.* **1979**, *A33*, 179.
(9) Ahrland, S. *Pure Appl. Chem.* **1979**, *51*, 2019.
(10) Persson, I.; Iverfeldt, Å.; Ahrland, S. *Acta Chem. Scand., Ser A* **1981**, *A35*, 295.
(11) Cannas, M.; Carta, G.; Cristini, A.; Marongiu, G. *J. Chem. Soc., Dalton Trans.* **1976**, 300.
(12) Srdanov, G.; Herak, R.; Prelesnik, B.; Jeremić, M. *Bull. Soc. Chim. Belg.* **1979**, *44*, 561.
(13) Aslanov, L. A.; Ionov, V. M.; Kynev, K. *Sov. Phys.—Crystallogr. (Engl. Transl.)* **1976**, *21*, 693.
(14) Taylor, K. A.; Long, T. V., II; Plane, R. A. *J. Chem. Phys.* **1967**, *47*, 138.
(15) Antić-Jovanović, A.; Jeremić, M.; Long, D. A. *J. Raman Spectrosc.* **1982**, *12*, 91.
(16) Doe, H.; Kitagawa, T. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 2975.
(17) Doe, H.; Kitagawa, T.; Sasabe, K. *J. Phys. Chem.* **1984**, *88*, 3341.
(18) *Shin Jikken Kagaku Koza*; Maruzen: Tokyo, 1976; Vol. 8, Chapters 1–3.

0020-1669/87/1326-2244$01.50/0

**Table I.** Data Relating to a Plot according to Eq 3b for a Cadmium Chloride System ($C^\circ_M = 4.419 \times 10^{-3}$ M; $C^\circ_I = 4.00 \times 10^{-2}$ M)

| $10^3C^\circ_X$/M | $10^5[X^-]$/M | $10^{-6}Y/y_{2+}$/M$^{-1}$ | $10^3[M^{2+}]$/M | $10^3[ClO_4^-]$/M | $10^2I$/M | $y_\pm$ | $y_{2+}$ | $\bar{n}$ |
|---|---|---|---|---|---|---|---|---|
| 0.955 | 0.2846 | 1.843 | 2.181 | 4.755 | 4.974 | 0.5116 | 0.083 20 | 0.215 |
| 1.306 | 0.4281 | 1.859 | 1.963 | 4.768 | 4.964 | 0.5118 | 0.083 32 | 0.295 |
| 1.663 | 0.6215 | 1.843 | 1.734 | 4.781 | 4.955 | 0.5120 | 0.083 45 | 0.375 |
| 1.982 | 0.8334 | 1.846 | 1.535 | 4.792 | 4.947 | 0.5122 | 0.083 56 | 0.447 |
| 2.892 | 1.908 | 1.850 | 0.9703 | 4.825 | 4.924 | 0.5128 | 0.083 86 | 0.650 |
| 3.172 | 2.499 | 1.862 | 0.8055 | 4.835 | 4.918 | 0.5129 | 0.083 94 | 0.712 |
| 3.442 | 3.325 | 1.877 | 0.6503 | 4.844 | 4.913 | 0.5130 | 0.084 01 | 0.771 |
| 3.706 | 4.513 | 1.900 | 0.5080 | 4.853 | 4.909 | 0.5131 | 0.084 07 | 0.828 |
| 3.935 | 6.076 | 1.926 | 0.3336 | 4.860 | 4.905 | 0.5132 | 0.084 11 | 0.877 |
| 4.192 | 8.894 | 1.965 | 0.2791 | 4.867 | 4.904 | 0.5133 | 0.084 13 | 0.928 |
| 4.604 | 17.61 | 2.064 | 0.1449 | 4.875 | 4.907 | 0.5132 | 0.084 09 | 1.002 |

