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Contribution from the Department of Inorganic and Structural Chemistry, The University, Leeds LS2 9JT, England

Computer-Based Study of the Electronic Absorption Spectra of Neutral Mercury(II) Mixed Halides in Methanol: Equilibrium Constants and Band Assignments

TREVOR R. GRIFFITHS* and RICHARD A. ANDERSON

Received October 3, 1978

The complete electronic spectra of the neutral mixed halogenomercurates HgXY , where X is one halogen atom, Y is another, and neither is fluorine, have been determined in methanol by using computational techniques to extract the spectra of the species free from the ever-present contributions of the neutral dihalides. Two ways are described and compared for calculating these spectra, and hence their equilibrium constants, K ($=[\text{HgXY}]^2/[\text{HgX}_2][\text{HgY}_2]$). The logarithm of K at 20 °C is 1.09 ± 0.13 (HgICl), 1.04 ± 0.08 (HgIBr), and 0.70 ± 0.10 (HgBrCl). The equilibrium $\text{HgX}_2 + \text{HgY}_2 \rightleftharpoons 2\text{HgXY}$ is exothermic. The spectra are resolved into their component bands. Since the neutral dihalides are linear in solution, their molecular orbital scheme provided the basis for that for HgXY , and the transitions are assigned. The nonappearance of the transition to $^1\Sigma^+$ is explained. It is suggested that in methanol, HgCl_2 and HgXY may be solvated by three rather than four methanol molecules in the equatorial plane.

The formation of mixed-halide complexes of the type HgXY , HgX_2Y^- , $\text{HgX}_2\text{Y}_2^{2-}$, and $\text{HgX}_3\text{Y}^{2-}$, where X is one halogen atom, Y is another, and neither is fluorine, has been studied by several workers and techniques. Eliezer¹ has reviewed mixed-halide chemistry and included a comprehensive treatment of the mercury complexes. The neutral mixed halides have been examined²⁻⁸ in some half-dozen solvents, but only Delwaille^{7,8} has investigated methanol solutions, finding new lines in the Raman spectrum of equimolar mixtures of HgX_2 and HgY_2 , which she attributed to HgXY .

The electronic spectra of the neutral mixed halogenomercurates in water have been discussed by Spiro and Hume.³ If the charge-transfer bands were the result of an electron transfer from anion to cation, one would expect the mixed-halide species to have spectra showing the same peaks as the parent complexes, but at intermediate frequencies. This has been found for the mixed bismuth-chloride-bromide system.⁹ However, if the transitions are localized on opposite definite ligands, mixed-complex absorption would be expected at the same frequency as for the parent complexes, but with intermediate intensity. The partial spectra reported³ followed neither pattern rigorously.

The structure of HgX_2 in the vapor state is linear, and the electronic spectra of HgI_2 and HgBr_2 in a variety of solvents resemble those recorded for the vapor state. These molecules have thus generally been considered linear in solution. The same configuration has been deduced for all the mercuric halides (except HgI_2) by Raman spectroscopy.¹⁰ The Raman spectra of HgCl_2 in a series of solvents showed a relative shift in the symmetrical stretching frequency compared to the spectrum of the vapor, and the shift correlated with the dielectric constant of the solvent.¹¹ However, no information

about the attached solvent molecules was obtained. Keck¹² has suggested that HgCl_2 in methanol is octahedral, with four equatorial solvent molecules attached. However, Eliezer¹³ proposed from an investigation of the solubilities of mercury halides in paraffinic and aromatic solvents, and dioxane, that donor-acceptor complexes are formed, the linear HgX_2 molecule being bent on coordination with the solvent and rehybridization taking place to accommodate the distorted tetrahedral species HgX_2D_2 (D = solvent). He claimed support for this view from UV studies in aromatic solvents, and Kolling¹⁴ has suggested that $\text{HgCl}_2 \cdot 2\text{HOAc}$ may be tetrahedral.

Raman spectra of HgCl_2 in molten KNO_3 at 350 °C indicate that the molecule is linear,¹⁵ though ion-induced dipolar solvation may occur. Zangen,¹⁶ however, has suggested that HgBr_2 is tetrahedral in a $\text{LiNO}_3\text{-KNO}_3$ eutectic at 150 °C, being of the type $\text{HgBr}_2(\text{NO}_3)_2^{2-}$, and that this also occurs in a polyphenyl mixture. Support for this comes from his studies of the mixed-halide species in molten salts,⁶ where the observed formation constants are best explained by assuming the presence of $\text{HgX}_2(\text{NO}_3)_2^{2-}$ in the medium, but the nitrate ligand could be bidentate and the complex octahedral.

We have recently examined the electronic spectra of HgX_2 in some 23 solvents. The spectra were resolved and assigned and showed linear excited states for all except HgI_2 in cyclohexane and 2,2,4-trimethylpentane.¹⁷ We now report an extension of that work to the charge-transfer spectra of the neutral mixed-halides in methanol, employing and extending the computer techniques we have established¹⁸⁻²² for treating absorption spectra. We here definitively establish the existence of these complexes and calculate their spectra over the complete spectral range, free from the absorptions of other

species. We hence calculate their equilibrium constants, resolve their spectra, assign their component bands, and establish the geometry of HgXY in methanol.

