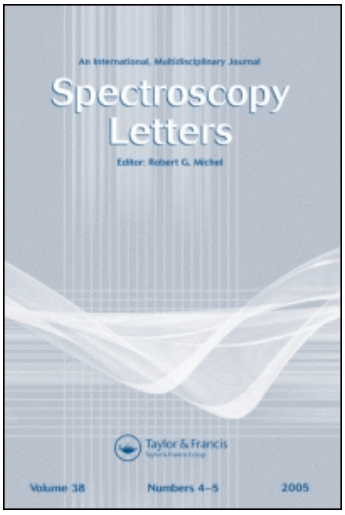

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Vibrational Parameters of Some Mixed Tetracoordinate Halogenomercurate(II) Complexes

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VIBRATIONAL PARAMETERS OF SOME MIXED TETRACOORDINATE HALOGENOMERCURATE(II) COMPLEXES

Key words: force constants,GQVFF, dynamic parameters, tetracoordinate halogenomercurates

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ABSTRACT

The normal coordinate analysis has been performed for the mercury(II) halogeno complexes HgX_3Y^{2-} ($X \neq Y$=Cl,Br,I) using latest Raman spectral data for the first time. The general quadratic valence force field has been used in this study. The results in turn are utilized to investigate the useful vibrational parameters such as compliance constants and mean amplitudes of vibration. The trends among the vibrational parameters are discussed and the bond

properties of the mercury(II) and related complexes are examined.

1. INTRODUCTION

In the studies of intramolecular force fields, it is a matter of great importance to determine reliable general valence force constants such as bond stretching, angle deformation, bond-bond interaction, angle-angle interaction and bond angle interaction in polyatomic molecules. For understanding the complete characterization of the side products of the reaction of a number of complexes of the type $Hg_2X_4Y_2^{2-}$ with the bridge breaking ligand 2,2'-bipyridyl Contreras and Seguel [1] have recorded the Raman spectra of the anionic halogenomercurate(II) complexes of the types HgX_3Y^{2-} and HgX_4^{2-} ($X \neq Y = Cl, Br$ or I) as salts of tetrapropylammonium cations (pr_4N). The vibrational spectra of these tetracoordinate mercurate(II) complexes have been interpreted on the basis of pseudotetrahedral (C_{3v}) and tetrahedral structures, respectively. Since we have been engaged in investigating the bond and molecular properties of anionic mixed halogeno complexes [2,3] and complete vibrational data of the above mentioned halide complexes of mercury(II) are now available for the first time, it seems timely to utilize these data for understanding the different vibrational parameters such

as force constants, compliance constants and mean amplitudes. A study of this kind is expected to give a better insight into the nature of chemical bonds in the complexes under present investigation as well as in related complexes.

2. METHOD OF COMPUTATION

The anions of the type HgX_3Y^{2-} have C_{3v} symmetry and their fundamental frequencies span the following irreducible representatios : $3A_1+3E$. The three A_1 species contain two stretching and one deformation mode, and the three E species involve one stretching and two deformation modes.

The normal coordinate analysis has been performed in Wilson's FG matrix framework [4] employing general quadratic valence force field (GQVFF). The determination of symmetrized force constants involved in the secular equation of order greater than one requires additional informations besides vibrational frequencies as observables. In absence of additional informations the matematical constraints are used in limiting the number of independent parameters in the force field. The method of kinetic constants [5] introduces mathematical constraints on the off diagonal elements relating them to the diagonal elements of the F-matrix through the relations:

$$\frac{F_{ij}}{F_{jj}} = \frac{K_{ij}}{K_{jj}} \qquad (i<j \;\; i,j=1,2,3)$$

where F_{ij} and K_{ij} stand for force constants and kinetic constants, respectively. This method thus provides a way for the determination of the force field once the kinetic constants are determined. The kinetic constants are easily evaluated from the atomic masses and the geometrical parameters of the molecules [5]. Therefore, the kinetic constants calculated from the masses and the structural parameters of the anions have been employed to solve the three dimensional secular determinants associated with each species in FG matrix framework. The compliance constants are determined by the method of Decius [6]. The vibrational amplitudes have been computed using the normal coordinate transformation matrix L in the relation $\Sigma = L \Delta L'$, where the symbols have their usual meanings [7].

3. RESULTS AND DISCUSSION

The vibrational wavenumbers for the HgX_3Y^{2-} species, required in the present study, are collected in Table 1. Since the vibrational wavenumbers for HgI_3Cl^{2-} and HgI_3Br^{2-} under the E species do not differ markedly, a value of 44 cm^{-1} has been assumed for the wavenumber corresponding to the unobserved wagging mode of HgI_3Br^{2-}, equal to that of HgI_3Cl^{2-}. It can be pointed out that in case f CdI_3Cl^{2-} and CdI_3Br^{2-} [8,9] similar situation occurs and $\nu_5(E) < \nu_6(E)$ as in the present case. The structural parameters for the

TABLE 1

Vibrational wavenumbers(cm^{-1}) for anionic halogenomercurate(II) complexes of the type HgX_3Y^{2-} ($X \neq Y = Cl, Br, I$)