## Data Treatment and Results

Considering the equilibria

$$\mathrm{CdX}_{n-1}^{3-n} + \mathrm{X}^- \rightleftarrows \mathrm{CdX}_n^{2-n} \quad (K_n;\ n = 1, 2) \qquad (1)$$

$$\mathrm{Cd}^{2+} + \mathrm{ClO}_4^- \rightleftarrows \mathrm{CdClO}_4^+ \quad (K_{1A}) \qquad (2)$$

in a sample solution with a relatively low $[X^-]$ in comparison with total cadmium concentration, $C^\circ_M$, we can write the following equation under some assumptions:[2]

$$Y = \Delta_X/([\mathrm{Cd}^{2+}][X^-]) = y_{2+}K_1 + 2y_{2+}y_\pm^2K_1K_2[X^-] \qquad (3a)$$

$$Y/y_{2+} = K_1 + 2K_1K_2(y_\pm^2[X^-]) \qquad (3b)$$

where

$$\Delta_X = C^\circ_X - [X^-]$$

$C^\circ_X$ is the total concentration of NaX, and $y_{2+}$ and $y_\pm$ are the ion activity coefficients of $\mathrm{Cd}^{2+}$ and $\mathrm{ClO}_4^-$ (or $\mathrm{Cl}^-$) ions, respectively. If $[\mathrm{CdX}_2]$, which is neglected in the previous works,[1-4] is taken into account, $[\mathrm{Cd}^{2+}]$ is calculated by the equation

$$y_{2+}K_{1A}[\mathrm{Cd}^{2+}]^2 + (y_{2+}K_{1A}(C^\circ_I + C^\circ_M + \Delta_X') + 1)[\mathrm{Cd}^{2+}] - (C^\circ_M - \Delta_X') = 0 \qquad (4)$$

where

$$\Delta_X' = \Delta_X - [\mathrm{MX}_2]$$

and $C^\circ_I$ is the total concentration of $\mathrm{NaClO}_4$. The ionic strength, $I$, of a solution is given by the equation

$$I = C^\circ_I + C^\circ_M + C^\circ_X + 2[\mathrm{Cd}^{2+}] \qquad (5)$$

By the use of eq 5, in the present study, the $I$ values of all solutions were computed, and from those, $y_{2+}$ and $y_\pm$ were evaluated by the Debye–Hückel second approximation with 5 and 4 Å for ion size parameters, $a$, respectively. Then, a quantity of $[X^-]$ that was calibrated at $I = 0.05$ M was corrected by the $y_\pm$ values at $I = 0.05$ M and at $I$ of the calculation. On the other hand, the average number of ligands, $\bar{n}$, is expressed as

$$\bar{n} = \Delta_X/C^\circ_M = (y_{2+}K_1[X^-] + 2y_{2+}y_\pm^2K_1K_2[X^-]^2)/(1 + y_{2+}K_{1A}[\mathrm{ClO}_4^-] + y_{2+}K_1[X^-] + y_{2+}y_\pm^2K_1K_2[X^-]^2) \qquad (6)$$

$[\mathrm{ClO}_4^-]$ is evaluated by the equation

$$[\mathrm{ClO}_4^-] = C^\circ_I + C^\circ_M + [\mathrm{M}^{2+}] + \Delta_X' \qquad (7)$$

In Figure 1, the plot of $Y/y_{2+}$ vs. $y_\pm^2[X^-]$ according to eq 3b is compared to a plot according to the previous treatment in which $[\mathrm{CdX}_2]$ is neglected. In a low-$[X^-]$ region, there is no difference in both plots, but the previous plot cannot maintain the straight line in a higher $[X^-]$ region. Therefore, the previous experiments had to be conducted in such a low-$[X^-]$ region.[1-4] Thus, the consideration of $[\mathrm{MX}_2]$ expands the range of $[X^-]$ in which the plot according to eq 3b is straight; that is, it makes the wide range of $[X^-]$ suitable for measurements.