Experimental Section

Apparatus and Materials. Spectra were recorded on an Applied Physics Cary 14 H spectrophotometer fitted with digitizing apparatus (Harrison Reproduction Equipment),^{19,20} and the solutions were thermostated at 20 ± 0.1 °C. The paper-tape output was analyzed on an ICL 1906A computer with graph-plotting facilities.

All chemicals were of analytical quality where available or were recrystallized twice. Methanol was of Spectro Grade quality. The mercuric halides are readily soluble in methanol, and solutions were prepared by dissolving a weighed quantity in methanol and making up to volume in a graduated flask. As mercuric halides ionize and disproportionate in some solvents, it was established that for the concentrations employed here, around 10^{-3} M, this did not occur and Beer's law was obeyed. Thus as no ions were present, solutions were not maintained at a constant ionic strength, especially since spectra of HgX₂ in water were found to be independent of added NaClO₄ up to 1.0 M, the maximum concentration employed.

Computing Section. Our previous work¹⁸⁻²² establishing various computational approaches to spectra had employed the "raw" data; now, because of the more subtle spectral changes, it was necessary to smooth the recorded spectra. Two methods were used: recording the spectra about five times and then either averaging in the computer or averaging mathematically by using a five-point convolution.^{23,24} Calculated spectra contained the original noise contribution enhanced by extrapolation and were treated with a 15-point smoothing convolution.

Derivative Spectra. The number and positions of component bands of an observed spectrum may be obtained by analysis of the derivative functions of that spectrum. We and others have discussed this technique.^{19-22,25,26} In this study second- and fourth-differential spectra were obtained of the calculated spectra and were essential for subsequent curve resolution since some profiles contained a band whose presence was not obvious to visual inspection.

Curve Resolution. Fitting bands to a profile requires a knowledge of the band shape. The commonly employed shape for electronic transitions is Gaussian, though precision fitting requires Gaussian-Lorentzian sum or product functions in some circumstances.²⁷ Within the accuracy of our calculated spectra a Gaussian function was found adequate. The program used was based on the least-squares minimization procedure of Fletcher and Powell²⁸ and adapted to include matrix inversion²⁹ to increase the rate of convergence of fit.

Calculation of Spectra. The mixed neutral halides of mercury(II), HgICl, HgIBr, and HgBrCl, are formed in the reaction $\text{HgX}_2 + \text{HgY}_2 \rightleftharpoons 2\text{HgXY}$. Two main methods have been here derived to calculate the spectrum of HgXY, and we discuss their various merits.

Displaced Equilibrium. If a large excess of HgX₂ is added to HgY₂, the solution will only contain HgX₂ and HgXY, i.e., the final concentrations will be $(a - b)$ and $2b$, respectively, where a and b are the initial concentrations of HgX₂ and HgY₂, respectively. If ϵ_a and ϵ_{ab} are the molar extinction coefficients of HgX₂ and HgXY, then

$$\epsilon_{ab} = (A - (a - b)\epsilon_a)/2 \quad (1)$$

where A is the observed absorbance. Thus from the known molar extinction coefficient of HgX₂ and a sample spectrum of a solution containing a large excess of HgX₂, the molar extinction coefficient of HgXY may be found at any wavelength. A simple computer program was written to implement this method over the complete wavelength range used.

The method has three disadvantages. First, if a very large excess of HgX₂ is used, only part of the desired spectrum is observable, the rest being hidden under the absorbance of HgX₂. Thus low concentrations must be used, and HgY₂ must have band maxima at higher energies than HgX₂. Second, as a consequence of low HgY₂ concentrations, the contribution of HgXY to the observed spectrum is small, and any noise is magnified in the calculation by fluctuations in the low values of $2b$ (eq 1). Third, the steep absorbance curves resulting from large concentrations of HgX₂ cause errors in the subtraction in eq 1 if there is any frictional pen lag or if encoding did not occur at precisely the same wavelength for all spectra. This last effect will be minimal in recent spectrophotometers where pen signal, and not pen position, is encoded and stepper motors are used to drive the wavelength mechanism.

Reference Point Method. If a solution contains three absorbing species, the molar extinction coefficient is given by eq 2. F represents

$$\epsilon = F_a\epsilon_a + F_b\epsilon_b + F_{ab}\epsilon_{ab} \quad (2)$$

the mole fraction, and $F_a + F_b + F_c = 1$. For the case when the mole fractions of HgX₂ and HgY₂ are equal then eq 2 becomes eq 3.

$$\epsilon = F_a(\epsilon_a + \epsilon_b) + (1 - 2F_a)\epsilon_{ab} \quad (3)$$

Obtaining data for solutions containing different mole fractions enables ϵ_{ab} to be evaluated as eq 4. ϵ_{a+b} is the reference spectrum and is the

$$\epsilon_{ab} = \epsilon + (F_a/(0.5 - F_a))(\epsilon - \epsilon_{a+b}) \quad (4)$$

mean of the known molar absorbances of HgX₂ and HgY₂, and eq 4 holds only for solutions containing equal quantities of HgX₂ and HgY₂.

