

Figure 3. Correlation of the observed electronic transitions with the calculation of Interrante and Messmer,<sup>11</sup> Piepho, Schatz, and McCaffery,<sup>10</sup> and Isci and Mason.<sup>8</sup> Asterisk signifies three singlet and six triplet energy levels in this region.

The assignment for the long-wavelength transition near  $35800\text{ cm}^{-1}$  is still in question because of the uncertainty in the ordering of the d levels. It is agreed<sup>8,10,11</sup> that the transition terminates on an  $a_{2u}\pi^*$  ligand level. The extinction coefficient and oscillator strength for this transition are small (Table I), and this is in qualitative agreement with the assignment as a singlet-triplet transition. Piepho et al.,<sup>10</sup> Isci and Mason,<sup>8</sup> and Interrante and Messmer<sup>11</sup> assigned the transitions for bands 2 and 3 as  $e_g \rightarrow a_{2u}$ , giving rise to  $E_u'$  and  $A_{2u}'$  states. Interrante and Messmer assigned both singlet and triplet transitions to the  $38835\text{-cm}^{-1}$  band. The shoulder near  $41000\text{ cm}^{-1}$  had not been assigned with certainty. The calculations of Piepho et al.<sup>10</sup> do not account for this transition, although they speculated on possible transitions. Isci and Mason<sup>8</sup> and Interrante and Messmer<sup>11</sup> on the other hand have calculated energy levels that agree fairly well with this shoulder and Interrante and Messmer<sup>11</sup> assigned the transition as  $a_{2g} \rightarrow a_{2u}$  with symmetry labels ( $A_{2u}, E_u'$ ). The less intense band near  $43500\text{ cm}^{-1}$  previously unreported in the literature can be accounted for by Piepho et al.<sup>10</sup> and Isci and Mason<sup>8</sup> who assigned a symmetry label of  $E_u'$  whereas Interrante and Messmer<sup>11</sup> have assigned the transition in this region as  $a_{2g} \rightarrow a_{2u}$  with symmetry label  $A_{1u}$ .

The assignments of the experimentally observed transitions in the region  $44000\text{--}50000\text{ cm}^{-1}$  are less clear. Interrante and Messmer<sup>11</sup> have calculated three singlet and six triplet energy levels to lie in that region but did not assign transitions for them. Isci and Mason<sup>8</sup> have calculated states near  $45000$  ( $A_{2u}$ ),  $45700$  ( $E_u'$ ), and  $47600\text{ cm}^{-1}$  ( $B_{1u}$ ), although they did not report the assignment of transitions at energies greater than these three.

The additional transition present at an energy greater than  $50000\text{ cm}^{-1}$ , band 8, is in closer agreement with the calculations of Interrante and Messmer.<sup>11</sup> They have calculated energy states at  $50800$  and  $52400\text{ cm}^{-1}$ . The transition at  $50800\text{ cm}^{-1}$  has been assigned as  $a_{1g} \rightarrow a_{2u}$  ( $A_{2u}$ ).<sup>11</sup>

Figure 3 shows the energy levels for states in  $\text{Pt}(\text{CN})_4^{2-}$  obtained by curve fitting experimental data. Shown also are the energy states calculated by Piepho et al.,<sup>10</sup> by Isci and Mason,<sup>8</sup> and by Interrante and Messmer.<sup>11</sup> This figure shows

the agreement between theory and experiment for the two very different approaches used by these authors. The calculations of Piepho et al.<sup>10</sup> and Isci and Mason<sup>8</sup> agree with the experimental results at low energies better than at higher energies, whereas calculations based on the  $X\alpha$  scattered-wave approach agree better at the higher energies. The latter calculations did not implicitly include spin-orbit coupling, which may have improved the agreement with the experimental data.

The assignments of the metal to ligand charge-transfer electronic absorption transitions for the  $\text{Pt}(\text{CN})_4^{2-}$  anion are still subject to question. It is hoped that this additional experimental evidence may stimulate further theoretical calculations on the interesting tetracyanoplatinate anion.

Registry No.  $\text{K}_2\text{Pt}(\text{CN})_4$ , 562-76-5;  $(\text{Bu}_4\text{N})_2\text{Pt}(\text{CN})_4$ , 21518-40-1.

