CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
CORNELL UNIVERSITY, ITHACA, NEW YORK 14850

Raman Study of Stepwise Formation of Bromide Complexes of Zinc, Cadmium, and Mercury in Aqueous Solution[1]

BY JOHN W. MACKLIN[2] AND ROBERT A. PLANE

Received September 2, 1969

Through a quantitative investigation of the variation in Raman spectra with solution composition and with temperature in the range 20–95°, spectra are found for the first time characteristic of the mono-, di-, tri-, and tetrabromo complexes of Zn, Cd, and Hg(II). In addition to symmetrical stretching frequencies for all twelve complexes, bending frequencies are found for all three tetrabromo species and for the tribromo complexes of Zn and Cd. A three-line spectrum is indicated for $ZnBr_2$ (polarized lines at 60 and 206 cm^{-1} and a depolarized line at 250 cm^{-1}) consistent with a nonlinear structure. In contrast, $CdBr_2$ appears to exist in water as a polymeric species. The molar intensities for the A_1 stretching mode of each of the aqueous complexes is determined and found to increase with the number of Br atoms bound per metal ion, except that the tribromo species gives slightly more intensity than does the tetrabromo species. From the molar intensities, species concentrations are determined along with their temperature dependence. These are used to calculate equilibrium concentration quotients and apparent thermodynamic parameters for the aqueous equilibria which are discussed in terms of ion hydration.

Introduction

Few methods for characterizing complex species in electrolyte solutions are as direct as the use of Raman spectroscopy. Unfortunately, in some cases the Raman method fails to detect certain species indicated by less direct techniques. A case in point is the bromides of zinc, cadmium, and mercury. Despite the fact that these salts are sufficiently soluble for Raman measurements to be made and the fact that their intensities are relatively high, no Raman studies to date[3-11] have found all the various MBr_n^{2-n} species indicated by other techniques.[12-14] The present study was undertaken to extend previous measurements to broader concentration ranges and to higher temperatures in order to see whether various species were detectable under any conditions and to characterize them as completely as possible. Of particular interest is the question whether or not the species having fewer than four bound bromides also contain solvent H_2O in the first coordination sphere.

Experimental Section

AR grade chemicals were used throughout. For determination of stoichiometric concentrations, solutions were prepared quantitatively in cases where reagents could be dried and weighed accurately. In other cases, standard analyses were performed. Zinc was precipitated and weighed as $ZnHg(SCN)_4$; bromide, as AgBr. Perchloric acid, which served as an internal Raman intensity standard, was determined by titration against sodium carbonate. All stock solutions were filtered under pressure through ultrafine sintered glass. All of the solutions studied were colorless.

Raman sample cells were constructed such that water from a thermostated bath could be circulated through a concentric jacket without affecting the spectral background. Such tubes had a 10-mm inside diameter and contained about 20 ml. Temperature differences between water entering the cell and leaving it never exceeded 2°. Raman spectra were measured with a Cary Model 81 Raman spectrophotometer using the 4358-Å line of a low-pressure mercury arc for excitation.

The Raman spectrum of any solution was measured repeatedly (4–16 times) with the internal standard (A_1 line of ClO_4^-) measured alternately with the M–Br Raman line. Such measurements were repeated at 20, 40, 60, 80, and 95°. In an attempt to eliminate error in fixing the (slanted) base line for each spectrum, the same solutions were run while wrapped with a polaroid film (plane of polarization parallel to cell axis) which for the polarized bands in question greatly lowered the intensity of the band while causing no significant changes in the background. Further blank runs using distilled water and NaBr and/or the group IIb metal perchlorate solutions having concentrations comparable to those containing group IIb bromides and using the same instrument settings at which the latter solutions were studied showed no bands due to water at 60 and 166 cm^{-1}. Overlapped bands were resolved with the aid of a Du Pont 310 analog computer.

The bands which could be isolated were copied on the curve resolver (*e.g.*, the A_1 line for $ZnBr_4^{2-}$) and this shape was used with varied band width for all bands near in frequency and due to vibrations of the same symmetry class. This approximation appears valid since the shapes of all the bands due to A_1 stretching modes of the MBr_n^{2-n} species in triethyl phosphate solutions are the same for a given metal and have the same shape as that found for the aqueous solutions. The empirical shape of the bands due to A_1 stretching modes is between Gaussian and Lorentzian, and that of the bending modes is closer to Gaussian.

Results

Zinc–Bromide Solutions.—In the first series of experiments, 12 solutions were prepared which contained zinc ion and bromide ion at a total concentration

---

[1] Supported by a research grant from the Office of Saline Waters, U. S. Department of Interior. Presented at the 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968.

[2] Presented in partial fulfillment of the requirements for the Ph.D. degree.

[3] H. Braune and G. Engelbrecht, *Z. Physik. Chem.*, **B19**, 303 (1932).

[4] M. L. Delwaulle, F. Francois, and J. Wiemann, *Compt. Rend.*, **208**, 1881 (1939).

[5] M. L. Delwaulle and F. Francois, *ibid.*, **212**, 761 (1941).

[6] J. A. Rolfe, D. E. Sheppard, and L. A. Woodward, *Trans. Faraday Soc.*, **50**, 1275 (1954).