To use this equation to calculate the neutral mixed-halide spectrum, one needs a reference point, and this was obtained from the above displaced equilibrium method (eq 1). An accurately known molar extinction coefficient of the mixed species is determined at a wavelength where there was as low a slope as possible in the spectrum and the difference between the calculated and the mean of the molar extinction coefficients of the spectra of HgX₂ and HgY₂ was greatest. This method produces the calculated spectra of HgXY, and their extinction coefficients, which are subsequently used in the calculation of equilibrium constants.

Calculation of Equilibrium Constants. If the molar extinction coefficients of all the species in a solution are known, then the equilibrium constants may be calculated from a series of solutions of different ligand concentrations, but equilibrium constants so calculated are very dependent on the molar extinction coefficient values used.^{30,31} Instead, therefore, the concentrations of the individual species were calculated as follows.

The absorbance A of a solution, at any given wavelength, is given by $A = \sum c_i \epsilon_i$, where c_i and ϵ_i are the molar concentration and molar extinction coefficients, respectively, of the i th species in solution. The ϵ_i values for each species in solution were either known or calculated as described above.

Hence if A is measured for n different wavelengths, then n linear equations of i unknowns may be derived. For $n \gg i$ these equations may be accurately solved for c_i by multiple linear regression analysis. A library computer program was amended to perform this analysis for up to six species in solution. The output consisted of the required concentrations, with their standard errors, and various parameters indicating the accuracy of the main computation and the precision of the fitted data. Equilibrium constants, with their standard errors, were computed from the regression coefficients.

Results

Experimental Observations. The behavior of the spectra of solutions containing varying proportions of HgX₂ and HgY₂ in methanol at 20 °C is shown in Figure 1. Isobestic points were not observed at wavelengths at which the two dihalides have equal molar extinction coefficients, thereby indicating the presence of a third absorbing species, and the calculated mean spectrum, assuming no reaction, was not identical with the observed spectrum. A plot of the difference between the calculated and the observed spectra (Figure 2) shows the wavelengths at which $\epsilon = 0$.

The molar extinction coefficient of the 270-nm peak of HgI₂ decreased with increase in the HgCl₂:HgI₂ ratio, and the peak simultaneously shifted to lower energies. A plot of this shift against mole ratio is shown in the insert in Figure 1, and this was used to determine the ratio at which complete conversion of HgI₂ to HgICl occurred.

Calculated Mixed-Halide Spectra. The spectra of the mixed neutral halides in methanol were calculated by using the displaced equilibrium method for solutions containing a large excess of one halide and the reference point method for solutions containing a mole ratio of unity. The absorbances at the points at which $\epsilon = 0$ were used to check the validity of the spectrum calculated by the former method. The spectra calculated by the different methods agreed within experimental error. They were smoothed with a 15-point convolution and are shown in Figure 3.

