X-RAY DIFFRACTION STUDIES ON THE STRUCTURES OF CADMIUM IODIDE COMPLEXES IN WATER AND IN DMSO SOLUTIONS

Hitoshi Ohtaki* and Georg Johansson**

*Department of Electronic Chemistry, Tokyo Institute of
Technology at Nagatsuta, Nagatsuta-cho, Midori-ku, Yokohama,
227 Japan
**Department of Inorganic Chemistry, Royal Institute of
Technology, S-10044, Stockholm 70, Sweden

Abstract - The structures of solvated cadmium ions and cadmium
iodide complexes in water and in DMSO solutions were studied by
means of X-ray diffraction at 25 °C. In an aqueous perchlorate
solution a cadmium ion has six water molecules in the first
coordination sphere with a Cd-O bond length of 2.292(5) Å. The
same value, 2.292(3) Å, is found in crystals of $[Cd(H_2O)_6](ClO_4)_2$.
The Cd-O bond length of the hexasolvated cadmium ion in a per-
chlorate solution in DMSO is 2.292(5) Å and the corresponding
value in crystal of $[Cd(DMSO)_6](ClO_4)_2$ is 2.291 Å (Sandström,
et al. (21)). The CdI^+ complex has five water molecules in the
coordination sphere in the aqueous solution. The Cd-I and Cd-O
bond distances within the $CdI(H_2O)_5^+$ complex is estimated to be
2.80(5) Å and 2.30(5) Å, respectively. Although the number of
solvent molecules combined with the CdI^+ complex in the DMSO
solution has not been determined with a reasonable accuracy, the
Cd-I bond distance within the complex is found to be about 2.75 Å.
The structure of the CdI_2 complex has not been determined in any
of the two solvents because of low concentrations of that species.
The CdI_3^- complex is pyramidal in DMSO with a Cd-I bond length
of 2.773(3) Å and an I-Cd-I angle of *ca*.112(1)°. However, no
structural measurement has been possible for the CdI_3^- complex
in the aqueous solution, because the concentration of the complex
in water is rather low. The CdI_4^{2-} complex has a tetrahedral
structure in both water and DMSO solutions. The Cd-I bond
distance within the complex is 2.79(1) Å and 2.790(3) Å in water
and DMSO, respectively.

The Raman spectrum of the CdI_4^{2-} complex in water show a pattern
typical of a tetrahedral complex, the bands appear at 34, 46, 117
and 142 cm^{-1}. A very similar spectrum of the complex is found
in DMSO (40 - 50, 115 and 142 cm^{-1}). For the CdI_3^- complex the
frequency of the Cd-I stretching vibration appears at 120 - 122
cm^{-1} in both water and DMSO. Thus, no significant difference is
observed in the structures, bond lengths or Raman spectra of the
CdI_4^{2-} (and perhaps CdI_3^-, too) complex in the two solvents.

Introduction

X-Ray diffraction techniques were applied to studies on structures of liquids
and amorphous solids almost immediately after the work of Bragg (1). Debye and
Scherrer (2) obtained diffraction patterns of paraffine in 1916. Even for
water, some pioneering works were done in 1930 - 1931 (3-5), which were follow-
ed by the famous work by Bernal and Fowler (6). Results of structure studies
on simple liquids such as argon (7) and krypton (8) have given an experimental
base for the theoretical treatment of liquids with the use of the methods of
statistical mechanics. Molecular dynamic simulations recently developed can
give radial distribution curves for atoms in liquids, which can be compared
with those experimentally obtained by X-ray and neutron diffraction measure-
ments.

Although structures of liquids have been investigated rather extensively by
X-ray and neutron diffraction methods, studies on structures of complexes which
only exist in solution are very limited. They are often deduced from crystallo-

graphic data by assuming them to have the same structures as complexes of similar composition in the solid phase. Knowledge of formation constants and other thermodynamic data for the complexes in solution can also give information on their structures, but conclusions based on this type of indirect evidence may sometimes lead to erroneous results.

Direct determinations of structures of molecules and complexes in solution by means of X-ray and neutron diffraction give more reliable results which can, in turn, be used for interpretations of thermodynamic data on liquids and solutions of complexes.

X-Ray diffraction methods have been used for structure determinations of several aqua complexes in solution. Early investigations include alkaline (9) and alkaline earth (10) metal ions in water. Structures of solvated metal ions, as well as some anions, in water and in other solvents have later been studied, and extensive information on structures of solvated ions in various systems is now being accumulated with the efforts of many workers in this fields (11-15).

