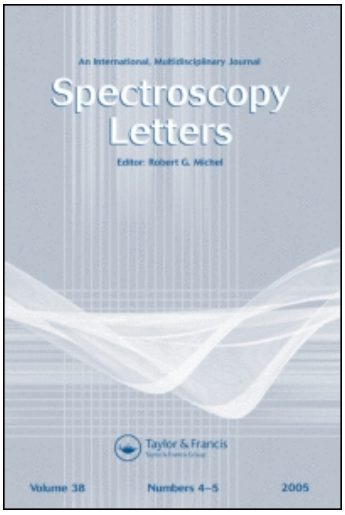

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Confirmation of Complex Formation Between Ethylene and Mercury Halides by Matrix-Isolation Infrared Spectroscopy

David Tevault[a]; Kazuo Nakamoto[a]
[a] Todd Wehr Chemistry Building, Marquette University, Milwaukee, Wis.

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CONFIRMATION OF COMPLEX FORMATION BETWEEN ETHYLENE AND MERCURY HALIDES BY MATRIX-ISOLATION INFRARED SPECTROSCOPY

KEY WORDS: Ethylene-mercury Halide Complexes, Matrix-Isolation Infrared Spectroscopy

David Tevault and Kazuo Nakamoto

Todd Wehr Chemistry Building, Marquette University, Milwaukee, Wis. 53233

Since DeKock[1] first prepared the $Ni(CO)_n$ (n = 1,2,3 and 4) series in argon matrices, a number of unstable and transient coordination compounds have been synthesized by reacting metal vapor directly with the ligand in inert gas matrices at low temperatures. These include metals such as Pt, Pd and Ni, and ligands such as CO, N_2, NO, O_2 and PF_3. Van Leirsburg and DeKock[2] prepared the MX_2-L type complexes by reacting metal halide vapor such as NiF_2 and $NiCl_2$ directly with ligands such as CO, NO and N_2 in argon matrices. Thus far, no reports are available on the synthesis of metal halid-ethylene complexes in inert gas matrices. In this letter, we wish to report the confirmation of such complex formation by matrix-isolation infrared spectroscopy.

The description of our apparatus and experimental procedures is given elsewhere.[3,4] Mercury halides were vaporized from a CaF_2 cell, and co-condensed with an argon/ethylene mixture (typically 200/1 ratio) onto a 10°K CsI window for infrared measurements.

The infrared spectra of mercury halides in krypton matrices have been reported previously.[5] The present results are in good agreement with those of previous investigators except for small shifts due to the difference in inert gases used. In argon matrices, we observed the Hg-F stretching at 645.9 cm^{-1}, and the Hg-Cl stretching bands at 416.3 ($Hg-^{35}Cl_2$) and 412.0 ($Hg-^{35}Cl^{37}Cl$) cm^{-1}. A doublet band at 941 and 937 cm^{-1} was reported previously for the infrared spectrum of ethylene in argon matrix at low dilution (30/1).[6] As is seen in the top trace of Fig. 1, our spectrum shows two bands at 959.2 (weak) and 946.8 (strong) cm^{-1}. This difference may suggest that the infrared spectrum of ethylene is affected by the change in the dilution ratio. The 946.8 cm^{-1} band is definitely due to the CH_2 wagging mode (ν_7, b_{1u}) which corresponds to the 949.2 cm^{-1} band of the gaseous phase.[7] The 959.2 cm^{-1} band is also due to some CH_2 vibration of ethylene since C_2D_4 does not show any band in this region. However, its assignment is not certain. This band is not our prime interest since it is not sensitive to complex formation with ethylene.

The second trace of Fig. 1 shows the spectrum obtained by reacting HgF_2 with ethylene in an argon matrix. It exhibits a new band at 972.6 cm^{-1} (marked by c) in addition to free ethylene bands (marked by m). The former must be due to the HgF_2-ethylene complex because its frequency changes as the halogen in mercury halides is changed (*vida infra*). In the case of Zeise's salt, $K[Pt(C_2H_4)Cl_3]\cdot H_2O$ in which ethylene is bonded strongly to the Pt atom, the CH_2 wagging band is observed at 1023 cm^{-1} which is 77 cm^{-1} higher than that of free ethylene.[8] In the present case, the shift is about one third (25.8 cm^{-1}) of that observed for Zeise's salt. In the low-frequency region, a new band appears at 620.9 cm^{-1} (marked by c) which is due to the Hg-F stretching mode of the complex. This mode is shifted by 25 cm^{-1} to a lower frequency by complex formation.