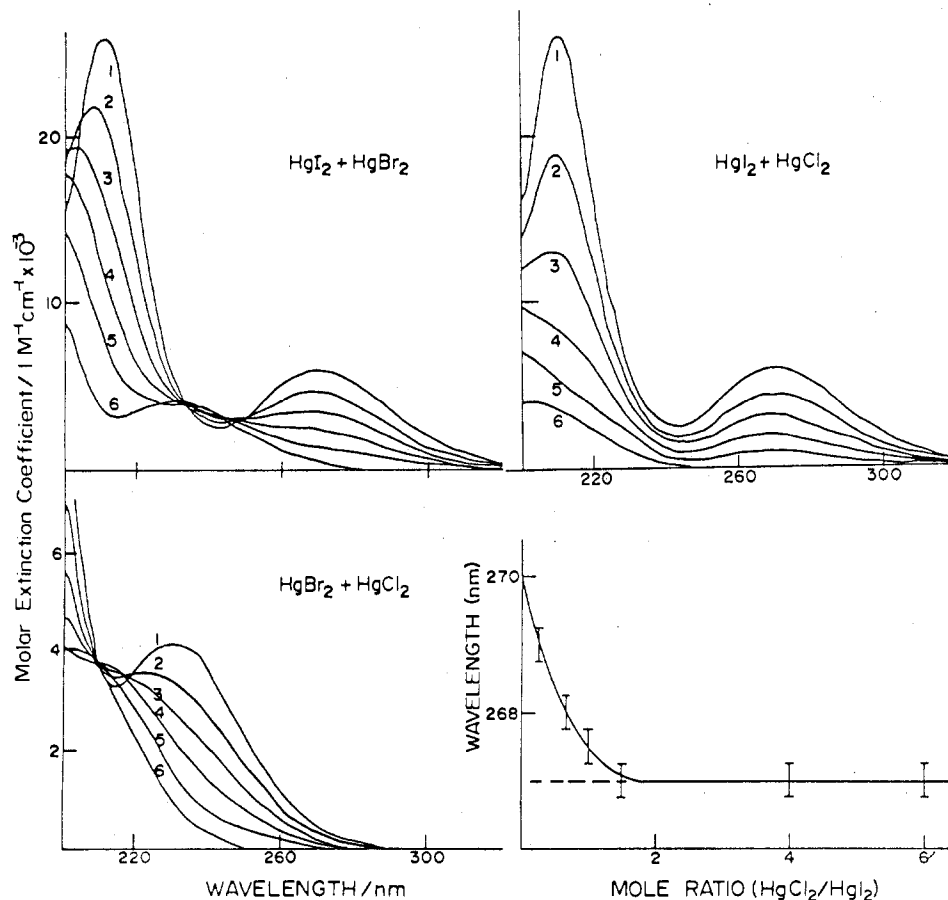


Figure 1. Spectra of methanol solutions of $\text{HgX}_2 + \text{HgY}_2$ in varying proportions at 20 °C (total mercury concentration maintained constant at 8.54×10^{-5} M): 1, HgX_2 ; 2–5, $\text{HgX}_2/\text{HgY}_2$ mole ratios of 4.0, 1.5, 1.0, 0.67, and 0.25, respectively; 6, HgY_2 . Insert: plot of E_{\max} (nm) for HgI_2 on addition of HgCl_2 .

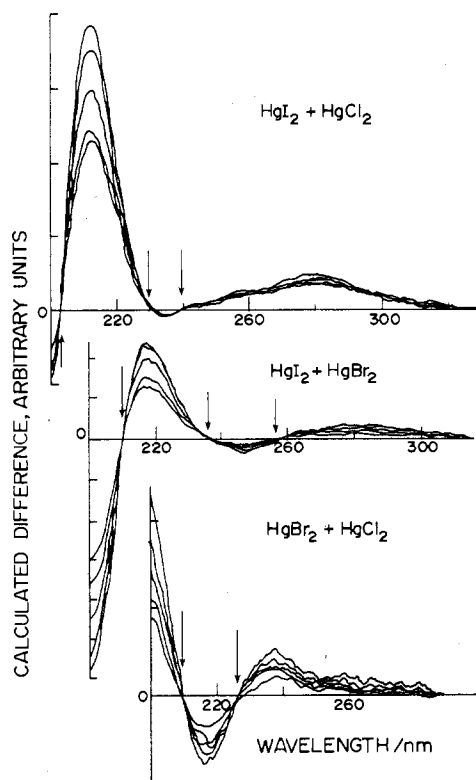


Figure 2. Calculated difference between observed and theoretical spectra for mixtures of the mercuric halides in methanol at 20 °C. Arrows indicate wavelengths at which $\epsilon(\text{HgXY}) = (\epsilon(\text{HgX}_2) + \epsilon(\text{HgY}_2))/2$.

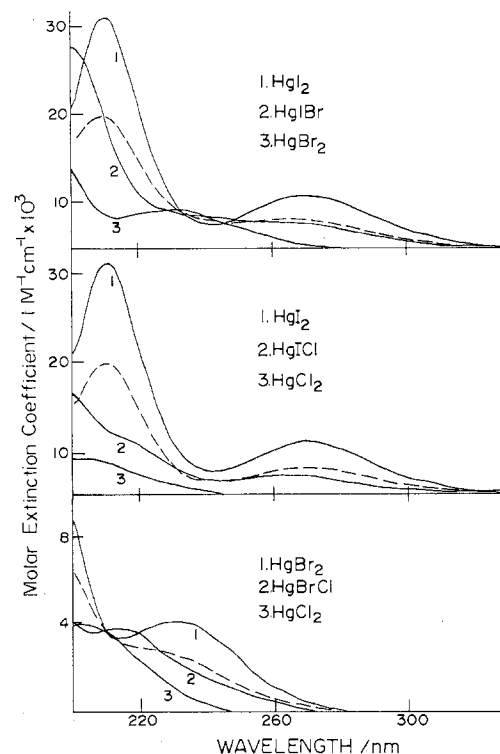


Figure 3. Spectra of the mixed mercuric halides in methanol at 20 °C. The dashed line is the median line of those of HgX_2 and HgY_2 .

Calculated Equilibrium Constants. The equilibrium constants of the neutral mixed halides were calculated by the

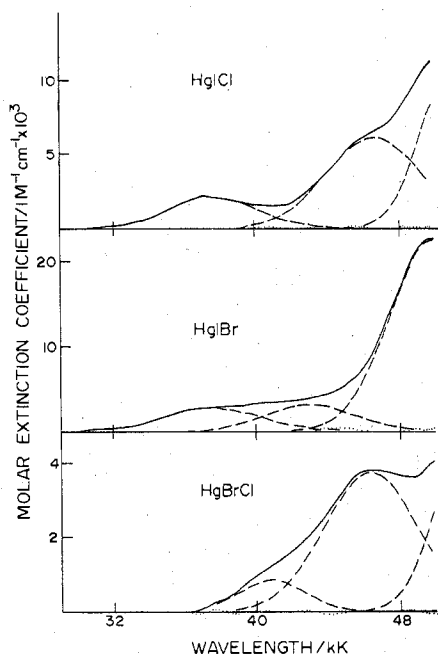


Figure 4. Resolution of the spectra of HgXY into Gaussian bands. Band parameters given in Table I.

regression-analysis procedure outlined above. The total mercury concentration was maintained close to 10^{-5} M. The wavelength ranges used in the computation were 205–300 nm for HgCl and HgBr and 205–265 nm for HgBrCl. The equilibrium constants are given in Table I.

