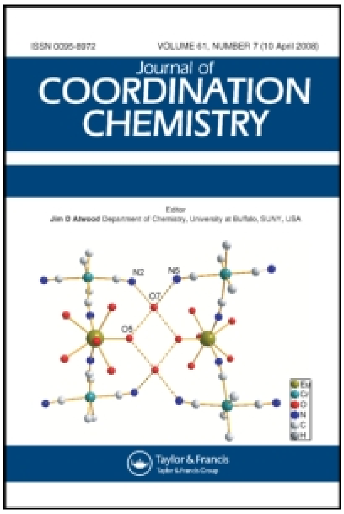

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

A SPECTRAL AND STRUCTURAL STUDY OF THE METAL-HALOGEN STRETCHING VIBRATIONS IN COORDINATION COMPOUNDS OF MERCURY(II)

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To cite this Article Konovalov, L. V. and Davarski, K. A.(1986) 'A SPECTRAL AND STRUCTURAL STUDY OF THE METAL-HALOGEN STRETCHING VIBRATIONS IN COORDINATION COMPOUNDS OF MERCURY(II)', Journal of Coordination Chemistry, 14: 3, 201 — 207

To link to this Article: DOI: 10.1080/00958978608073908

URL: http://dx.doi.org/10.1080/00958978608073908

J. Coord. Chem. 1986, Vol. 14, p. 201-207
0095-8972/86/1403-0185 $18.50/0

A SPECTRAL AND STRUCTURAL STUDY OF THE METAL-HALOGEN STRETCHING VIBRATIONS IN COORDINATION COMPOUNDS OF MERCURY(II)

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(Received April 4, 1985)

The relation between the position of the highest-frequency component of $\nu_{Hg\text{-}X}$ (X = Cl, Br, I) and the corresponding interatomic distances $r_{Hg\text{-}X}$ has been studied. In a number of compounds it was established that there exists a clear correlation which makes it possible to determine $r_{Hg\text{-}X}$ from the long-wave IR spectra with an accuracy of ± 0.05 Å. The dependences $\nu_{Hg\text{-}X}/r_{Hg\text{-}X}$ may be used to determine the boundaries within which the vibrations of the fragment HgX_n have a group character. The weak effect of the configuration of the coordination polyhedron on the dependences $\nu_{Hg\text{-}X}/r_{Hg\text{-}X}$ hinders its identification from the IR spectral data.

Keywords: Mercury, halide, infrared, bondlengths, correlations

INTRODUCTION

In a study of the dependence of the degree of covalency of the Hg-Cl coordination bond on its length, Scaife[1] established a correlation between the value of $r_{Hg\text{-}Cl}$ and the frequencies of the stretching vibrations $\nu_{Hg\text{-}Cl}$. Because of the limited experimental data used at the time of the publication, his conclusions are rather incomplete. For example, no consideration is given to the elongated coordination bonds characteristic for Hg and complementing the main polyhedron of the octahedron. The corresponding dependences for bromide and iodide complexes were not discussed.

There is interest in similar dependences from another point of view. For example, they could be used in structural analysis for rapid quantitative determination of $r_{Hg\text{-}X}$ (X = Cl, Br, I) from long-wave IR spectra. In studying the normal vibrations, these results make it possible to determine the boundaries of application of the models for the group vibrations of the HgX_n fragment of the complex polyhedron and the ratio between the kinematic and dynamic parameters which determine the $\nu_{Hg\text{-}X}$ vibrations as characteristic. The aim of the present work is to make a more detailed study of these problems on the basis of published material on the structure and long-wave IR spectra of coordination compounds of Hg.

RESULTS AND DISCUSSION

This study is based on the assumption that the monotony of the correlation between the interatomic distances Hg-X and the corresponding frequencies of the stretching vibrations $\nu_{Hg\text{-}X}$ is disturbed due to both mixing the Hg-X vibrations with the vibrations of neighbouring bonds in the coordination polyhedron (the group character of the vibrations of the HgX_n fragment is upset) and the change in the kinematic parameters of the investigated vibrations with the change in the configuration of the complex. The frequency of the highest-frequency component of the absorption $\nu_{Hg\text{-}X}$ was chosen to be the spectroscopic criterion (for convenience it will be denoted here as $\nu^{as}_{Hg\text{-}X}$). The dependences $\nu^{as}_{Hg\text{-}X}/r_{Hg\text{-}X}$

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TABLE I

Stretching vibrations $\nu^{as}_{Hg\text{-}Cl}$ and interatomic distances $r_{Hg\text{-}Cl}$ for the chloride complexes of Hg(II).