Structures of halido complexes of metal ions in solution have been studied rather extensively compared with other complexes. Structural changes of halido complexes sometimes occur in solution when solvent molecules in the first coordination sphere of a metal ion are replaced by ligand atoms. Such changes are often indicated by thermodynamic measurements when irregular changes in enthalpies and entropies of formation of complexes are observed. Even colors of solutions can change when coordination numbers of metal ions are changed. However, direct evidence for structural changes of complexes in solution is obtainable only by applying X-ray diffraction techniques to the systems.

Solvent effects on complex formation have usually been estimated from thermodynamic data. Dielectric constants of solvents have been believed to be the essential factor for the solvent effect (16). However, behavior of electrolytes in different solvents having similar dielectric constants show that the dielectric constant is not only the factor which controls solute-solute and solute-solvent interactions in a solution.

Various attempts have so far been made by many workers to interpret the solvent effects in non-aqueous solutions. Gutmann's donor and acceptor numbers (17) are known to be useful as measures of solvent effects. The bond-length variation rules proposed by Gutmann (18) can qualitatively explain experimental observations of structural changes of molecules and complexes in solutions. However, very few experimental determinations of bond lengths within molecules and complexes in solutions have been reported. Here, again, X-ray and neutron diffraction and X-ray absorption (EXAFS) methods become indispensable for determination of bond lengths between atoms in various media.

In this paper, the structures of cadmium iodide complexes in water (19) and in DMSO (20) solutions are given, and bond lengths within the complexes are compared for the two solvents. A comparison of the structures of complexes with different numbers of iodide ions are also made in the two solvents. Results of Raman spectroscopic measurements are helpful for the discussion.

Experimental procedures

Sample Solutions. The solutions were prepared by dissolving weighed amounts of $\overline{CdI_2}$ and NaI in water or in DMSO. The compositions of the solutions are listed in Table 1. In solution A, $Cd(ClO_4)_2$ was used instead of CdI_2, and in solution B a suitable amount of $Cd(ClO_4)_2$ was added to a CdI_2 solution. The structure of the solvated cadmium ion in DMSO solution has been determined by Sandström, et al. (21), and the results is also included in this paper (solution D in Table 1) in order to allow a comparison with the corresponding aqua ion.

Method of Measurements and Treatment of Data. X-Ray diffraction measurements were carried out at 25 °C by using a θ-θ type X-ray diffractometer (JEOL, Tokyo). MoKα radiation ($\lambda = 0.7107$ Å) was used. The range of the scattering angle (2θ) was 2° to 140°, which corresponds to the range 0.31 Å$^{-1} < s < 16.6$ Å^{-1} ($s = 4\pi\lambda^{-1}\sin\theta$).

The measured intensities were scaled in the usual way (22,23), and the reduced intensities $i(s)$ were obtained (24) as follows:

$$i(s) = I(s) - \sum_i n_i \{(f_i(s) + \Delta f_i')^2 + (\Delta f_i'')^2\} + \Phi(s) I_i^{inco}(s) \qquad (1)$$

TABLE 1. Compositions of sample solutions (g-atom dm^{-3})

Sample	Water			DMSO			
	A	B	C	D[a]	E	F	G
Cd	2.920	1.265	2.246	0.685	2.49	1.70	1.33
I	-	0.917	11.39	-	4.98	5.03	5.04
Cl	6.303	2.552	-	1.370	-	-	-
Na	-	0.917	6.899	-	-	1.62	2.38
S	-	-	-	13.33	11.52	11.28	11.20
O	66.02	58.33	30.60	18.81	11.52	11.28	11.20
C	-	-	-	26.66	23.0	22.6	22.4
H	81.15	96.27	61.21	79.98	69.1	67.7	67.2
I/Cd	0.00	0.725	5.07	0.00	2.00	2.96	3.79

[a] M. Sandström, I. Persson and S. Ahrland, <u>Acta Chem. Scand.</u>, <u>A32</u>, 607 (1978).

where $I(s)$ denotes the scaled intensities, f_i the scattering factor of atom i, $\Delta f'_i$ and $\Delta f''_i$ the real and imaginary parts of the anomalous dispersion, respectively. $\Phi(s)$ represents the fraction of the incoherent scattering, $I_i^{inco}(s)$, reaching the counter.

