

Structural studies on solvation and complexation of metal ions in nonaqueous solutions

Hitoshi Ohtaki

Department of Electronic Chemistry, Tokyo Institute of Technology at Nagatsuta,
Nagatsuta, Midori-ku, Yokohama, 227 Japan

Abstracts – Structures of solvated metal ions and metal complexes in non-aqueous solvents have been investigated by means of X-ray diffraction and the results are discussed in connection with thermodynamic quantities and spectroscopic data of these species. Solvation structures of alkali metal ions with special reference to lithium ion in formamide, of copper(II) in *N,N*-dimethylformamide (DMF) and in DMF - acetonitrile (AN) mixtures, and of cadmium(II) ion in DMF are discussed. Chloro and bromo complexes of copper(II) ion have been investigated in DMF, AN, DMF-AN mixtures and dimethyl sulfoxide (DMSO) solutions by spectrophotometric and calorimetric measurements, and the structure of the complexes with varying numbers of ligands is estimated. The X-ray diffraction analysis of the structures of the stepwise complexes has not been carried out in these solvents. Structural studies of copper(II)-chloro complexes in methanol by the X-ray diffraction and EXAFS methods and those of copper(II)-bromo complexes in methanol and in AN by the EXAFS method have been carried out to obtain the average structure of mixtures of the complexes. The structure of the tetrathiocyanatocadmiate(II) complex in DMF and DMSO has been compared with that in water. It has been found that the tetrathiocyanatocadmiate(II) complex has a regular tetrahedral structure and it has two N and two S atoms in water, while it contains three N and one S atoms in the first coordination sphere in DMF and DMSO.

INTRODUCTION

A number of methods have been proposed for the determination of solvation numbers of ions in water and in other solvents. In the historical point of view, such works have already appeared in the literature of the 1900's. Studies on solvation numbers of ions were extensively carried out in the 1930's and improvement of methods was continued until the 1960's. The methods so far employed in the classical studies are those of measuring static and dynamic properties of ions in solution in which solvated solvent molecules and bulk solvent are conventionally separated under some assumptions. Methods such as measurements of transference numbers and diffusion velocities of ions, conductivities and compressibilities of electrolyte solutions, emf's of electrolytic cells, various thermodynamic measurements (mean activity coefficients and solubilities of electrolytes, enthalpies and entropies of solvation of ions, heat capacities of solutions, etc.), dielectric constant measurements of electrolyte solutions, and so on, have been examined and various results have been reported. Excellent reviews have been published for the problem of ionic solvation in solution by several authors with critical surveys of solvation numbers of ions so far reported in the literature (refs. 1–5).

When nuclear magnetic resonance spectroscopy was applied to the determination of solvation numbers of ions in solution in the 1960's, a remarkable accumulation of data resulted, and it was believed that this modern method provides the most reliable result. However, when people tried to employ this method for some electrolyte solutions, metal ions which exchange solvent molecules very rapidly (substitution labile), they found that the analysis of NMR data is very difficult and sometimes leads to erroneous results. For this reason and others, few NMR measurements have been used in recent years for the determination of solvation numbers of ions in solutions.

The X-ray diffraction method of solutions has long been used for structural studies of molecular liquids, molten salts and liquid metals. However, the structural analysis of dissolved species in solution was not easy, because the necessary information is usually hidden behind structural data of solvents themselves, and therefore, we had to wait until high speed electronic computers and reliable equipment became available in order to apply this method to the structural analysis of electrolyte solutions.

By the X-ray diffraction method, as well as the neutron diffraction and EXAFS (Extended X-ray Absorption Fine Structure) methods, solvation numbers of ions and the bond lengths between ions and coordinated solvent molecules have been determined with high accuracies (ref. 5). The time and space averaged solvation numbers of ions thus determined are sometimes discussed in terms of the number of solvent molecules around the relevant ions in the instantaneous structure (structure within 10^{-15} s) estimated by computer simulations such as molecular dynamics (MD) and Monte Carlo (MC) methods.

Most studies on the structure of solvated ions and complexes in solution have been carried out in water, and very few results have been reported for non-aqueous systems. In this review, we summarize results obtained for the structures of solvated ions and complexes in some non-aqueous solvents and the structural data are discussed in connection with thermodynamic and spectroscopic data of the species found in the same solvents.

STRUCTURE OF SOLVATED METAL IONS IN NON-AQUEOUS SOLVENTS

Alkali metal ions

Solvation numbers of alkali metal ions in various non-aqueous solvents have mostly been determined by measuring the transference number of the ions in solvents. A few results have been obtained from conductivity measurements of alkali halides in organic solvents. Only one experiment, as far as I know, has been carried out by the X-ray diffraction method for the determination of the solvation number of lithium ion in formamide (the solvation number of chloride ion has also been determined in the same solvent). The results so far reported for solvation numbers of alkali metal ions in various non-aqueous solvents are summarized in Table 1.

The fractional solvation number of lithium ion in formamide obtained by the X-ray diffraction method indicates that it is an averaged number of various solvation numbers of lithium ions but the distribution of the solvation numbers remains unchanged with time, according to the view from studies of molecular dynamics simulations in aqueous solutions of lithium salts (refs. 15, 16). It may be surprising to see that the averaged solvation number of lithium ion in formamide determined by the X-ray diffraction method accidentally coincides with the value from the measurement of the transference number of the ion in the same solvent. It should be noted that the hydration number of lithium ion obtained by the measurement of the transference number in water is sometimes extremely large ($n = 22$ (ref. 17) and $13 - 14$ (ref. 18)) compared with that from the X-ray diffraction measurement ($n = 4 - 6$) (refs. 15, 16, 19).

