

## Infrared Studies of Mixed Ligand Complexes of Mercuric Cyanide

By A. K. AGRAWAL and B. N. TRIPATHI\*)

With 1 Figure

### Abstract

The structure of (i)  $\text{NaHg}(\text{CN})_2(\text{Cl})(\text{H}_2\text{O})$ , (ii)  $\text{NaHg}(\text{CN})_2(\text{Br})(\text{H}_2\text{O})$ , (iii)  $\text{NaHg}(\text{CN})_2(\text{CNS})(\text{H}_2\text{O})$ , (iv)  $\text{KHg}(\text{CN})_2(\text{Br})$  and (v)  $\text{KHg}(\text{CN})_2(\text{CNS})$  has been studied by infrared spectroscopy. The structure of the anions of I, III and V complexes have been derived on the basis of characteristic absorption frequencies and other known properties and of II and IV on the basis of analogy as the CN groups in these complexes are infrared inactive. CN in these anions are linked as cyanide groups and SCN as isothiocyanate group in V. In III SCN is present both as thiocyanate and isothiocyanate group. III is monomeric with water as a coordinating group. In I and II water is not expected to be a ligand to Hg. Anions of I, II, IV and V are predominantly dimeric with CN as bridging group in the first three and SCN in V.

Hg (II) usually forms tetrahedral complexes with  $\text{Sd}^3$  hybridization. The existence of complexes having odd cyanide coordination number has also been inferred by spectroscopic data<sup>1)</sup>. Mercuric cyanide forms mixed ligand complexes with halides and pseudo-halides having apparently odd coordination number<sup>2) 3) 4)</sup>. Therefore it would be of interest to investigate the structure of mixed ligand complexes of mercuric cyanide having three halide or pseudo-halide ligands. The preparation of such compounds having stoichiometric compositions  $\text{NaHg}(\text{CN})_2(\text{Cl})(\text{H}_2\text{O})$ ,  $\text{NaHg}(\text{CN})_2(\text{Br})(\text{H}_2\text{O})$ ,  $\text{NaHg}(\text{CN})_2(\text{CNS})(\text{H}_2\text{O})$ ,  $\text{KHg}(\text{CN})_2\text{Br}$  and  $\text{KHg}(\text{CN})_2(\text{CNS})$  has been reported earlier<sup>5) 6) 7)</sup>. In this particular investigation, the structure of these compounds has been studied with the help of infrared spectroscopy and the results reported.

\*) Defence Science Laboratory, Delhi (India).

<sup>1)</sup> R. A. PENNEMAN and L. H. JONES, *J. Inorg. Nuclear Chem.* **20**, 19 (1961).

<sup>2)</sup> R. C. AGGARWAL and R. C. MEHROTRA, *Z. anorg. allg. Chem.* **297**, 65 (1958).

<sup>3)</sup> L. NEWMAN and D. N. HUME, *J. Amer. chem. Soc.* **81**, 5901 (1959).

<sup>4)</sup> H. POULET and J. P. MATHIEN, *C. R. Acad. Sci. Paris* **248**, 2079 (1959).

<sup>5)</sup> A. K. AGRAWAL and R. C. MEHROTRA, *Z. anorg. allg. Chem.* **312**, 230 (1961).

<sup>6)</sup> A. K. AGRAWAL and R. C. MEHROTRA, *Z. anorg. allg. Chem.* **317**, 343 (1962).

<sup>7)</sup> A. K. AGRAWAL and R. C. MEHROTRA, *Z. anorg. allg. Chem.* **336**, 66 (1965).

## Experimental

Perkin Elmer 221 infrared spectrophotometer was used for recording the spectra of the complexes. The spectra were taken in nujol mull.

## Results

The spectra of the complexes in ranges 2.5–3.25, 4.5–5.0 and 6–6.5  $\mu$  corresponding to OH stretching, CN stretching and OH bending are given in Fig. 1. The complexes do not exhibit any other peak in non-finger print region. In the finger print region the absorption peaks have not helped in the elucidation of structure, hence they have not been given.

