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An X-Ray Diffraction Study on the Structure of Hexaamminecadmium(II) Ion in Aqueous Solution

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Synopsis. The structure of the hexaamminecadmium(II) ion in an ammoniacal aqueous solution of cadmium chloride was determined by the X-ray diffraction method at the NH_3/Cd mole ratio of 9.9. The result showed that a cadmium(II) ion is octahedrally surrounded by six ammonia molecules at the distance of (2.37±0.03) Å.

A number of equilibrium studies have been reported[1] for the complex formation between cadmium(II) ion and ammonia molecules, and structures of the complexes have mainly been investigated by spectroscopic ways.[2–5] The structure of the hexaamminecadmium(II) complex in the solid phase has also been studied by the Raman spectroscopy.[3] However, no X-ray crystallographic data are available, because no stable single crystal of the hexaamminecadmium(II) complex, as well as other cadmium ammine complexes, could be prepared. Therefore, we undertook to determine the structure of the hexaamminecadmium(II) complex in an aqueous solution by the X-ray diffraction method. An ammoniacal aqueous solution of $CdCl_2$ at the NH_3/Cd mole ratio of 9.9 has been used as a sample solution. In solutions of the NH_3/Cd mole ratio lower than 9.9, various ammine complexes can coexist, and thus, structural analyses of such solutions are not examined in the present work.

Experimental

The sample solution was prepared as previously described.[6] The solution was almost saturated with both cadmium(II) ion and ammonia. The concentration of cadmium(II) ion in the solution was determined both by EDTA titration using a BT indicator and by electrogravimetry. The results obtained by the two methods agreed each other within 0.2 %. Concentrations of ammonia and chloride ions were determined as described previously.[6] The atomic composition of the sample solution is given in Table 1.

X-Ray scattering data were obtained at (25±1) °C with a θ-θ diffractometer (JEOL Co., Tokyo) equipped with a Philips Mo-tube (Mo $K\alpha$: λ=0.7107 Å). Details of measurements and treatment of data are described elsewhere.[6,7] A Raman spectrum of the sample solution was measured with a JEOL JRS-S1 spectrophotometer using the 4880 Å Ar^+ laser excitation.

Table 1. The atomic composition (g-atoms/dm^3) and the stoichiometric volume V per cadmium atom for the solution

Cd	1.336
Cl	2.671
N	12.53
O	36.31
H	110.2
NH_3/Cd	9.9
density/g cm^{-3}	1.112
V/Å^3	1243

Results and Discussion

The $(D(r)-4\pi r^2\rho_0)$ and $D(r)$ curves obtained for the solution are shown in Figs. 1a and 1b, respectively. As can be seen from Fig. 1a, five peaks appear around 1.0, 2.4, 2.8, 3.2 and 4.6 Å (indicated by arrows). The small and broad peak at 1.0 Å is due to both O–H and N–H bonds within water and ammonia molecules, respectively. A shoulder locates at *ca.* 2.4 Å, the position being expected from the sum of the sizes of a cadmium(II) ion and an ammonia molecule (0.97 Å[8]+1.40 Å[9]= 2.37 Å). The peak around 3.2 Å can be ascribed to the Cl–O bond within the hydrated chloride ion.[10] The nearest O–O contacts in the bulk water-structure contribute to the shoulder around 2.8 Å.[11] The interatomic N–O distance of the NH_3–H_2O contacts in the ammoniacal aqueous solution[9] is almost the same as the O–O distance of the H_2O–H_2O contacts in the bulk.

In order to deduce the peak due to the Cd–N bond, the contributions of the nearest O–O and N–O contacts in the bulk medium and the Cl–O bonds within the hydrated chloride ions were subtracted from the $D(r)$ curve according to the following procedures. Since the X-ray method could hardly distinguish O from N atoms, the effective scattering factor, $f_X(s)=xf_N(s)+(1-x)f_O(s)$, was introduced in order to calculate the H_2O–H_2O and NH_3–H_2O interactions in the bulk phase (the NH_3–NH_3 contact was neglected because of the relatively low concentration of ammonia compared with the water concentration). The same scattering factor was used for the calculation of theoretical intensities of scattered X-rays from chloride ions solvated with water and, possibly, ammonia molecules. x represents the mole fraction of free ammonia: $x=[NH_3]_F/([NH_3]_F+[H_2O]_T)$, where $[NH_3]_F$ is assumed to be $[NH_3]_T-6[Cd^{2+}]_T$,[12] subscript T denoting the total concentration. f_N and f_O are the scattering factors of nitrogen and oxygen atoms, respectively. The values of 2.78 Å and 0.008 Å^2 were used as the distance and the temperature factor, respectively, of the H_2O–H_2O interaction in aqueous ammonia solution.[11] The same distance and temperature factor were used for the calculation of the NH_3–H_2O contacts.[9] The result is shown in Fig. 1b. Figure 1c shows the theoretical peak shapes of the atoms pairs which are taken into account in the present consideration. In this picture X means either O or N. A definite peak at 2.4 Å (chain line in Fig. 1b) can be ascribed to the Cd–N bond. The area under the peak