TABLE 1. Solvation numbers of alkali metal ions in non-aqueous solvents

Solvent	Li ⁺	Na ⁺	K ⁺	Rb ⁺	Cs ⁺	Method	Ref.
Methanol	5.0	4.6	3.9	3.7	3.3	T	7
	3.3	3.9	3.6	-	-	C	8
Ethanol	5.8	3.8	3.3	3.1	2.9	T	7
	1.4	0.9	-	-	-	C	8
Acetone	2.7	2.6	2.5	-	-	T	7
Formamide	5.4	4.0	2.5	2.3	1.9	T	9
	5.4 ^a	-	-	-	-	X	10
<i>N</i> -Methylformamide	5.5	2.6	1.0	-	-	T	11
<i>N,N</i> -Dimethylformamide	5.2	3.3	2.9	-	-	T	11
	5.0	3.0	2.6	2.5	2.3	T	12
Acetonitrile	9	6	3	-	-	T	1
<i>N</i> -Methylacetamide	5.1	3.5	3.3	-	2.6	T	1
Dimethyl sulfoxide	3.3	3.1	2.8	2.3	2.0	T	13
Hexamethylphosphoramide	3.4	1.8	1.6	1.3	1.2	T	14
Propylene carbonate	3.4	2.9	2.4	1.7	1.6	T	13

T = Transference number, C = Conductivity, X = X-ray diffraction;

^a $r_{\text{Li-O}} = 224$ pm.

The length of the lithium-oxygen bond within the formamide-solvated lithium ion has been determined to be 224 pm (Fig. 1a) (ref. 10). The Li-O distance in water is 195 – 225 pm (Fig. 1b) (refs. 15, 16, 19-23) according to X-ray and neutron diffraction experiments, and thus similar distances are expected for any Li-solvent bonds in the non-aqueous solvents in Table 1, because all the solvents in the table have oxygen atoms as the coordinating ligand ones.

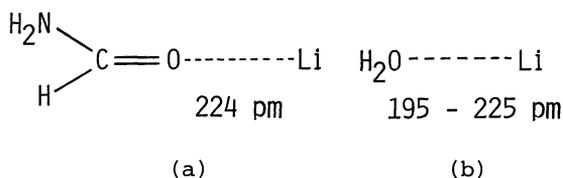


Fig. 1. The coordination structure of lithium ion with formamide (a) and water (b)

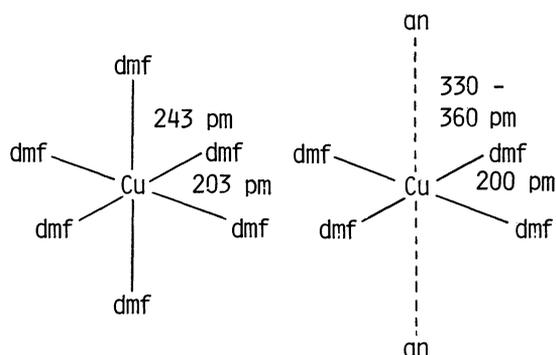


Fig. 3. The structure of solvated complexes of copper(II) ion. (a) $[\text{Cu}(\text{dmf})_6]^{2+}$ in DMF, (b) $[\text{Cu}(\text{dmf})_4]^{2+}$ in a mixture DMF:AN = 1:2 ($[\text{Cu}^{2+}] = 0.9388 \text{ mol dm}^{-3}$)

Copper(II) ion

Solvation of multi-charged ions, except for metal ions in group 2A, in non-aqueous solvents has scarcely been investigated, because most of these ions associate with counter anions in such solvents with relatively low dielectric constants, and thus reliable information for solvation of naked multi-charged ions is difficult to obtain in non-aqueous systems. Solvation equilibria of the copper(II) ion are calorimetrically and spectrometrically studied in pure DMF and in DMF-AN mixtures in which perchlorate ions are contained as the counter anions.

It is known that copper(II) ion has a distorted octahedral structure with an elongated axis in water, and the Cu-OH₂ distances are 194 pm within the plane and 243 pm along the axis (ref. 24). According to calorimetric studies on solvation of copper(II) ion with DMF in DMF-AN mixtures, solvated complexes $[\text{Cu}(\text{dmf})_n]^{2+}$ ($n = 1 - 4, 6$) form; the formation of $[\text{Cu}(\text{dmf})_3]^{2+}$ has not been confirmed. The distribution of the complexes is shown in Fig. 2 (ref. 25).

The $[\text{Cu}(\text{dmf})_6]^{2+}$ complex has a distorted octahedral structure, which is similar to that of the hexaqua copper(II) ion (see Fig. 3a) (ref. 26).