Anion	$\nu_1(A_1)$	$\nu_2(A_1)$	$\nu_3(A_1)$	$\nu_4(E)$	$\nu_5(E)$	$\nu_6(E)$
$HgCl_3Br^{2-}$	217	156	142	248	118	137
$HgBr_3Cl^{2-}$	151	242	104	163	93	122
$HgBr_3I^{2-}$	148	118	103	159	97	116
HgI_3Cl^{2-}	113	225	62	117	39	44
HgI_3Br^{2-}	116	151	61	119	38	44*

* not observed, see text

investigated pyramidal anionic systems are [10]: Hg-Cl= 227 pm, Hg-Br= 244 pm, Hg-I= 261 pm and $X-\widehat{Hg}-X = X-\widehat{Hg}-Y = 109.5°$.

The GQVFF model for HgX_3Y^{2-} species includes the bond stretching force constants f_d(Hg-X) and f_D(Hg-Y), and deformation force constants f_α ($X-\widehat{Hg}-X$) and f_θ ($X-\widehat{Hg}-Y$). The force constants f_{dd} and f_{Dd} stand for stretch-stretch interaction, and $f_{\alpha\alpha}$ and $f_{\alpha\theta}$ take into account the bending interactions. The remaining force constants $f_{D\alpha}$, $f'_{d\alpha}$, $f''_{d\alpha}$ and $f'_{d\theta}$ show stretch-bend interactions. The values calculated for these force constants are summarized in Table 2. An inspection of the results shows that the stretching force constant varies in the sequence $f_{Hg-Cl} > f_{Hg-Br} > f_{Hg-I}$. The

TABLE 2

Force constants (in $10^2 Nm^{-1}$) for HgX_3Y^{2-} anions

Anion	f_d	f_{dd}	f_α	$f_{\alpha\alpha}$	$f'_{d\alpha}$	$f''_{d\alpha}$
	f_D	f_{Dd}	f_θ	$f'_{\alpha\theta}$	$f_{D\alpha}$	$f'_{d\theta}$
$HgCl_3Br^{2-}$	0.891	0.170	0.092	-0.031	0.004	0.005
	0.596	0.055	0.034	-0.015	-0.030	0.003
$HgBr_3Cl^{2-}$	0.756	0.057	0.093	-0.026	-0.011	0.017
	1.056	0.001	0.025	-0.015	-0.002	0.013
$HgBr_3I^{2-}$	0.778	0.144	0.066	-0.024	-0.054	0.035
	0.661	0.074	0.032	-0.003	-0.025	0.002
HgI_3Cl^{2-}	0.420	0.208	0.053	-0.022	-0.060	0.038
	0.909	0.066	0.005	-0.002	-0.004	0.004
HgI_3Br^{2-}	0.444	0.224	0.054	-0.023	-0.064	0.038
	0.800	0.058	0.006	-0.002	-0.008	0.003

trend is consistent with the corresponding bond lengths. The deformation force constant f_α decreases with the increase of the mass of the X atom and $f_\alpha > f_\theta$. The stretch-stretch interactions (f_{dd} and f_{dD}) are greater than bend-bend interactions ($f_{\alpha\alpha}$ and $f'_{\alpha\theta}$). This shows that the stretch-stretch interaction dominates over the bend-bend interaction in mixed halogenomercurate(II) complexes. Similar conclusion has also been drawn for InX_3Y^- [2] and CdX_3Y^{2-} [3] halogeno

TABLE 3

Compliance constants (in 10^{-2}m/N) for HgX_3Y^{2-} anions

Anion	n_d	n_{dd}	n_α	$n_{\alpha\alpha}$	$n'_{d\alpha}$	$n''_{d\alpha}$
	n_D	n_{Dd}	n_θ	$n'_{\alpha\theta}$	$n_{D\alpha}$	$n'_{d\theta}$
$HgCl_3Br^{2-}$	1.284	-0.416	2.133	-0.078	-0.055	-0.071
	1.930	-0.096	5.615	-0.521	0.337	0.028
$HgBr_3Cl^{2-}$	1.362	-0-071	1.973	-0.133	-0.087	-0.129
	0.947	-0.004	9.807	-0.311	0.013	0.053
$HgBr_3I^{2-}$	1.554	-0.409	3.516	0.181	0.634	0.515
	1.935	-0.160	5.840	-1.479	0.558	0.076
HgI_3Cl^{2-}	8.496	-3.579	8.343	-0.162	5.048	2.811
	1.130	-0.100	53.854	-2.493	0.176	-0.267
HgI_3Br^{2-}	8.204	-3.517	8.165	-0.191	4.984	2.744
	1.311	-0.104	33.861	-2.518	0.341	-0.246

complexes. The remaining interaction force constants vary in the order $f'_{d\alpha} > f_{D\alpha}$ and $f''_{d\alpha} > f'_{d\theta}$, but their magnitudes are such that they do not influence the force field markedly.

The compliance constants are collected in Table 3. These constants are invariant to the choice of coordinates defining the force field and they may be used as a measure of the rigidity of the bonds and interactions instead of potential energy constants as

pointed out by Decius [6] and Jones [11]. It may also be noted that the compliance constants exhibit trends opposite to those of the corresponding force constants.