No.	Complex	$r_{Hg\text{-}Cl}$(Å)	Ref.	$\nu^{as}_{Hg\text{-}Cl}$(cm^{-1})	Ref.
1.	$[HgCl_2]$ (gas)	2.25 − 2.34	2,4	413	16
2.	$[CH_3HgCl]$	2.282 3.27	3	304–315 ?	3,17,18
3.	$[HgCl_2]$ (solid)	2.25 3.34 3.63	1,5	368–378 ? ?	1,5,7,16
4.	$K_2[HgCl_4]\cdot H_2O$	2.383 2.797 3.249	23	286–305 ? ?	1,6,24
5.	$[HgCl_2]_3[(CH_3)_2SO]_2$	2.31 3.0–3.4	7	345 ?	7
6.	$[HgCl_2(PyO)_2]$	2.33 ?	6	310 ?	6
7.	$\{HgCl_2[(C_6H_5)_2SO]\}$	2.290 3.3	8	362 ?	7,8
8.	$[HgCl(SCN)]$	2.29 3.08	1	331 ?	1
9.	$[HgCl_2(thiophan)]$	2.30 2.6–3.1	9	304 ?	19
10.	$[HgCl_2]_2[S(C_2H_5)_2]$	2.315 2.35	9	342 311	7.19
11.	$[HgCl_2(dioxan)]$	2.34 2.7–3.2	1,9	350 ?	1,16,20
12.	$[Hg_2Cl_2]$	2.42 3.18–3.21	1,29	255 ?	1,21,22
13.	$[HgCl_2Py_2]$	2.34 3.25	1	? 168	10
14.	$[HgCl_2(biuret)]$	2.30 ?	11	324[†] 175	11
15.	(*N*-benzylpiperazin-H) $[Hg_2Cl_5]$	2.26 2.40 2.69 3.62	6	363 280 178 ?	6
16.	$[NH_4][HgCl_3]$	2.34 2.96	1,6	304 ?	1,6
17.	$Cs[HgCl_3]$	2.29 2.70	1,6	320 ?	1
18.	$[HgCl_2(thio)_2]$	2.57 3.22	12	215 119[†]	13
19.	α-$[N(C_2H_5)_4][HgCl_3]$	2.43 3.1–3.2	2	252 ?	30
20.	$Cs_2[HgCl_4]$	2.386 2.455	25	269 228	26
21.	$\{HgCl_2[(C_6H_5)_2AsO]_2\}$	2.335	1,9	310	
22.	$\{HgCl_2[(C_6H_5)_3P]\}$	2.370 2.64	14	287–297 180–188	14,27,28
23.	$[HgCl_2(triphenylphosphol)]$	2.404 2.542 2.747	14	283 219 156	14
24.	$[\{p\text{-}(CH_3)_2C_6H_4\}_2Pt][HgCl_4]$	2.316 2.84 3.24	15	343 295 ?	15

[†] Our assignment.

TABLE II
Stretching vibrations $\nu^{as}_{Hg\text{-}Br}$ and interatomic distances $r_{Hg\text{-}Br}$ for the bromide complexes of Hg(II).

No.	Complex	$r_{Hg\text{-}Br}$(Å)	Ref.	$\nu^{as}_{Hg\text{-}Br}$(cm^{-1})	Ref.
1.	$[HgBr_2]$ (gas)	2.38–2.44	4	293	16
2.	$[HgBr_2]$ (solid)	2.43–2.49 3.25	5,31	247–258 ?	5,16,33
3.	*trans*-[HgBr(CHCHCl)]	2.43 ?	31	222 ?	34
4.	$[(CH_3)_4N][HgBr_3]$	2.48–2.56 2.92	31	185 ?	30,35
5.	$[(CH_3)_4N]_2[HgBr_4]$	2.587	32	160†	35

†A value, obtained by analogy with the data for $[(C_2H_5)_4N]_2[HgBr_4]$ (ν_3(IR) = 154 cm^{-1}) and $[(CH_3)_4N]_2[HgBr_4]$ (ν_1(R) = 164 cm^{-1}).[35]

TABLE III
Stretching vibrations $\nu^{as}_{Hg\text{-}I}$ and interatomic distances $r_{Hg\text{-}I}$ for the iodide complexes of Hg(II).