[7] M. L. Delwaulle, *Bull. Soc. Chim. France*, 1294 (1955); *Compt. Rend.*, **240**, 2132 (1955).

[8] J. P. Mathieu, *J. Inorg. Nucl. Chem.*, **8**, 33 (1958).

[9] W. Yellin and R. A. Plane, *J. Am. Chem. Soc.*, **83**, 2448 (1961).

[10] D. F. C. Morris, E. L. Short, and D. N. Waters, *J. Inorg. Nucl. Chem.*, **25**, 975 (1963).

[11] J. H. R. Clarke and L. A. Woodward, *Trans. Faraday Soc.*, **61**, 207 (1965).

[12] L. G. Sillén, *Acta Chem. Scand.*, **2**, 828 (1948).

[13] L. Eriksson, *ibid.*, **7**, 1146 (1953).

[14] A. Swinarski and M. Baranowna-Tarasiuk, *Chem. Anal.* (Warsaw), **11**, 563 (1966).

of 4.0 *M*, plus ClO_4^- to serve as Raman intensity standard. In the series, the ratio of total Br^- to Zn^{2+} varied from 0.18 to 6.0. Raman spectra were measured at 20 and 95°. Each spectrum contained at least one polarized Raman line in the 200 ± 50 cm^{-1} region. Particularly at the higher temperature it was evident that four separate polarized lines are present at various concentration ratios throughout the series. These frequencies, characteristic of four chemical species, occur at 240, 206, 183, and 171 cm^{-1}. The area of each band is given in Table I. All but the first of these have been observed previously.[9,10] The previous failure to observe it results from its very low intensity at room temperature and the fact that it obtains its maximum intensity for solutions containing less than one Br^- per Zn^{2+}. Thus, the previous assignments must be revised. With large excess of Br^-, only the species characterized by the polarized 171-cm^{-1} band is evident. This species which also shows depolarized Raman bands at 214, 81, and 57 cm^{-1} has previously been characterized as tetrahedral $ZnBr_4^{2-}$.[7-10] From the fact that this highest species has but four coordinated bromides and the observation that the other three species occur at progressively lower Br^- to Zn^{2+} ratios allows unequivocal assignment of the 183-cm^{-1} band to the 3:1 complex, 206 cm^{-1} to the 2:1 complex, and 240 cm^{-1} to the 1:1 complex.

TABLE I

MEASURED RAMAN INTENSITIES FOR AQUEOUS ZINC–BROMIDE SOLUTIONS

$[Br^-]/[Zn^{2+}]$	Areas at 20°				Boltzmann corrected areas at 95°			
	240	206	183	171	240	206	183	171
0.18	0.84	8.10	5.9	4.5	5.43	13.2	3.7	3.3
0.37	0.35	8.94	10.7	5.7	3.81	19.2	8.9	3.4
0.60	1.34	8.96	13.4	8.3	3.87	26.3	16.9	4.6
0.90	1.93	8.58	14.2	10.3	1.34	28.6	19.6	8.6
1.50		6.60	15.5	10.9	1.65	25.6	25.0	12.2
2.00		6.25	17.1	13.4	0.37	22.3	32.0	15.4
2.50		5.36	16.9	16.1		20.7	33.0	17.8
3.00		5.46	16.8	19.7		18.4	33.2	21.6
3.50		4.39	15.2	20.4		16.5	33.1	23.5
4.00		4.26	14.2	22.1		14.7	32.0	27.0
5.00		3.68	12.7	24.5		11.2	27.7	31.3
6.00		2.22	11.1	23.7		7.8	24.9	35.6

In order to obtain the complete Raman spectrum of each complex, a series of seven experiments was performed in which the concentration of zinc ion was maintained at 2.0 *M* while bromide was increased from 1.0 to 12.0 *M*. Some of the spectra from this series are given in Figure 1. Included in the figure is an analysis of the low-frequency, bending, region. For the highest ratio, two low-frequency bands are observed (81, 57 cm^{-1}). At lower bromide to zinc ratios two additional bands are seen (71, 49 cm^{-1}). Also at lower ratios, it is noted that although the intensity of the 81-cm^{-1} band of the 4:1 species has decreased markedly, the lower frequency band has not shown a corresponding decrease. This is attributed to the appearance of another low-frequency band, near 60 cm^{-1}, characteristic of the 2:1 species. Further support of this result comes from the fact that, in polarization studies, the new band appears to be polarized while the 57-cm^{-1} band is not. Polarization measurements are also useful in analyzing the higher frequency region for the appearance of additional depolarized bands. All the bands are listed in Table II.

TABLE II

RAMAN BANDS OF ZINC–BROMIDE COMPLEXES[a]

Complex	Freq, cm^{-1}			
$ZnBr^+$		240 (p)		
$ZnBr_2$	250	206 (p)		60 (p?)
$ZnBr_3^-$	244	183 (p)	71	49 (p?)
$ZnBr_4^{2-}$	214	171 (p)	81	57

[a] Polarized bands indicated by p.