The radial distrinution function $D(r)$ were calculated as

$$D(r) = 4\pi r^2 \rho_o + 2r\pi^{-1}\int_0^{s_{max}} s\cdot i(s)\cdot M(s)\cdot\sin(rs)\,ds \qquad (2)$$

where $M(s) = \{f_A^2(0)/f_A^2(s)\}\exp(-0.01s^2)$. A represents Cd in the aqueous system (19), while A denotes I in the DMSO system (20). ρ_o is the average scattering density.

Contributions to the reduced intensity function from a pair interaction "ij" were calculated from the expression

$$i_{calc}(s) = \sum_i\sum_j n_{ij}\{(f_i(s) + \Delta f'_i)(f_j(s) + \Delta f'_j) + (\Delta f''_i)(\Delta f''_j)\}$$

$$\cdot\frac{\sin(r_{ij}s)}{(r_{ij}s)}\cdot\exp(-b_{ij}s^2) \qquad (3)$$

Here, r_{ij} is the distance between the two atoms, n_{ij} is the number of such interactions, and b_{ij} is a coefficient related to the root-mean-square variation in the distance. Parameter values were refined by means of a least-squares procedure in which the sum $U = \Sigma s^2\{i(s) - i_{calc}(s)\}^2$ was minimized.

Scattering factors f_i for the neutral atoms (25.26), correction terms for anomalous scattering (27) and values for the incoherent scattering (28,29) were taken from the literature. Corrections for the Breit-Dirac factor (30-32) were made.

Results and Discussion

When several complexes coexist in a solution, it is usually necessary to know the formation constants of the complexes for analyzing X-ray scattering data. The formation constants of $CdI_n^{(2-n)+}$ complexes ($n = 1 - 4$) have been reported in both water (19b,33) and DMSO (34). Since concentrations of metal ions, as well as anions, are so high in the sample solutions used in the present X-ray diffraction measurements, the formation constants determined in solutions of relatively low ionic media should be used with caution. The formation constants sometimes vary markedly with concentrations of reacting species and medium salts. For the analysis of the X-ray data, we used formation constants of the complexes given for the highest ionic strengths so far reported. In aqueous solutions, values determined in a 4 mol dm^{-3} $NaClO_4$ medium are available (19b). However, in DMSO solutions, the highest concentration of medium salts is 1 mol dm^{-3} NH_4ClO_4 (34). Although the concentrations of the sample solutions used in the present X-ray diffraction measurements are much higher than 1 mol dm^{-3} in the DMSO system, we used the literature values as a first approach for analyzing the data.

In solution A (and also D) only solvated cadmium ions are present, since complexes are not formed between Cd^{2+} and ClO_4^- ions. In the other solutions containing iodide ions several complexes may coexist. In solution B, Cd^{2+} and CdI^+ exist, together with very small amounts of CdI_2^0, CdI_3^- and CdI_4^{2-}, which are neglected in the course of the analysis of the scattering data. In solution C, only the CdI_4^{2-} complex is formed, since the solution contains a large excess of iodide ions. In solution E, almost all kinds of complexes from Cd^{2+} to CdI_4^{2-} can be formed, and therefore, analysis of the data is difficult and the result obtained for this solution may be less certain compared with the results in the other systems. In solutions F and G, both CdI_3^- and CdI_4^{2-} are present. In the former solution, the CdI_3^- complex may be the main species, while in the latter, CdI_4^{2-} is predominant.

Details of the analytical procedures of the scattering data obtained for these solutions have been described elsewhere (19b,20). Therefore, the final results are summarized in Table 2.

TABLE 2. Structural parameters for the cadmium iodide complexes in water and in DMSO.

Complex	Water	DMSO
$Cd(solvent)_n^{2+}$	$n = 6$ $r_{Cd-O} = \begin{cases} 2.31(2) \text{ Å} \\ 2.292(5) \text{ Å}^a \end{cases}$	$n = 6^b$ $r_{Cd-O} = 2.292(5)$ Å^b $r_{Cd\cdots S} = 3.42(1)$ Å^b
$CdI(solvent)_n^+$	$n = 5$ $r_{Cd-O} = 2.30(5)$ Å $r_{Cd-I} = 2.80(5)$ Å	$n = ?$ $r_{Cd-O} = 2.3(1)$ Å $r_{Cd\cdots S} = 3.4(1)$ Å $r_{Cd-I} = 2.75(1)$ Å
$CdI_2(solvent)_n^0$	-	-
$CdI_3(solvent)_n^-$	-	$n = 1$ $r_{Cd-O} = 2.3(1)$ Å $r_{Cd\cdots S} = 3.4(1)$ Å $r_{Cd-I} = 2.773(3)$ Å $r_{I-I} = 4.61(2)$ Å $\angle I-Cd-I = 112(1)°$
$CdI_4(solvent)_n^{2-}$	$n = 0$ $r_{Cd-I} = 2.79(1)$ Å $r_{I-I} = 4.56(2)$ Å $\angle I-Cd-I = 109°$	$n = 0$ $r_{Cd-I} = 2.790(3)$ Å $r_{I-I} = 4.57(1)$ Å $\angle I-Cd-I = 110.0(5)°$