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## Extraction of Molybdenum(VI) from Hydrochloric Acid Solutions by Triisooctylamine in Organic Diluents

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There exist only a few detailed investigations of the extraction of molybdenum(VI) by long-chain alkylammonium salts, and these deal mainly with the influence of acidity and diluents on the extraction.<sup>1-7</sup> For example, the equilibria involved in extracting Mo(VI) from aqueous nitric acid solutions were found to depend upon the diluent.<sup>1,8</sup>

In nonpolar diluents, third-phase formation was observed when the aqueous molybdenum(VI) concentration was increased. No definite formula could be given to the organic compound as was found from molecular weight determinations. In 1,2-dichloroethane and 1,2-dichlorobenzene, no third-phase formation occurred nor did extraction lead to aggregation.

In hydrochloric acid medium, the formation of a third phase has been reported in the extraction of Mo(VI) by hydrochloride salt solutions of triisooctylamine in benzene and xylene.<sup>9</sup> This, however does not occur when extractions are performed with those diluents at a high acidity (from 1 to 6 M HCl) or at relatively low acidity (0.01 M HCl) when the ammonium salt is dissolved in moderately polar diluents.<sup>10</sup>

These observations seem to indicate that third-phase formation depends both on diluent characteristics, such as polarity, and on the initial aqueous solution.

The present study was undertaken to obtain further information on the extraction of molybdenum(VI) from hydrochloric acid solutions of high acidity by triisooctylamine, a suitable extractant whose properties have been previously reported in numerous metal extraction systems. We have also investigated the influence of the following diluents: carbon tetrachloride, 1,2-dichlorobenzene, and 1,2-dichloroethane. Some additional data are given for solutions in benzene and xylene. With all of these diluents there is normally no extraction of the metal complexes from aqueous solutions.

Both chemical and spectrophotometric methods were used in this study. Our results are discussed in light of the known chemistry of molybdenum(VI) in aqueous HCl media.

### Experimental Section

The amine ( $R_3N$ ) and the diluents have been purified as previously described.<sup>11</sup> The hydrochloride salt of triisooctylamine in various diluents was obtained as indicated in earlier reports.<sup>12,13</sup> The chemicals, Merck analytical reagent grade, were used without further purification. The chloride content of the aqueous molybdenum(VI) solutions of various concentrations and acidities was kept constant at 6 M using NaCl. Extractions were performed by equilibrating initially equal volumes of aqueous and organic phases at room temperature ( $25 \pm 2^\circ\text{C}$ ). Fifty-milliliter amounts of each phase were added in a glass-stoppered Erlenmeyer flask and were shaken for 20 min. This time was sufficient for attaining equilibrium at high acidity and sufficient to obtain reproducible results at low acidity. Equilibrium-phase volumes were estimated to  $\pm 0.2$  ml by draining each phase from a separatory funnel into 50-ml graduated tubes. In no case did the volume of each phase differ from that of the initial phase.

The chloride ion concentration of the organic phase after molybdenum(VI) extraction was determined in the organic phase with the Volhard<sup>14</sup> method using nitrobenzene, starting from a homogeneous water-alcohol phase consisting of 10% organic solution studied, 75% ethanol, and 15% water or from the aqueous phase by Volhard's method after triple reextraction with equal volumes of a 0.4 N NaOH solution. The molybdenum concentration in the organic phase was determined after reextraction (triple) into the aqueous phase as mentioned above. High concentrations of Mo(VI) were determined gravimetrically<sup>15</sup> and low concentrations colorimetrically.<sup>16,17</sup>

Blanks were run to determine the uptake of chloride by solutions of  $R_3NHCl$  in the diluents, in the absence of Mo(VI) from the initial aqueous solutions. Corrections were made if needed. It was also ascertained that in the absence of  $R_3NHCl$ , no molybdenum(VI) was extracted into the diluents.

