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Donor Induced Vibrational Effects in Mercury(II) Halide Complexes and Some Metal(II) Halide–1,4-Dioxanate Stability Correlations

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The mercury(II) halides (Cl, Br, I) show a variation in Hg–X stretching motions in 24 class (a) donor solvents that correlates with the pK_a of the donor. In several solvents ν_3(Hg–Cl) becomes weakly active in the Raman implying that slightly non-centrosymmetric units exist, but this behavior is not a function of the solvent basicity. The decomposition profile of a series of $MX_2\cdot n$dioxane complexes were studied by TGA and the temperatures corresponding to the loss of dioxane follow the trend in the softness parameters of M^{2+}.

Introduction

The mercury(II) halides are tractable Lewis acids from which a great deal of ligand–metal bonding information can be learned. The mercury atom is sterically and electronically flexible enough to accomodate a variety and variable number of donor molecules.[1] Indeed, numerous solid-state donor–acceptor complexes involving the mercuric halides have been reported with widely ranging stoichiometries, structures and stabilities. For the donor molecules, the electronic character of the donor site appears to be of prime importance in modifying the HgX_2 molecule, but steric demands also play a significant role. The gross electronic contribution seems to be adequately classified according to the hard–soft formalism of Pearson[2] and Ahrland, Chatt and Davies.[3] For example, X-ray studies reveal that softer (class (b)) donors like phosphines,[4] arsines,[4] sulfides[5–9] and selenides[10] usually produce four coordinate mercury. Accompanying this geometry is often a significant bending of the HgX_2 unit and Hg–X bond lengthening of 0.1–0.3 Å over that of the uncomplexed HgX_2 molecule. The harder (class (a)) donors, such as the weakly basic amines,[11,12] ethers,[13–17] alcohols,[18] ketones,[19–22] N-oxides,[23,24] and sulfoxides[25–27] lead to highly associated crystal lattices containing 5 or 6 coordinate mercury and relatively weak donor–acceptor interactions. Some overlap of these classes could be expected and does exist. For example, $(C_6H_5)_3AsO$[28] behaves more like a class (b) donor toward $HgCl_2$, whereas the sulfur atom in phenoxathiin[29] is more like a class (a) donor toward $HgCl_2$.

Within a series of closely related donor molecules, details of the differences at the donor site add a complicating feature. It is also rather more difficult to characterize the class (a) interactions in solution because even with some more stable class (b) complexes of HgX_2, a significant amount of dissociation has been noted.[30–31] However, by inference to the solid state it might be expected that the donor site electronic character will play an important role in modifying the structure and bonding of the HgX_2 molecule. The conclusion that the solvent dielectric constant is the origin of solvent induced Hg–Cl frequency shifts was advanced by Allen and Wahrhurst[32] who examined $\nu_1(\Sigma g^+)$ and $\nu_3(\Sigma g^-)$ of $HgCl_2$ in 13 class (a) solvents. A crucial, yet uncertain, frequency in their correlation was that produced by benzene and this number is known to be in error.[33] Replotting the data including frequencies determined in this work reveals that no correlation of note exists between the Hg–Cl frequencies and the dielectric constant. Moreover, no other bulk property of the solvent yields a correlation. Such observations are not surprising if HgX_2 structural changes and thus Hg–X vibrational effects are indeed primarily manifestations of donor site characteristics. In the present study we find that a better parameter for correlating solvent effects with ν_{Hg-Cl} is simply the solvent basicity.

The structure of these aggregates in class (a) donor solvents is of interest because the possibility of nonlinearity of the HgX_2 molecule in solution has been the subject of some discussion over the years.[33–41] The latest opinions favor approximate linearity of the HgX_2 unit at least in benzene and dioxane.[33,41] While the vibrational spectra do not give decisive structural assignments, they are of some utility because the observation of the antisymmetric stretch, ν_3, in the Raman implies that a non-centrosymmetric structure exists for the HgX_2 unit.

In the overall picture of weak donor–acceptor interactions we wished also to investigate whether a simple

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model could be used to explain metal(II) halide complexation differences with a common donor molecule. The dioxanate complexes of Group IIA and IIB halides would appear to be a suitable class of compounds to extract this information. The vibrational spectra of solids and solutions of these compounds are not particularly informative,[42–45] so we have determined by thermogravimetric analysis their stability with respect to loss of the dioxane base. Correlations of these data with metal softness parameters verify the validity of the hard–soft model for qualitative trending in the stability of these complexes.