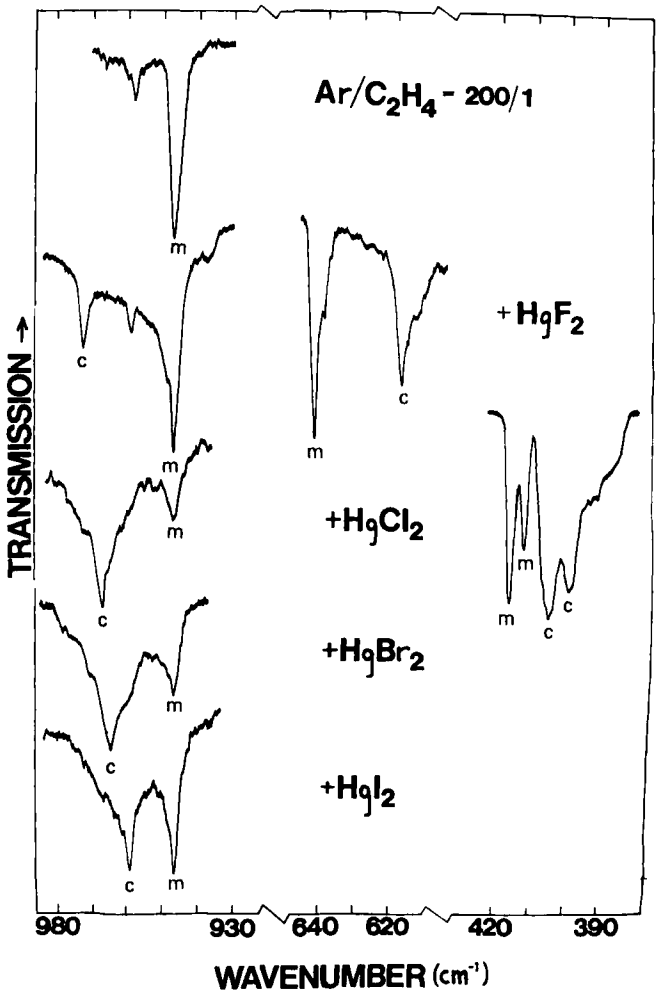

Fig. 1- Infrared Spectra of C_2H_4 and HgX_2-C_2H_4 in argon matrices at 10°K.

The third trace of Fig. 1 shows the spectrum of the $HgCl_2$-ethylene system in an argon matrix. The CH_2 wagging frequency of the $HgCl_2$ complex (967.6 cm^{-1}) is by 5 cm^{-1} lower than that of the HgF_2 complex. In the low-frequency region, two bands at 416.3 and 412.0 cm^{-1} are due to

free $HgCl_2$, and two bands at 404.7 and 399.6 cm^{-1} are attributed to the complex. The average negative shift of two chlorine isotope bands by complex formation is ca. 12 cm^{-1}.

The fourth and fifth traces of Fig. 1 show the spectra of ethylene reacted with $HgBr_2$ and HgI_2, respectively. The CH_2 wagging modes are observed at 965.5 and 960.1 cm^{-1}, respectively. The low-frequency spectra of these systems were not studied due to experimental difficulties below 300 cm^{-1}.

Evidently, the present results are not sufficient to discuss the structure and bonding of the HgX_2-C_2H_4 type complex. The observed spectra show that mercury halide and ethylene are mixed roughly at an equimolar ratio, leading to the formation of the 1:1 complex as the predominant species. A side-on structure in which ethylene is bonded to the Hg atom with the C_2H_4 plane parallel and the C=C axis perpendicular to the Hg-X axis is probable.

By combining the present result with the HgF_2L series[9], we obtain the following order of the Hg-F stretching frequencies (cm^{-1}):

L	=	C_2H_4	CO	NO	N_2
ν(Hg-F)	=	620.9 <	638.3 <	641.7 <	643.2

C_2H_4 is the best σ-donor in the above series since the greater the σ-donation from L to the Hg atom, the lower the Hg-F stretching frequency.[9] It is anticipated that the σ-accepting property of HgX_2 decreases as X is changed in the order F > Cl > Br > I because the polarity of the Hg-X bond decreases in this order. Then, the HgX_2-ethylene interaction also becomes weaker in the same order. This is reflected in the order of the CH_2 wagging frequencies (cm^{-1}):

X	=	F	Cl	Br	I
$\rho_\omega(CH_2)$		972.6 >	967.6 >	965.5 >	960.1

A more complete work including deuterated ethylene and other mono-olefins is now in progress.

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