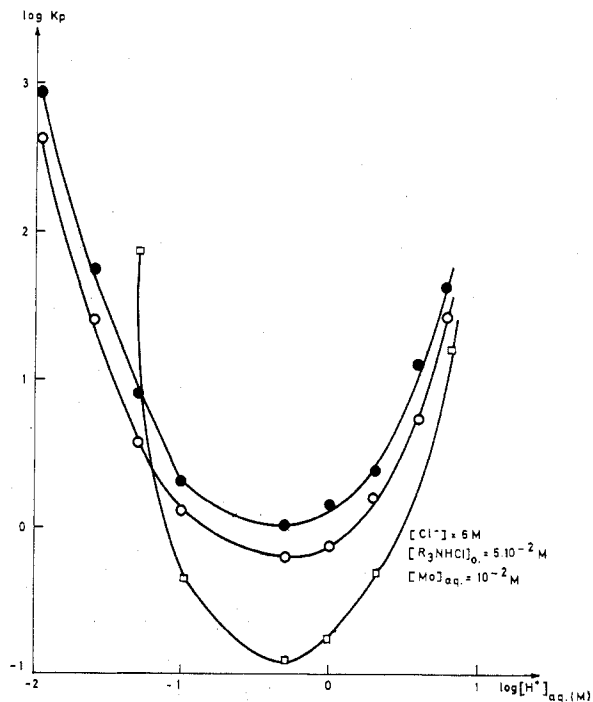
The results reported are the average of at least three determinations. Experimental data were consistent to within  $\pm 1\%$ . The molar distribution ratio is given as  $K_p = [Mo]_o/[Mo]_{aq}$  where the subscripts o and aq stand for organic and aqueous phase, respectively.

The uv absorption spectra were run on a Perkin-Elmer 350 spectrophotometer against reference solutions.

### Results and Discussion

**Dependency of the Distribution Ratio of Mo(VI) on HCl Concentration.** The effect of the aqueous phase hydrochloric acid concentration on the extraction of molybdenum(VI) by triisooctylamine in carbon tetrachloride, 1,2-dichlorobenzene, and 1,2-dichloroethane is shown in Figure 1, at constant ionic strength ( $[Cl^-] = 6$  M).

The shapes of the curves are qualitatively similar to those obtained for triisooctylamine solutions of benzene and xylene<sup>9</sup> and also to those obtained using an anion resin<sup>18</sup> or tetrahexyl-, tetrabutyl-, and tetrapropylammonium chloride in methyl isobutyl ketone.<sup>19</sup> The extraction is almost 100% complete from acidic solutions of low hydrogen ion concentrations. The decrease in the distribution coefficient observed in all of these systems from  $10^{-2}$  to 2 M HCl may imply successive protonation of anionic species<sup>20</sup> to give  $HMo_4O_{13}^-$  or a complex metal acid such as  $H_2Mo_4O_{13}$ , the formation of cationic species



**Figure 1.** Hydrogen ion dependency of the distribution ratio of Mo(VI) in hydrochloride salt of triisooctylamine. Diluents: carbon tetrachloride ( $CCl_4$ ),  $\square$ ; 1,2-dichloroethane (DCE),  $\bullet$ ; 1,2-dichlorobenzene (DCB),  $\circ$ .

$HMo_2O_6^{+21}$  which will not extract, and the rather unstable cationic chloride complex  $MoO_2Cl^+$  ( $pK = -0.4$ ).<sup>22</sup>

The increase in extraction observed in the range of high acidity upon increasing the hydrogen ion concentration was attributed by Selmer-Olsen<sup>23</sup> to the increasing concentration of anionic chloro complexes in the aqueous phase.

The diluent appears to influence the extraction process. For example, in the range of rather low hydrogen ion concentrations, third-phase formation occurs for organic solutions in carbon tetrachloride, whereas this is not observed at higher hydrogen ion concentrations nor in the range of low hydrogen ion concentrations in the other systems which we studied. For extractions from 1 to 0.01 M hydrochloric acid solutions, with triisooctylamine solutions in benzene and xylene, the formation of a greenish oily phase was also observed, whereas this phenomenon does not occur at higher acid concentrations.<sup>9</sup>

**Determination of the Formula of the Complex.** To determine the stoichiometry of the extracting species, extraction isotherms were determined for the various systems. The extraction isotherms indicate, for the asymptotic part of the curves, a limiting loading ratio of ammonium salt to molybdenum of approximately 2.