The mean amplitude of vibration for both bonded and non-bonded distances at 298.16° K are tabulated in Table 4. In order to search the characteristicness of the mean amplitudes for bonded distances we examine the corresponding values. The characteristic nature of mean amplitudes is found for the bond Hg-Cl in $HgCl_3Br^{2-}$ and $HgBr_3Cl^{2-}$, the bond Hg-Br in $HgCl_3Br^{2-}$, $HgBr_3I^{2-}$, HgI_3Br^{2-} and the bond Hg-I in HgI_3Cl^{2-} and HgI_3Br^{2-}. It is also evident that $l_d(Hg\text{-}Cl) < l_d(Hg\text{-}Br) < l_d(Hg\text{-}I)$.

It is interesting to compare the principal force constants and bonded mean amplitudes of tetracoordinate halogenomercurates(II) with those of the halogenocadmates(II). The results are compared in Table 5. Keeping the ligand atoms the same in anions it is seen that the bond stretching force constant and the bending force constant f_θ decrease with the increase of the mass of the central atom and the bending force constant f_α shows in general an increasing tendency. These trends suggest that the mercury-halogen bond is comparatively weaker than the cadmium-halogen bond. The bonded mean amplitude in general varies as $l_{Cd\text{-}X} < l_{Hg\text{-}X}$ as expected. This also favours the trend in bond stretching force constants as discussed above.

TABLE 4

Mean amplitudes of vibration (in 10^{-20} Å) for HgX_3Y^{2-} anions

Anion	l_d	l_D	$l_{(X..X)}$	$l_{(X..Y)}$
$HgCl_3Br^{2-}$	5.344	7.353	12.721	15.933
$HgBr_3Cl^{2-}$	10.357	5.539	8.457	14.406
$HgBr_3I^{2-}$	7.970	10.429	11.119	10.488
HgI_3Cl^{2-}	20.390	8.123	18.538	17.667
HgI_3Br^{2-}	20.898	7.779	18.436	19.893

TABLE 5

Comparison of stretching and deformation force constants (in $10^2 Nm^{-1}$) and bonded mean amplitudes (in Å) between CdX_3Y^{2-} and HgX_3Y^{2-} anions

Anion	f_d	f_D	f_α	f_β	Bond	l_d
$CdCl_3Br^{2-}$	1.025	0.793	0.062	0.054	Cd-Cl	0.070
$HgCl_3Br^{2-}$	0.891	0.596	0.092	0.034	Hg-Cl	0.063
$CdBr_3Cl^{2-}$	0.869	1.143	0.057	0.073	Cd-Br	0.077
$HgBr_3Cl^{2-}$	0.756	1.056	0.093	0.025	Hg-Br	0.083
$CdBr_3I^{2-}$	0.833	0.614	0.057	0.033	Cd-I	0.086
$HgBr_3I^{2-}$	0.778	0.661	0.066	0.032	Hg-I	0.172
CdI_3Cl^{2-}	0.690	1.061	0.056	0.046		
HgI_3Cl^{2-}	0.420	0.909	0.053	0.005		
CdI_3Br^{2-}	0.715	0.999	0.051	0.059		
HgI_3Br^{2-}	0.444	0.888	0.054	0.006		

TABLE 6

Bond stretching force constants($10^2 Nm^{-1}$) and vibrational amplitudes l_{Hg-X}(Å) at 298.16°K for anionic halide complexes of mercury(II)

Bond	HgX_2 ($D_{\infty h}$) Ref.[12]	HgX_3^- (D_{3h}) Ref.[13]	HgX_3Y^{2-} (C_{3v})	HgX_4^{2-} (T_d)
f_{Hg-Cl}	2.61	1.403	0.952	1.798
f_{Hg-Br}	2.24	1.170	0.732	1.707
f_{Hg-I}	1.83	0.914	0.508	1.592
l_{Hg-Cl}	0.044		0.063	0.088
l_{Hg-Br}	0.043		0.083	0.090
l_{Hg-I}	0.043		0.172	

In order to provide some information on the bonding properties of the halide complexes of mercury(II) possessing different coordination number, we have collected the relevant bond parameters, namely the bond stretching force constants and bonded mean amplitudes in Table 6. From a survey of the results it is observed that the bond stretching force constants exhibit the following trend: $f_{Hg-X}(D_{\infty h}) > f_{Hg-X}(D_{3h}) > f_{Hg-X}(C_{3v}) < f_{Hg-X}(T_d)$. This trend is further supported by the corresponding variation in mean amplitudes. It is, therefore, inferred that as one moves from planarity to non-planarity the relative strength of the identical

chemical bond decreases, but as the configuration approaches to tetrahedral (T_d) from pseudotetrahedral (C_{3v}) the relative strength of the chemical bond gets increased. Similar conclusion has been also drawn for CdX_3Y^{2-} anions by Pandey et al. [2].

The results presented in this paper besides their usefulness in understanding the bond properties in tetracoordinate halogenomercurate(II) and related complexes, will be very useful as starting values for deriving the molecular force fields of more complicated mercury complexes.

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