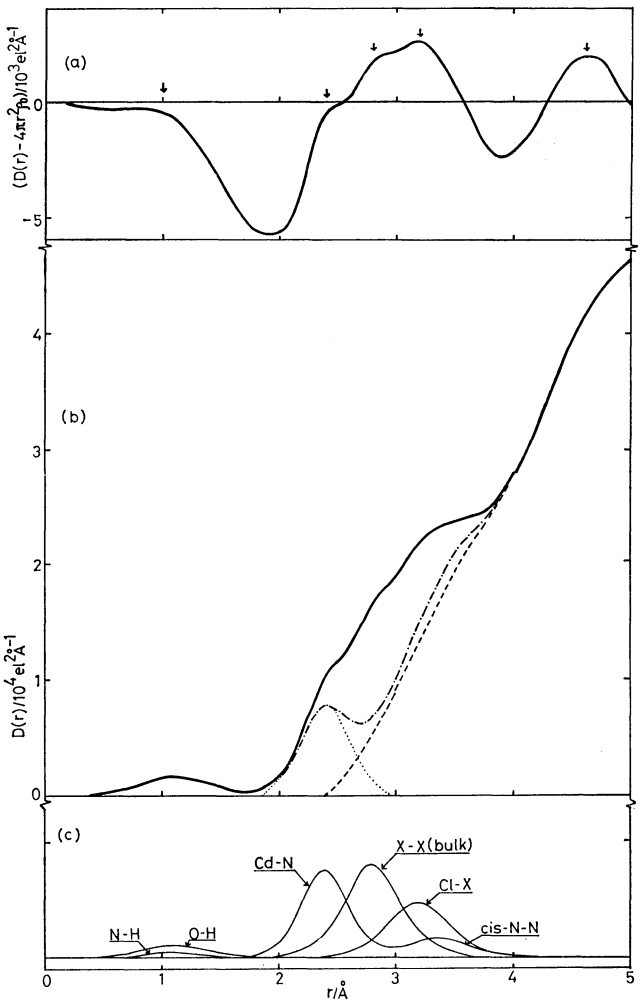

Fig. 1. The radial distribution curve of the sample solution. (a) The $(D(r)-4\pi r^2\rho_0)$ curve. (b) The $D(r)$ curve (solid line). The chain line shows the curve after subtraction of the theoretical peak shapes for the O–H and N–H bonds within H_2O and NH_3 molecules, respectively, the nearest neighbors X–X (*i.e.*, O–O and N–O) interactions in the bulk structure and the Cl–X bonds within the solvated chloride ions from the $D(r)$ curve. The dashed line shows the residual curve after subtraction of the theoretical peak shapes for the Cd–N and *cis*-N–N interactions within the hexaamminecadmium(II) complex. The dotted line is drawn by assuming that the curve having the maximum at 2.4 Å is Gaussian. (c) Theoretical peak shapes for each atom pair.

(dotted line) gave about six ammonia molecules neighboring with the central cadmium(II) ion. The peak can also be explained in terms of the formation of the $Cd(NH_3)_5(OH_2)^{2+}$ complex, because we cannot distinguish $Cd(NH_3)_6^{2+}$ ion from $Cd(NH_3)_5(OH_2)^{2+}$ ion by the present X-ray diffraction technique as far as the Cd–N bond length does not significantly differ from the length of the Cd–O bond. However, the Raman spectrum of the solution revealed a polarized band at (341 ± 2) cm^{-1}, which is assigned to the totally symmetric Cd–N stretching vibration. The frequency agreed well with that of the hexaamminecadmium(II) complex in the solid phase.[3] Therefore, we concluded that the hexaamminecadmium(II) complex is the main species in the present sample solution and that the peak at 2.4 Å is due to six Cd–NH_3 bonds. Subtraction of the theoretical peak due to the Cd–NH_3 bonds, together with the peak due to the *cis*-N–N contacts within the complex, from the residual curve (chain line in Fig. 1b) led to a smooth background curve (dashed line). The Cd–N bond distance finally determined was (2.37 ± 0.03) Å. The bond is slightly longer than the Cd–OH_2 bond (2.31 Å) within the hexaaquacadmium(II) ion.[7]

No other intramolecular interaction could be found, since no appreciable peak was observed in the background curve in the range of $r<4$ Å.

The broad peak around 4.6 Å may be related to the interactions between cadmium(II) ions and ligand molecules (water and ammonia molecules and chloride ions) in the second coordination layer.

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