Besides an amine:metal ratio of 1 for the extraction of metal giving chloro complexes,<sup>24,25</sup> an amine:metal ratio of 2 has often been reported, in particular for U(VI).<sup>26-31</sup> Bullock et al.<sup>32</sup> have also found for the neptunium(VI) hydrochloric acid-MDOA-chloroform system an amine:metal ratio of 2. According to an earlier report,<sup>33</sup> the neptunium species extracted into a solution of long-chain quaternary ammonium salt is the tetrachlorodioxoneptunium(VI) anion,  $NpO_2Cl_4^{2-}$ . Additional evidence was obtained by saturating with molybdenum(VI) an organic solution containing a known quantity of the amine salt. The organic solution was extracted four times with fresh aqueous solutions. No more uptake of Mo(VI) could be detected after mixing together the resulting organic solution and fresh aqueous phases.

The ratio of the concentrations of  $R_3N$ , Mo(VI), and chloride in the organic solutions saturated with molybdenum(VI) remains virtually constant at 2:1:4 and is independent

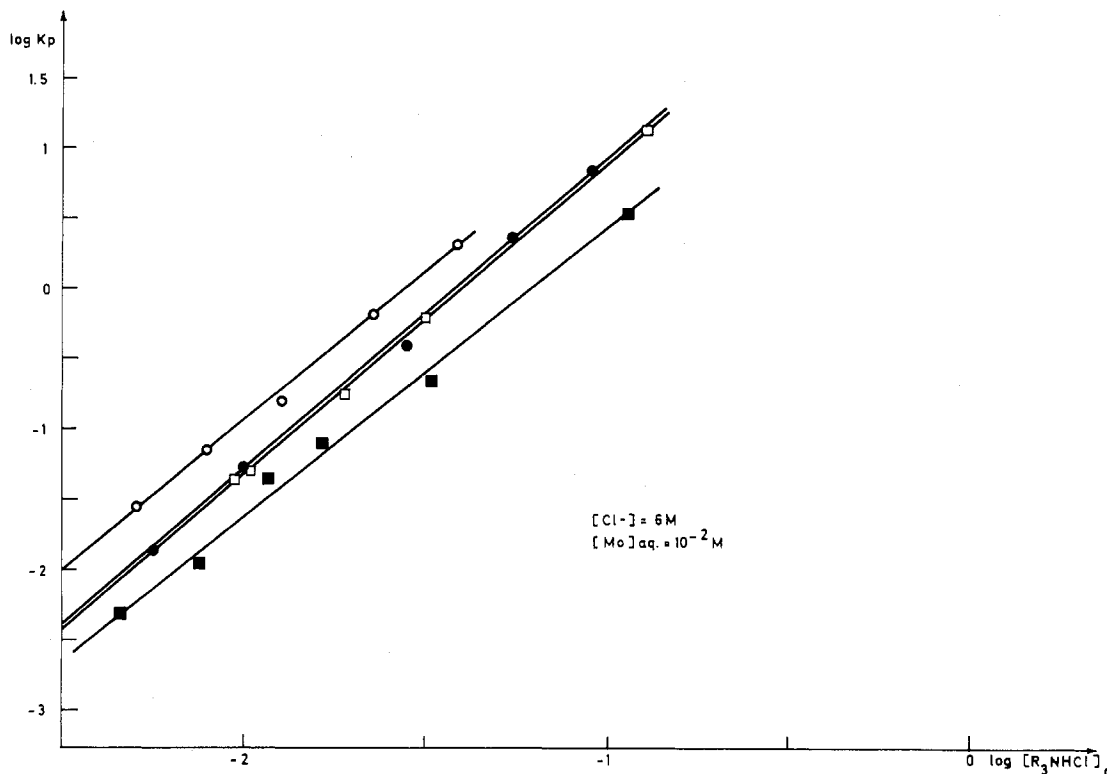


Figure 2. Log-log plots of the free ammonium salt vs. the partition coefficient of Mo(VI):  $\circ$ , in 1,2-dichlorobenzene,  $[H^+] = 6$  M;  $\bullet$ , in 1,2-dichlorobenzene,  $[H^+] = 4$  M;  $\blacksquare$ , in 1,2-dichloroethane,  $[H^+] = 4$  M.

of the diluent, the amine concentration, and the acidity.