On the other hand, in a DMF-AN mixture with the mole ratio of 1 : 2 which contains copper(II) ion at $0.9366 \text{ mol} \cdot \text{dm}^{-3}$, Cu^{2+} ion forms a square planar complex. Neither DMF molecules nor AN molecules are along the elongated axis (ref. 26). The acetonitrile molecules detected at 330 – 360 pm from the central copper(II) ion are considered to be those in the bulk, because the distance is too long to have a direct interaction between copper(II) ion and the acetonitrile molecules. The absence of the axial solvent molecules within the complex is due to an insufficient amount of DMF molecules in the solvent which contains a relatively high concentration of copper(II) ions and to the weak solvation ability of AN to the ion (a small donor number of AN). The structure of solvated copper(II) ion in AN has not been determined by the X-ray diffraction method due to a low solubility of copper(II) perchlorate in the solvent.

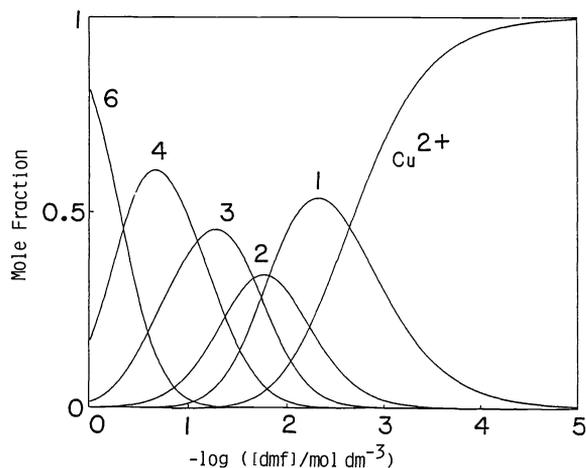


Fig. 2. Distribution of $[\text{Cu}(\text{dmf})_n]^{2+}$ complexes in DMF-AN mixtures as a function of the concentration of DMF in the solution. Numbers in the figure indicate the n values within the complexes (ref. 25).

According to Libús *et al.* (ref. 27), copper(II) ion is hexa-solvated with acetonitrile molecules in pure AN. In DMF-AN mixtures, acetonitrile molecules at the corners of the square plane of the complex are successively replaced with DMF molecules with increasing concentration of DMF. The axial Cu-AN bond may gradually elongate in the course of the substitution reaction due to strong electron donation from DMF molecules to the central ion and thus the copper(II) solvate complex with four DMF molecules forms a practically square planar structure. By the addition of more DMF molecules the $[\text{Cu}(\text{dmf})_4]^{2+}$ complex combines with two more DMF molecules to complete the distorted octahedral structure, as we observe in pure DMF solution.

The enthalpy of transfer of copper(II) ion from water to another solvent ($\Delta H_f^{\circ}(\text{Cu}^{2+}, \text{W-S})$) reflects the difference in the solvation energies of copper(II) ion in the solvents. As we can see from Fig. 4, the enthalpy of transfer of copper(II) ion from water to another solvent changes linearly with the donor number of the solvent (ref. 28).

Cadmium(II) ion

Structural determination of cadmium(II) ion in water has been carried out by the X-ray diffraction method and it is found that cadmium ion has six water molecules within the first coordination shell with the Cd-OH₂ distance of 231 pm (ref. 29). The structure of the solvated complex of cadmium(II) ion in DMSO has been studied by Sandström, *et al.* by the X-ray diffraction method (ref. 30) and they found that cadmium(II) ion is hexa-solvated with DMSO molecules through the oxygen atom and the Cd-O distance is 229.2 pm. The DMF-solvate complex of Cd²⁺ ion has a Cd-O bond length of 229.6 pm in the $[\text{Cd}(\text{dmf})_6]^{2+}$ complex which is very close to that in $[\text{Cd}(\text{dmsO})_6]^{2+}$ (ref. 31).

Other ions

The structures of the hexa-solvated complexes of zinc(II) and mercury(II) ions in DMSO have been investigated by Sandström, *et al.* (ref. 30) by using the X-ray diffraction method and Raman and infrared spectroscopies. It has been found from this work that the Hg-O distance is 239.3 pm, which is significantly longer than the length in the solid hexa-solvate. Although the octahedral structure of the solvated zinc(II) ion with DMSO molecules is elucidated by the spectroscopic methods, the length of the Zn-O bond has not been reported. The Zn-O and Hg-O bond lengths in water are 210 (ref. 32) and 240 pm (ref. 30), respectively. Both of the hydrated ions have the regular octahedral structure in water.

STRUCTURE OF COMPLEXES IN NON-AQUEOUS SOLVENTS

A number of investigations have been carried out for determining structures of metal complexes in various solvents and for studies of the solvent effect on the formation of various complexes. Thermodynamic measurements and spectroscopic investigations have most widely been employed for the studies. However, a very limited number of investigations have been reported in which the X-ray and neutron diffraction methods have been applied. NMR measurements have sometimes provided very useful information for the structure of complexes in non-aqueous solvents, and the method is extremely useful for kinetic studies of complex formation reactions in solutions.

It has often been pointed out that most complexes existing in non-aqueous solvents have similar structures to those in water, except for coordinated solvent molecules, but there are exceptions in which the structure of complexes in non-aqueous solvents differs remarkably from that in aqueous solutions.

Interesting work has been carried out by a group of Swedish solution chemists in the structural investigation of complexes in non-aqueous solutions. They also reported valuable data of thermodynamic quantities for complex formation reactions in various systems. In this review we focus our attention on the structure of thiocyanato complexes of some divalent metal ions in DMF and DMSO and then we try to elucidate the role of solvents in the formation reactions of the thiocyanato complexes of cadmium(II) ion in the solvents. Structures of some halogeno complexes of copper(II) ion in methanol, DMF, AN, DMF-AN mixtures and in DMSO have been reviewed in this paper, most of these investigations were carried out by Japanese solution chemists.