In addition to the bands listed in Table II, zinc solutions show a characteristic band at higher frequency (382 cm^{-1}) which is due to symmetric stretching of waters of hydration of the zinc ion. To see whether this band arises only from zinc ion free of bromide or whether it also reflects hydration of zinc–bromide complexes, its band profile and intensity were measured as a function of bromide to zinc concentration ratio. Qualitatively, there were no changes in the band shape. Quantitatively, the intensity decreased with added bromide at least as fast as the concentration of uncomplexed zinc decreased. Therefore, it seems that this band is characteristic of uncomplexed zinc, and Raman frequencies characteristic of hydration of zinc–bromide complexes have intensities too low to be seen.

Cadmium–Bromide Solutions.—Spectroscopic studies were made on four series of solutions. In two of these, the total concentration of cadmium plus bromide was constant (at 2.70 and at 4.0 *M*) while the bromide to cadmium ratio varied between 0.25 and 8.0. In the other two series, cadmium was maintained constant at 0.5 *M* with bromide varied from 0.5 to 6.0 *M* and at 3.0 *M* with bromide varied from 0.3 to 3.0 *M*. In all cases, the Raman spectra consisted of a broad band in the stretching region (near 166 cm^{-1}) and a lower frequency envelope centered between 50 and 60 cm^{-1}. Unlike the zinc bromide case, the spectra do not resolve into distinct maxima. In this case, frequencies due to different chemical species apparently are more badly overlapped. That there is more than a single complex species was shown previously through measurements of intensity changes with bromide to cadmium ratio.[9] This result is also found in the present studies, reinforced by observations on changes of band shape with solution composition. These changes include a shift of asymmetry from one side of the peak maximum to the other, an 8–10-cm^{-1} shift in position of the maximum, a variation of more than a factor of 2 in band width at half-height, and a variation in depolarization ratio for the total area under the contour.

In order to analyze the changes in contour, two procedures were used. In the first, band height, normalized through use of perchlorate internal intensity standard, at 5-cm^{-1} intervals, was plotted *vs.* bromide to cadmium ratio. Such plots are not smoothly varying

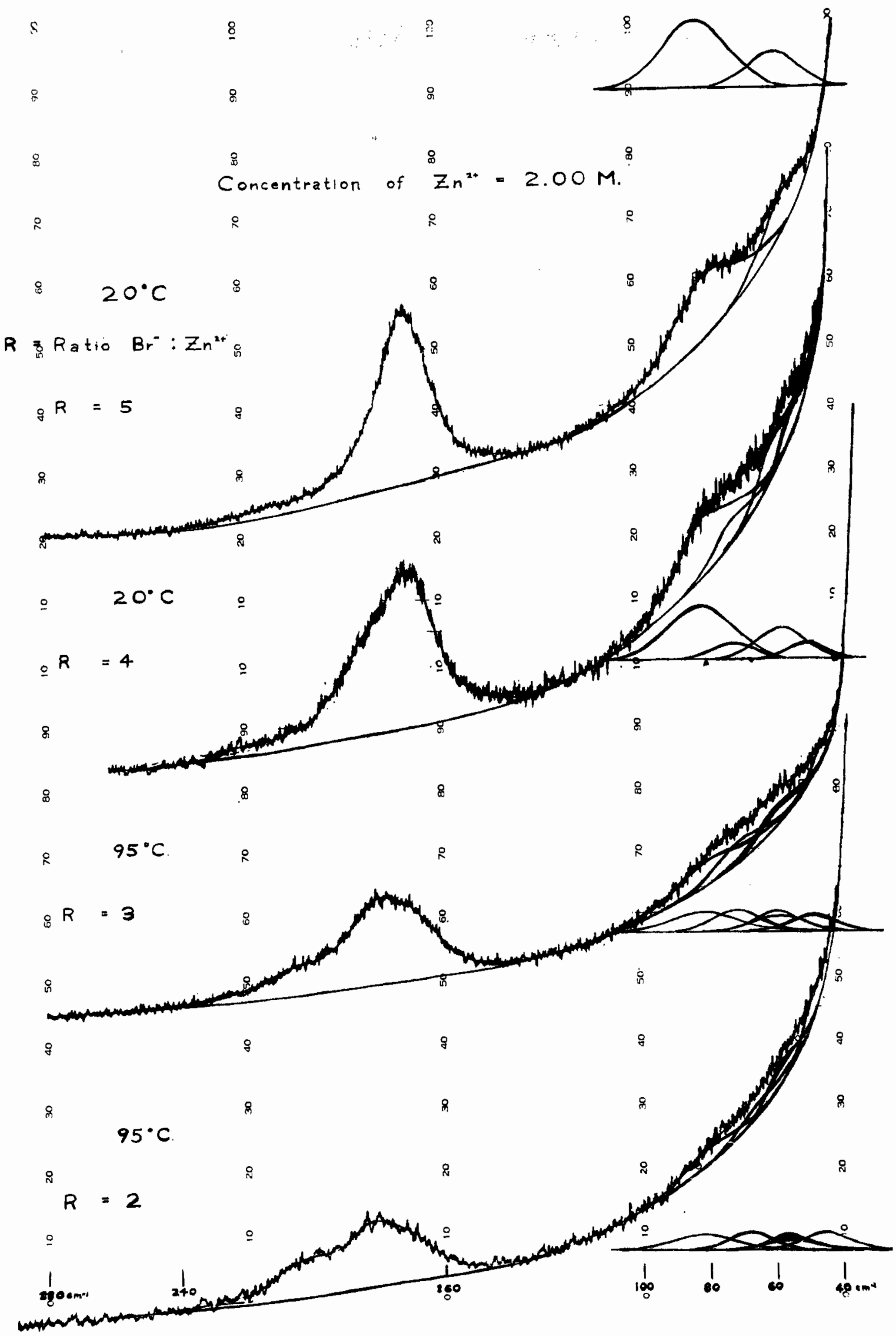

Figure 1.—Raman spectra of zinc–bromide solutions.