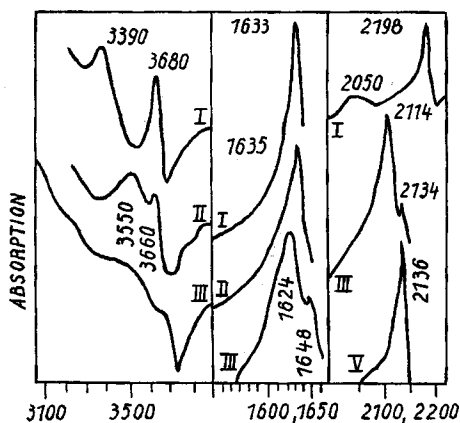


Fig. 1. Infra-red absorption spectra of mixed ligand complexes of mercuric cyanide in non-finger print region

## Discussion

The complexes containing  $H_2O$  exhibit absorption frequencies in OH stretching and OH bending frequency ranges. In OH stretching region,  $NaHg(CN)_2(Cl)(H_2O)$  absorbs at 3680 and 3390  $cm^{-1}$  and  $NaHg(CN)_2(Br)(H_2O)$  at 3660 and 3550  $cm^{-1}$ .  $NaHg(CN)_2(CNS)(H_2O)$  exhibits a broad band in this region. In HOH bending frequency region first two compounds exhibit peaks at 1633 and 1635  $cm^{-1}$  respectively. The third complex exhibits peaks at 1624 and 1648  $cm^{-1}$ , at least one of which is expected to be due to HOH bending. Therefore  $H_2O$  is present in all these complexes as H—O—H entity. In the first two complexes, the higher stretching frequency corresponds to free OH and lower to OH group involved in hydrogen bonding. The donor atom for the hydrogen bond formation, appears to be the halogen atom, especially in the case of chloro complex, as the thiocyanato complex having no halogen atom exhibits only a broad OH band.

Bands associated with strongly coordinated water molecules in aquo complexes have been reported<sup>8)</sup> in the range 1000—800  $\text{cm}^{-1}$ . These bands have been tentatively assigned to wagging, twisting and rocking modes of vibration of water ligand. But the spectra do not provide any conclusive evidence regarding these modes of vibration of HOH. In the finger print region all the five complexes exhibit weak and broad absorption bands at  $\sim 1165$  and  $\sim 975$   $\text{cm}^{-1}$  and, with the exception of  $\text{NaHg}(\text{CN})_2\text{Br} \cdot \text{H}_2\text{O}$ , at  $\sim 785$   $\text{cm}^{-1}$ . As the potassium complexes do not contain any water, no band can be conclusively assigned to any HOH vibration modes. These bands may be due to water, in case of hydrated sodium complexes, or overtones and combination bands of Hg—C or Hg—S band or, in case of thiocyanato complexes, to SC bonds. They may also be spurious bands.

Excepting the bands given earlier, the complexes exhibit absorption in the range 2220—2000  $\text{cm}^{-1}$ . This is a general frequency range for inorganic cyanides and thiocyanates of all types.

**$\text{NaHg}(\text{CN})_2(\text{Cl})(\text{H}_2\text{O})$ .** Because of the following reasons it is expected that this is not an aquo complex :

(i) The corresponding potassium complex crystallises out from water without any molecule of hydration. Thus the complex anion  $\text{Hg}(\text{CN})_2\text{Cl}^-$  is stable without coordinated water.

(ii) In  $\text{Hg}(\text{CN})_2-\text{Hg}(\text{CN})_4^{--}$  system in water, the intermediate complex exists in dimeric form  $\text{Hg}_2(\text{CN})_6^{--}$ . If the compound is an aquo complex of coordination number 4, dimerisation should not normally occur. Therefore  $\text{Hg}(\text{CN})_2\text{Cl}^-$  entity may also be stable without water of coordination.

(iii) As discussed below CN stretching frequency shown by  $\text{NaHg}(\text{CN})_2(\text{Cl})(\text{H}_2\text{O})$  corresponds to bridged cyanide group. Therefore CN functions as bidentate ligand, each atom of which combines with different Hg atoms. Thus 4 coordination number of Hg is completely accounted for. If water is present as a ligand, the bridge structure is not possible for the complex.