Experimental

The Lewis bases employed in this work were either of Spectral Grade quality and not purified further, or, in the case of the cyclic ethers, were first purified by methods described in Riddick and Bunger[46] or Jolly.[47] The metal(II) halides were of commercial reagent grade quality and were not purified further except in the case of BaI_2. BaI_2 was first exhaustively extracted with dioxane to remove the I_2 present and used immediately.

Raman spectra were recorded on a Spex Ramalog 1401 double monochrometer spectrometer employing photon counting. Laser excitation was obtained with either a CRL Model 54 argon-ion laser operating at 4800 Å and about 150 mW power or a Spectra Physics Model 164 argon-ion laser operating at the same wavelength but at 1.4 w power. Samples were run as saturated solutions in sealed capillary tubes. The ir spectra were recorded between 400–200 cm^{-1} on a Perkin–Elmer Model 180 spectrometer in 0.1 mm polyethylene cells. The errors in spectral frequencies are estimated to be no more than ± 2 cm^{-1}.

The thermogravimetric analysis studies of the dioxanate complexes were carried out on a DuPont 950 TGA.

Results and Discussion

HgX_2–Donor Studies

The donor molecules studied here, except possibly for pyridine, are most notable for their low tendency

TABLE I. Vibrational Stretching Modes in cm^{-1} of HgX_2 in Various Solvents.

Medium	$HgCl_2$			$HgBr_2$	HgI_2
	ν_1(R)[a]	ν_3(IR)[a]	ν_3(R)	ν_1(R)[a]	ν_1(R)[a]
Gas[b]	355	413		255	156
1. Benzene	339	392	–	213	[e]
2. Furan	339	386	–	212	155
3. Nitrobenzene	337	[c]	[c]	213	156
4. Acetic acid	332	380	383 vvw	208	[e]
5. Benzonitrile	332	[c]	[c]	210	[e]
6. Diethyl ether	332	380[d]	[c]	210	152
7. Acetone	328	375[d]	376 vvw	207	151
8. Methyl formate	328[d]	376[d]	–	205	150
9. Acetonitrile	325	372[d]	[c]	208	[e]
10. Methanol	324	365	363 vvw	206	151
11. 3,4-Dihydropyran	323	375	380 vvw	207	151
12. Tetrahydrofuran	323	368	366 vvw	207	154
13. Dioxane	322	375	–	203	156
14. Tetrahydropyran	322	368	370 vvw	204	151
15. 1-Butanol	321	366	[c]	203	151
16. Ethanol	321	366	363 vvw	202	149
17. 1-Propanol	321	365	366 vvw	205	151
18. 2-Propanol	320	[c]	[c]	206	150
19. H_2O	320	[c]	–	205	[e]
20. t-Butanol	318	[c]	[c]	209	153
21. Formaldehyde	318	[c]	–	204	[e]
22. N,N-Dimethylformamide	308[d]	[c]	[c]	195	146
23. Dimethylsulfoxide	305[d]	[c]	[c]	198	148
24. Pyridine	282	[c]	–	185	141

[a] All modes are very strong. [b] From D. M. Adams, "Metal–Ligand and Related Vibrations," St. Martins Press, New York, 1968, p. 52. [c] Solvent interference makes assignment impossible. [d] Some solvent interference. [e] Insoluble.

to form covalent interactions with acceptor molecules.[48] The HgX_2 interactions with these solvents should be primarily charge controlled. In accordance with this, the range of ν_1 frequencies in Table I as a function of the donor molecule is $HgCl_2$ (57 cm^{-1}) > $HgBr_2$ (28 cm^{-1}) > HgI_2 (15 cm^{-1}). It follows that the decreasing Hg–X bond polarity diminishes the positive charge on the mercury atom which makes the molecule progressively less sensitive to perturbation upon interaction with these class (a) donor molecules. Even though the range of ν_1 varies widely with X, a good correlation exists between the frequencies of $HgCl_2$, $HgBr_2$ and HgI_2 in respective solvents. It is thus evident that variations in the solvent donor properties and steric requirements affect all of the mercuric halides in approximately the same way. ν_3 was often interfered with by solvent bands. Perusal of the data reveals that ν_3 is affected by the solvent in a manner very similar to that of ν_1, however.