^{a} Unpublished data. ^{b} M. Sandström, I. Persson and S. Ahrland, Acta Chem. Scand., A32, 607 (1978)

Raman spectra of aqueous cadmium iodide solutions with various $\bar{n}$ values ($\bar{n}$ = the ligand number: average number of iodide ions combined per cadmium atom) are shown in Fig. 1 (19b). Very similar spectra, except bands due to DMSO molecules, have been found for cadmium iodide solutions of DMSO (35).
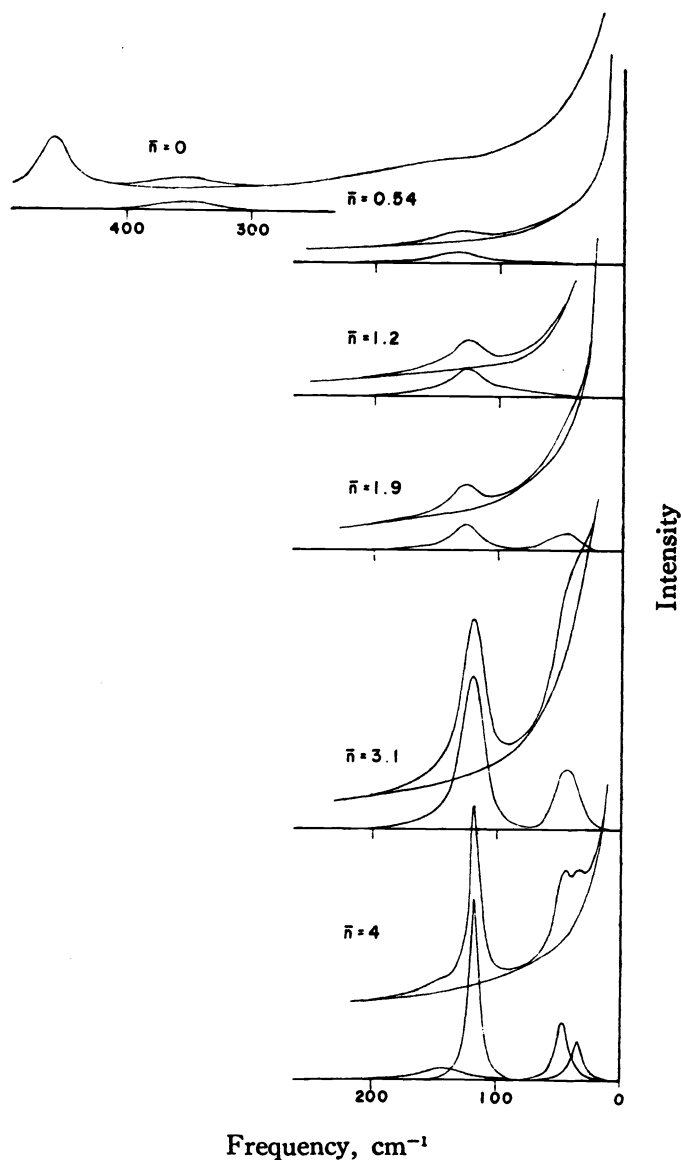

Fig. 1. Raman spectra of aqueous cadmium iodide solutions with various $\bar{n}$ values, together with resolved bands on the horizontal background (reproduced from Denki Kagaku, 45, 367 (1977)).

