Molecular Species in Concentrated Aqueous Solutions of Cadmium Halides as Inferred from the Raman Spectra

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Dedicated to Jannik Bjerrum on the occasion of his 70th birthday

The depolarization ratio of the (strong) totally symmetric Raman bands from aqueous solutions of $CdCl_2$ and of $CdBr_2$ has been measured and interpreted as evidence for molecular species of cubic symmetry. A comparison of the band frequencies with those obtained from single crystal spectra indicates that cadmium chloride complexes of octahedral as well as of tetrahedral symmetry exist in such solutions, but lends no support for assuming the presence of octahedral (besides tetrahedral) $CdBr_n^{(n-2)-}$-species.

In connection with a systematic investigation of the Raman spectra of solid cadmium halogen complexes it became of interest to have some quantitative idea about the depolarization ratios for cadmium halides in aqueous solutions. Although the Raman spectra of solutions of these compounds have been investigated several times in the past[1-5] numerical data for the depolarization ratios have apparently not been published.

EXPERIMENTAL

From concentrated or saturated aqueous stock solutions of pure LiCl, LiBr, $CdCl_2$ or $CdBr_2$, solutions as indicated in the first column of Table 1 were prepared. The halogen contents in the stock solutions were determined by Volhard titration and the densities were obtained by weighing a fixed volume of each solution. These data together with a knowledge of the volumes of the solutions which have been mixed together allow a calculation of the concentrations of cadmium and halogen in each solution given in the second and third column of Table 1.

The Raman spectra were recorded on a spectrometer equipped with a Jarrel-Ash model 25–101 double grating monochromator and an EMI 9659 extended S-20 photomultiplier tube. The source of excitation was the 4880 Å line from a Spectra-Physics model 165-00 argon ion laser. The spectra were recorded with the electric vector of the scattered radiation being perpendicular as well as parallel (*i.e.* horizontal) to that of the exciting light. A polarization scrambler was placed immediately before the entrance slit of the spectrometer. During two such consecutive recordings all other experimental conditions were kept constant. The intensities were measured by drawing the intensity curves and the estimated background curves on tracing paper, cutting out the areas framed of the two curves and weighing the paper cuts. The main contribution to the uncertainty of the intensities originates from the difficulty in estimating the background curve. Calibration of wavelengths (and depolarization ratios) was done with carbon tetrachloride, the Raman spectrum of which was recorded on top of the solution spectra all starting from the same nominal wavelength. The uncertainty on the wavenumbers for the peak intensities is usually $2-3$ cm^{-1}, but may be as high as 5 cm^{-1} when it is difficult to localize the peak of intensity as in the case of the two $CdCl_2$-solutions in the third and fourth rows of Table 1.

For the depolarization ratios the uncertainty varies because new bands develop and overlap with the bands in which we are mainly interested. For the solutions of $CdCl_2$, except the one in the fourth row of Table 1, it is presumably less than 0.02. In the case of $CdBr_2$ the measured depolarization ratio for the symmetrical stretching mode

Table 1. Measured Raman frequencies $\Delta\tilde{v}$ in cm^{-1} and depolarization ratios for the symmetrical stretching modes of CdX_n-complexes in aqueous solutions with varying amounts of halide ions.

	C_{Cd} mol/l	C_X mol/l	Density g/cm³	$\Delta\tilde{v}$ cm⁻¹	ρ_1
$CdCl_2$(sat.)	4.5	9.0	1.66_9	233	0 – 0.02
1 vol $CdCl_2$(sat.) + 1 vol H_2O	2.3	4.6	1.34_7	233	0
1 vol $CdCl_2$(sat.) + 5 vol H_2O	0.7_7	1.5_3	1.13_3	240	0
1 vol $CdCl_2$(sat.) + 11 vol H_2O	0.3_8	0.7_6	1.06_6	broad, overlapped	
1 vol $CdCl_2$(sat.) + 1 vol LiCl (conc.)	2.3	10.4	1.46_8	256	0.02
1 vol $CdCl_2$(sat.) + 5 vol LiCl (conc.)	0.7_6	11.3	1.32_1	250	0
1 vol $CdCl_2$(sat.) + 11 vol LiCl (conc.)	0.3_7	11.2	1.25_2	250	0
$CdBr_2$(sat.)	3.1_5	6.3	1.71_7	159	0.05
1 vol $CdBr_2$(sat.) + 1 vol H_2O	1.5_7	3.1_5	1.35_8	160	0.08
1 vol $CdBr_2$(sat.) + 5 vol H_2O	0.5_4	1.0_7	1.14_3	162	0.18
1 vol $CdBr_2$(sat.) + 11 vol H_2O	0.2_6	0.5_3	1.06_8	161	0.3_4
1 vol $CdBr_2$(sat.) + 1 vol LiBr (conc.)	1.5_3	8.6	1.66_0	162	0.06
1 vol $CdBr_2$(sat.) + 5 vol LiBr (conc.)	0.5_1	10.3	1.66_2	159	0.05
1 vol $CdBr_2$(sat.) + 11 vol LiBr (conc.)	0.2_6	10.4	1.65_2	161	0.07

varies from 0.05 to 0.34 indicating that we are dealing with overlapping bands with different depolarization ratios.

