

overlap population at the observed bond length of 2.587 Å is 0.402.

The net atom charges for the various types of atoms are +0.414 for Mo₁₁, +0.731 for Mo₂₁, -0.629 for Br₁₁, -0.082 for Br₂₁, -0.938 for O₁₁, and +0.483 for H. The Mo₂₁ charge could be selectively reduced slightly by choosing VSIP's for oxygen based on the ionization potential of H₂O.⁴⁵ However, no additional calculations with altered *H_{ii}*'s were done since they would not affect the qualitative effects we were seeking.

The charge distribution and the overlap populations are intimately related and result from the nature of the terminal atoms. The larger the differences in the

(45) A. Viste and H. B. Gray, *Inorg. Chem.*, **3**, 1113 (1964).

VSIP's (electronegativities may be used as a rough guide) of the terminal atoms the greater will be the differences in the charges of the equatorial and axial Mo's. In general the Mo atom with the largest charge will be associated with the largest overlap populations and the shortest bonds and *vice versa*. This simple concept is consistent with our calculations and our observed structural parameters; it should have some predictive power with respect to structural parameters of other substituted Mo₆X₈⁴⁺ clusters.

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Studies on the Chemistry of Halogens and of Polyhalides. XXIX. Complex Compounds of Bromine Chloride

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Bromine chloride complexes with pyridine, 4-picoline, 2,3- 2,4-, 2,5-, 2,6-, 3,4-, and 3,5-lutidines, and 2,3,6-collidine were prepared. The lutidine complexes, except that of 3,4-lutidine, are quite stable at room temperature under anhydrous conditions. Formation constants of these complexes were determined in carbon tetrachloride solutions. Comparison of these values with the formation constants of iodine(I) chloride and iodine bromide shows that the order of the Lewis acid strength is ICl > IBr > BrCl. Far-infrared spectra of the complexes indicate that the fundamental Br-Cl vibration band is shifted from 430 to 280 cm⁻¹ by complexation with pyridine.

Introduction

While numerous halogen complexes involving iodine, bromine, iodine(I) chloride, iodine(III) chloride, and iodine bromide have been reported in the literature, it is interesting to note that with two exceptions, no mention is made of the compounds of bromine chloride. In 1931, Williams briefly mentioned the preparation of the pyridine-bromine chloride complex,¹ but no details are given on the properties of the resulting compound. More recently, preparation of 4-*n*-amylpyridine-bromine chloride complex was reported by Zingaro and Witmer.²

Bromine chloride is a rather unstable compound, and so far, it has not been obtained in the pure state. It is highly dissociated in the vapor phase and in solutions, the equilibrium constant for the reaction 2BrCl ⇌ Br₂ + Cl₂ being 0.145 at 25° in carbon tetrachloride solutions.³ This instability of bromine chloride very probably discouraged in the past the investigation of its complexing ability. It should be noted, however, that Scott calculated the electron-accepting ability of bromine chloride (Lewis acid strength) on the basis of the free energy of the formation of trihalide ion

Br₂Cl⁻ in aqueous solutions.⁴ On the basis of these calculations, Scott obtained the following order of Lewis acid strengths for the halogens: ICl ≫ BrCl > IBr ≫ I₂ > Br₂ ≫ Cl₂.

This work was undertaken in order to study possible formation of bromine chloride complexes with heterocyclic amines and to compare its complexing ability with that of other halogens and interhalogen compounds.

Experimental Section

Reagents.—Technical grade pyridine was refluxed for 2 hr over granulated barium oxide and then slowly distilled through a 100-cm helices-packed column. The middle fraction of the distillate was used.

All of the substituted pyridines used in the investigation were obtained from the Aldrich Chemical Co. These were used without further purification aside from drying. Bromine and chlorine were obtained from J. T. Baker Chemical Co. and Matheson Co., respectively, and were used without further purification.