Effect of Temperature. A qualitative survey of the effect of temperature upon solutions in methanol equimolar in HgX₂ and HgY₂ showed that with increasing temperature the equilibrium was displaced in favor of the dihalides. The reaction $\text{HgX}_2 + \text{HgY}_2 \rightleftharpoons 2\text{HgXY}$ is thus exothermic.

Table I. Equilibrium Constants ($\log K$)^a for HgXY in Methanol at 20 °C

HgCl	HgBr	HgBrCl
1.09 ± 0.13	1.04 ± 0.08	0.70 ± 0.10

$$^a K = [\text{HgXY}]^2 / [\text{HgX}_2][\text{HgY}_2].$$

Resolved Mixed-Halide Spectra. The calculated HgXY spectra, after smoothing, were analyzed for their component bands. All had hidden bands and required derivative analysis to reveal the number of component bands. Both HgCl and HgBrCl gave derivative spectra indicating two bands in the observed spectral range, and inspection showed the presence of another band at higher energies. A good fit to the data was obtained for three component bands in the spectra of these species. For HgBr in methanol only two bands were evidenced in derivative spectra, but a third, with a band maximum outside the range covered by derivative analysis, was obvious from the spectrum. A good fit was also subsequently obtained for three bands within the HgBr profile. The resolutions are shown in Figure 4 and Table II.

Interpretation of the Electronic Spectra. In order to assign the transitions of the resolved bands in HgXY it is necessary to know if the molecule is linear, since bent HgX₂ molecules in solution have been proposed.^{6,13,14,16} We shall first assume, and then demonstrate, that HgXY is linear in methanol, on the basis of our recent successful assignment and interpretation of HgX₂ in solution as a linear molecule.¹⁷ Figure 5 shows the molecular orbital scheme for HgX₂ (after Walsh³²) and our extension to linear HgXY with $C_{\infty v}$ symmetry. The introduction of the Y atom causes the degeneracy of the π orbitals to be lifted. The nonbonding orbital ($2\pi_u$) and the first antibonding orbital ($3\pi_u$) are of the same energy as those in HgX₂ (corresponding in HgX₂ to $1\pi_g$ and $2\pi_u$, respectively).

The ground-state configuration is $\dots(2\pi_u)^2(2\pi_g)^2$, giving a $^1\Sigma^+$ term, and the first excited state is $\dots(2\pi_u)^2(2\pi_g)^1(3\pi_u)^1$, giving the excited terms $^1\Sigma^+$, $^1\Sigma^-$, and $^1\Delta$ (neglecting mul-