To find the composition of the molybdenum(VI) compound extracted by triisooctylammonium chloride from HCl solutions when the organic phase is far from saturated with molybdenum(VI), organic solutions in equilibrium with aqueous HCl solutions of various Mo(VI) concentrations were analyzed to determine their chloride content and Mo(VI) concentration. Blanks were run by equilibrating organic phases containing no molybdenum(VI) with aqueous HCl solutions of the same concentrations. The results in Table I show that at different concentrations of molybdenum(VI) in the organic phase, the concentration of chloride in the organic phase can be represented as equal to the organic ammonium chloride salt concentration plus twice the number of gram-atoms of Mo(VI) extracted. This result is independent of the hydrogen ion concentration in the aqueous phase within the limits of 4–6 M HCl. Therefore, when the organic phase is far from saturated, molybdenum(VI) is extracted as  $(R_3NH^+)_2MoO_2Cl_4^{2-}$  or  $(R_3NHCl)_2MoO_2Cl_2$  as previously found.

All of these results suggest a correlation between the species extracted and the reported evidence of the chemistry of Mo(VI) in aqueous hydrochloric acid solution. According to Neumann and Cook<sup>34</sup> 79% of the molybdenum species in a 4 M HCl solution can be represented by the formula  $MoO_2Cl_2$ , and in a 6 M HCl solution, 93%. The anionic complex  $MoO_2Cl_3^-$  begins to occur at higher acid concentrations. More highly chlorinated complexes do not seem to occur at higher acid concentrations.

From the nature of the absorption curves between 270 and 400  $m\mu$  for HCl solutions between 2 and 12 N, Wendling<sup>35</sup> concluded that the molybdenum oxydichloride is formed between 2 and 5 N HCl solutions. At these concentrations, the cation  $HMo_2O_6^+$  also exists in the aqueous phase. Between 5 and 6 N HCl the formation of  $MoO_2Cl_2$  would become complete. Chauveau reached the same conclusions.<sup>36</sup> In 6 N HCl,  $MoO_2Cl_2$  transforms itself progressively into the more highly chlorinated anionic species  $MoO_2Cl_4^{2-}$ , this trans-

formation becoming complete at 11 N HCl.

Heitner-Wirguin and Cohen<sup>18</sup> arrived at similar conclusions using ion-exchange and spectroscopic techniques. According to these authors, however, the monoanionic complex  $MoO_2Cl_3^-$  is formed after  $MoO_2Cl_2$  when the acidity is increased. At even greater acidities, perhaps the tetrachlorinated anion is formed.

Log-log plots of the free ammonium salt vs. the partition coefficient of Mo(VI) were drawn in order to explore the dependence of the latter on the former, if any. The value of the  $[R_3NHCl]_0$  concentration was calculated as the difference between its initial concentration and twice the concentration of molybdenum(VI) in the organic phase, according to the previously mentioned results on the stoichiometry of the complex formed. Since Figure 2 is a straight line of slope 2, this indicates an amine:metal ratio of 2 and leads to the assumption that probably no polymeric species of the extracted compound are formed in the organic layer.

**Spectroscopic Study.** We have compared the spectra of the organic phase with those already published.<sup>34–37</sup> The spectra of the organic phase correspond to Heitner-Wirguin's spectra<sup>18</sup> in aqueous HCl media, 4.4 M or higher molarity, a maximum occurring at 220  $m\mu$  and a shoulder at 265  $m\mu$ . According to Neuman and Cook<sup>34</sup> all Mo–Cl compounds have a maximum at 226  $m\mu$  but compounds with a Mo:Cl ratio of 1:2 are characterized by a maximum at 240–250  $m\mu$ ; 1:3 compounds are characterized by a second maximum at 290  $m\mu$ ; and for the compound 1:4, if it exists, the second maximum should normally occur at a wavelength greater than or equal to 310  $m\mu$ . These results from the literature appear to indicate that under the experimental conditions we have employed, it is impossible to determine the exact formula of the molybdenum(VI) species in the aqueous phase. Also, our data do not allow us to choose between the two formulas proposed earlier for the organic compound. However, because of the fact that the anionic exchange mechanism is generally accepted, the formula  $(R_3NH^+)_2MoO_2Cl_4^{2-}$  best describes the extracted complex.