The purification of carbon tetrachloride has been discussed in previous publications.⁵ 1,1,2-Trichlorotrifluoroethane was refluxed for 24 hr over barium oxide and then distilled slowly through a 1-m helices-packed column.⁶ 1,2-Dichloroethane was washed successively with sodium bicarbonate solution and water and then dried over calcium sulfate. It was then refluxed for

(1) G. Williams, *J. Chem. Soc.*, 2783 (1931).

(2) R. A. Zingaro and W. B. Witmer, *J. Phys. Chem.*, **64**, 1705 (1960).

(3) A. I. Popov and J. J. Mannion, *J. Am. Chem. Soc.*, **74**, 222 (1952).

(4) R. L. Scott, *ibid.*, **75**, 1550 (1953).

(5) A. I. Popov and W. A. Deskin, *ibid.*, **80**, 2976 (1958).

(6) F. L. Greenwood, *J. Org. Chem.*, **10**, 416 (1945).

TABLE I
 BROMINE CHLORIDE COMPLEXES WITH PYRIDINE AND PYRIDINE DERIVATIVES

Compound	Mp, °C	Analyses, %							
		Carbon		Hydrogen		Nitrogen		Iodometric equiv	
		Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
py·BrCl	106-107 ^a	97.2	97.8
2,4-lut·BrCl	96-98	37.75	37.43	4.05	3.97	6.29	6.20	111.3	112.9
2,5-lut·BrCl	94-96	37.75	37.62	4.05	3.97	6.29	6.26	111.3	112.7
2,6-lut·BrCl	99-100	37.75	37.50	4.05	3.99	6.29	6.24	111.3	112.7
3,4-lut·BrCl	93-94	37.75	37.52	4.05	4.03	6.29	6.35	111.3	112.3
3,5-lut·BrCl	106-108	37.75	37.71	4.05	4.07	6.29	6.32	111.3	111.6
2,3,6-coll·BrCl	102-104	40.62	40.39	4.69	4.63	5.92	6.04	118.6	121.0
4-pic·BrCl	89-90	104.2	103.6

^a Literature¹ mp 107-108°.

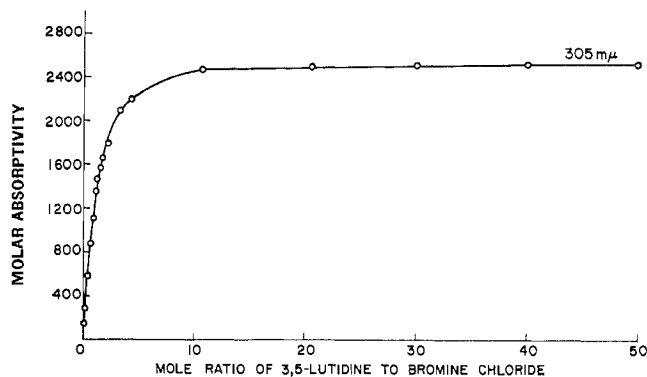


Figure 1.—Molar absorptivity of the 3,5-lutidine-bromine chloride system at 305 mμ. The limiting value gives the molar absorptivity of the complex.

24 hr and distilled through a 1-m helices-packed column.⁷ Dichloromethane was refluxed for 24 hr over barium oxide and distilled through a 1-m helices-packed column.

Physical constants of the above solvents were checked against literature values, and in all cases close agreement was obtained.