Correlations between bulk properties of the solvent and ν_1 are not very good. It is more likely that properties specific to the donor site are responsible for modifications of the HgX_2 molecule. For most of the solvents in Table I, the pK_a values in H_2O solution are known[49] and these should reflect the electrostatic differences at the donor site. It cannot be tacitly expected that basicity toward the proton is quantitatively comparable to that toward Hg(II), but Figure 1 demonstrates that within reasonable limits pK_a of the solvent does reproduce shifts in ν_1 of $HgCl_2$ in the expected way. That is, weakly basic donors generate the smallest $HgCl_2$ frequency shifts compared to $HgCl_2$ (gas) whereas more strongly basic donors produce the larger shifts. Thus over a wide range of class (a) donor basicities ν_1(Hg–Cl) is primarily sensitive to the σ-electron donating power of the solvent.

The pattern of point distribution in Figure 1 seems to be significant. Steric crowding has been encountered for diethyl ether in other Lewis acid–base studies.[48] Most of the bases expected to have sterically somewhat crowded donor sites lie below the line, meaning that the shift in ν_1 of $HgCl_2$ is less than expected from the pK_a value. Many of the less hindered donor sites yield data points above the average line. This distribution very likely results from real differences in complex formation, perhaps in which solvents having crowded donor sites either coordinate fewer molecules on average or coordinate less strongly than pK_a suggests compared to solvents with more available donor sites.

A good correlation is also noted between ν_1 of $HgCl_2$ and solvents for which Gutmann[50] has determined donor numbers. Of the eleven solvents common to Gutmann's $SbCl_5$ studies and the present $HgCl_2$ analysis, only pyridine and diethyl ether produce data points at variance to an otherwise linear correlation between solvent donicity and $\nu_1(HgCl_2)$.

In the hope of providing a better structural picture of the Hg(II) coordination sphere in these solutions, a very careful examination of the Raman spectra was made under high sensitivity conditions in the ν_3 region. In many instances solvent bands were found to obscure this range, but very weak ν_3 activity was noted in several solvents where no interference exists. An example is shown in Figure 2 for $HgCl_2$ in tetrahydrofuran. The only explanation for ν_3 activity in the Raman is that a mild disruption of the molecular center of symmetry in the $HgCl_2$ unit has occurred. It is clear, however, that the activity of ν_3 is not related to the magnitude of pK_a for the class (a) donor. The two compounds representing the extreme limits of pK_a in this study (pyridine and benzene) do not produce ν_3 activity, whereas ν_3 is frequently, but not always, observed for donor molecules having intermediate pK_a values. Unfortunately, further correlations are made very difficult because solvent interference limits the number of useful spectra. At least a 100-fold excess of solvent molecules over HgX_2 molecules exists in these solutions so that several solvent molecules are

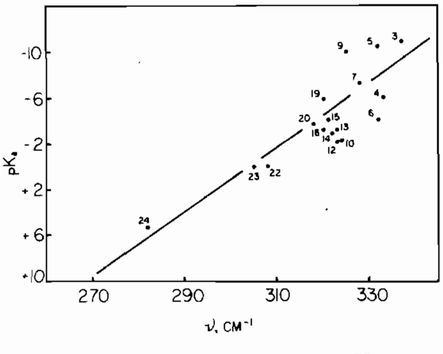

Figure 1. The relationship between pK_a of the solvent and ν_1 of $HgCl_2$ in solution.

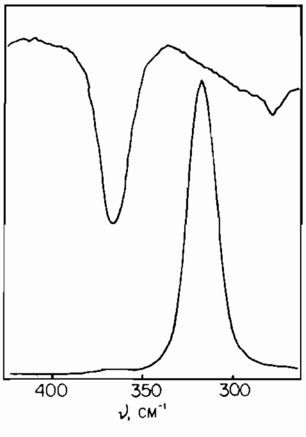

Figure 2. The IR (upper trace) and Raman (lower trace) spectra of $HgCl_2$ in tetrahydrofuran solution.

probably associated with HgX_2. A solubility study has been interpreted as showing that a ratio of two solvent molecules to one HgX_2 molecule exists in benzene and dioxane.[51] Molecular weight[40,41] and Kerr effect studies[40] of $HgCl_2$ in benzene suggest dimers are present but other studies are consistent with monomers.[52] The molecular weights of the mercuric halides in acetone are said to be close to those of the uncomplexed monomeric species.[53] As a consequence it seems impossible to speculate on the structures of these species in solution in view of the conflicts in the data usually accepted as clarifying the aggregate dimensions. This study does suggest that while different structures very likely are present depending on the solvent, the $HgCl_2$ unit is essentially linear in all cases.