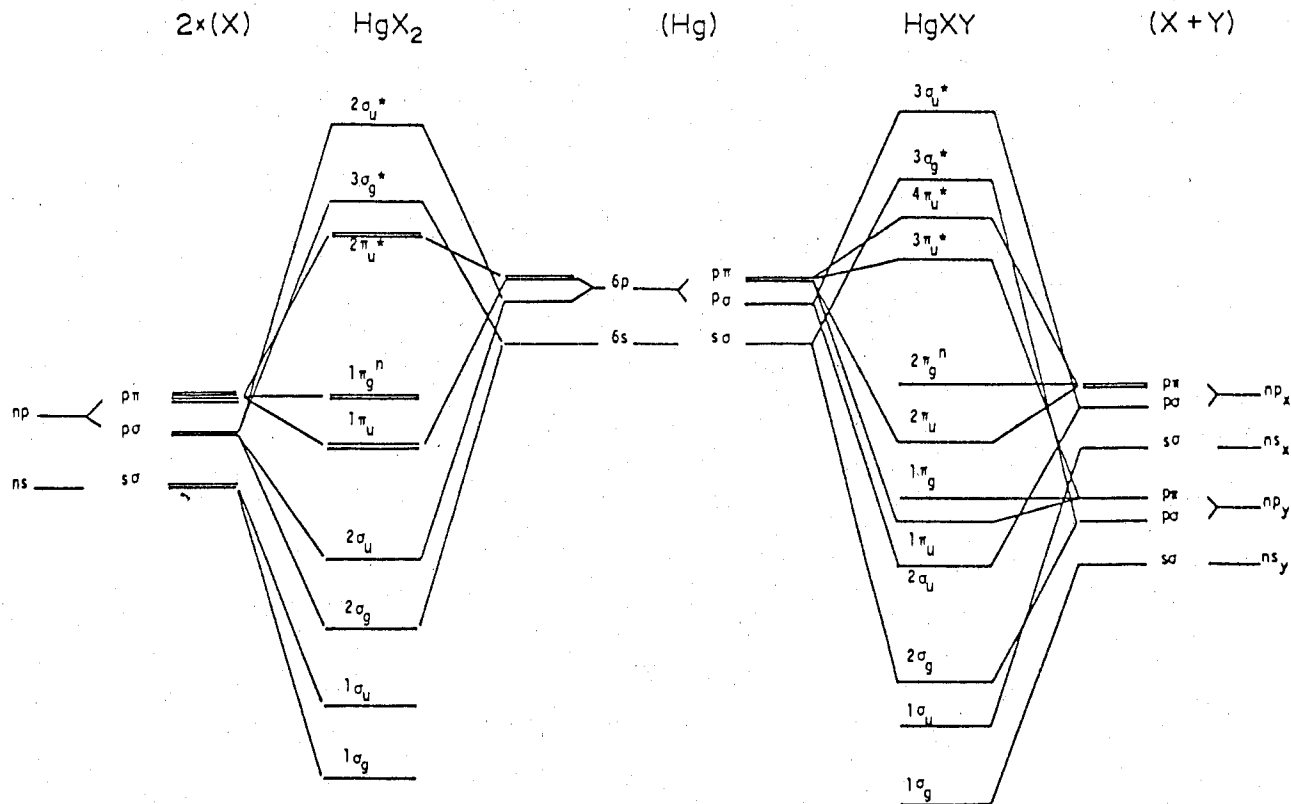
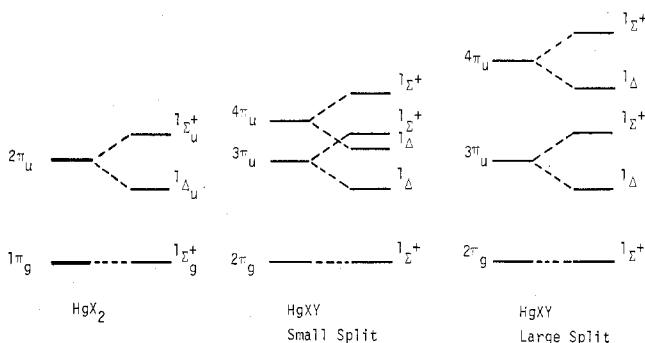
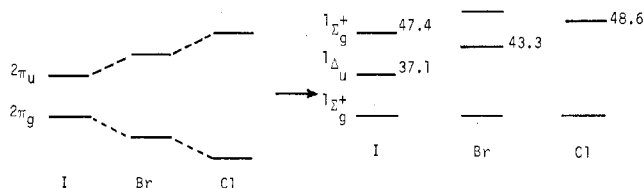


Figure 5. Correlation diagrams for the orbitals in HgX₂ molecules ($D_{\infty h}$ symmetry) and HgXY ($C_{\infty v}$ symmetry). Superscripts: asterisk, antibonding orbital; n, nonbonding orbital.

Table II. Absorption Band Parameters for HgXY in Methanol at 20 °C^a

species	obsd peaks		resolved bands				
	E_{\max}	ϵ_m	E_{\max}	ϵ_m	w	A	OS
HgI ₂	37.45	2110	37.60	2100	5.70	2.55	1.10
			46.60	6000	6.06	7.75	3.35
			50.60	9500	3.81	7.71	3.33
HgIBr	46.73	3820	37.50	2800	6.28	3.75	1.62
			43.00	3100	5.53	3.66	1.58
			49.80	22400	5.53	26.4	11.4
HgBrCl	46.73	3820	40.90	850	4.44	0.81	0.35
			46.40	3750	6.06	4.84	2.09
			52.00	5000	4.44	4.73	2.04

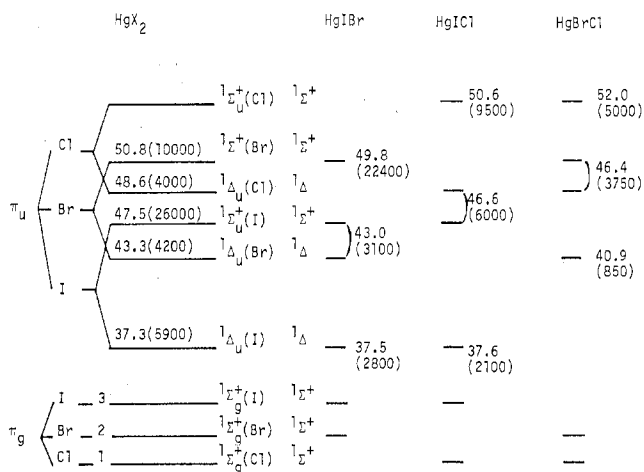
^a ϵ_m = molar extinction coefficient ($M^{-1} \text{ cm}^{-1}$); E_{\max} = peak maximum ($\text{cm}^{-1} \times 10^3$); w = band width at half-height ($\text{cm}^{-1} \times 10^3$); A = band area ($M^{-1} \text{ cm}^{-1} \times 10^{-4}$); OS = oscillator strength.