As is seen from Table 2, the Cd-I bond distance within the CdI[+] complex is essentially the same as that within the CdI_4^{2-} complex in water. The bond length within the latter complex is not dependent on the solvent. These results are different from those found in mercury halide solutions (36,37). Raman spectra of solution C (aqua solution) show four peaks over the range < 200 cm^{-1} (the lowest curve in Fig. 1), that is, 34, 46, 117 and 142 cm^{-1}, which are attributed to the frequencies due to the CdI_4^{2-} complex of T_d symmetry. A DMSO solution which contains the CdI_4^{2-} complex as the major species also shows Raman bands at 40 - 50, 115 and 142 cm^{-1} (35). Within experimental uncertainties, no significant difference can be found between the two spectra. Since

the bond lengths of the CdI_4^{2-} complex in water and in DMSO are the same, the strength of the Cd-I bond within the complex in these solvents is concluded to be the same, independent of the solvents (the b_{Cd-I} values of the CdI_4^{2-} complex in water and in DMSO are 0.004 Å^{-2} and 0.0035 Å^{-2}, respectively).

Although the bond lengths within the CdI_3^- complex in the aqueous solution have not been determined in the present study, a similar conclusion to that derived for the CdI_4^{2-} complex described above may be drawn for the CdI_3^- complex, because the Raman bands of the aqueous and DMSO solutions containing the CdI_3^- complex as a predominant species appear at similar positions in both solutions, i.e., 120 - 122 cm^{-1} (35). Although resolution of the peaks to bands attributed to each complex in the solutions could not be achieved, it may be expected that frequencies of the Cd-I bonds within the CdI_3^- complex are not significantly different in the solutions, and thus, the bond strengths within the complex may be similar in the two solvents.

However, enthalpies of formation of the CdI_3^- and CdI_4^{2-} complexes, as well as CdI^+ and CdI_2, are very different in these solvents (38). Values of $\Delta H°$ are more negative in water than in DMSO. On the other hand, $\Delta S°$ is more positive for all the complexes in DMSO than in water. As a result, $\Delta G°$ values of the complexes become similar in the two solvents (34) (see Table 3).

TABLE 3. Values of $\Delta G°$, $\Delta H°$ (kJ mol^{-1}) and $\Delta S°$ (J K^{-1} mol^{-1}) for the overall formation of the complexes $CdI_n^{(2-n)+}$ in water and in DMSO (34,38).

	Water (1 mol dm^{-3} NaClO$_4$)	DMSO (1 mol dm^{-3} NH$_4$ClO$_4$)
$\Delta G_1°$	-10.7	-12.5
$\Delta G_2°$	-15.3	-20.3
$\Delta G_3°$	-24.9	-37.1
$\Delta G_4°$	-32.5	-43.8
$\Delta H_1°$	-10.2	2.4
$\Delta H_2°$	-12.3	29.4
$\Delta H_3°$	-18.2	24.4
$\Delta H_4°$	-35.0	14.9
$\Delta S_1°$	2	50
$\Delta S_2°$	10	167
$\Delta S_3°$	22	207
$\Delta S_4°$	-11	197

Since the strengths of the Cd-I bonds within the CdI_4^{2-} complex (and perhaps within the CdI_3^- complex, too) may be approximately the same in water and in DMSO, the enthalpies and entropies of formation of the complexes can not be explained by different interactions between cadmium and iodide ions in these solvents, and the difference should be interpreted in terms of different ion-solvent interactions, i.e., cadmium and perhaps also iodide ions — water and DMSO molecules, in these media.

Since DMSO has a larger donor number (and a smaller acceptor number and a lower dielectric constant) than water, DMSO molecules probably react more strongly with the soft cadmium ions to form stable solvated ions than water molecules do.

Therefore, when DMSO molecules in the solvation shell are replaced by iodide ions, less negative $\Delta H°$ values than in the aqueous system may result. According to Ahrland, *et al.* (39), the enthalpy of solvation of free cadmium ion in DMSO is more negative by -67 kJ mol^{-1} than that in water.

On the other hand, release of solvent molecules which are strongly coordinated and well oriented to the central metal ion from the solvated cadmium ions may give rise to a larger entropy gain in DMSO than in water. As we see in Table 3 the entropies of formation of the $CdI_n^{(2-n)+}$ complexes in DMSO are always much more positive than those in water (38). Solvation of iodide is weak in both solvents (39). Interactions between the solvent molecules in the bulk and the iodide ions in the coordination sphere of a cadmium ion do not appreciably influence the strength of the Cd-I bonds, because no significant difference has been observed in the bond lengths and frequencies within the complexes examined in the two solvents.