Chloro and bromo complexes of copper(II) ion

According to calorimetric and spectrophotometric studies of complex formation reactions of copper(II) chloro complexes in DMF, AN, DMF-AN mixtures and DMSO solutions, copper(II) ion forms a series of complexes $[\text{CuCl}_n]^{(2-n)+}$ ($n = 1 - 4$) (refs. 28, 33 - 35). Although no structural analysis by diffraction methods has yet been carried out, the $[\text{CuCl}_4]^{2-}$ complex is no doubt tetrahedral from the absorption spectra of the complex in these solvents. The formation of the $[\text{CuCl}_2]^0$ complex is weakest among the four of these solvents except in pure AN, in which the formation of the $[\text{CuCl}_2]^0$ complex is even stronger than the $[\text{CuCl}]^+$ and $[\text{CuCl}_3]^-$ complexes (see Fig. 5) (ref. 34). It should be noted that the formation of the $[\text{CuCl}_2]^0$ complex is suddenly suppressed when a small amount (0.025 mole fraction) of DMF is added to AN. The formation of $[\text{CuCl}]^+$ is also decreased by the addition of DMF

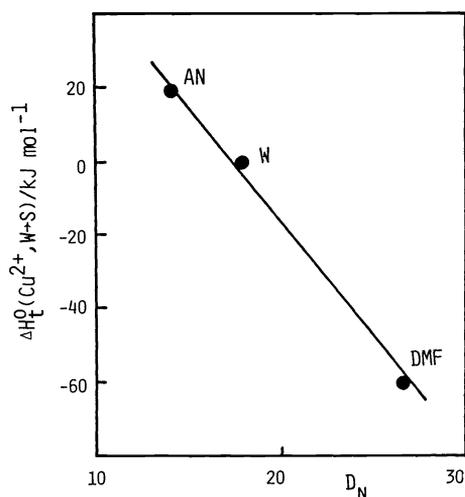


Fig. 4. Enthalpies of transfer of Cu^{2+} ion from water to acetonitrile (AN) and N,N -dimethylformamide (DMF) plotted against the donor number (D_N) of the solvents

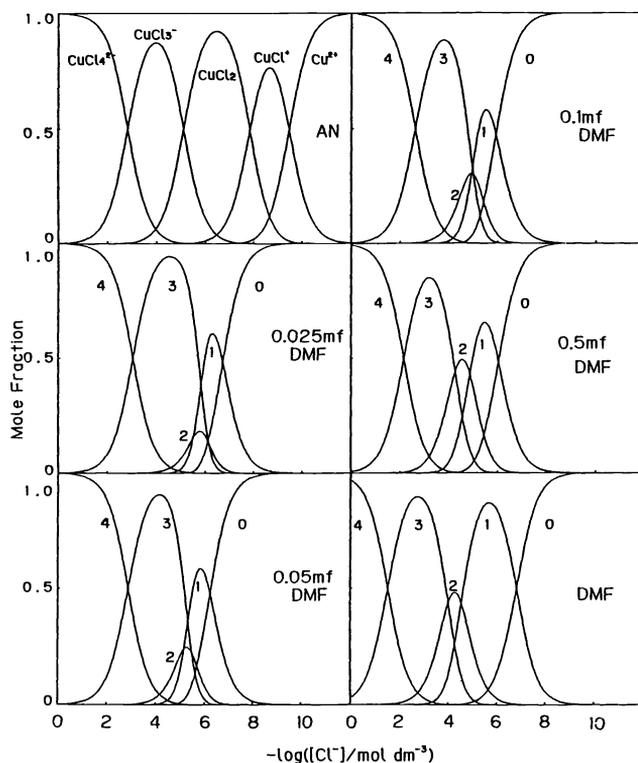


Fig. 5. Distribution curves of the copper(II) chloro complexes in various DMF-AN mixtures containing $0.2 \text{ mol dm}^{-3} (\text{C}_2\text{H}_5)_4\text{NClO}_4$ at 25°C (ref. 34)

to AN, but the formation is relatively enhanced when the concentration of DMF is increased. In pure DMF the $[\text{CuCl}]^+$ complex can exist as a main species under a suitable condition (*ca.* 90 mole % at $-\log([\text{Cl}^-]/\text{mol dm}^{-3}) \approx 6$). Distribution curves of the complexes in DMF and in DMSO containing $0.2 \text{ mol dm}^{-3} (\text{C}_2\text{H}_5)_4\text{NClO}_4$ as a constant ionic medium are similar but in a DMSO solution containing $1 \text{ mol dm}^{-3} \text{LiClO}_4$ as an ionic medium in which lithium ion forms ion-pairs with chloride ion, and the formation of the chloro complexes in the solution is more suppressed than in $0.2 \text{ mol dm}^{-3} (\text{C}_2\text{H}_5)_4\text{NClO}_4$ DMSO solution.