**Figure 6.** Splitting of the $2\pi_u$ orbital of HgX_2 on replacement of one X by Y.**Figure 7.** Separation of the $1\pi_g$ and $2\pi_g$ energy levels in HgX_2 and the observed transitions for HgX_2 in methanol at 20 °C.

tiplicity changes). By comparison with HgX_2 , the transition to $^1\Sigma^+$ is allowed and expected to be intense. Transitions to $^1\Sigma^-$ and $^1\Delta$ are forbidden, but as in HgX_2 transitions to $^1\Delta$ are considered to occur.¹⁷ Promotion to the second antibonding orbital, giving the configuration $\dots(2\pi_u)^2(2\pi_g)^1(4\pi_u)^1$, can also occur, yielding the same terms and transitions. The splitting of the $2\pi_u$ orbital of HgX_2 to the $3\pi_u$ and $4\pi_u$ orbitals in HgXY will determine the order of the excited states and is shown schematically in Figure 6.

The $1\pi_g - 2\pi_u$ energy difference in HgX_2 increases from HgI_2 to HgCl_2 . This difference (Figure 7) is sufficient in methanol for HgCl_2 to make the $^1\Delta_u$ transition (at $48.6 \text{ cm}^{-1} \times 10^3$) of greater energy than the $^1\Sigma_u^+$ transition of HgI_2 ($47.4 \text{ cm}^{-1} \times 10^3$). However, in HgXY molecules the $2\pi_g$ orbital (corresponding to $1\pi_g$ in HgX_2) does not change in energy from, for example, HgIBr to HgICl ; the nonbonding level corresponds to the p_π orbital of the least electronegative halogen atom. The order of the states thus deduced for the mixed-halide species in methanol is given in Figure 8 and the band analysis results are also included.

Assigning now the resolved spectra, we note that the two low-energy transitions in HgIBr and HgICl have low intensity and indicate transition to a forbidden $^1\Delta$ state. In both species the third transition is intense and is associated with excitation to a $^1\Sigma^+$ state. The order of the low-intensity transitions should be $^1\Delta(\text{I}) < ^1\Delta(\text{Br}) < ^1\Delta(\text{Cl})$ as shown in Figure 8. The lowest

**Figure 8.** Energy level diagram for HgXY molecules in methanol at 20 °C. Numbers are computed band positions (in $\text{cm}^{-1} \times 10^3$) with their molar extinction coefficients ($M^{-1} \text{ cm}^{-1}$) in parentheses.

transition in HgIBr and HgICl should correspond to the transition to $^1\Delta_u$ in HgI_2 and have the same energy. Within experimental error this is found.

The second transition of HgIBr corresponds to the transition to the $^1\Delta_u$ state in HgBr_2 but should be of lower energy as the ground state of HgIBr is derived from the $2\pi_g$ orbital from the iodine atom (level 3 in Figure 8), whereas in HgBr_2 it is derived from the lower energy $1\pi_g$ orbital from the bromine atom (level 2). This is observed: the transition is at $43.3 \text{ cm}^{-1} \times 10^3$ in HgBr_2 but at $43.0 \text{ cm}^{-1} \times 10^3$ in HgIBr . The third, intense band of HgIBr was found at $49.8 \text{ cm}^{-1} \times 10^3$. This would be expected for an allowed transition to the $^1\Sigma^+$ state, corresponding to that in HgBr_2 , where it is at about $50.8 \text{ cm}^{-1} \times 10^3$ ³³ and a decrease in this value is expected because the $^1\Sigma^+$ ground state in HgIBr is derived from the iodine and not the bromine ligand. However, this leaves the $^1\Sigma^+$ state derived from the iodine atom unused, and an intense transition at about $47 \text{ cm}^{-1} \times 10^3$ would therefore be expected, but none is observed, and the intense band at $49.8 \text{ cm}^{-1} \times 10^3$ could not be assigned to this transition, its energy being too high.

The nonappearance of the transition to $^1\Sigma^+(\text{I})$ may be understood since $^1\Sigma^+(\text{I})$ and $^1\Delta(\text{Br})$ lie close together and can therefore interact under the influence of spin-orbit coupling. The direct product of the $^1\Sigma^+$ and $^1\Delta$ representations (species) in $C_{\infty v}$ symmetry is $^1\Delta$, and hence transitions to this are forbidden. The transition found at $43.0 \text{ cm}^{-1} \times 10^3$ thus represents transition to this resultant state rather than simply to $^1\Delta(\text{Br})$.

A similar argument is invoked to explain the second and third bands found for HgICl . The intense band at $50.6 \text{ cm}^{-1} \times 10^3$ is at too high an energy to correlate with $^1\Sigma^+(\text{I})$ and must therefore be due to transitions to $^1\Sigma^+(\text{Cl})$. The two states interact giving a new $^1\Delta$ state, thus explaining the band at $46.6 \text{ cm}^{-1} \times 10^3$. This band, correlating mainly with $^1\Delta(\text{Cl})$, is expected to be at lower energy than that due to excitation to the $^1\Delta_u$ state in HgCl_2 as the ground state of HgICl (mentioned previously) is derived from the $^1\Sigma^+(\text{I})$ ground state (level 3). The increase in intensity compared to the corresponding transition in HgIBr is attributed to the large difference in the energies of the chlorine and iodine atomic orbitals, causing the coupling of $^1\Sigma^+(\text{I})$ with $^1\Delta(\text{Cl})$ to be less effective.

The band resolutions for HgBrCl showed greater uncertainty than those for HgIBr and HgICl , but the band structure is explained on similar lines.