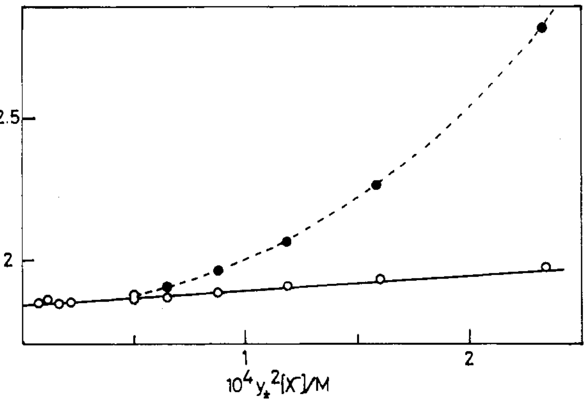

**Figure 1.** $Y/y_{2+}$ vs. $y_\pm^2[X^-]$ plots according to eq 3b: (○) present calculation; (●) previous calculation. For a cadmium chloride system, $C^\circ_M = 4.419 \times 10^{-3}$ M and $C^\circ_I = 4.00 \times 10^{-2}$ M.

**Table II.** Results of Plots Based on Eq 3b for Cadmium Chloride, Bromide, Iodide, and Thiocyanate Systems

| $10^3C^\circ_M$/M | $10^2C^\circ_I$/M | $10^{-6}K_1$/M$^{-1}$ | $10^{-3}K_2$/M$^{-1}$ | $N$[a] | $r$[b] |
|---|---|---|---|---|---|
| | | 1. Cadmium Chloride | | | |
| 2.223 | 4.50 | 1.838 ± 0.004 | 0.82 ± 0.02 | 11 | 0.9986 |
| 4.419 | 4.00 | 1.838 ± 0.004 | 1.35 ± 0.06 | 11 | 0.9920 |
| 6.588 | 3.50 | 1.810 ± 0.004 | 0.70 ± 0.33 | 13 | 0.5362 |
| | | 2. Cadmium Bromide | | | |
| 2.223 | 4.50 | 3.25 ± 0.26 | 4.2 ± 0.4 | 10 | 0.9884 |
| 4.419 | 4.00 | 3.618 ± 0.007 | 4.1 ± 0.6 | 10 | 0.9259 |
| 6.588 | 3.50 | 3.564 ± 0.006 | 5.0 ± 0.7 | 7 | 0.9532 |
| | | 3. Cadmium Iodide | | | |
| 2.223 | 4.50 | 7.69 ± 0.19 | 27.2 ± 1.2 | 14 | 0.9923 |
| 4.419 | 4.00 | 7.96 ± 0.05 | 23.0 ± 1.3 | 13 | 0.9841 |
| 6.588 | 3.50 | 7.58 ± 0.15 | 24.8 ± 1.1 | 8 | 0.9937 |
| | | 4. Cadmium Thiocyanate | | | |
| 4.419 | 4.00 | 0.723 ± 0.003 | 1.91 ± 0.02 | 16 | 0.9996 |
| 6.588 | 3.50 | 0.710 ± 0.001 | 1.54 ± 0.04 | 8 | 0.9974 |
| 6.588 | 3.50 | 0.720 ± 0.002 | 1.65 ± 0.04 | 11 | 0.9978 |
| 8.728 | 3.00 | 0.709 ± 0.002 | 1.68 ± 0.04 | 17 | 0.9969 |
| 8.728 | 3.00 | 0.721 ± 0.001 | 1.67 ± 0.05 | 15 | 0.9932 |

[a] The number of data points. [b] Correlation coefficient.