but show four maxima. Curiously the one which occurs near a bromide to cadmium ratio of 2 is most pronounced for frequencies lower than 160 cm^{-1} which is near the maximum for the 4:1 complex. The other two maxima are prominent at higher frequencies and occur at ratios near 3:1 and 1:1. Thus, some of the difference between the cadmium and zinc systems is apparently due to the unusual situation for cadmium that progressive addition of bromide to the complex does not cause a progressive lowering of the observed A_1 frequency. Instead, the 2:1 species seems to have the lowest frequency.

The second method for analyzing the overlapped spectra involved use of the analog computer to reconstruct all observed spectra from four individual spectra maintaining constant frequency and empirically determined band shape for each of the four components. Such fitting was completely successful and correlated

TABLE III

MEASURED RAMAN INTENSITIES FOR AQUEOUS CADMIUM–BROMIDE SOLUTIONS

$[Br^-]/[Cd^{2+}]$	Areas at 20°				Boltzmann corrected areas at 95°			
	200	146	173	161	200	146	173	161
0.25	2.74	14.6	8.2	4.9	3.34	13.4	18.2	4.7
0.50	2.68	21.5	11.2	9.4	3.42	21.8	22.6	9.8
0.75	1.92	23.5	11.0	11.5	4.10	24.4	27.8	12.8
1.00	3.46	29.6	12.9	17.0	5.62	31.6	36.7	20.9
1.50	2.95	36.6	17.7	26.9	3.64	35.9	44.0	39.3
2.00	2.02	37.3	21.2	40.4	2.85	31.4	50.3	60.0
2.50	1.08	29.1	22.6	55.0	2.38	22.7	52.7	82.8
3.00	0.61	19.0	23.3	79.7	1.80	16.5	52.4	110.8
3.50		9.5	19.0	107.3	0.94	13.0	43.9	126.3
4.00		7.3	16.0	123.9		6.5	33.8	143.5
5.00		2.8	9.7	126.3		1.8	20.8	151.8
6.00			4.8	115.0			11.0	147.8

with the results obtained by the alternate method. Results, including the areas used, are listed in Table III.

Other frequencies were similarly analyzed and polarization measurements were made. These are summarized in Table IV. The Cd–H_2O stretching frequency occurs at *ca.* 356 cm^{-1}. As for zinc, it showed a progressive decrease in intensity on addition of Br^- and so provided no evidence for hydration of the bromo complexes. Except for the anomalously low frequency observed for the polarized band of $CdBr_2$, the results are quite similar to those for zinc. The difference could arise if $CdBr_2$ polymerized in solution. Several experimental observations support such polymerization. (1) The Raman intensity due to $CdBr_2$ has a temperature dependence which is opposite from that of any other included in this study; that is, the intensity is decreased with increasing temperature as is likely for depolymerization. (2) $CdBr_2$ dissolved in triethyl phosphate is expected to be monomeric and the Raman spectrum of this solution shows one polarized band at 185 cm^{-1}, consistent with this expectation but clearly different from that for $CdBr_2$ in water. (3) The behavior of the 166-cm^{-1} band contour with varying concentrations of $CdBr_2$ in water indicates a concentration dependence of the spectral intensity at 146 cm^{-1} and higher frequencies consistent with an equilibrium of the type: $CdBr_4 \rightleftharpoons CdBr^+ + CdBr_3^-$. (4) The Raman spectrum of the monomeric cadmium bromide–triphenylphosphine complex $((C_6H_5)_3P)_2CdBr_2$[15] has a CdBr stretching frequency near 185 cm^{-1} while solid complexes with *o*-toluidine, *m*-toluidine, and aniline, which are known to contain bromide bridges,[16] have a broad feature near 146 cm^{-1} characteristic of the aqueous species.

TABLE IV

RAMAN BANDS OF CADMIUM–BROMIDE COMPLEXES

Complex	Freq, cm^{-1}			
$CdBr^+$		200 (p)		
$(CdBr_2)_x$	*Ca.* 240	146 (p)		
$CdBr_3^-$		173 (p)	73 (p?)	44
$CdBr_4^{2-}$	183	161 (p)	59	49

