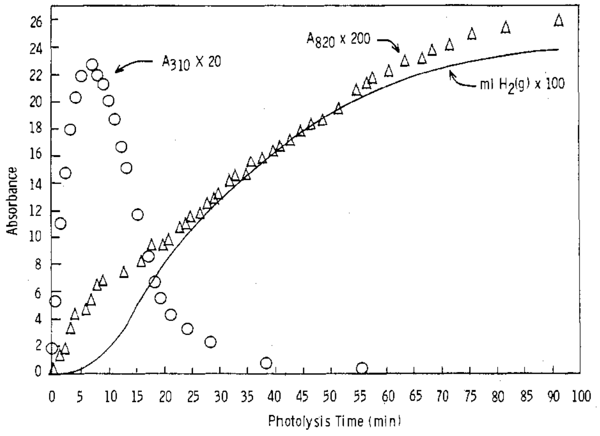

Figure 4. Reaction curves for the photolysis at 274 nm in terms of the absorbances at 310 and 820 nm and the volume of $H_2(g)$ in milliliters for 1.0 mL of 0.020 M CuCl in solution containing 1 M H^+–0.4 M Cl^-; $\mu = 1$ M, $I_0 = 9.7 \times 10^{-9}$ einstein s^{-1}, $T = 301$ K, $P = 740$ torr, and $l = 0.45$ cm.

not change while the blue absorbance disappears (see also Figure 5), indicating that Cu(II) is indeed formed simultaneously with the yellow species and that the 820-nm band is indicative of the amount of Cu(II) formed. In fact, the reduction in copper(I)–chloro complex concentration, as determined by the decrease in absorbance at 274 nm after complete thermal decay of the yellow species, is equal to the amount of Cu(II) species formed as determined by the appearance of the band at 820 nm. Thus it became clear that the course of the reaction could best be followed by monitoring the absorbances at 310 and 820 nm, corresponding to the yellow species and Cu(II) products, respectively.

Figure 4 shows a complete photolysis run in terms of the absorbances at 310 and 820 nm, as well as the volume of H_2 produced. It is apparent that the yellow species and Cu(II) products are produced before any H_2 is evolved and that H_2 evolves only after the onset of decay of the yellow species. Figure 5 illustrates what happens when the photolysis is interrupted at the peak of yellow species concentration. As the yellow species decays thermally between 9 and 70 min on the time scale, there is production of H_2 but no apparent formation of Cu(II) product. Upon resumption of photolysis the yellow species forms again, but to a lesser extent.

The yellow species is easily formed nonphotochemically by adding very small amounts of $NaBH_4$ to the same solutions used in photolysis, giving absorption spectra virtually identical with those of the photochemically produced yellow species. This yellow species, whether formed by photolysis or with $NaBH_4$, is readily adsorbed on an anion-exchange resin (Dowex 1-X8) but not on a cation resin, indicating that it is negatively charged. Unfortunately, it cannot be eluted from the anion resin without being decomposed so that it cannot be obtained in a form which can be easily characterized. Nevertheless, it seems reasonable to suggest that this species may be a hydrido–chlorocuprate(I) complex such as $HCuCl_2^{2-}$ or $HCuCl_3^{3-}$ or some dimeric or polymeric species such as $HCu_2Cl_3^{2-}$ or $HCu_2Cl_4^{3-}$ or a complex mixture of these.

In order for such a copper(I)–hydrido complex to be consistent with the Ferraudi mechanism above, it would have to be formed in a side reaction following step 4. Such a side reaction would involve an electron or H-atom transfer such as

$$HCuCl_2^- + CuCl_2^- \rightleftharpoons HCuCl_2^{2-} + CuCl_2 \qquad (4a)$$

Unfortunately, this system does not yield results as reproducible as one would like in order to make a more detailed analysis of the mechanism and the nature of the yellow species.