The first step of a data treatment was the determination of $K_1$, which was evaluated from the intercept of a plot according to eq 3b. Initially, it was assumed that $[\mathrm{MX}_2] = 0$ and $I = 0.05$, and then $[\mathrm{M}^{2+}]$ was calculated by eq 4, because $y_{2+}$ was evaluated by the Debye–Hückel equation, because $K_{1A}$ had already been determined conductometrically, and because $\Delta_X'$ was equal to $\Delta_X$. Once $[\mathrm{M}^{2+}]$ was determined, the next value of $y_{2+}$ was calculated from a next $I$ evaluated by eq 5. Using the next $y_{2+}$ and $[X^-]$, which was corrected by the equation $(y_\pm(I = 0.05))[X^-] = (y_\pm(\text{next}))[X^-]$, the calculation of $[\mathrm{M}^{2+}]$ was repeated until $I$ became constant. Then we were able to calculate $K_2$ by using eq 6, because $K_1$ and $[\mathrm{ClO}_4^-]$ (by eq 7) were known. Here, we can write the relation

$$\Delta_X' = \Delta_X(1 + y_\pm^2K_2[X_-])/(1 + 2y_\pm^2K_2[X_-]) \qquad (8)$$

because $y_\pm^2K_2 = [\mathrm{CdX}_2]/([\mathrm{CdX}^+][X^-])$ and $[\mathrm{CdX}^+] = \Delta_X - 2[\mathrm{CdX}_2]$. By the use of eq 8, a next $\Delta_X'$ value was calculated. Then we were able to return to the start of calculations with the next $\Delta_X'$. For every piece of data, this series of calculations was repeated until $\Delta_X'$ became constant.

**Table III.** Thermodynamic Stability Constants of Cd(II)–$X^-$ and Zn(II)–$X^-$ Systems in Methanol

| | Cd ($K_{1A}$ = 149 $M^{-1}$) | | Zn ($K_{1A}$ = 144 $M^{-1}$) | |
|---|---|---|---|---|
| $X^-$ | $K_1/M^{-1}$ | $K_2/M^{-1}$ | $K_1/M^{-1}$ | $K_2/M^{-1}$ |
| Cl | $(1.83 \pm 0.01) \times 10^6$ | $(9.4 \pm 3.4) \times 10^2$ | $(9.4 \pm 0.2) \times 10^3$ | $(1.63 \pm 0.06) \times 10^4$ |
| Br | $(3.5 \pm 0.2) \times 10^6$ | $(4.4 \pm 0.7) \times 10^3$ | $(2.7 \pm 0.1) \times 10^3$ | $(1.4 \pm 0.1) \times 10^4$ |
| I | $(7.8 \pm 0.2) \times 10^6$ | $(2.5 \pm 0.2) \times 10^4$ | $(8.0 \pm 0.4) \times 10^2$ | $(9.6 \pm 0.6) \times 10^3$ |
| NCS | $(7.2 \pm 0.1) \times 10^5$ | $(1.7 \pm 0.1) \times 10^3$ | $(2.09 \pm 0.05) \times 10^5$ | $(1.0 \pm 1.6) \times 10^3$ |

**Table IV.** Concentration Stability Constants of Cd(II)–$X^-$ and Zn(II)–$X^-$ Systems in Methanol at 25.0 °C ($I = 5.00 \times 10^{-2}$ M)

| | Cd | | Zn | |
|---|---|---|---|---|
| $X^-$ | $y_{2+}K_1/M^{-1}$ | $y_\pm^2K_2/M^{-1}$ | $y_{2+}K_1/M^{-1}$ | $y_\pm^2K_2/M^{-1}$ |
| Cl | $(1.51 \pm 0.01) \times 10^5$ | $(2.5 \pm 0.9) \times 10^2$ | $(9.2 \pm 0.2) \times 10^2$ | $(4.3 \pm 0.2) \times 10^3$ |
| Br | $(2.9 \pm 0.2) \times 10^5$ | $(1.1 \pm 0.2) \times 10^3$ | $(2.66 \pm 0.13) \times 10^2$ | $(3.7 \pm 0.3) \times 10^3$ |
| I | $(6.4 \pm 0.2) \times 10^5$ | $(6.6 \pm 0.6) \times 10^3$ | $(7.8 \pm 0.4) \times 10$ | $(2.49 \pm 0.14) \times 10^{13}$ |
| NCS | $(5.94 \pm 0.05) \times 10^4$ | $(4.5 \pm 0.3) \times 10^2$ | $(2.05 \pm 0.05) \times 10^4$ | $(2.6 \pm 4.2) \times 10^2$ |