**Table I.** Composition of Organic Solutions on Varying the Molybdenum(VI) Concentration in the Initial Aqueous Phase<sup>a</sup>

Diluent <sup>b</sup>	[Mo] <sub>aq</sub> , M	[Mo] <sub>o</sub> , M	10 <sup>2</sup> [Cl] <sub>o</sub> , M
DCB <sup>c</sup>	1.40 × 10 <sup>-4</sup>	6.60 × 10 <sup>-4</sup>	5.20
	1.60 × 10 <sup>-3</sup>	3.40 × 10 <sup>-3</sup>	5.60
	3.70 × 10 <sup>-3</sup>	6.20 × 10 <sup>-3</sup>	6.00
	1.28 × 10 <sup>-2</sup>	1.16 × 10 <sup>-2</sup>	7.10
	2.27 × 10 <sup>-2</sup>	1.73 × 10 <sup>-2</sup>	8.50
	3.86 × 10 <sup>-2</sup>	2.13 × 10 <sup>-2</sup>	9.30
	5.10 × 10 <sup>-2</sup>	2.38 × 10 <sup>-2</sup>	9.82
	7.52 × 10 <sup>-2</sup>	2.47 × 10 <sup>-2</sup>	10.1
DCE <sup>c</sup>	2.61 × 10 <sup>-5</sup>	6.4 × 10 <sup>-4</sup>	5.10
	1.01 × 10 <sup>-4</sup>	3.93 × 10 <sup>-3</sup>	5.72
	2.16 × 10 <sup>-3</sup>	7.08 × 10 <sup>-3</sup>	6.47
	8.21 × 10 <sup>-3</sup>	1.53 × 10 <sup>-2</sup>	8.10
	2.47 × 10 <sup>-2</sup>	2.05 × 10 <sup>-2</sup>	9.02
	4.50 × 10 <sup>-2</sup>	2.11 × 10 <sup>-2</sup>	9.30
DCE <sup>d</sup>	4.0 × 10 <sup>-5</sup>	7.84 × 10 <sup>-4</sup>	5.20
	5.1 × 10 <sup>-4</sup>	1.80 × 10 <sup>-3</sup>	5.42
	1.00 × 10 <sup>-3</sup>	3.17 × 10 <sup>-3</sup>	5.66
	2.52 × 10 <sup>-3</sup>	6.84 × 10 <sup>-3</sup>	6.22
	7.90 × 10 <sup>-3</sup>	1.23 × 10 <sup>-2</sup>	7.46
	2.67 × 10 <sup>-2</sup>	2.00 × 10 <sup>-2</sup>	9.07
	4.40 × 10 <sup>-2</sup>	2.09 × 10 <sup>-2</sup>	9.35
CCl <sub>4</sub> <sup>c</sup>	3.0 × 10 <sup>-5</sup>	9.4 × 10 <sup>-4</sup>	5.26
	1.4 × 10 <sup>-4</sup>	4.80 × 10 <sup>-3</sup>	6.28
	6.0 × 10 <sup>-4</sup>	9.30 × 10 <sup>-3</sup>	6.68
	7.10 × 10 <sup>-3</sup>	1.88 × 10 <sup>-2</sup>	7.80
	2.90 × 10 <sup>-2</sup>	1.98 × 10 <sup>-2</sup>	8.92
	4.84 × 10 <sup>-2</sup>	2.00 × 10 <sup>-2</sup>	9.20

<sup>a</sup> [R<sub>3</sub>NHCl]<sub>o</sub> = 5 × 10<sup>-2</sup> M. <sup>b</sup> Diluents: 1,2-dichlorobenzene, DCB; 1,2-dichloroethane, DCE; carbon tetrachloride, CCl<sub>4</sub>.

<sup>c</sup> [H<sup>+</sup>]<sub>aq</sub> = 6 M = [Cl<sup>-</sup>]<sub>aq</sub>. <sup>d</sup> [H<sup>+</sup>]<sub>aq</sub> = 4 M; [Cl<sup>-</sup>]<sub>aq</sub> = 6 M.