Preparation of Solutions.—Stock solutions of the halogens were prepared by dissolving appropriate amounts of the halogens in the respective solvents. The concentration was then determined by iodometric titration and the solutions were diluted to the desired concentration. Stock solutions of the respective pyridines were made by weighing the respective compound into a volumetric flask and diluting with purified solvent. Bromine chloride solutions were prepared by mixing the carbon tetrachloride solutions of the two halogens. In the mole ratio study the concentration of the BrCl was calculated from the known value of the dissociation constant.³ The mixed solutions of bromine chloride and of the respective pyridine were prepared just before each measurement. Contact of solutions with the atmosphere was kept to a minimum, but no attempt was made to do all of the transfers in a completely inert atmosphere. Preliminary results have indicated that brief contacts of the solution with the atmosphere did not alter the experimental data. Likewise, it was found that carbon tetrachloride solutions of bromine chloride and the pyridines were stable for at least 2 hr after mixing, while, in general, spectral measurements were completed within 5-10 min of the initial mixing. Concentration of the solutions was kept low ($<10^{-3}$ M) in order to avoid the formation of the solid complex.

Preparation of Bromine Chloride Complexes.—Equimolar solutions ~ 0.1 M of bromine chloride and the respective pyridine were prepared in 1,1,2-trichlorotrifluoroethane. It had been found that purer products were obtained if the preparation was carried out at lower temperatures. For this reason, 1,1,2-trichlorotrifluoroethane was used as a solvent, since its freezing point (-36.9°) was below that of carbon tetrachloride. These solutions were cooled in a carbon tetrachloride-monochlorobenzene slush and then rapidly mixed in a drybox in an anhydrous

nitrogen atmosphere. The precipitate was filtered, washed with purified 1,1,2-trichlorotrifluoroethane, and dried under vacuum. The list of complexes prepared, their melting points, and the analytical data are given in Table I.

In all cases, the complexes were obtained as yellow or light yellow microcrystalline powders. They slowly reacted with atmospheric moisture. When the complexes were kept in a desiccator, the pyridine, 4-picoline, and 3,4-lutidine complexes lost bromine chloride after several days. However, the 2,4-lutidine, 2,5-lutidine, 2,6-lutidine, 3,5-lutidine, and 2,3,6-collidine complexes of bromine chloride remained unchanged for at least 8 weeks.

Attempts to make bromine chloride complexes with 2-fluoropyridine, 4-hydroxypyridine, 2-chloropyridine, and 2-bromo-5-nitropyridine were unsuccessful. Obviously the inductive effects of the halogen and the OH group decreased the donor strength of the pyridine to the point where interaction with BrCl was too weak to produce a solid complex. Attempts to make the 3,4-lutidine complex in dichloromethane and 1,2-dichloroethane solutions were also unsuccessful.

Absorption Spectra.—Ultraviolet absorption spectra were obtained on a Cary Model 14 spectrophotometer. Either 1- or 5-cm path length cells were used. All measurements were carried out at room temperature of $\sim 25^\circ$. The donor:acceptor ratio was varied within such limits so as to give a good spread of experimental points. The concentration of bromine chloride was held constant in all cases.

Spectral data obtained on the bromine chloride-respective pyridine mixtures were used to calculate the formation constants of the complexes using the mole ratio method described in a previous publication.⁸ The formation constants of the complexes were determined in carbon tetrachloride solutions.

In a mixture containing bromine chloride and a base B, the total absorbance at a given wavelength in a 1-cm cell is expressed by

$$A = \epsilon_{\text{BrCl}}C_{\text{BrCl}} + \epsilon_{\text{B}}C_{\text{B}} + \epsilon_{\text{C}}C_{\text{C}} \quad (1)$$

where ϵ_{BrCl} , ϵ_{B} , and ϵ_{C} are the molar absorptivities of BrCl, B, and the complex, and C_{BrCl} , C_{B} , and C_{C} are the equilibrium concentrations of the three species. Assuming a 1:1 complex in solution, the absorbance equation becomes

$$A = \epsilon_{\text{BrCl}}(C_{\text{BrCl}}^0 - C_{\text{C}}) + \epsilon_{\text{B}}(C_{\text{B}}^0 - C_{\text{C}}) + \epsilon_{\text{C}}C_{\text{C}} \quad (2)$$

where C_{BrCl}^0 and C_{B}^0 are the stoichiometric concentrations of BrCl and of the base, respectively

The molar absorptivity of bromine chloride complex was determined by the limiting absorbance measurement³ (Figure 1), while ϵ_{B} was determined from measurements on solutions of the pyridines in CCl_4 . Once these values are determined, the equilibrium concentrations of the complex and hence the formation constant can be calculated from eq 2. Correction was applied for the dissociation of uncomplexed bromine chloride.³

Spectra of bromine chloride-base solutions containing a fixed amount of bromine chloride and a variable amount of the respec-

(7) A. I. Vogel, *J. Chem. Soc.*, 644 (1948).