The absorption spectra of each complex in DMF, AN and DMSO solutions are shown in Figs. 6 – 8. The absorption spectra of the complexes are similar in general for all the solvents examined and the position of the peaks around 300 nm for the $[\text{CuCl}]^+$ and $[\text{CuCl}_2]^0$ complexes shifts slightly toward the higher wavelength side in AN compared to the peak positions of the complexes in DMF and DMSO. The formation constants of individual complexes are in the order $K_n(\text{AN}) > K_n(\text{DMF}) > K_n(\text{DMSO})$ at all n values. The enthalpy and entropy values of the complex formation reactions vary in a complicated manner in these solvents due probably to the structural changes in the course of individual complex formation reactions. The order of ΔH_n° and ΔS_n° values at a given n is not the same as that of K . It is suggested from the variation of the values of K_n (and ΔG_n°), ΔH_n° and ΔS_n° and the changes in the donor and acceptor numbers of the solvents, that the $[\text{CuCl}]^{n+}$ complex may have a distorted octahedral structure as $[\text{Cu}(\text{solvent})_6]^{2+}$ has, and $[\text{CuCl}_2]^0$ may also have a distorted octahedral structure in DMF and DMSO. However, the absorption spectrum of $[\text{CuCl}_2]^0$ in AN is rather different from that in the other two solvents, the result suggests that in AN the $[\text{CuCl}_2]^0$ complex may be in equilibrium between the Oh and Td structures. The $[\text{CuCl}_3]^-$ complex may be a distorted tetrahedron with weak bonding of one solvent molecule. The bonding may be weakest for AN, the donor number of the solvent ($D_N(\text{AN}) = 14.1$) being the smallest among water ($D_N = 18.0$), DMF (26.6), DMSO (29.8) and AN. The $[\text{CuCl}_4]^{2-}$ complex shows a typical absorption spectrum of the tetrahedral structure in all the solvents.

The X-ray diffraction analysis of the structure of chloro complexes of copper(II) ion in non-aqueous solutions has been demonstrated in methanol (ref. 36). When a certain amount of copper(II) chloride was dissolved ($1.055 - 3.251 \text{ mol dm}^{-3}$) in methanol, Ichihashi, *et al.* found that a mixture of octahedral complexes $[\text{CuCl}_n(\text{CH}_3\text{OH})_{6-n}]^{(2-n)+}$ ($n = 1 - 3$) was formed, the Cu–O(eq), Cu–O(ax) and Cu–Cl(eq) distances being determined to be 192.6 – 196.0, 242.3 – 247 and 223.0 – 223.8 pm, respectively. Unfortunately, they could not separate the radial distribution curve of the mixture into individual ones, since they did not determine the formation constants of the complexes in methanol in advance, and thus the result they obtained is not conclusive. Tajiri and

Wakita (ref. 37) have applied the EXAFS method to analyse the structure of methanolic CuCl_2 solutions, but the conclusion derived by the diffraction method previously examined by themselves was not improved from the EXAFS experiment.

Similar experiments have been carried out for CuBr_2 methanol solutions (ref. 38) and $\text{CuBr}_2 + x\text{LiCl}$ ($x = 1$ and 2) acetonitrile solutions (ref. 39). The structural data obtained from the EXAFS measurement gave average bond distances and average coordination numbers of $[\text{CuBr}_n]^{(2-n)+}$ complexes in the solutions and no further analysis of the data to separate into those of individual complexes was not possible.