The complex exhibits absorption frequency at 2198  $\text{cm}^{-1}$  which corresponds to CN stretching vibration. This value is much greater than the stretching frequency for cyanide ion ( $\sim 2050$   $\text{cm}^{-1}$ ) and nonbridged cyanide group ( $\sim 2150$   $\text{cm}^{-1}$ )<sup>9)10)</sup> but in the range of bridged cyanide group ( $\sim 2200$   $\text{cm}^{-1}$ ). The occurrence of single sharp peak at 2198  $\text{cm}^{-1}$  indicates that the compound exists predominantly in the complex form, otherwise

<sup>8)</sup> F. FUJITA, K. NAKAMOTO and KOBAYASHI, J. Amer. chem. Soc. 78, 3963 (1956).

<sup>9)</sup> P. C. H. MITCHELL and R. J. P. WILLIAMS, J. chem. Soc. 1912 (1960).

<sup>10)</sup> C. N. R. RAO, J. RAMACHANDRAN and P. S. SHANKAR, J. Sci. Ind. Research (India), 18 B, 169 (1959).

another sharp and medium peak due to cyanide ion formed by the following exchange reaction should have been obtained.



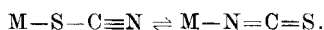
Howsoever a broad and very weak frequency is exhibited at  $\sim 2050$ . This corresponds to slight disproportionation of the complex according to the second step.

The difference between the electronegativities of Hg and C is of very small order and the isocyanide group  $-\text{N}\equiv\text{C}$  does not possess any non-bonded electron to form a bridge between two Hg atoms. Therefore CN is linked to Hg atoms in cyanide form and in the bridged structure lone pair of electrons of nitrogen atom is involved.<sup>11)</sup>

Based on these factors it is concluded that the complex exists in polymeric form. But it has been deduced<sup>4)</sup> from RAMAN and I.R. Spectra of  $\text{Hg}(\text{CN})_2-\text{Hg}(\text{CN})_4^{--}$  system in water, that the intermediate complex is a dimer  $\text{Hg}_2(\text{CN})_6^{--}$ . Hence it is expected that this complex also exists principally in dimeric form  $(\text{Cl})(\text{CN})\text{Hg} \begin{matrix} \swarrow \text{CN} \\ \searrow \text{NC} \end{matrix} \text{Hg}(\text{CN})(\text{Cl}) \cdot 2\text{H}_2\text{O}$ .

$\text{NaHg}(\text{CN})_2(\text{CNS})(\text{H}_2\text{O})$ . This complex exhibits two absorption frequencies at  $2140\text{ cm}^{-1}$  and  $2110\text{ cm}^{-1}$ . The higher frequency is in the range assigned for stretching vibration of CN of non-bridging cyanide group ( $\sim 2150\text{ cm}^{-1}$ ) and of bridging thiocyanate<sup>12)</sup> group ( $2180-2150\text{ cm}^{-1}$ ). The lower one is in between the two ranges for the stretching mode of ionic ( $\sim 2050\text{ cm}^{-1}$ ) and nonbridging cyanide group ( $\sim 2150$ ) and in the range of stretching mode of CN in nonbridged thiocyanate<sup>12)</sup> group ( $2120$  to  $2100\text{ cm}^{-1}$ ). As the complex can have only bridged or non-bridged cyanide and thiocyanate, it is very likely that the higher valency corresponds to non-bridging cyanide and lower to nonbridging thiocyanate group.

For transition metals including Hg the following equilibrium is balanced<sup>9)</sup> far to the left.



Therefore linkage between Hg and thiocyanate group is expected to be predominantly through S atom. This complex exhibits two absorption frequencies at  $1624\text{ cm}^{-1}$  and  $1648\text{ cm}^{-1}$ . It is expected that former frequency is due to HOH bending and the latter due to  $\text{C}=\text{N}$ . In organic compounds the range for  $\text{C}=\text{N}$  stretching vibration is  $1700-1630$ . Therefore appre-

<sup>11)</sup> M. H. FORD-SMITH, The Chemistry of Complex Cyanides (Her Majesty's Stationery's Office, London), p. 2 (1964).