(8) A. I. Popov and R. H. Rygg, *J. Am. Chem. Soc.*, **79**, 4622 (1957).

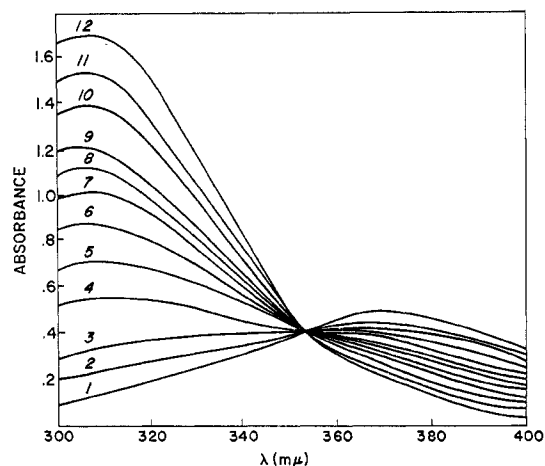


Figure 2.—Absorption spectra of the 3,4-lutidine-bromine chloride system in carbon tetrachloride solutions where $C_{\text{BrCl}} = 6.62 \times 10^{-4} M$. $C_{\text{lut}} \times 10^{-4} (M)$: (1) 0.0; (2) 0.62; (3) 1.24; (4) 2.47; (5) 3.71; (6) 4.94; (7) 6.18; (8) 7.42; (9) 8.65; (10) 12.6; (11) 18.5; (12) 61.8.

tive base were obtained in the 450–300- $m\mu$ spectral range. A typical set of spectral curves is illustrated in Figure 2. All pyridine derivatives listed in Table II gave essentially ideal isosbestic points. In general, the position of the absorption band of the complex did not change appreciably with the nature of the base. It varied from 304 $m\mu$ for the 3,4-lut·BrCl complex to 310 $m\mu$ for 2,6-lut·BrCl.

TABLE II

FORMATION CONSTANTS OF AMINE-BROMINE CHLORIDE COMPLEXES IN CARBON TETRACHLORIDE AT 25°

Complex	$10^{-3}K_f, M^{-1}$	Complex	$10^{-3}K_f, M^{-1}$
py·BrCl	1.2 ± 0.1^a	2,6-lut·BrCl	1.5 ± 0.1
4-pic·BrCl	2.1 ± 0.2	3,4-lut·BrCl	4.2 ± 0.4
2,4-lut·BrCl	6.7 ± 0.7	3,5-lut·BrCl	6.8 ± 0.8
2,5-lut·BrCl	5.2 ± 0.4		

^a Standard deviations for independent runs.

Studies of absorbance *vs.* time were conducted using bromine chloride as the solute in 1,2-dichloroethane and in dichloromethane. It was found that the solutions were quite unstable and the spectra changed rapidly with time.

Far-infrared absorption spectra were obtained with a Perkin-Elmer 301 spectrophotometer, on the Nujol mulls of the solid complexes. Prior to use the frequency scale was carefully calibrated in the usual manner using water vapor as reference. Typical absorption curves are shown in Figure 3. The mulls were placed between two polyethylene disks separated by a polyethylene spacer. In order to obtain the absorption bands of the respective pyridines, polyethylene liquid cells obtained from Barnes Engineering Co. were used. The instrument was continuously purged with nitrogen while in use. The bands obtained for the uncomplexed pyridines agreed closely with those obtained by Frank and Rogers.⁹

Analyses.—Microanalyses for carbon, hydrogen, and nitrogen were made at Spang Microanalytical Laboratory, Ann Arbor, Mich. Iodometric equivalent was determined by dissolving the complexes in aqueous acetic acid solution and titrating the resulting solution by standard iodometric technique.