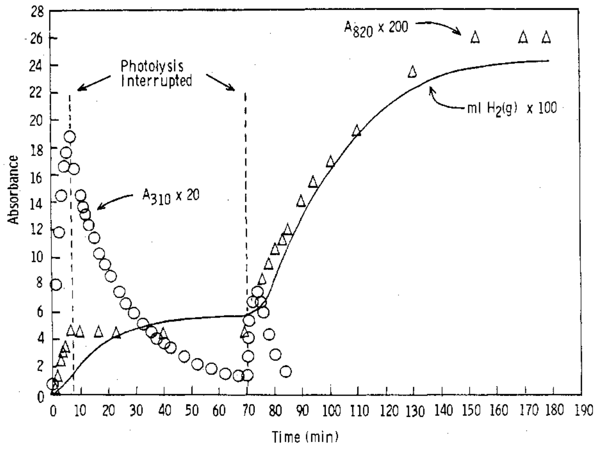

Figure 5. Photolysis and thermal decay curves of same solution as in Figure 4.

For example, the photolysis of identical solutions does not always produce the same maximum amount of yellow species, nor does the yellow species decay at the same rate in the dark. In fact, the decay of the yellow species seems to be sensitive to $[Cu^{2+}]$, to $[H^+]$, and very much to $[Cl^-]$, but it does not appear to decay via any simple rate law. Thus, we are forced to conclude that we may be dealing with a very complex mixture of species rather than a simple monomeric copper(I)–hydrido complex.

Recently, it has been reported that hydride intermediates are observed in the photolytic production of H_2 from acidic solutions of dimeric molybdenum(II)–halo complexes,[10] an anionic system roughly similar to the Cu(I) system we have studied. Indeed, it may well turn out that hydride intermediates are common in many of the H_2-producing reactions involving CTTS photolysis of transition-metal cations or complexes.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Registry No. $CuCl_2^-$, 15697-16-2; $CuCl_3^{2-}$, 29931-61-1; CuCl, 7758-89-6; $CuCl_2$, 7447-39-4.

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The Structure of $HGaCl_2$—a Chlorine-Bridged Dimer

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Received June 11, 1979

The compounds of groups 2A and 3A (primarily Be, Mg, B, and Al) which incorporate both hydrogen and halogen ligands have been the subject of numerous chemical investigations and spectroscopic studies. Interesting structural questions arise for this class of compounds because both hydrogen and halogen atoms can be bridging ligands between metal atoms. The spectroscopic properties of the dimeric group 2A molecules $[HClBeO(C_2H_5)_2]_2$ and $[HClMgO(C_2H_5)_2]_2$ are consistent with structures having bridging hydrogen atoms.[1,2] The hydrogen bridge is also a dominant feature in

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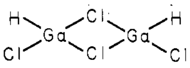
[1] Ashby, E. C.; Goel, A. B. *Inorg. Chem.* **1977**, *16*, 2941.

boron chemistry[3] whereas aluminum compounds[3] are known with both bridging hydrogen and halogen atoms. Bond energy correlations for dimeric Al_2X_6 compounds[4] suggest the following order of bridging potential: $Cl > Br > I > H > CH_3$. This sequence suggests that two-center two-electron bridge bonds are stronger than three-center two-electron bonds in aluminum chemistry.[4] The compound $HAlCl_2$ would provide a test of this hypothesis, but a simple dimeric species has not been observed.[2,5-7] It is of interest that both AlH_3 and $AlCl_3$ have solid-state structures with extended lattices involving six-coordinate aluminum with bridging hydrogen and chlorine atoms.[8] Thus, the question of which ligand, hydrogen or halogen, will be the preferential bridging ligand in group 3A compounds remains unanswered.

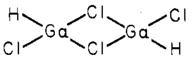
The gallium compound[9] $HGaCl_2$ is known and exists as a simple dimeric species in benzene solution according to cryoscopic molecular weight measurements. However, no experimental data have been reported to ascertain whether $H_2Ga_2Cl_4$ exhibits hydrogen or chlorine bridging or whether the compound is dimeric or more highly associated in the solid state. The task of answering these questions is hindered by the thermal instability of $H_2Ga_2Cl_4$ as it readily eliminates H_2 at temperatures above 20 °C to form Ga_2Cl_4. Thus, the most applicable techniques available for studying the structure of $HGaCl_2$ are low-temperature Raman and infrared spectroscopies. In this paper we report the results of our investigations of $HGaCl_2$ and $DGaCl_2$. All spectroscopic data are consistent with the hypothesis that the dimeric molecule, which also exists in the solid state, has chlorine atoms in the bridging positions. The corresponding bromine compound $HGaBr_2$ was also prepared and was observed to decompose even more readily than $HGaCl_2$.