Registry No. Mo, 7439-98-7; triisooctylamine, 25549-16-0.

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## Nature of B-Monosubstituted Dimethylaminoboranes<sup>1</sup>

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Monaminoboranes with various substituents (R<sub>2</sub>BNR'<sub>2</sub>) have been observed as monomers, dimers, trimers, or higher polymers. The degree of polymerization is considered to be related to the interplay of a variety of factors<sup>2</sup> which include electronic, steric, thermodynamic, and mechanistic effects. When monomers are observed, the electronic effect, π bonding, has generally been considered to be sufficient to prevent association with subsequent σ-bond formation.<sup>2</sup> For example, the monomeric molecule,<sup>3</sup> (CH<sub>3</sub>)<sub>2</sub>BN(CH<sub>3</sub>)<sub>2</sub>, is planar and has a relatively short B-N bond, which would be consistent with π bonding. However, it should be noted that essentially all similarly organo-substituted aminoboranes are monomeric. This observation might suggest that steric factors play a significant role. For comparison, the compounds X<sub>2</sub>BN(CH<sub>3</sub>)<sub>2</sub> (X = H, F, Cl, Br, I), which do not have an organo substituent on boron, have been observed as monomers and dimers depending on the phase and experimental conditions.<sup>4,5</sup> The monomers which are believed to be planar<sup>5</sup> are usually observed in the gas phase at higher temperatures. The dimers, for example [Cl<sub>2</sub>BN(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>, exist as planar four-membered rings<sup>6</sup> at room temperature.

The B-monosubstituted aminoboranes, HXBN(CH<sub>3</sub>)<sub>2</sub>, offer interesting opportunities for research. The single substituent on boron in the aminoborane might have some unusual effects on the properties and structures of the compounds. In addition it might be possible to evaluate the significance of π-bonding and steric effects to the stability of the monomeric species and to the equilibrium between the monomeric and dimeric species. In this paper we report the results of our investigation of the preparation and physical and spectral properties of HClBN(CH<sub>3</sub>)<sub>2</sub> and HBrBN(CH<sub>3</sub>)<sub>2</sub>. Attempts to extend this study to other monosubstituted derivatives with more unusual substituents, such as -CN, -NCO, and -NCS, were unsuccessful. The compounds could not be prepared.

## Experimental Section

All compounds described in this investigation were manipulated in a vacuum system or a purified nitrogen atmosphere. The solvents and reagents were purified by conventional means.

**Preparation of HXBN(CH<sub>3</sub>)<sub>2</sub> (X = Cl, Br).** The compounds HClBN(CH<sub>3</sub>)<sub>2</sub> and HBrBN(CH<sub>3</sub>)<sub>2</sub> were prepared by heating [H<sub>2</sub>BN(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub> and HgCl<sub>2</sub> or HgBr<sub>2</sub> at 110 °C. In a typical reaction, 1.11 g (9.93 mmol) of [H<sub>2</sub>BN(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub> was vacuum distilled into a pyrolysis tube containing 2.74 g (10.1 mmol) of HgCl<sub>2</sub>. The tube, equipped with a break-seal side arm, was sealed under vacuum. The mixture was heated at 110 °C for 24 h. Hydrogen (9.73 mmol) and elemental Hg were produced in the reaction. A small pressure of a condensable gas, believed to be monomeric HClBN(CH<sub>3</sub>)<sub>2</sub>, was observed in the pyrolysis tube after the H<sub>2</sub> had been removed. The crystalline product remaining in the tube was purified by vacuum sublimation at 25 °C to a Dry Ice cold finger and identified as [HClBN(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub> by its melting point, 96–97 °C (lit.<sup>7</sup> mp 95–97 °C). The compound [HBrBN(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>, which was prepared and purified in an identical manner, was also identified by its melting point, 122–124 °C (lit.<sup>8</sup> mp 122–124 °C). Both compounds were further confirmed by elemental analyses and molecular weight studies. The molecular weights of [HClBN(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub> and [HBrBN(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub> as measured