Mercuric Bromide Solutions.—The Raman spectra of aqueous solutions of mercuric bromide with either excess bromide ion or excess mercuric ion were measured at 20 and 95°. Six solutions with excess Br^- and total concentration of $Hg(II) + Br^- = 4.0\ M$ were investigated. The stoichiometric ratios of Br^- to Hg(II) in these solutions were 12, 7, 6, 5, 4, and 3, with the last two having some solid $HgBr_2$ in equilibrium with the solution. The Raman spectra of solutions with $[Br^-]/[Hg(II)]$ equal to or greater than 5 were all identical at both 20 and 95°. This spectrum, attributed to $HgBr_4^{2-}$, consists of a very intense polarized line at 165 cm^{-1} and two weak bands at 47 and 52 cm^{-1} appearing as shoulders on the Rayleigh line. Although the spectrum is similar to that reported previously,[4,6] we note an asymmetry on the low-frequency side of the 165-cm^{-1} band which becomes especially apparent when the spectrum is measured with parallel polarized light. A band placed near 150 cm^{-1} makes up the asymmetry. An asymmetric stretching frequency has been assigned below the symmetric frequency in other mercury halide complexes.[17] This asymmetry is also evident in the spectrum of a triethyl phosphate solution having $[Br^-]/[Hg(II)]$ equal to 4.

In the Raman spectra of the remaining solutions of the series, the 165 cm^{-1} band is broadened by an asymmetry on its high-frequency side at 95° for the $[Br^-]/[Hg(II)] = 4$ solution and at 20 and 95° for the one with the lower ratio. The excess width in these spectra is fit perfectly by a band at 180 cm^{-1} having the same shape as the 165-cm^{-1} band. The 180-cm^{-1} band is also polarized. Previous workers have found a polarized line at 180 cm^{-1} in the Raman spectrum of an equimolar solution of $HgBr_2$ and LiBr in triphenyl phosphate.[18] We observe the same line in such mixtures in triethyl phosphate and so attribute it to ν_1 of $HgBr_3^-$.

Solutions were also studied in which Hg(II) greatly exceeded total bromide ($[Br^-]/[Hg(II)] = 0.20$, 0.15, 0.09). In these cases, the strongest feature is a polarized line at 238 cm^{-1}. A band near this frequency has previously been assigned to $HgBr^+$.[11] However, in order to account for the entire spectrum, some intensity must be attributed to the 180-cm^{-1} band of $HgBr_3^-$ and to the 165-cm^{-1} band of $HgBr_4^{2-}$ and in addition a polarized band located near 206 cm^{-1}. This band we assign to the symmetric stretching of $HgBr_2$ and note that a polarized band is found at 206 cm^{-1} for solutions of $HgBr_2$ in triphenyl phosphate[18] and in triethyl phosphate. The assignments for the mercuric bromide complexes are summarized in Table V.

TABLE V

RAMAN BANDS OF MERCURIC BROMIDE COMPLEXES

Complex	Freq, cm^{-1}			
$HgBr^+$		238 (p)		
$HgBr_2$		204 (p)		
$HgBr_3^-$		180 (p)		
$HgBr_4^{2-}$	150	165 (p)	51	47

---

[15] R. C. Evans, F. G. Mann, H. S. Peiser, and D. Purdie, *J. Chem. Soc.*, 1209 (1940).

[16] J. M. Haigh, M. A. Van Dam, and D. Thornton, *Z. Anorg. Allgem. Chem.*, **355**, 94 (1967).

[17] G. B. Deacon, J. H. S. Green, and W. Kynaston, *Australian J. Chem.*, **19**, 1603 (1966).

[18] D. F. C. Morris, E. L. Short, and D. N. Waters, *J. Inorg. Nucl. Chem.*, **26**, 902 (1964).

Molar Intensities and Species Concentrations.—In order to convert measured Raman intensities to species concentrations, it is necessary to know the proportionality constant, or molar intensity. This quantity can be obtained for solutions where the stoichiometric concentration of one component is known to be completely converted to a single species or to more than one species if the concentrations of all but one are independently known. For the present systems this procedure could be employed for a limited number of species as listed in Table VI. For the other species, two different methods were used. The first involved computer solutions to a series of linear equations for mass balances in terms of measured Raman intensities and unknown but constant molar intensities for each species. Because free Br^- has no Raman spectrum and free Zn^{2+} has only the single weak band due to the stretching mode of the hydrated ion, which could not be measured with sufficient accuracy, additional input was necessary in order to solve the simultaneous equations. This was done by assuming that free Zn^{2+} varied as a function of R, the stoichiometric ratio of Br^- to Zn^{2+} according to the expression $(\alpha + R)^{-\beta}$ where α and β are variable parameters. These parameters were each varied over the range 0.3–4, and best values of the resulting molar intensities were picked according to the following criteria: free Br^- concentration must increase with R, no negative values of any concentration or molar intensity can be allowed, values of independently measured molar intensities must be obtained, and the squared deviations of resultant molar intensities must be as near minimal as permitted by the other criteria. The results for zinc and cadmium are listed in Table VI. Because of solubility restrictions, mercuric bromide solutions could not be treated in this manner.

TABLE VI
COMPARISON OF MOLAR INTENSITIES DETERMINED BY VARIOUS METHODS

Method	M	MBr^+	MBr_2	MBr_3^-	MBr_4^{2-}
Direct—from solution stoichiometry	Zn			1.7	1.75
	Cd				3.30
	Hg	2		12	12.8
Least-squares computer fit	Zn	0.4	0.9	1.5–1.6	1.75
	Cd	0.5	0.7	3.5–3.6	3.30
Triethyl phosphate solutions	Zn		0.8	1.4	
	Cd		1.5[a]	3.2	3.1
	Hg		5.1	13	12.8
Values accepted	Zn	0.4	0.85	1.8	1.75
	Cd	0.5	0.7	3.7	3.30
	Hg	2.0	5.1	13	12.8

[a] For monomer.