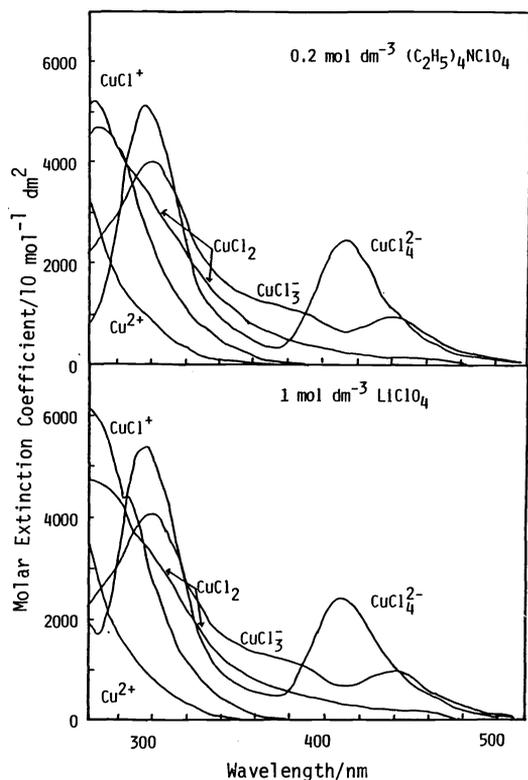


Fig. 6. Electronic spectra of individual copper(II) chloro complexes in DMF

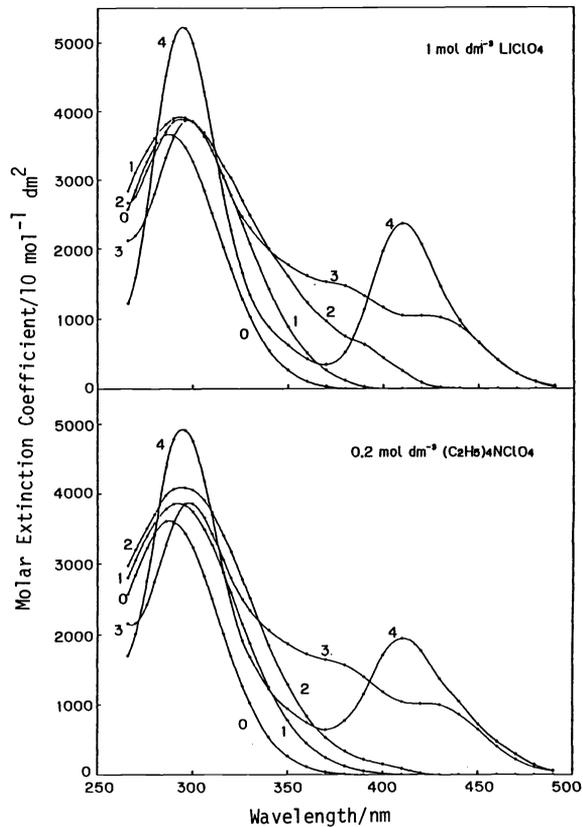


Fig. 8. Electronic spectra of individual copper(II) chloro complexes in DMSO

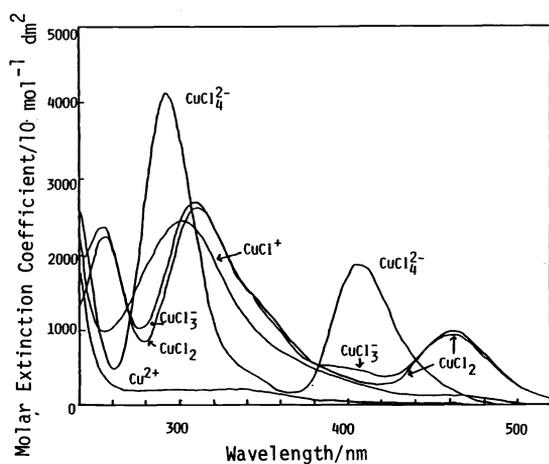


Fig. 7. Electronic spectra of individual copper(II) chloro complexes in AN

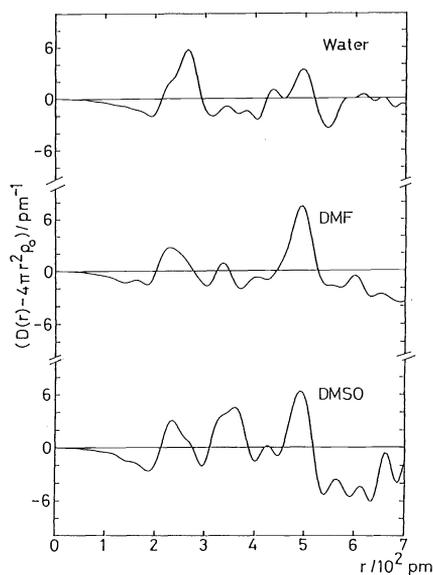


Fig. 9. Differential radial distribution curves of the tetrathiocyanatocadmate(II) complex in water, DMF and DMSO (refs. 40, 43)

Thiocyanato complexes of divalent metal ions

It has been found that the tetrathiocyanatozincate(II) and tetrathiocyanatomercurate(II) complexes are nitrogen- and sulfur-coordinated ones, respectively, *i.e.*, $[\text{Zn}(\text{NCS})_4]^{2-}$ and $[\text{Hg}(\text{SCN})_4]^{2-}$, in water, while the tetrathiocyanatocadmiate(II) complex has two nitrogen and two sulfur atoms in the coordination shell of the complex in water (refs. 40, 41). From calorimetric, Raman and NMR spectroscopic measurements, the coordination sequence of thiocyanate ions to a cadmium ion in water was considered as follows: $[\text{Cd}(\text{SCN})\text{Cd}]^{3+}(\text{Oh}) \rightarrow \text{Cd}^{2+}(\text{Oh}) \rightarrow [\text{Cd}(\text{NCS})]^+(\text{Oh}) \rightarrow [\text{Cd}(\text{NCS})(\text{SCN})](\text{Oh}?) \rightarrow [\text{Cd}(\text{NCS})_2(\text{SCN})]-(\text{Td}?) \rightarrow [\text{Cd}(\text{NCS})_2(\text{SCN})_2]^{2-}(\text{Td})$. Oh and Td denote the octahedral and tetrahedral structures of the complexes, respectively, and ? means that the structure suggested is not confirmed.