References

1. a) W. H. Bragg and W. L. Bragg, Proc. Royal Soc. (London), A88, 428 (1913), b) W. L. Bragg, Proc. Royal Soc. (London), A89, 298 (1913), c) W. L. Bragg, Proc. Camb. Phil. Soc., 17, 43 (1913).
2. P. Debye and P. Scherrer, Nachr. Ges. Wiss. Göttingen, 1, 1 (1916).
3. H. H. Meyer, Ann. Physik, 5, 701 (1930).
4. G. W. Stewart, Phys. Rev., 35, 1426 (1930), 37, 9 (1931).
5. E. Amaldi, Physik. Z., 32, 914 (1931).
6. J. D. Bernal and R. H. Fowler, J. Chem. Phys., 1, 515 (1933).
7. a) A. Einstein and N. S. Gingrich, Phys. Rev., 57, 1054 (1940), 58, 307 (1949), 62, 261 (1942), b) D. G. Henshaw, Phys. Rev., 105, 976 (1957).
8. G. T. Clayton and L. Heaton, Phys. Rev., 121, 649 (1961).
9. R. M. Laurence and R. F. Kruh, J. Chem. Phys., 47, 4758 (1967).
10. J. N. Albright, J. Chem. Phys., 56, 3783 (1972).
11. F. Franks, Ed., Water - A Comprehensive Treatise, Vol. 1 - 6, Plenum Press, New York (1972 - 1979).
12. H. Ohtaki, Pure and Appl. Chem., in press.
13. A. K. Soper, G. W. Neilson, J. E. Enderby and R. A. Howe, J. Phys. Chem., 10, 1793 (1977).
14. M. Magini, J. Inorg. Nucl. Chem., 40, 43 (1978).
15. R. Caminiti, G. Licheri, G. Piccaluga and G. Pinna, J. Chem. Phys., 69, 1 (1978).
16. M. Born, Z. Physik., 1, 45 (1920).
17. a) V. Gutmann and E. Wychera, Inorg. Nucl. Chem. Letters, 2, 257 (1966), b) U. Mayer, V. Gutmann and W. Greger, Mh. Chem., 106, 1235 (1975).
18. V. Gutmann, The Donor-Acceptor Approach to Molecular Interactions, Plenum Press, New York (1978).
19. a) H. Ohtaki, M. Maeda and S. Ito, Bull. Chem. Soc. Jpn., 47, 2217 (1974), b) M. Tsurumi, M. Maeda and H. Ohtaki, Denki Kagaku, 45, 367 (1977).
20. S. Pocev, R. Triolo and G. Johansson, Acta Chem. Scand., A31, 179 (1979).
21. M. Sandström, I. Persson and S. Ahrland, Acta Chem. Scand., A32, 607 (1978).
22. J. Krogh-Moe, Acta Crystallogr., 9, 951 (1956).
23. N. Norman, Acta Crystallogr., 10, 370 (1957).
24. G. Johansson and M. Sandström, Chem. Scr., 4, 195 (1973).
25. D. T. Cromer and J. T. Waber, Acta Crystallogr., 18, 104 (1965).
26. R. F. Stewart, E. R. Davidson and W. T. Simpson, J. Chem. Phys., 42, 3175 (1969).
27. D. T. Cromer, Acta Crystallogr., 18, 17 (1965).
28. D. T. Cromer, J. Chem. Phys., 50, 4857 (1969).
29. A. H. Compton and S. K. Allison, X-Ray in Theory and Experiment, Van Norstrand, New York (1935).
30. G. Breit, Phys. Rev., 27, 362 (1926).
31. P. A. Dirac, Proc. Royal Soc. (London), A111, 405 (1926).
32. C. W. Dwiggins and D. A. Park, Acta Crystallogr., A27, 264 (1971).
33. L. G. Sillén and A. E. Martell, Ed., Stability Constants of Metal-Ion Complexes, Chem. Soc., Special Publications, Nos. 17 and 25, London (1964, 1971).

34. S. Ahrland and N.-O. Björk, Acta Chem. Scand., A30, 249 (1976).
35. H. Ohtaki and M. Maeda, unpublished data.
36. M. Sandström and G. Johansson, Acta Chem. Scand., A31, 132 (1977).
37. M. Sandström, Acta Chem. Scand., A32, 627 (1978).
38. S. Ahrland and N.-O. Björk, Acta Chem. Scand., A30, 257 (1976).
39. S. Ahrland, L. Kullberg and R. Portanova, Acta Chem. Scand., A32, 251 (1978).