The final method for determining molar intensities is based on the work of Morris, Short, and Waters.[18] It involves use of an organic solvent to change association constants such that solution species will closely correspond to stoichiometric concentrations. Thus, if a solution is prepared from equimolar $ZnBr_2$ and LiBr, the species $ZnBr_3^-$ will predominate. Implicit in this method is the assumption that solvation of the species does not affect Raman intensity. Since frequencies and band shapes do not seem to be affected significantly, this may be a valid assumption. Solutions were prepared of dry MBr_2 (0.4 M) and LiBr at molar ratios of 1:0, 1:1, and 1:2 in triethyl phosphate. Intensities were measured relative to a polarized solvent band at 735 cm^{-1} which was in turn measured relative to the standard 933-cm^{-1} line of ClO_4^-. Correction was made for variation in solvent concentration with added salt. The intensity of the band given by a triethyl phosphate solution of $ZnBr_2$ was measured at 30 and at 80°. The decrease in intensity at 80° could be accounted for by the Boltzmann intensity temperature factor.[19] This result is taken to indicate that all bromide is bound at both temperatures. The molar intensity values obtained from triethyl phosphate solutions are listed in Table VI. Agreement with the other methods used for aqueous solutions seems satisfactory.

Included also in Table VI are the values chosen as the most reliable, based on the various methods of determination, for the molar intensity of each complex species. The uncertainty limits of these accepted values are considered to be $\pm 5\%$ for the tetrabromo complexes, $\pm 10\%$ for the dibromo, and $\pm 20\%$ for both the monobromo and the tribromo. It should be noted that all values are relative to the A_1 line of ClO_4^- and contain no correction for sensitivity of our instrument, which is such that the values can be corrected by multiplying by 1.2. Also, it was found that the values did not show exactly the temperature dependence given simply by a Boltzmann correction. Such deviations have been noted previously.[20] For 20°, the values accepted are lower than those calculated using a Boltzmann correction and the 90° values by 3% for Zn, 5% for Cd, and 9% for Hg.

From the molar intensity values and measured Raman intensities, molar concentrations of individual complex species can be calculated. This has been done and is plotted in Figures 2 and 3 for zinc and cadmium solutions in which the sum of metal and bromide ion concentrations is 4.0 M in each case.

Conclusions

For the zinc bromide complexes, all but the 1:1 complex seem to show more than one Raman band as noted in Table II. The four-band spectrum found for $ZnBr_4^{2-}$ has previously been used to assign it a tetrahedral structure.[7,9,10] For $ZnBr_3^-$, the four-band spectrum, with two polarized bands, would indicate a pyramidal, C_{3v}, structure. Similarly, the three bands, two polarized for $ZnBr_2$(aq), indicate a bent, C_{2v}, structure. Additional evidence for the bent structure of $ZnBr_2$(aq) comes from contrast of the stretching frequencies with those of the anhydrous solid where the symmetric stretching frequency is *ca.* 165 cm^{-1} and the asymmetric, 276 cm^{-1}. Large frequency shifts do not usually accompany dissolution. The strong shift of the stretching frequencies toward each other in aqueous solution may indicate that the frequencies are due to a

---

(19) G. W. Chantry, *J. Chem. Phys.*, **32**, 222 (1960).

(20) A. I. Sokolovskaya, *Tr. Fiz. Inst., Akad. Nauk SSSR*, **27**, 61 (1965).

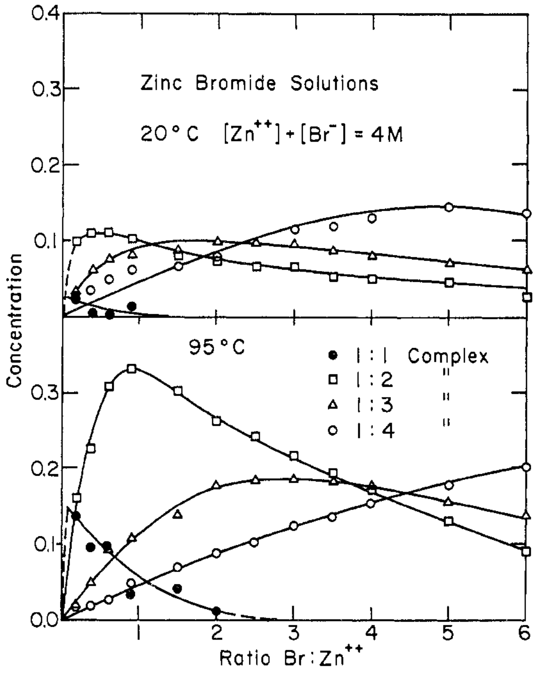

Figure 2.—Concentration of complex species in solutions of zinc and bromide.