The structures of the tetrathiocyanatozincate(II) and tetrathiocyanatomercurate(II) complexes in DMSO have been determined by the X-ray diffraction method and it is seen that they have the same coordination structures as those in water (ref. 42). According to the results of Persson, *et al.* (ref. 42), cadmium(II) ion is coordinated with sulfur atoms in the $[\text{Cd}(\text{SCN})_2]$ and $[\text{Cd}(\text{SCN})_3]^-$ complexes in DMSO. However, in the structural analysis of cadmium thiocyanate DMSO solution with an excess amount of ammonium thiocyanate, with the average ligand number n of the complexes existing in the solution being 2.0, we did not find evidence for the sulfur coordination of cadmium(II) ion from the radial distribution curve of the solution. The tetrathiocyanatocadmiate(II) complex in DMSO and DMF has been determined to have the structure $[\text{Cd}(\text{NCS})_3(\text{SCN})]^{2-}$, which is different from that in water. The difference is clearly seen from the differential radial distribution curves of the complex in water, DMF and DMSO (Fig. 9) (ref. 43) which are obtained by subtracting contributions of the intramolecular and intermolecular interactions of solvent molecules and intramolecular interactions within ammonium and thiocyanate ions. The first peak appearing around 220 – 270 pm is attributed to the Cd–N and Cd–S bonds within the complex in these solvents, while the peak observed at about 500 pm is due to nonbonding Cd...S interactions. Nonbonding Cd...N interaction is clearly observed in the differential radial distribution curve in the water system as a small peak at about 240 pm, but in the DMF and DMSO systems the peak arising from the Cd...N interaction is not well distinguishable from the main peak. The first peak is larger in the water systems than in the DMF and DMSO solutions, whereas the peak due to nonbonding Cd...N and Cd...S interactions is larger in the latter systems than in the former. The analysis of the radial distribution curves, as well as the structural functions of the tetrathiocyanatocadmiate(II) complex in water, DMF and DMSO solutions reveals that the complex has the structure of $[\text{Cd}(\text{NCS})_2(\text{SCN})_2]^{2-}$ in water, but $[\text{Cd}(\text{NCS})_3(\text{SCN})]^{2-}$ in DMF and DMSO. The bond lengths within the complexes are shown in Fig. 10. The formation of the binuclear $[\text{Cd}_2\text{SCN}]^{3+}$ complex was not detected in DMF and DMSO.

The different coordination structures of the tetrathiocyanatocadmiate(II) complex in water, DMF and DMSO may be ascribed to different solvation structures of thiocyanate ions in the solvents. Water having a large acceptor number may strongly solvate to the nitrogen site which is harder than the sulfur site, and thus the nitrogen atom less solvated in DMF and DMSO than in water may preferably coordinate to cadmium(II) ion. The electron acceptability of cadmium(II) ion may also be affected by the coordinating atoms. When a less solvated nitrogen atom which is a stronger electron donor compared to that of solvent molecules is coordinated to a cadmium(II) ion, the cadmium(II) ion may become softer than that within the hexa-solvated cadmium(II) complex. The second coordinating atom is either a softer sulfur atom or a less solvated nitrogen atom to combine with $[\text{Cd}(\text{NCS})(\text{solvent})_2]^+$ complex. Probably $[\text{Cd}(\text{NCS})]^+$ prefers the soft sulfur atom in water, because the nitrogen atom in water is still rather well solvated. On the other hand, in DMF and DMSO the less solvated nitrogen atom can attack the cadmium(II) ion to replace one solvent molecule with it to form $[\text{Cd}(\text{NCS})_2]$.

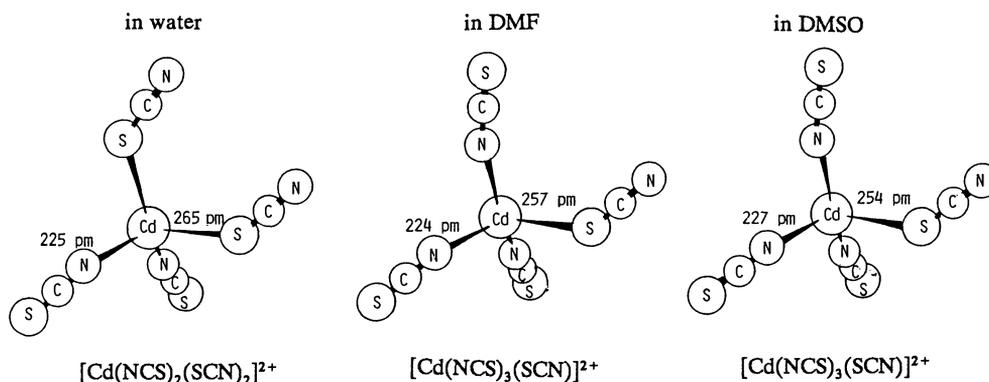


Fig. 10. The structure of the tetrathiocyanatocadmiate(II) complex in water, DMF and DMSO

The [Cd(NCS)(SCN)] complex in water changes the structure from octahedral to tetrahedral at the formation of the third complex. Libration of three solvent molecules from the coordination shell at the structural change may lead to decrease in the electron density of the cadmium(II) ion. Again a harder nitrogen atom may preferably combine with the cadmium(II) ion. We could not determine the structure of the trithiocyanatocadmium(II) complex in DMF and DMSO and the above described explanation for the change in the coordinating atoms is tentative and needs further studies to confirm. However, it is very interesting to note that the coordination structure of a complex is affected by the solvent.

Acknowledgement The financial support from the Ministry of Education, Culture and Science of Japan should be noted (Grant-in-Aid for Special Project Research, 61134043) for the achievement of this work. Computer calculations were carried out in the Tokyo Institute of Technology and the Institute for Molecular Science. Professor A. D. Kowalak kindly corrected the English.