Finally, using $[M^{2+}]$ and $[X^-]$ that were determined by the above calculation, we plotted $Y/y_{2+}$ against $y_\pm^2[X^-]$ and determined $K_1$ and $K_2$ values. The results of the calculation are shown in Table I for a cadmium chloride system in detail. The plot of the data in Table I according to eq 3b is shown in Figure 1. For all the systems, the results from such plots are summarized in Table II. Thermodynamic stability constants were determined by computing an arithmetic mean of the results in Table II, considering the number of data points, *N*. The thermodynamic stability constants are summarized in Table III, in which those of Zn(II)–$X^-$ systems are included. The $y_{2+}$ values of $Cd^{2+}$ and $Zn^{2+}$ are 0.082 85 ($a$ = 5 Å) and 0.098 07 ($a$ = 6 Å) at $I$ = 0.05 M in methanol ($\epsilon$ = 32.66 at 25.0 °C), respectively. The $y_\pm$ value is 0.5110 for both Cd(II) and Zn(II) systems. Table IV shows the concentration stability constants of these complexes at $I$ = 0.05, near which the measurements were carried out.

Between the present and the previous[1] calculations for Zn(II)–$X^-$ systems, there are two differences: one is the $K_{1A}$ value; the other, the degree of approximation (corrections about $[MX_2]$ and $I$). For example, if we calculate the stability constants with the present $K_{1A}$ value (144 $M^{-1}$) by using the previous data treatment, we get $K_1 = 9.1 \times 10^3$ and $K_2 = 1.66 \times 10^4$ for Zn(II)–$Cl^-$ (previously, $K_1 = 7.76 \times 10^3$ and $K_2 = 1.74 \times 10^4$) and $K_1 = 2.05 \times 10^5$ and $K_2 = 1.2 \times 10^3$ for Zn(II)–$NCS^-$ (previously, $K_1 = 1.74 \times 10^5$ and $K_2 = 4.4 \times 10^2$). This indicates that the difference of $K_{1A}$ is a main cause of the difference between the present and the previous $K_n$'s. It will be a natural conclusion because the experimental conditions of the previous study are well selected for the variations in $[MX_2]$ and $I$. However, the correction about $I$ is effective on $K_2$ of Zn(II)–$NCS^-$ to some extent because $K_1 \gg K_2$.

## Discussion

The thermodynamic stability constants (Table III) have been graphically summarized in Figure 2.

**Halide Complex.** As shown in Figure 2, there are two main differences between the cadmium and the zinc systems as follows: (1) $K_1$ is larger than $K_2$ for all the cadmium halides, contrary to the zinc halides; (2) both $K_1$ and $K_2$ of the cadmium halides increase in the order of Cl < Br < I, while those of the zinc halides decrease in that order.

In the case of difference 1, $K_1 > K_2$ for the cadmium halides is a normal result, though the ratios of $K_1/K_2$ appear to be extremely large. As to difference 2, Cd(II) is evidently a soft acid (HSAB principle),[19-22] while Zn(II), a borderline element between hard and soft acids, seems to behave as a hard acid at least before a trihalide complex is formed.

We previously discussed the abnormal result of $K_1 < K_2$ of the zinc halides, namely cooperativity, considering the structural change of the dihalide complex from an octahedral to a tetrahedral configuration.[1,2] According to this discussion, it is inferred that such a structural change for the cadmium halides does not occur at the step of dihalide complexation at least. It is not reasonable that the cadmium monohalide complex already changes its structure to a tetrahedrally four-coordinated $CdXS_3^+$ (where S is a solvent molecule), because the monohalide complex of Zn(II), having a smaller coordination sphere than Cd(II), still keeps a six-coordinating octahedral structure ($ZnXS_5^+$). Consequently, if the cadmium dihalide complex keeps the six-coordinated octahedral configuration, its ligands must become very crowded. This will probably cause the $K_2$ values of cadmium halides to become small.