The dimer $H_2Ga_2Cl_4$ can have structures with bridging chlorine and hydrogen atoms. Structures which incorporate both a bridging chlorine and hydrogen were also possible but seem less likely. Three lines of experimental data suggest that $HGaCl_2$ exists at low temperature in the solid state as the geometrical isomers of the dimer with bridging chlorine atoms, structures I and II: (1) the relative position of the GaH vibrational frequencies when compared with those of analogous group 3A compounds, (2) the comparision of the Raman spectra of $H_2Ga_2Cl_4$, $(CH_3)_2Ga_2Cl_4$, and $(C_6H_5)_2Ga_2Cl_4$, and (3) the assignment of the vibrational modes ν_2 and ν_3 for a chlorine-bridged dimeric skeleton.

bridging chlorine atoms

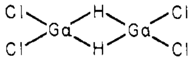


I
cis isomer



II
trans isomer

bridging hydrogen atoms

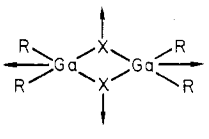


III

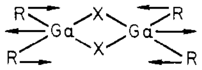
The gallium–hydrogen and gallium–chlorine vibrational motions are expected to give independent frequencies and not to be coupled. Thus, pure Ga–H modes are readily assigned by comparing the infrared and Raman spectra of $H_2Ga_2Cl_4$ and $D_2Ga_2Cl_4$. In contrast, the motions of the terminal and bridging chlorine atoms will be coupled. The infrared Ga–H stretching frequencies have been observed as sharp bands at 2047 cm^{-1} for $H_2Ga_2Cl_4$ and 1465 cm^{-1} for $D_2Ga_2Cl_4$. The $\nu(GaH)/\nu(GaD)$ ratio for these frequencies is 1.40. The corresponding Raman bands occur at 2051 cm^{-1} ($H_2Ga_2Cl_4$) and 1468 cm^{-1} ($D_2Ga_2Cl_4$) with a $\nu(GaH)/\nu(GaD)$ ratio of 1.40. The positions of these bands are consistent with terminal gallium–hydrogen bonds. If the hydrogen atoms had been in bridging positions, the vibrational modes of mainly stretching character should have absorptions at frequencies well below 2000 cm^{-1}. For comparison,[3] terminal B–H bonds lead to absorptions in the 2500–2600-cm^{-1} region, whereas the vibrational modes of bridging hydrogens occur at 1500–1610 cm^{-1}. In addition to the bands for the stretching motions, lower energy bond deformation modes were observed in the infrared spectrum of $H_2Ga_2Cl_4$ at 557 and 551 cm^{-1}. It is unfortunate that the KBr windows of the low-temperature infrared cell prevented the observation of the bond deformation modes in $D_2Ga_2Cl_4$. The Ga–H bond deformation bands in the Raman spectra were observed at 518 cm^{-1} ($H_2Ga_2Cl_4$) and 419 cm^{-1} ($D_2Ga_2Cl_4$) with a ν H/D ratio of 1.39. These observations of the low-energy bond deformation modes further support our hypothesis that the dimer has only terminal gallium–hydrogen bonds. The comparison of the number of observed Raman-active bands (11) with those predicted by symmetry considerations further supports our hypothesis. The cis and trans isomers of the chlorine-bridged structure should have 11 and 9 Raman-active bands, respectively. The dimer with the bridging hydrogen atoms should have only 9 bands, two fewer than that observed.

Further support for our hypothesis that the hydrogen atoms occupy terminal positions comes from comparing the Ga–H infrared stretching frequencies in $H_2Ga_2Cl_4$ with a variety of simple donor–acceptor adducts. All of these compounds involve four-coordinate gallium. The GaH stretching bands for $H_2Ga_2Cl_4$, $HCl_2Ga{\cdot}N(CH_3)_3$, $HCl_2Ga{\cdot}$dioxane, and $HCl_2Ga{\cdot}$bpy occur as sharp bands at 2047, 1986, 1975, and 1855 cm^{-1}, respectively. If there had been a major change in structure from bridging hydrogen in $H_2Ga_2Cl_4$ to terminal hydrogens in the adducts, a large change in frequency would have been expected.