<sup>12)</sup> C. N. R. RAO, Chemical Applications of Infrared Spectroscopy Academic Press, New York, p. 361 (1963).

ciable amount of linkages of Hg to thiocyanate group through nitrogen atom may also be present.

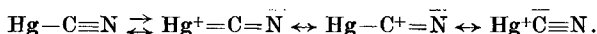
Based on these factors and that Hg(II) forms complexes with 4 coordination number it is concluded that the complex is monomeric and the water molecule is coordinating. The broad band in the OH stretching region may be considered as an evidence for water coordination. But the two frequencies at 2140 and 2110  $\text{cm}^{-1}$  correspond to the stretching vibration of identical group CN of cyanide and thiocyanate groups. Therefore coupling of vibrations of the two groups can occur. This will result in the displacement of natural frequencies. Even if such a coupling occurs, the possibility that the uncoupled frequencies correspond to nonbridging cyanide and bridging thiocyanate groups is very remote because the coupled frequencies lie in between the uncoupled frequency ranges of the non-bridging groups, and there is no possibility of appreciable amount of cyanide ions in the complex.

**KHg(CN)<sub>2</sub>CNS.** This complex exhibits only one absorption frequency at 2136  $\text{cm}^{-1}$  in the region of stretching frequencies of cyanide and thiocyanate group. Therefore CN stretching frequencies of both the groups have merged together. The frequency corresponds to CN stretching vibrations of non-bridged cyanide and bridged thiocyanate group. Unlike the previous compound, C=N stretching frequency corresponding to Hg-N=C=S is not exhibited by this compound. Therefore Hg is linked solely through S atom and the complex exists in polymeric form with thiocyanate bridge. The dimeric form  $(\text{CN})_2\text{Hg} \begin{matrix} \swarrow \text{S}-\text{C}\equiv\text{N} \\ \searrow \text{N}\equiv\text{C}-\text{S} \end{matrix} \text{Hg}(\text{CN})_2$  may be predominant as the structure requires small distortion from normal bond angles.

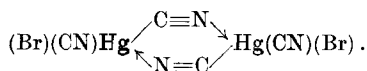
**NaHg(CN)<sub>2</sub>(Br)(H<sub>2</sub>O) and KHg(CN)<sub>2</sub>(Br).** These complexes do not exhibit any absorption frequency corresponding to CN stretching mode. It would be of interest to note that in case of NaF-Hg(CN)<sub>2</sub> system in aqueous solution no infrared absorption has been observed<sup>1)</sup> in the range 2200 to 2000  $\text{cm}^{-1}$  assigned for CN groups in various forms. Howsoever it has been reported that the complex formed between KBr and Hg(CN)<sub>2</sub> in water gives absorption band at 2189  $\text{cm}^{-1}$ . In water solution Hg (II) forms aquo complex of 6 coordination number<sup>13)</sup>. Therefore it is a chemical entity different from the complexes under discussion. The CN bonds in these complexes are infrared inactive. This indicates that the stretching vibration of CN bond in these complexes is not associated with change in the dipole moment. It is due to the electron displacements in the molecule induced by

<sup>13)</sup> M. M. JONES, Elementary Coordination Chemistry, Prentice Hall Englewood Cluff. N. J., p. 120 (1964).

introduction of Br ligand. The principal canonical forms of cyanide group in combination with Hg are



Thus N atom is the negative center of the dipole. When  $\text{Br}^-$  combines with  $\text{Hg}(\text{CN})_2$ , its negative charge is shared by carbon atoms of the cyanide group, thereby the contribution of the last canonical form becomes more predominant. By the introduction of  $\text{Br}^-$  the electron density over carbon atom increases to such a measure that its vibration is not associated with change in dipole moment of CN group and it becomes infrared inactive. Therefore on the basis of infrared spectroscopy, conclusions regarding the nature of CN linkage with Hg cannot be arrived at. However on the analogy of the structure of  $\text{NaHg}(\text{CN})_2(\text{Cl})(\text{H}_2\text{O})$ , it is proposed that the complex anion exists in polymeric form with predominance of the dimer



Gorakhpur (India), Chemical Laboratories, M.M.M. Engineering College.

Bei der Redaktion eingegangen am 27. Juli 1966.