BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 264—265 (1970)

Study of Raman Spectra of Complex Halide Anions of Mercury(II) in Solution

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(Received April 2, 1969)

From a study of Raman spectra, Delwaulle[1–3] obtained evidence for the existence of mixed halide complex anions $[HgI_nCl_{4-n}]^{2-}$ and $[HgI_nBr_{4-n}]^{2-}$, but she failed to get definite evidence for the corresponding complex anions containing bromide and chloride. Woodward and co-workers[4] confirmed the formation of complex anions $[HgI_nBr_{4-n}]^{2-}$. Aggarwal[5] estalbished the existence of the complex anion $[HgCl_2Br_2]^{2-}$ from physico-chemical studies of the system $HgCl_2$-KBr-H_2O.

The aim of the present work is to investigate the formation of mixed halide (Cl^- and Br^-) complex anions of mercury(II) with the help of Raman spectra.

TABLE 1. [$HgCl_2$:KCl=1:2]-KBr-H_2O SYSTEM

Solution No.	Relative concentration			$\Delta\nu$ cm^{-1}	Intensity (visual)
	[Hg^{II}]	[Cl^-]	[Br^-]		
1	1	4	0	270	s
2	¼	4	0	272	s
3	¼	3⅞	⅛	270	s
4	¼	3¾	¼	255	m
5	¼	3½	½	191	w
				256	w
6	¼	3	1	190	m
7	¼	2½	1½	191	m
8	¼	2	2	191	s
9	¼	1¾	2¼	191	s
10	¼	1½	2½	188	s
11	¼	1¼	2¾	183	s
12	¼	1	3	182	s
13	1	0	4	170	s

The solutions corresponding to Table 1 were prepared by dissolving different amounts of KBr in solutions containing $HgCl_2$ and KCl always in the molar ratio$\geqslant$0.5. The Hg^{II}/(Halide) ratio was kept constant at 1/16 in all the solutions except solution Nos. 1 and 15. This ratio was selected to enable us to observe the changes in the Raman shifts due to successive replacement of Cl^- by Br^- from the complex $[HgCl_4]^{2-}$ on the progressive addition of KBr.

From the table it is seen that with a gradual increase in the ratio Br^-/Cl^-, hereinafter to be represented by x, the shift due to $[HgCl_4]^{2-}$ ($x=0$), is lowered in value. These results may be explained by assuming that Br^- ions take part in the formation of mixed halide species and thus the shift in the position of maximum intensity to a lower value is, presumably, due to the successive replacement of chloride ions by bromide ions.

The solutions corresponding to Table 2 were prepared by dissolving varying quantities of KBr

TABLE 2. [$HgCl_2$:KCl=1:1]-KBr-H_2O SYSTEM

Solution No.	Relative concentration			$\Delta\nu$ cm^{-1}	Intensity (visual)
	[Hg^{II}]	[Cl^-]	[Br^-]		
1	1	3	0	295	s
				320	m
2	1	3	⅑	295	s
				320	m
3	1	3	⅙	293	m
				320	w
4	1	3	⅓	292	w
				320	w
5	1	3	1	256	m
6	1	3	1½	255	m
7	1	3	2	192	m
				256	w
8	1	3	3	190	s
9	1	3	4	188	s
10	1	3	6	183	s
11	1	3	9	180	s
12	1	3	12	176	s
13	1	3	21	175	s
14	1	0	4	170	s
15	1	0	3	183	s

s, strong m, medium w, weak

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2) M. L. Delwaulle, *C. R. Congr. Soc. Sevantes Paris Dept., Secti. Sci.*, **41**, (1955).

3) M. L. Delwaulle, *C. R. Acad. Sci., Paris*, **206**, 1108 (1938).

4) T. A. Ralfe, D. E. Sheppard and A. Woodward, *Trans. Faraday Soc.*, **50**, 1275 (1954).

5) R. C. Aggarwal, unpublished work (1958).