The organogallium dichloride compounds $(CH_3)_2Ga_2Cl_4$ and $(C_6H_5)_2Ga_2Cl_4$ have chlorine-bridged dimeric structures analogous to that proposed for $H_2Ga_2Cl_4$. The structure of the methyl compound was determined by an X-ray study[10] whereas Raman and NQR data[11] were used to assign a structure for the phenyl derivative. The comparison of the Raman spectra of these compounds supports our hypothesis. The frequencies of the Raman-active vibrational modes ν_2 and ν_3 are related to the bridged dimeric skeleton and are dependent on the nature of the bridging atom.[12-16] In the series of compounds $(C_6H_5)_2Ga_2X_4$ (X = Cl, Br, I), the frequencies[11] assigned to ν_2 for different halogens are 279 cm^{-1} (Cl), 185



ν_2



ν_3

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cm^{-1} (Br), and 153 cm^{-1} (I). Similarly, bands for $(C_6H_5)_4Ga_2X_2$ (X = Cl, Br, I) occur at 263 cm^{-1} (Cl), 181 cm^{-1} (Br), and 150 cm^{-1} (I). Consequently, ν_2 is assigned to the band at 320 cm^{-1} for $H_2Ga_2Cl_4$, 311 cm^{-1} for $(CH_3)_2Ga_2Cl_4$, and 330 cm^{-1} for Ga_2Cl_6.[12-16] The vibrational mode ν_3 is also dependent on the nature of the bridging and terminal groups in dimeric structures. Assignments for ν_3 are 167 cm^{-1} (Ga_2Cl_6),[12-16] 140 and 133 cm^{-1} ($(C_6H_5)_2Ga_2Cl_4$),[11] 165 and 132 cm^{-1} ($(CH_3)_2Ga_2Cl_4$), and 160 and 148 cm^{-1} ($H_2Ga_2Cl_4$). In conclusion, all spectroscopic data are fully consistent with a dimeric structure involving bridging chlorine atoms for $H_2Ga_2Cl_4$.

An attempt was made to differentiate the cis and trans isomers of $H_2Ga_2Cl_4$ by variable-temperature ^1H NMR spectroscopy. However, the broadness of the single observed line prevented isomer identification. The increased broadness of the line with increased temperature is consistent with the high spin and quadrupole moments of the two gallium isotopes.

All data are consistent with the hypothesis that $H_2Ga_2Cl_4$ has a chlorine-bridged dimeric skeleton. Thus, when there is a choice between hydrogen and chlorine as bridging atoms, beryllium, magnesium, and boron have bridging hydrogen; gallium has bridging chlorine. The preference of gallium for chlorine bridges may be attributed to several factors. The greater bond energy for the gallium–chlorine bond would favor chlorine bridges. The longer gallium–chlorine bonds will also minimize repulsions between gallium atoms. Furthermore, internuclear and interelectronic repulsion terms will be greater for bridged bonds than terminal bonds, thus making the weak gallium–hydrogen bond even weaker, if it is in a bridging position. Consequently, chlorine bridges are favored in gallium chemistry. Since the other elements have more stable bonds to hydrogen, hydrogen bridges with their greater angular variation can be accommodated.

Experimental Section

Materials. All compounds described in this investigation were manipulated in a standard vacuum system. The stopcocks were lubricated with Halocarbon 25-5S grease, which is not reactive to gallium(III)–chlorine compounds. The solvents were dried by conventional means. The reagents were purified by sublimation and/or fractionation. The gallanes[9] $H_2Ga_2Cl_4$ and $D_2Ga_2Cl_4$ were prepared by reacting 1 mol of $GaCl_3$ with 1 mol of $HSi(CH_3)_3$ or $DSi(CH_3)_3$ at −23 °C for 8 h. The $DSi(CH_3)_3$ was prepared by reacting $ClSi(CH_3)_3$ with $LiAlD_4$ and dry dibutyl ether at 0 °C and purified by trap to trap fractionation. Its purity was confirmed by spectroscopy and vapor pressure measurements. The compound $HGaBr_2$ was prepared from $GaBr_3$ and $HSi(CH_3)_3$ by the analogous procedure but it was observed to be significantly more unstable at room temperature than $H_2Ga_2Cl_4$.