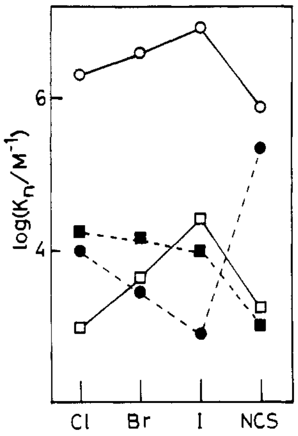

**Figure 2.** Stepwise thermodynamic stability constants of zinc and cadmium halides and thiocyanates in methanol at 25.0 °C: (○) $K_1$ of Cd(II); (□) $K_2$ of Cd(II); (●) $K_1$ of Zn(II); (■) $K_2$ of Zn(II).

Furthermore, we previously stated that the $K_2/K_1$ ratios of zinc halides become large as the size of a halogen atom increases (the ratios are 1.7, 5.2, and 12 for Cl, Br, and I, respectively), because a steric hindrance among ligands is stronger in the crowded octahedral monohalide, $ZnXS^5$, than in the tetrahedral dihalide, $ZnX_2S_2$. On the other hand the $K_2/K_1$ ratios of cadmium halides also increase in a similar proportion to the zinc systems ($0.5 \times 10^{-3}$, $1.3 \times 10^{-3}$, and $3.2 \times 10^{-3}$ for Cl, Br, and I, respectively). If a discussion is done in the same manner, contrary to the experimental results those ratios must decrease as halogen sizes increase, because the dihalide complex is more crowded than the monohalide one in the case of those cadmium halides with the same configurations. Thus the steric effect caused by halogen atoms may be of little importance in the cadmium halides, and then another discussion will be made as follows.

Properties of a hard acid (HSAB principle) are a small size, a high positive charge, and a small polarizability. Halide complexes of hard acids increase their stabilities in the order I < Br < Cl, and those of soft acids, in the order Cl < Br < I. In the individual reactions of zinc and cadmium halide complexes (eq 1), the acid in the first reaction ($K_1$) is $M^{II}S_6^{2+}$ and that in the second one ($K_2$) is $M^{II}XS_5^+$. If one compares $M^{II}S_6^{2+}$ and $M^{II}XS_5^+$, it will probably be seen that $M(II)S_6^{2+}$ is a harder acid

---

(19) Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533.
(20) Pearson, R. G. *Science (Washington D.C.)* **1966**, *151*, 172.
(21) Pearson, R. G. *Chem. Br.* **1967**, *3*(3), 103.
(22) Pearson, R. G. *J. Chem. Educ.* **1968**, *45*, 581, 643.

than $M(II)XS_5^+$. That is to say because $ZnXS_5^+$ is a weaker hard acid than $ZnS^{62+}$, a decrease in $K_2$ from Cl to I (Figure 2) is smaller than that in $K_1$. On the other hand, because $CdXS_5^+$ is a stronger soft acid than $CdS_6^{2+}$, an increase in $K_2$ from Cl to I is larger than that in $K_1$. Thus, we conclude that the $K_2/K_1$ ratio increases in going from Cl to I.

**Thiocyanate Complex.** We have the following knowledge on the structure of cadmium thiocyanate complexes (cf. Introduction). The cadmium thiocyanate complexes seem not to change their structure, keeping a six-coordinated octahedral configuration, contrary to the zinc thiocyanate complexes. According to the previous discussion,[1] the zinc thiocyanate complexes have a four-coordinated tetrahedral structure; that is, the structural change from an octahedral to a tetrahedral configuration occurs at the formation of a monothiocyanate complex. Cd(II) may be partly coordinated through a sulfur atom (S-coordination) in methanol as in water, though Zn(II) is coordinated through a nitrogen atom of $NCS^-$ (N-coordination).