Results and Discussion

Formation constants for the heterocyclic amine-bromine chloride complexes are given in Table II. The measurements were carried out on solutions of dif-

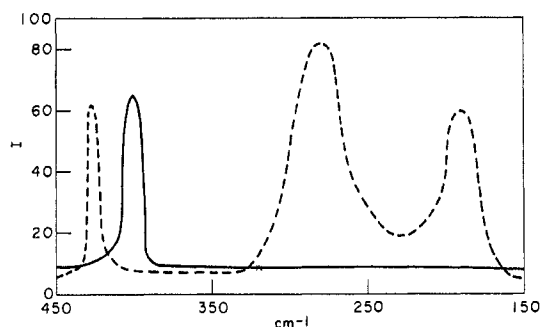


Figure 3.—Far-infrared spectra of pyridine (—) and of the py·BrCl complex (---).

ferent concentrations and at least at three different wavelengths. The wavelengths were selected so that there was minimum interference from the absorption of uncomplexed BrCl.

With one exception, the complex-forming ability of the amines is directly proportional to their basic strength. That is, the stability of the bromine chloride complexes is in the order lut > pic > py. The exception occurs in the case of the 2,6-lutidine complex, where the order is pic > 2,6-lut > py. This inversion is not particularly surprising, since in the case of iodine(I) chloride, it has been shown⁸ that because of the steric hindrance of the two methyl groups of the 2,6-lutidine, this compound forms weaker complexes with large ligands than does pyridine. Also, pyridine forms a stronger complex with boron trifluoride than 2,6-lutidine.¹⁰ Bromine chloride is not as large a ligand as iodine monochloride or boron trifluoride; therefore, in this case, the 2,6-lutidine complex is still stronger than the pyridine complex, but weaker than the picoline complex. On the other hand, the 2-methyl group of the 2,4-lutidine and 2,5-lutidine does not interfere with the complex formation and since these amines are stronger bases than either picoline or pyridine, they form stronger complexes with bromine chloride.

The comparison of the formation constants for the complexes of iodine(I) chloride, iodine bromide, and bromine chloride shows that the order differs somewhat from that predicted by Scott.⁴ The results, shown in Table III, indicate that the order of Lewis acid strength is ICl > IBr > BrCl. It is possible that the order may be dependent on the reaction medium. In any case, the difference in the acceptor strengths of BrCl and of IBr is not great.

TABLE III

COMPARISON OF THE FORMATION CONSTANTS OF PYRIDINE COMPLEXES WITH ICl, IBr, AND BrCl IN CARBON TETRACHLORIDE AT 25°

Amine	K_f, M^{-1}		
	ICl ^a	IBr ^a	BrCl
Pyridine	4.8×10^5	1.3×10^4	1.2×10^3
2-Picoline	8.9×10^5	2.4×10^4	2.1×10^3
2,6-Lutidine	8.9×10^4	3.7×10^3	1.5×10^3

^a Reference 8.

(9) C. W. Frank and L. B. Rogers, *Inorg. Chem.*, **5**, 615 (1966).

(10) H. C. Brown, H. I. Schlesinger, and S. F. Cardon, *J. Am. Chem. Soc.*, **64**, 325 (1942).