In conclusion, the spectra of the mixed neutral mercuric halides in methanol are readily explained by assuming linear species and derive from transitions of electrons from ligand-localized to mercury-localized molecular orbitals. The

forbidden transitions observed in HgXY have approximately half the intensity shown for corresponding transitions in HgX_2 , as expected for a reduction in the populations of the ground state by half. The allowed transitions are relatively unaffected. HgXY is, however, expected to be solvated in methanol. Since it is linear, the methanol molecules must be in the equatorial plane about mercury and could be four in number, making an approximately octahedral solvate similar to that suggested for HgCl_2 in methanol.¹² But a trigonal-bipyramidal species cannot be ruled out, since the resolved charge-transfer spectrum of HgCl_3^- in water has been assigned to this structure³³ and $[\text{HgCl}_3(\text{MeOH})]^-$ has been reported.¹² The readiness with which Cl^- added on could imply the presence of HgCl_2 (and HgXY) solvates with one rather than two methanol molecules to be eliminated.

Acknowledgment. We thank the Science Research Council for the purchase of the Cary 14 H spectrophotometer. The digitizing attachment was purchased out of Harwell Contract EMR 1913. We thank the University of Leeds Computing Service for assistance, and R.A.A. acknowledges a Leeds University postgraduate award. T.R.G. thanks the Royal Society for a travel grant and the Chemistry Department, Michigan State University, East Lansing, MI 48824, for hospitality and facilities during the preparation of this paper.

Registry No. HgI_2 , 7774-29-0; HgI_2Br , 13444-76-3; HgBr_2 , 7789-47-1; HgICl , 13444-77-4; HgCl_2 , 7487-94-7; HgBrCl , 13595-89-6.

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Contribution from the Chemistry Department and Energy and Mineral Resources Research Institute of Iowa State University, Ames, Iowa 50011

Polarized Electronic Absorption Spectra for Dimolybdenum(II) Tetraacetate

DON S. MARTIN,* ROBERT A. NEWMAN, and PHILLIP E. FANWICK

Received November 27, 1978

Polarized spectra with rich vibrational detail are reported for two faces of single crystals of $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ at temperatures down to 5 K. Evidence, which includes the orientation in space of transition moments for individual vibrational lines, hot bands, and Franck-Condon factors, is presented that the $23\,000\text{-cm}^{-1}$ band is the electric-dipole-allowed $^1A_{2u} \leftarrow ^1A_{1g}$ or $\delta^* \leftarrow \delta$ with an origin at $21\,700\text{ cm}^{-1}$. However, the intensities are sufficiently low that lines excited vibrationally, although somewhat weaker, approach the intensity of the dipole-allowed progression. A second transition at $26\,500\text{ cm}^{-1}$ is evident as well from the low-temperature spectra. The spectra of a number of dimeric carboxylate complexes of molybdenum(II) are compared and the possible cause of the exceptionally low intensity for an electric-dipole-allowed transition is discussed.

Introduction

Single-crystal electronic absorption spectra are now available for several compounds which contain dimeric complexes with multiple metal-metal bonds. Studies¹⁻³ of crystals with $\text{Re}_2\text{Cl}_8^{2-}$ together with results⁴ for $\text{Mo}_2\text{Cl}_8^{4-}$, which have quadruple metal-metal bonds, have confirmed that the electronic absorption band at the lowest observed energy is polarized with the electric vector of the light wave in the direction of the metal-metal bond. In the D_{4h} symmetry of these ions, the spin-allowed $\delta^* \leftarrow \delta$ excitation is $b_{1u}^* \leftarrow b_{2g}$, and the transition is therefore $^1A_{2u} \leftarrow ^1A_{1g}$. This transition should be electric dipole allowed for polarization in the direction of the z axis which is coincident with the metal-metal bond. The assignment of the first electronic band to this $\delta^* \leftarrow \delta$ transition is predicted by $X\alpha$ -scattered wave calculations,^{2,5} although the calculated energies for the transition have

been generally much lower than the observed values. Polarized crystal spectra⁶ for $\text{K}_4\text{Mo}_2(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$, in which the $\text{Mo}_2(\text{SO}_4)_4^{4-}$ ion has four bridging sulfato ligands, have indicated a band at $19\,400\text{ cm}^{-1}$ with a polarization again consistent with a $\delta^* \leftarrow \delta$ assignment. Also, for $\text{K}_3\text{Mo}_2(\text{SO}_4)_4 \cdot 3.5\text{H}_2\text{O}$, in which one electron from the quadruple bond has been lost by oxidation, the first band with an origin at about $6\,300\text{ cm}^{-1}$ has the polarization predicted for the $\delta^* \leftarrow \delta$ assignment.⁷ The spectra of the chloro and sulfato complexes have, therefore, presented a coherent pattern with the first electronic transition assignments of $\delta^* \leftarrow \delta$.

A group of tetra- μ -carboxylato-dimolybdenum(II) complexes have, however, presented a conflicting situation. These complexes are also generally considered under the D_{4h} point group about the metal-metal bond since the atomic positions out through the α carbon follow this symmetry. The spectra