As for the N- or S-coordination, it was reported that the change from M–NCS to M–SCN bonding coincides approximately in the periodic table with the change in relative binding of halide ions from $F^- > Cl^- > Br^- > I^-$ to $I^- > Br^- > Cl^- > F^-$.[23,24] Hence, it is probable that the existence of S-coordinated species in the cadmium thiocyanate complexes in methanol is supported by our results of halide complexes. If so, *S*-coordination may appear easily in complexes containing many $NCS^-$ ions such as $Cd(CNS)_3S_3^-$ or $Cd(CNS)_4S_2^{2-}$ because the coordination of $NCS^-$ probably increases the softness of Cd(II). According to a Raman study in water,[14] in $Cd(CNS)_4^{2-}$ (even in the complexes containing less $NCS^-$) some of the $NCS^-$ is bound to Cd(II) through the N and some through the S.

In comparison with those of the iodide complexes, the stabilities of the thiocyanate complexes in methanol indicate some tendency similar to that in water: in water, at 25 °C and $I = 0$ M, log $K_1$(Zn–I) = −1.5 ($I$ = 3.0 M), log $K_1$(Zn–NCS) = 1.33, log $K_2$(Zn–NCS) = 0.58, log $K_1$(Cd–I) = 2.28, log $K_2$(Cd–I) = 1.64, log $K_1$(Cd–NCS) = 1.89, log $K_2$(Cd–NCS) = 0.89[25] (cf. log $K_1$(Zn–I) = −2.93 and log $K_2$(Zn–I) = 1.17 at $I$ = 4.5[26]). Why $K_1$(Zn–NCS) is large was previously explained by the structural change of zinc monothiocyanate. The results of $K_1$(Cd–I) > $K_1$(Cd–NCS) and $K_2$(Cd–I) > $K_2$(Cd–NCS) seem to be normal because Hg(II) of S-coordination also gives the same results in water: log $K_1$(Hg–I) = 12.87 ($I$ = 0.5), log $K_2$(Hg–I) = 10.95 ($I$ = 0.5), log $K_1$(Hg–NCS) = 9.08 ($I$ = 1), log $K_2$(Hg–NCS) = 7.78 ($I$ = 1).[25] However, considering $K_1$(Hg–NCS) > $K_1$(Hg–Cl) in water (log $K_1$(Hg–Cl) = 6.74 at $I$ = 0.5), $K_1$(Cd–NCS) appears to be too small in methanol. This may support a prediction that the N-coordination dominantly exists in the cadmium monothiocyanate complex. As $K_2$(Zn–NCS) < $K_2$(Zn–I), we think that $K_2$(Zn–I) is too large if it is considered that the Zn–N bond is just slightly covalent (less than that in Zn–Br).[14] For this reason, it is thought that the zinc dihalide complex is stabilized significantly by the structural change.

The $K_2/K_1$ ratio of cadmium thiocyanate is considerably small, like those of its halides, $2.4 \times 10^{-3}$. Thus, if the cadmium thiocyanate complex changes its structure, the structural change in the tri- or tetrathiocyanate complex might be predicted. However, if there is no probability of structural change in the cadmium thiocyanate complex contrary to the zinc thiocyanate complex, we will expect that this structural property of cadmium thiocyanate is related to ambidentate binding of $NCS^-$ to Cd(II).

**Acknowledgment.** C.Y. and H.O. thank Associate Professor Shigeo Sawada of Kinki University for his kind direction. K.N.S. thanks Professor Dr. Ko Ko Gyi of Rangoon University, Rangoon, Burma, for his kind permission to do research work in Japan.

---

(23) Lindquist, I.; Standberg, B. *Acta Crystallogr.* **1957**, *10*, 173.

(24) Mitchell, P. C. H.; Williams, R. J. P. *J. Chem. Soc.* **1960**, 1912.

(25) Smith, R. M.; Martell, A. E. *Critical Stability Constants*; Plenum: New York, 1976; Vol. 4.