No.	Complex	$r_{Hg\text{-}I}$(Å)	Ref.	$\nu^{as}_{Hg\text{-}I}$(cm^{-1})	Ref.
1.	$[HgI_2]$ (gas)	2.55–2.61	4	237	16
2.	$[HgI_2]$ (yellow)	2.62 3.5	36	187–200 ?	37,16
3.	$[(CH_3)S][HgI_3]$	2.71 3.5–3.6	38	144 ?	30
4.	$[HgI_2]$ (red)	2.783	36	116–105	39
5.	$[(C_4H_9)_4N]_2[Hg_2I_6]$	2.7 2.9	40	145† 114†	40
6.	Ag_2HgI_4	2.77	45	116	our data‡

†Our assignment. ‡Unpublished results.

(X = Cl, Br, I) for halide complexes of Hg (solid phases) for which the two parameters are known, are presented in Tables I-III and Figs. 1-3.

Tables I-III and Figs. 1-3 show that, except for three of the investigated compounds, a clear correlation exists between the studied frequencies and the corresponding interatomic distances. The data for the gaseous phases HgX_2 also fit well in the general dependence. The greater number of the question marks in the $\nu^{as}_{Hg\text{-}X}$ column refer to the fact that the corresponding authors either did not have the equipment necessary for measurements or did not analyze the IR spectra below 200 cm^{-1}. The data for the elongated bonds in the complex $[\{p\text{-}(CH_3)_2C_6H_4\}_2Pt][HgCl_4]$ (No. 24) lie away from the general dependence but it is almost sure this is due to the fact that Baker *et al.*,[15] adopted for the bond $\nu^{(bridge)}_{Hg\text{-}Cl}$ = 295 cm^{-1}, a value $r^{(bridge)}_{Hg\text{-}Cl}$ = 2.8 Å. Unfortunately, it is not possible to correct the assignment since they confined themselves to studying the IR spectrum above 200 cm^{-1}.

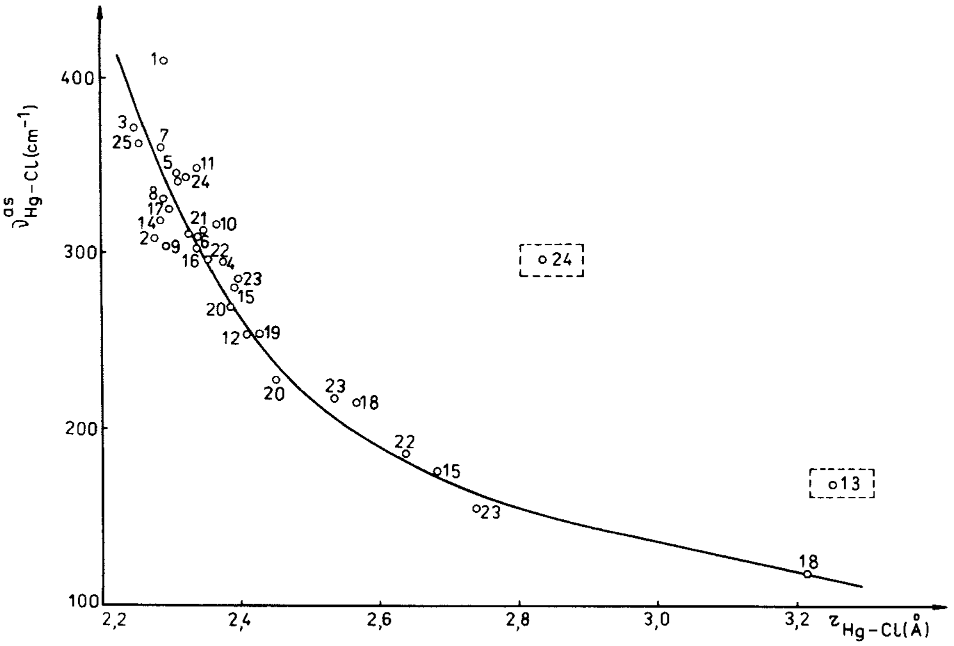

FIGURE 1 Dependence $\nu^{as}_{Hg-Cl}/r_{Hg-Cl}$ (numbering of the compounds is the same as in Table I.