6) M. R. Nayer and J. R. Saraf, Jr., *Indian Chem. Soc.*, **20**, 312 (1943).

in solutions containing $HgCl_2$ and KCL always in 1 : 1 molar ratio. In a solution No. 1, with $x=0$, two lines are observed corresponding to $[HgCl_3]^-$ and $HgCl_2$ in agreement with the observations of earlier workers.[6] The intensity of these lines decreases with increasing value of x (soln. 1 to 4). With further increase in the value of x, Raman shifts are obtained at lower $\Delta\nu$ values which are more or less similar to those observed in the solutions of Table 1 containing Hg^{2+}, Br^- and Cl^- ions. The similarity of the Raman shifts observed in solutions of Tables 1 and 2 suggests the formation of similar mixed halide anions in the two different series of solutions.

A comparison of the results of Tables 1 and 2 further shows that the position of maximum intensity falls to a minimum value of 183 cm^{-1} in Table 1 as against 175 cm^{-1} in Table 2. This suggests that the Cl^- ions are more labile in the complex anion $[HgCl_3]^-$ as compared to $[HgCl_4]^{2-}$. The greater lability of $[HgCl_3]^-$ enables the formation of mixed halide complexes of Hg^{II} in which the number of the Br^- ions appears to be greater than those formed from $[HgCl_4]^{2-}$.

Another series of solutions was prepared by dissolving varying amounts of KCl in solutions containing $HgBr_2$ and KBr always in 1 : 1 molar ratio. When $x=0$ a line 183 cm^{-1} corresponding to the complex anion[7] $[HgBr_3]^-$ is obtained. With the addition of Cl^- ions this line shifts gradually to a minimum value 175 cm^{-1} when $x=1/7$. Since the bromo complexes of Hg^{2+} are more stable than the corresponding chloro complexes, the replacement of Br^- ions by Cl^- ions is not favoured and hence the observed shifts to lower $\Delta\nu$ side produced on addition of Cl^- ions to $[HgBr_3]^-$ ions can only be due to formation of a four-coordinated complex of Hg^{2+} *viz.* $[HgBr_3Cl]^{2-}$.

The fourth series of solutions was prepared by dissolving $HgCl_2$ and KBr in different molar proportions *viz.* 1 : 2, 1 : 3, 1 : 4 and 1 : 6. In 1 : 2 solution two strong lines at $\Delta\nu$ 191 and 270 cm^{-1} are observed. The shifts at 270 may be attributed to the anion $[HgCl_4]^{2-}$ while the other at 191 cm^{-1} is, in all probability, due to the mixed halide complex anion formed in solutions.

It is interesting to note that in all the series of solutions except that in Table 1 the minimum shift is almost the same indicating the existence of similar species in these solutions at some state.

Our observations compare favourably with those made by Delwaulle and Woodward from a study of mixed halide complex anions of mercury(II). We find that the shifts, in each series, lie between the $\Delta\nu$ values of $[HgCl_4]^{2-}$ and $[HgBr_4]^{2-}$ suggesting the formation of mixed halide complex anions as shown below:

	$[HgCl_4]^{2-}$	increasing Br^-/Cl^-	$[HgBr_4]^{2-}$
$\Delta\nu$ (cm^{-1})	270	255 ⟶ 176	170

With the increasing Br^-/Cl^- ratio anions likely to be formed are $[HgCl_4]^{2-}$, $[HgCl_3Br]^{2-}$, $[HgCl_2Br_2]^{2-}$, $[HgClBr_3]^{2-}$ and $[HgBr_4]^{2-}$— the shifts decreasing in the order given. Broadness of the lines in many cases suggests the simultaneous existence of more than one complex anion in solution. The position of maximum intensity corresponds to the species present in relatively greater concentration.

The authors wish to express their grateful thanks to Dr. B. G. Gokhale, Professor and Head of the Physics Department, Lucknow University for providing all possible facilities and for his keen interest in the progress of the work.

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