(26) Shchukarev, S. A.; Lilich, L. S.; Latysheva, V. A. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1956**, *1*(2), 36.

---

Contribution from the Research School of Chemistry, Australian National University, Canberra, ACT 2601, Australia, and Chemistry Department, University of Tasmania, Hobart, Tasmania 7001, Australia

# Electronic Spectrum of $Cs_3Mo_2Cl_9$

Lucjan Dubicki,*[†] Elmars Krausz,[‡] Robert Stranger,[§] Peter W. Smith,[§] and Yukito Tanabe[‖]

*Received December 10, 1986*

The single-crystal absorption, MCD, and Zeeman spectra are reported for $Cs_3Mo_2Cl_9$. The highly structured absorption at ~13 000 $cm^{-1}$ has no MCD and consists of spin-singlet and orbitally nondegenerate states. New absorption lines are observed near 11 600 and 7800 $cm^{-1}$. The main spectroscopic features can be qualitatively explained on the basis of an exchange-coupled-pair model with strong $\sigma$ Mo–Mo bonding. The $\sigma$ bonding preferentially stabilizes the pair states derived from the $t_{2e}^2t_{2e}^2$ configuration. However, the $t_{2z}$ electrons are not fully paired and the ground singlet–triplet separation is dominated by $t_{2z}$–$t_{2z}$ kinetic exchange. The bonding in $Mo_2Cl_9^{3-}$ and $W_2Cl_9^{3-}$ is considered to be qualitatively the same, with one strong $\sigma$ bond and two weak $\pi$ interactions.

## Introduction

The anion of the title compound is a member of the classic series $M_2X_9^{3-}$ (M(III) = Cr, Mo, W; X = Cl, Br) in which the strength of the M–M bonding is reflected in the structural distortions of the bridging group and a progressive reduction in M–M separations.[1-4] Direct Cr–Cr bonding is very weak and the ground singlet–triplet separation[5] is very small, $E_{10} \sim 13$ $cm^{-1}$. $Cs_3Mo_2Cl_9$ is weakly paramagnetic. The magnetic susceptibility[5] can be fitted to either a $d^3d^3$, $d^2d^2$, or $d^1d^1$ model and gives $E_{10} \sim 840$ $cm^{-1}$. The $W_2Cl_9^{3-}$ anion is diamagnetic[6] at 298 K. The changes in the structural and magnetic properties have been interpreted[7] by assigning no M–M bonds in $Cr_2Cl_9^{3-}$, one bond in $Mo_2Cl_9^{3-}$, and three bonds in $W_2Cl_9^{3-}$.

The electronic spectra of $Cr_2X_9^{3-}$ have been studied by many workers.[8-10] The exchange interactions are small and together

---

[†] Visiting Fellow, Research School of Chemistry, Australian National University.

[‡] Australian National University.

[§] University of Tasmania.

[‖] Present address: Department of Applied Physics, University of Tokyo, Tokyo, Japan

(1) Wessel, G. J.; Ijdo, D. J. W. *Acta Crystallogr.* **1957**, *10*, 466.

(2) Watson, W. H., Jr.; Waser, J. A. *Acta Crystallogr.* **1958**, *11*, 689.

(3) Saillant, R.; Jackson, R. B.; Streib, W. E.; Folting, K.; Wentworth, R. A. D. *Inorg. Chem.* **1971**, *10*, 1453.

(4) Cotton, F. A.; Ucko, D. A. *Inorg. Chim. Acta* **1972**, *6*, 161.

(5) Grey, I. E.; Smith, P. W. *Aust. J. Chem.* **1971**, *24*, 73.

(6) Saillant, R.; Wentworth, R. A. D. *Inorg. Chem.* **1968**, *7*, 1606.

(7) Summerville, R. H.; Hoffmann, R. *J. Am. Chem. Soc.* **1979**, *101*, 3821.

0020-1669/87/1326-2247$01.50/0