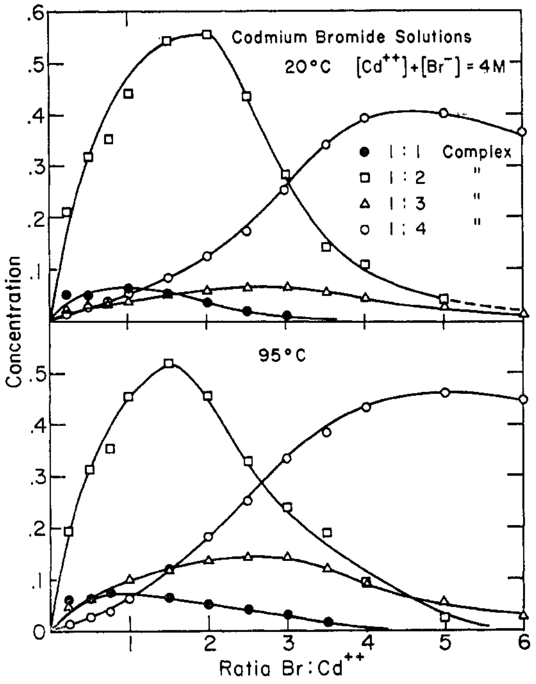

Figure 3.—Concentrations of complex species in solutions of cadmium and bromide.

bond disposition of lower symmetry. The lack of higher symmetry for aqueous $ZnBr_2$ and $ZnBr_3^-$ can be the result of hydration, and it was for this reason that Raman spectral evidence was sought for such hydration. The lack of such evidence, however, does not rule out the hydration because Raman bands due to hydration of simple cations with charge less than 2+ have never been observed. Apparently, in the species $ZnBr_2$ and $ZnBr_3^-$, the effective charge on Zn is less than sufficient to cause measurable Raman intensity.

Like the corresponding zinc complexes, $CdBr_4^{2-}$ and $CdBr_3^-$ are apparently tetrahedral and pyramidal, respectively. Failure to observe the asymmetric stretching mode of $CdBr_3^-$ is probably due to the severe overlapping of the various bands. Of greater importance in making the structure assignment is the presence of two low-frequency, bending modes as expected for C_{3v} symmetry but not for D_{3h}. The main difference between the cadmium and zinc bromide complexes lies in the apparent polymeric nature of $CdBr_2$. Cadmium halides are known to form polymeric compounds in cases where the corresponding zinc and cadmium compounds are monomeric,[16] a fact attributed to increased π-bond formation for cadmium. Also, there is evidence for polymerization of $CdCl_2$ in aqueous solution.[21]

Spectra of the mercuric bromide complexes are less complete than those determined for zinc and cadmium. This is principally due to solubility problems, although it is noted that for $HgBr_4^{2-}$ the A_1 mode is of greater intensity relative to the other bands than is true for zinc and cadmium. Thus the absence of detectable mercury bands should not be taken as indicative of structural differences. In fact, the A_1 frequencies for the mercuric bromide complexes are all quite similar to those for zinc bromides as would be demanded by similar structures.

Table VII

Stepwise Thermodynamic Parameters at 20° and a Total Concentration of M^{2+} + Br^- = 4 *M*

	MBr^+	MBr_2	MBr_3^-	MBr_4^{2-}
		Zn		
Log *Q*	−1.9	1.4	−0.2	−0.3
ΔH, kcal/mol	5.1	−3.1	−0.8	−0.3
$\Delta S°$, eu	8.7	−3.8	−3.5	−2.5
		Cd		
Log *Q*	−1.2	1.4[a]	−1.0[a]	0.4
ΔH, kcal/mol	2.7	−0.1[a]	3.8[a]	−0.4
$\Delta S°$, eu	3.7	6.0[a]	8.4[a]	0.7

[a] Consider polymer species in terms of $(1/n)(CdBr_2)_n$.

The molar intensities for the various complexes as listed in Table VI exhibit some interesting regularities. On the basis of simple theory,[9,22] it is to be expected that for the same metal, the molar intensity will be roughly proportional to the number of M–Br bonds. In fact, such a generalization further supports the conclusion that the aqueous $CdBr_2$ species is not monomeric (molar intensity based on assumption of monomeric species is much too low) while that in triethyl phosphate is monomeric. However, there is one significant departure of the data of Table VI from the approximate rule. It is the fact that in every case, the molar intensity of MBr_3^- is too large, slightly larger than that for MBr_4^{2-}. One cause for this discrepancy can be the fact that for symmetric species (*e.g.*, MBr_4^{2-}) only diagonal elements in the derived polarizability tensor contribute to Raman intensity while in less symmetric species (*e.g.*, MBr_3^-)

---

(21) J. E. D. Davies and D. A. Long, *J. Chem. Soc., A*, 2054 (1968).

(22) M. Wolkenstein, *Compt. Rend. Acad. Sci. URSS*, **32**, 185 (1941).

off-diagonal elements contribute as well.[23,24] Furthermore, at some point in the stepwise series, addition of a further Br^- would cause bond covalency to decrease preventing the metal ion from becoming too negatively charged. This decrease would in turn decrease the Raman intensity.[25] In any case it seems significant that the molar intensities of the various stepwise complexes formed from the same elements roughly obey the rule and do not vary by orders of magnitude. This is important since it means that if Raman studies fail to observe one or more of the stepwise complexes, these species do not occur in significant concentrations.