TABLE IV
 INFRARED ABSORPTION BANDS OF BROMINE CHLORIDE-PYRIDINE
 AND SUBSTITUTED PYRIDINE COMPLEXES IN THE 667-130-CM⁻¹ REGION

Compound	Bands, cm ⁻¹									
Bromine chloride	430 ^a									
Pyridine	602	402								
py·BrCl	631	427		280 ± 4 ^b		211 vw		192 ± 1 ^c		
4-picoline	513	482								
4-pic·BrCl	542	481		266 ± 3 ^b		173 ± 1 ^c				
2,4-Lutidine	551	513	426	402	281	221	194			
2,4-lut·BrCl	540	438		288 ± 3 ^b		174 ^c				
2,5-Lutidine	642	474	429	401	390	292	220			
2,5-lut·BrCl		545	501	431			212			
2,6-Lutidine	549	534	412	286						
2,6-lut·BrCl	565	534	476	281 ^b		219	186 ^c			
3,4-Lutidine	592	524	501	412	253					
3,4-lut·BrCl	602	540	517	420						
3,5-Lutidine	528	429	390		272	280 ^b	206			
3,5-lut·BrCl	539			242, 233	214		174 ^c			

^a G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., Princeton, N. J., 1965, p 512. ^b $\nu_{\text{Br-Cl}}$. ^c $\nu_{\text{N-Br}}$.

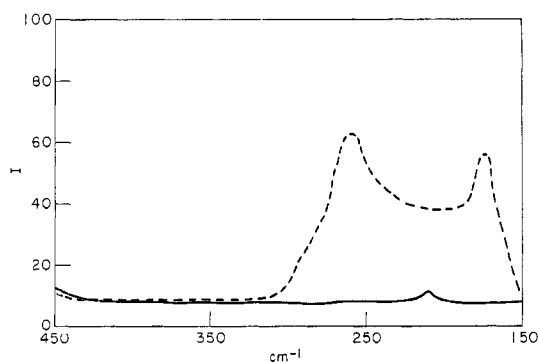


Figure 4.—Far-infrared spectra of 4-picoline (—) and of the 4-pic·BrCl complex (---).

Far-infrared bands of the pyridine and of the pyridine-bromine chloride complexes are shown in Table IV. The analysis of the spectrum is complicated by numerous bands of the amines in this spectral region. Tentative assignments are possible in the case of pyridine which does not have bands below 402 cm⁻¹. In this case, it seems reasonable to assume that the 280-cm⁻¹ band is due to the BrCl stretch. It is interesting to note that this shift from the 430-cm⁻¹ band of the uncomplexed BrCl is much larger than the one observed for the ICl stretch which is at 375 cm⁻¹ for uncomplexed molecule and 280 cm⁻¹ in the

pyridine-iodine(I) chloride complex.¹¹ The shift seems to be even larger for the 2,4-lutidine-bromine chloride complex where the BrCl stretch appears to be at 238 cm⁻¹. Analogous to the case of ICl, the $\nu_{\text{Br-Cl}}$ band, upon complexation, becomes broader and more intense.

Bands have been tentatively assigned to the bromine-nitrogen stretching vibrations at 192 cm⁻¹ for the pyridine complex and down to 174 cm⁻¹ for the other complexes. As in the case of the bromine-chlorine stretch, a bromine-nitrogen stretch is not observed in the 2,5-lutidine or 3,4-lutidine complexes. Further work, however, is necessary to elucidate the far-infrared spectra of bromine chloride complexes.

After the completion of this work, a paper appeared in the literature by Ginn, *et al.*,¹² which reports far-infrared spectra of the pyridine-bromine chloride complex. These authors report a BrCl stretching frequency at 296 cm⁻¹ and an N-Br band at 196 cm⁻¹. Our values are 280 and 192 cm⁻¹, respectively. At this time, we cannot account for this difference in the $\nu_{\text{Br-Cl}}$ frequency.

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(11) J. Yarwood and W. B. Person, *J. Am. Chem. Soc.*, **90**, 3930 (1968).

(12) S. G. W. Ginn, I. Hague, and J. L. Wood, *Spectrochim. Acta*, **24A**, 1531 (1968).