REFERENCES

1. J. F. Hinton and E. S. Amis, *Chem. Rev.*, **71**, 627 (1971).
2. J. Burgess, *Metal Ions in Solution*, Ellis Horwood, Chichester, UK (1978).
3. K. Burger, *Solvation, Ionic and Complex Formation Reactions in Non-Aqueous Solvents*, Akademiai Kiado, Budapest, Hungary (1983).
4. Y. Marcus, *Ion Solvation*, John Wiley & Sons, Chichester, UK (1985).
5. H. Ohtaki, *Solution Chemistry* (in Japanese), Shokabo, Tokyo (1985).
6. H. Ohtaki, *Rev. Inorg. Chem.*, **4**, 103 (1982).
7. R. Gopal and H. M. Husain, *J. Indian Chem. Soc.*, **40**, 981 (1963).
8. D. S. Allam and W. H. Lee, *J. Chem. Soc.*, **A5**, 426 (1966).
9. J. M. Motley and M. Spiro, *J. Phys. Chem.*, **70**, 1502 (1966).
10. H. Ohtaki and H. Wada, *J. Solution Chem.*, **70**, 1502 (1966).
11. V. M. Ryabikova, B. S. Krumgal'z and K. P. Mishchenko, *Russ. J. Phys. Chem.*, **45**, 1451 (1971).
12. R. C. Paul, J. P. Singla, D. S. Gill and S. P. Narula, *J. Inorg. Nucl. Chem.*, **33**, 2953 (1971).
13. N. Matsuura, K. Umemoto and Y. Takeda, *Bull. Chem. Soc. Jpn.*, **48**, 2253 (1975).
14. R. C. Paul, J. S. Banait and P. Narula, *Z. phys. Chem., Frankfurt*, **94**, 199 (1975).
15. I. Okada, Y. Kitsuno, H.-G. Lee and H. Ohtaki, *Ions and Molecules in Solution*, Eds. N. Tanaka, H. Ohtaki and R. Tamamushi, Elsevier, Amsterdam, p. 81 (1983).
16. P. Bopp, I. Okada, H. Ohtaki and K. Heinzinger, *Z. Naturforsch.*, **40a**, 116 (1985).
17. A. J. Rutgers and Y. Hendrix, *Trans. Faraday Soc.*, **58**, 2184 (1962).
18. J. Baborovsky, *Z. phys. Chem.*, **A168**, 135 (1934).
19. T. Radnai, G. Pálkás, Gy. I. Szász and K. Heinzinger, *Z. Naturforsch.*, **36a**, 1076 (1981).
20. A. H. Narten, F. Vaslow and H. A. Levy, *J. Chem. Phys.*, **58**, 5017 (1973).
21. G. Licheri, G. Piccaluga and G. Pinna, *J. Appl. Crystallogr.*, **6**, 392 (1973).
22. J. E. Enderby and G. W. Neison, *Advan. Phys.*, **29**, 323 (1980).
23. N. Ohtomo and K. Arakawa, *Bull. Chem. Soc. Jpn.*, **52**, 2755 (1979).
24. H. Ohtaki and M. Maeda, *Bull. Chem. Soc. Jpn.*, **47**, 2197 (1974).
25. S. Ishiguro, B. G. Jeliaskova and H. Ohtaki, *J. Solution Chem.*, **16**, 1 (1987).
26. K. Ozutsumi, S. Ishiguro and H. Ohtaki, to be published.
27. W. Libús, M. Mečík and H. Strezelecki, *J. Solution Chem.*, **9**, 723 (1980).
28. S. Ishiguro, B. G. Jeliaskova and H. Ohtaki, *Bull. Chem. Soc. Jpn.*, **58**, 1749 (1985).
29. H. Ohtaki, M. Maeda and S. Itoh, *Bull. Chem. Soc. Jpn.*, **47**, 2217 (1974).
30. M. Sandström, I. Persson and S. Åhrland, *Acta Chem. Scand.*, **A32**, 607 (1978).
31. T. Takamuku, S. Ishiguro and H. Ohtaki, to be published.
32. H. Ohtaki, T. Yamaguchi and M. Maeda, *Bull. Chem. Soc. Jpn.*, **49**, 701 (1976).
33. S. Ishiguro, B. G. Jeliaskova and H. Ohtaki, *Bull. Chem. Soc. Jpn.*, **58**, 1143 (1985).
34. S. Ishiguro, B. G. Jeliaskova and H. Ohtaki, *Bull. Chem. Soc. Jpn.*, **59**, 1073 (1986).
35. S. Ishiguro, H. Suzuki, B. G. Jeliaskova and H. Ohtaki, *Bull. Chem. Soc. Jpn.*, **59**, 2407 (1986).
36. M. Ichihashi, H. Wakita and I. Maeda, *Bull. Chem. Soc. Jpn.*, **56**, 3761 (1983).
37. Y. Tajiri and H. Wakita, *Bull. Chem. Soc. Jpn.*, **59**, 2285 (1986).
38. Y. Tajiri and H. Wakita, *Nippon Kagaku Kaishi*, 1531 (1986).
39. M. Sano, T. Maruo and H. Yamatera, *J. Chem. Phys.*, **84**, 66 (1986).
40. T. Yamaguchi, K. Yamamoto and H. Ohtaki, *Bull. Chem. Soc. Jpn.*, **58**, 3235 (1985).
41. S. Ishiguro, K. Yamamoto and H. Ohtaki, *Bull. Chem. Soc. Jpn.*, **59**, 1009 (1986).
42. I. Persson, Å. Iverfeldt and S. Åhrland, *Acta Chem. Scand.*, **A35**, 295 (1981).
43. T. Takamuku, S. Ishiguro, K. Ozutsumi and H. Ohtaki, to be published.