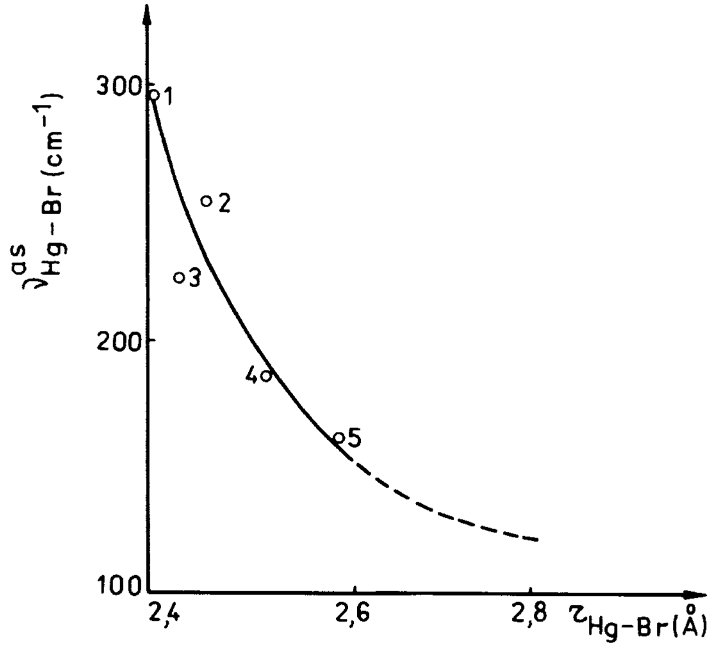

FIGURE 2 Dependence $\nu^{as}_{Hg-Br}/r_{Hg-Br}$ (numbering of the compounds is the same as in Table II.

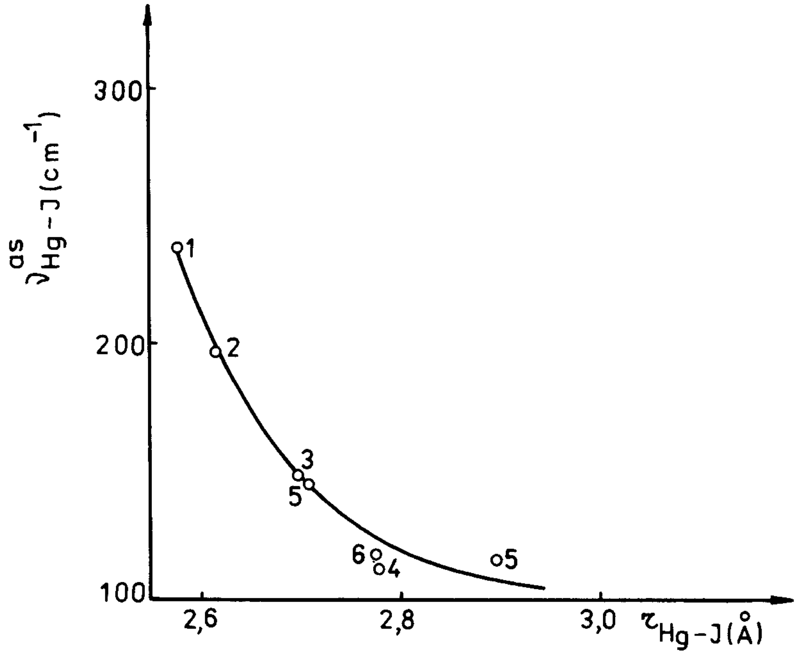

FIGURE 3 Dependence $\nu^{as}_{Hg\text{-}I}/r_{Hg\text{-}I}$ (numbering of the compounds is the same as in Table III.