In the way of a sidelight, it would be interesting to know whether the Hg–Cl frequency shifts produced by other donors, particularly soft (class (b)) donor sites, can also be correlated with basicity. The data most needed for comparison are often lacking because the insolubility of many complexes makes it impossible to record solution spectra. Also structural differences in the degree of HgX_2 bending often are present. It could be anticipated beforehand that correlations will be less satisfactory. Considering a few complexes of 1/1 stoichiometry, trialkyl-[54,55] and triarylphosphines[55] yield Hg–Cl modes in the 270–290 cm^{-1} range in the Raman and have pK_a values of 2–9.[49] Sulfides have pK_a values around –5[49] and generate somewhat higher Hg–Cl modes at 295–315.[56] Solid pyridine-1-oxide complexes give ν_1(Hg–Cl) at about 280 cm^{-1} [57] and the donor has pK_a values in the 3–5 range.[49] $(CH_3)_3AsO$ has a pK_a of 4[49] and ν_1(Hg–Cl) in the phenyl analog is a 278 cm^{-1} [58]. Thus very rough trending is found in these solid complexes of other donor molecules but it is not nearly systematic enough to be reliable.

MX_2·ndioxane Complexes

A number of MX_2·ndioxane (n = 1,2) complexes can be prepared in crystalline form.[59] The metal atom, M, can be varied through both the group IIA and IIB series and in some cases the halogen, X, through X = Cl, Br, I. A complete series of complexes cannot be prepared in every case, however. Vibrational analyses have been published for some of the compounds,[42–45] but they do not lead to a satisfactory description of bonding trends because of normal mode coupling and structural differences in the complexes. On the other hand, a useful indicator could be merely the thermal stability of the solid complexes as indicated by the temperature required to remove the dioxane molecules. Barnes[60] has obtained a stability trend of HgX_2·dioxane of X = Cl > Br > I, which is consistent with the trend established by vibrational[61] and nuclear quadrupole resonance studies[62] as well as symbiosis expectations.[63] CdX_2·dioxane (X = Cl, Br, I) also follow this trend based on differential scanning calorimeter measurements.[45]

TABLE II. Temperatures of Dioxane Loss from Group II Metal Halide Dioxanates.

	T_2°C	T_1°C	σ_p[b]	σ_A[c]
$HgCl_2$·dioxane		126	0.064	4.6
$HgBr_2$·dioxane		123		
$HgCl_2$·(dioxane)$_2$	65	120		
$CdCl_2$·dioxane[a]		188	0.081	3.5
$CdBr_2$·dioxane[a]		170		
CdI_2·dioxane[a]		143		
ZnI_2·(dioxane)$_2$	70	157	0.115	3.1
$SrBr_2$·(dioxane)$_2$	121	207	0.172	0.6
BaI_2·(dioxane)$_2$	136	175	0.184	0.5

[a] Reference 45. [b] Reference 64. [c] Reference 66.

Table II summarizes the thermochemical data obtained along with the softness parameters for M given by Pearson and Mawby[64] and Ahrland.[65] Two reactions occur in the low temperature thermal decomposition of the 1/2 complexes.

$$MX_2 \cdot 2\ \text{dioxane} \xrightarrow{T_2} MX_2 \cdot \text{dioxane} + \text{dioxane}$$

$$MX_2 \cdot \text{dioxane} \xrightarrow{T_1} MX_2 + \text{dioxane}$$

T_2 is substantially less than T_1 as expected. T_1, of course, is the temperature that must be used when comparing the 1/2 complexes to the 1/1 complexes. Looking at T_1 values for MI_2·ndioxane, the trend is $M^{2+} = Ba^{2+} > Zn^{2+} > Cd^{2+} > Hg^{2+}$ which follows the trend in increasing softness of metals and thus decreasing stability of the complexes toward the class (a) donor, dioxane. The T_1 values of MBr_2·ndioxane follow the order $M^{2+} = Sr^{2+} > Cd^{2+} > Hg^{2+}$ in accordance with the increasing softness trend of M^{2+}. The correlation is not quantitative because of possible structural variations. But coupled with the correct ordering of the HgX_2·dioxane and CdX_2·dioxane values, these results suggest that a simple hard–soft model can be used to broadly classify the donor–acceptor stability trends in these complexes.

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