Raman spectra of single crystals of hexagonal K_4CdCl_6 and of hexagonal $CsCdBr_3$ were also obtained. The crystals were prepared by slow evaporation of aqueous solutions containing the constituent compounds. In K_4CdCl_6 we have isolated $CdCl_6^{4-}$-octahedra,[6] but in $CsCdBr_3$ the $CdBr_6^{4-}$-octahedra are stacked on top of one another so as to share the basal faces.[7] The frequencies measured for the symmetrical stretching modes were: 231 cm⁻¹ for K_4CdCl_6 and 169 cm⁻¹ for $CsCdBr_3$ which are in reasonable agreement with published data: 229 cm⁻¹ for K_4CdCl_6,[8] 172 and 143 cm⁻¹ for orthorhombic $RbCdBr_3$.[9]

DISCUSSION

Offhand it would not appear to be too difficult from the Raman spectra of an aqueous solution of a cadmium halide to deduce which molecular species exist in it. But practically it turns out that often there are not sufficient details in the spectra as only the most prominent bands (such as the symmetric stretching modes) show up. Hence the usual arguments based on application of the selection rules to molecular species of an assumed symmetry become of dubious value. Also, in aqueous solutions of complexes several molecular species arising from chemical equilibria may co-exist and thus give rise to extra bands in the Raman spectra. On the other hand some species may be very labile and con-

tinuously exchanging water molecules or other ligands so quickly that the vibrational states of such species become ill-defined. For these reasons we must resort to a comparison of characteristic features of the Raman bands such as frequency at peak intensity, depolarization ratio, band shape *etc.* with those of the same compounds obtained under different circumstances — or of related compounds. Raman spectra of crystals with their structure known from X-ray analysis and which contain the assumed molecular species may often prove helpful. An analysis of the Raman spectra of molten cadmium chloride, molten cadmium bromide and their molten mixtures with alkali metal halides has actually been performed along these lines by Clarke, Hartley and Kuroda.[8]

In special cases measurements of the depolarization ratio, ρ_1, of the Raman bands due to totally symmetric stretching modes may be useful, namely when as here the result it close to zero. For molecules of cubic symmetry (octahedral or tetrahedral) it can be shown that for the totally symmetric stretching modes $\rho_1 = 0$.[10] Hence the measured depolarization ratios of aqueous solutions of $CdCl_2$ are strong evidence for the existence of octahedral or tetrahedral species, $CdCl_n^{(n-2)-}$. For $CdBr_2$ in aqueous solution the increase of ρ_1 with dilution shows that the Raman band around 160 cm⁻¹ is composite and not single. The lowest value for ρ_1 is measured for $CdBr_2$ in LiBr-solutions and it is likely that in these solutions we also have $CdBr_n^{(n-2)-}$-species with either tetrahedral or octa-

hedral symmetry. To decide between the latter two possibilities we may draw on arguments given by Clarke, Hartley and Kuroda.[8] These authors make the following proposition on the basis of a comparison of Raman frequencies measured for the symmetrical stretching modes of complex Cd-halides in the crystalline and molten states: High vibrational frequencies for the symmetric stretching modes are associated with terminal Cd-X-bonds involving Cd with low net coordination numbers and low charge neutralization. According to the same authors Raman frequencies in the range $219-250$ cm^{-1} from cadmium chloride complexes may be associated with stretching modes involving octahedral complexes with shared or unshared Cl-ligands. Frequencies above this region should then be evidence of a lower coordination number for Cd.

The Raman frequencies given in Table 1 agree fairly well with published frequencies for aqueous solutions of tetrahedral $CdCl_4^{2-}$: 250,[3] 260 cm^{-1},[4] and of tetrahedral $CdBr_4^{2-}$: 166,[1] 163,[3] 159,[4] 161 cm^{-1}.[5] But the assumption of tetrahedral CdX_4^{2-}-species being present in aqueous solutions leans heavily on the interpretation of the Raman spectra given by Delwaulle et al.[1,3] which is based on the agreement between the number of observed Raman bands and their state of polarization with the selection rules applied to tetrahedral species. In the light of what has been said above, this procedure may be questionable. However, if we accept the higher Raman frequencies (above 250 cm^{-1} for $CdCl_2$-solutions) as being evidence for tetrahedral species and the lower Raman frequencies as evidence for octahedral species then the shift of peak intensity in the $CdCl_2$-solutions from 233 to 250 cm^{-1} for the totally symmetric Raman band indicates a change from octahedral to tetrahedral coordination around the Cd-atoms.

As for $CdBr_2$ in aqueous solutions the low values of the depolarization values for the Raman band with peak intensity about 161 cm^{-1} indicates the presence of molecular species with cubic symmetry. From the work in Ref. 8 it appears that in molten solutions of $CdBr_2$ in KBr there are trends similar to those observed for the $CdCl_2-KCl$-system and the Raman frequency is close to that assigned to $CdBr_4^{2-}$ in molten sodium or potassium nitrate. From investigations of the Raman spectra of crystals of $RbCdBr_3$ and $CsCdBr_3$ the $Cd-Br$-stretching modes for $CdBr_6^{4-}$-octahedra sharing Br-atoms are associated with frequencies at 169 and 172 cm^{-1}. In this case there is no real evidence from the

Raman spectra for octahedral $CdBr_6^{4-}$-complexes in aqueous solutions.

In view of the uncertainties which still exist about which molecular species occur in aqueous solutions of the cadmium halogen complexes, Raman investigations of crystals where cadmium is tetrahedrally coordinated ($RbCdI_3.H_2O$) or trigonal bipyramidally coordinated ($[Cr(NH_3)_6][CdCl_5]$) will be interesting and are in progress.

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