The second exception established here, [$HgCl_2py_2$] (No. 13), may allow various interpretations of the data. The absence of the $\nu_{Hg\text{-}Cl}$ bands which may be related to $r_{Hg\text{-}Cl} = 2.34$ Å was explained by the great mixing of the vibrations of the short and long Hg-Cl bonds.[10] To a certain degree, the observed deviation of the point $\nu^{as}_{Hg\text{-}Cl} = 168$ cm^{-1}/$r_{Hg\text{-}Cl} = 3.25$ Å from the general dependence presented in Fig. 1 speaks in favour of that conclusion. On the other hand, it should be noted that the complex is unstable and rapidly becomes [$HgCl_2py$] in air, a strong band $\nu_{Hg\text{-}Cl} = 290$ cm^{-1} comparable with the value $r_{Hg\text{-}Cl} = 2.34$ Å appearing in the spectrum.[10] This fact makes us treat the structural data with caution since they may refer to the product of the [$HgCl_2py_2$] → [$HgCl_2py$] transition or to a mixture of the two.

For the biuret complex (No. 14), we suggest a correction of the band assignment reported in Ref. 11 as shown below.

$$\begin{array}{lcl} \nu_{Hg\text{-}Cl} = 175\ \text{cm}^{-1} & & \nu_{Hg\text{-}Cl} = 324\ \text{cm}^{-1} \\ & \longrightarrow & \\ \nu_{Hg\text{-}O} = 324\ \text{cm}^{-1} & & \nu_{Hg\text{-}O} = ? \end{array}$$

In assigning the bands, Birker *et al.*,[11] made a misplaced analogy with the [$CdCl_2(biuret)_2$] complex. The assignment suggested here agrees with the dependence in Fig. 1. Analyzing the reasons for the deviation of that complex, one should also have in mind the ability of biuret to coordinate with different donor atoms in three different forms.[11]

In any case, the reasons for the deviation of the data for these compounds from the general dependence need a special study.

Independent of the deviations and stipulations pointed out above, the conclusion may be made that the dependence in ν^{as}_{Hg-X}/r_{Hg-X} is general enough. It is natural to expect that similar dependences exist for the dependence of ν^{as}_{Hg-X} and r_{Hg-X} on the stretching force constants of Hg-X. The results obtained make it possible to draw some conclusions about the peculiarities of the studied vibrations.

The widely used *a priori* assumption about the group character of the vibrations of the HgX_n fragment in coordination compounds is correct and well grounded from a physical point of view in certain cases only. The limits of using this approach are determined by the maximum values for the deviations ν^{as}_{Hg-X} from the general dependences presented in Figs. 1-3. For a more detailed analysis of that problem it is necessary to employ a computational approach. The problem of the necessity of such a treatment of the spectrum should be solved for each case proceeding from the degree of deviation of the observed frequency from the dependences illustrated in the Figures.

The dominating factor determining the ν^{as}_{Hg-X} frequencies as characteristic is the change in the stretching force constants. The total effect of the rest of the factors on the value of ν^{as}_{Hg-X} is secondary and, in the extreme cases, does not exceed $\Delta\nu = 40\ cm^{-1}$. On the basis of the data from ref. 42, the whole variety of the Hg-X bonds comprising a wide range of values for r_{Hg-Cl} (for example, in the case of the chlorides, they vary from 2.25 Å to 3.5 Å) may be accounted for by the monotonous decrease of the share of 5d-orbitals and the corresponding increase of the share of 6d-orbitals of Hg in the bonding molecular orbitals.

Analogous conclusions were made for the complexes of Re, Os and Ir,[41] which are also remarkable for the variety of their configurations. The discussed properties seem to be characteristic for coordination compounds of all metals from the middle of the VI period in the Periodic Table.

In structural analysis, the dependences in Figs. 1-3 may be recommended for determining the quantities r_{M-X} from the long-wave IR spectra with an accuracy of $\Delta r = \pm\ 0.05$ Å. In analyzing the mutual effect of the ligands, it is possible to determine the correctness and incorrectness of the frequent use of the ν_{M-X} frequencies as a quantitative criterion for *cis* and *trans* influences. In addition, by using the value for ν^{as}_{Hg-X} and r_{Hg-X}, and empirical formulae and correlation dependences, a number of characteristics of the Hg-X bonds may be determined, such as the bond order,[31,43] the difference in the electronegativity of the bond forming atoms Hg and X[44] and the degree of covalency.[1]

It should be noted that, as Tables I-III show, the structures of the coordination environment of the mercury atoms have little effect on the values for ν^{as}_{Hg-X} and r_{Hg-X}. This fact greatly complicates the determination of the coordination polyhedron configuration from the data concerning long-wave IR spectra.

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