Methylgallium dichloride,[17] $(CH_3)_2Ga_2Cl_4$, was synthesized by reacting equimolar quantities of $GaCl_3$ and $Si(CH_3)_4$ in benzene at 35 °C for 4 h.

Analyses. Gallium was determined by EDTA titration.[18] Chlorine was determined by standard gravimetric procedures. Hydrogen was measured after acid hydrolysis with a Toepler pump–gas buret assembly. Anal. Calcd for $H_2Ga_2Cl_4$: Ga, 49.2; Cl, 50.1; H, 0.71. Found: Ga, 49.3; Cl, 50.0; H, 0.68. Calcd for $D_2Ga_2Cl_4$: Ga, 48.9; Cl, 49.7. Found: Ga, 48.9; Cl, 49.8.

Infrared Spectra. The infrared spectra were recorded in the range 4000–250 cm^{-1} by using a Perkin-Elmer Model 457 spectrometer. Condensed-phase spectra were observed by using a low-temperature cell[19] equipped with KBr optics. The sample was cooled by a cold finger which contained liquid nitrogen.

Raman Spectra. The Raman spectra were recorded by using a Spex Model 14018 double monochromator instrument and the 5145- or 4880-Å line of a coherent radiation argon ion laser. Spectra were observed when the sample was cooled to 120 K. Direct-current detection was employed. Band positions were measured relative to the laser line and should be accurate to ±1 cm^{-1}.

The IR spectra are as follows [frequency, cm^{-1} (intensity: vs, very strong; s, strong; m, medium, w, weak; sh, shoulder)]. $H_2Ga_2Cl_4$: 2051 (vs), 581 (vs), 338 (s), 320 (m), 202 (m), 160 (m), 148 (m), 136 (m), 114 (m), 105 (m), 52 (vs). $D_2Ga_2Cl_4$: 1468 (vs), 419 (vs), 383 (s), 321 (m), 314 (m), 202 (m), 160 (m), 148 (m), 135 (m), 112 (m), 103 (m), 52 (vs).

Nuclear Magnetic Resonance Spectra. The ^1H NMR spectra were recorded at 100 MHz by using the Varian XL-100 spectrometer equipped with variable-temperature capability. The solvent for the 25% solution of $H_2Ga_2Cl_4$ was toluene-d_8. Tetramethylsilane was used as internal reference. The following are the temperature (°C), chemical shift (δ ppm), and width of line at half-height (Hz): −10, 4.06, 64; −60, 4.58, 22; −80, 4.86, 21.

Acknowledgment. This work was supported in part by the Office of Naval Research. We also wish to thank Professors P. Prasad of this department and T. B. Brill, University of Delaware, for the Raman spectral data. The XL-100 NMR spectrometer was obtained by a grant from the National Science Foundation.

Registry No. $H_2Ga_2Cl_4$, 72214-14-3; $D_2Ga_2Cl_4$, 72214-15-4.

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Ionic Species in HF–SbF_5 Solutions. An Infrared Spectroscopy Investigation

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Infrared spectra of HF–SbF_5 solutions were measured previously by Hyman et al.[1] More recently, Couzi et al.[2] reported the infrared spectra of a crystalline solid at 77 K, formulated as $H_2F^+SbF_6^-$. However, these results have been criticized by Christe et al.,[3] who suggested that this compound should be better formulated as $SbF_5{\cdot}HF{\cdot}H_2O$.

In a previous paper[4] we reported the phase diagram of the HF–SbF_5 system and confirmed the existence of the $2HF{\cdot}SbF_5$ adduct postulated by Couzi and co-workers. However, the infrared spectra given by Couzi et al. for HF–SbF_5 solutions presented some features, not easily reconcilable with the earlier data of Hyman and co-workers. Further, Gillespie and Moss[5] have conclusively shown from electrical conductivity and NMR measurements that polymeric anions such as $Sb_2F_{11}^-$ are present in solution even at relatively low concentration in SbF_5 (below 22 mol % of SbF_5, which is significantly lower than the 33.33 mol % of SbF_5 concentration for $H_2F^+SbF_6^-$). This leads to the suggestion that cationic species also could be solvated, giving rise to the $H_3F_2^+$ ion, analogous to the $H_5O_2^+$ grouping which has been recently shown by Zundel and co-workers[6] to play a major role in aqueous solutions of strong

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