From the molar intensities, molar concentrations were determined. These are as displayed in Figures 2 and 3. If the molar concentrations are used to find equilibrium quotients as a function of temperature, apparent thermodynamic parameters may be derived. Values are listed in Table VII. All values refer to stepwise association equilibria $MBr_{n-1}^{(3-n)+} + Br^- = MBr_n^{(2-n)+}$ at 20° and a total concentration of $M + Br^- = 4\ M$. Within the range of 12 solutions there are no significant trends in the variation of Q with the ratio of Br^- to M^{2+}. Individual values of Q show a mean deviation of $\pm 40\%$. These deviations along with uncertainties in determination of molar intensities should mean that thermodynamic values have reliabilities corresponding to ± 1 kcal/mol. Because the standard states involved are those of concentrated solutions, the magnitude of the values should not be compared to that of the values obtained for the usual standard states. However, trends within the present values should be meaningful.

The enthalpy and entropy changes found for the zinc complexes are interesting in that both show special values for the first step of complex formation. These values are consistent with the indication from the Raman spectra that on formation of even the first bromide complex, hydration of the zinc ion is noticeably weakened. After the first step, the values follow a trend to be expected for addition of a Br^- to a progressively less positive, weakly hydrated zinc ion. For the cadmium complexes, a similar but somewhat smaller effect is observed for the first and last steps. Values for the two intermediate steps are not comparable since they involve the polymeric species characteristic of this system.

[23] L. A. Woodward, *Quart. Rev.* (London), **10**, 185 (1956).

[24] G. W. Chantry and R. A. Plane, *J. Chem. Phys.*, **32**, 319 (1960).

[25] T. V. Long, II, and R. A. Plane, *ibid.*, **43**, 457 (1965).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
MICHIGAN STATE UNIVERSITY, EAST LANSING, MICHIGAN 48823

The Preparation and Far-Infrared and Proton Magnetic Resonance Spectra of Some Tungsten(IV) and Tungsten(V) Chloride Alkoxide Dimers

BY WILLIAM J. REAGAN AND CARL H. BRUBAKER, JR.

Received October 27, 1969

Solutions of WCl_5 in several alcohols that were basic with alkoxide ions were investigated and the diamagnetic alkoxide compounds $W(OC_2H_5)_5$ and $W_2Cl_4(OC_3H_7)_6$ and the yellow, paramagnetic solid $NaW(OC_2H_5)_6$ were isolated. The reaction of WCl_4 with alcohols was also studied. Green, diamagnetic dimers $W_2Cl_4(OR)_4(ROH)_2$ ($R = CH_3$, C_2H_5, 1-C_3H_7, 2-C_3H_7) were obtained. The far-ir, optical, and pmr spectra of these compounds are presented.

In previous studies[1,2] of tungsten(V) alkoxide compounds, both monomers and dimers have been reported. We have now prepared and characterized several new W(V) and W(IV) dimers. The far-ir, optical, and pmr spectra of these compounds have been measured.

Experimental Section

Materials.—Solvents and other starting materials were purified as described in previous work.[1,2] All operations were carried out under dry N_2.

Tungsten tetrachloride was prepared by the red phosphorus reduction of WCl_6.[3] Some preparations were contaminated with small amounts of unreacted phosphorus. *Anal.* Calcd for WCl_4: W, 56.54; Cl, 43.54. Found: W, 55.70; Cl, 43.10.

$W_2Cl_4(OC_2H_5)_6$ and $W_2Cl_2(OC_2H_5)_8$.—These compounds were prepared as previously reported.[1]

$W_2Cl_4(OC_3H_7)_6$ (I).—A 4.9-g portion of WCl_5 (0.014 mol) was added to 15 ml of 1-propanol cooled to −78°. The temperature of the solution was gradually increased to 0°. A sodium propoxide solution (prepared by treating 0.66 g of Na, 0.028 g-atom, with 35 ml of 1-propanol) was added to the dark green solution. The solution became green-brown and sodium chloride separated. The sodium chloride was removed by centrifuging and decanting the supernatant liquid. The resulting solution was allowed to reflux for 1.5 hr and was then stored overnight at −10°. The dark red crystals were filtered, washed with a small amount of 1-propanol, and dried *in vacuo*. *Anal.* Calcd for $WCl_2C_9H_{21}O_3$: W, 42.58; Cl, 16.42; C, 25.01; H, 4.86. Found: W, 42.67; Cl, 16.49; C, 25.16; H, 4.88. The theoretical molecular weight of the dimer is 864. The mass spectrum gave a series of peaks in the region of 862–868 mass units.

$W_2Cl_2(OC_3H_7)_8$ (II).—This impure substance was prepared by the same procedure as I except that a sodium propoxide solution

---

[1] D. P. Rillema, W. J. Reagan, and C. H. Brubaker, Jr., *Inorg. Chem.*, **8**, 587 (1969).

[2] D. P. Rillema and C. H. Brubaker, Jr., *ibid.*, **8**, 1645 (1969).

[3] G. I. Novikov, N. V. Andeeva, and O. G. Polyachenok, *Russ. J. Inorg. Chem.*, **9**, 1019 (1961).