

that this resonance is indicative of an exchange system, since if a paramagnetic Rh(II) species were being formed, its presence in solution would cause a broadening of the former resonance. After 27 hr the two resonances are of similar size, but it is noteworthy that although the initial well-resolved resonance is slowly replaced by this second broad resonance, it does not appear to become involved in the exchange since the resolution of the former peak remains unaffected. It has also been found that although compound **3** shows an  $^1\text{H}$  nmr spectrum analogous to the trifluoroacetate one, this second complex shows a much more rapid conversion, the broad resonance being of comparable size after about 30 min, and essentially complete conversion occurs after 20 hr. This observation of the rapid growth of a broad resonance in the  $^1\text{H}$  nmr shows that care should be taken in the interpretation of such spectra.

Although we have been unable to characterize compound **2**, it is significant that we have been able to obtain the trifluoroacetate hydride in 73% yield from this compound, and, in addition, by reaction with ammonium hexafluorophosphate, the complex  $[(\text{POMePh}_2)_4\text{Rh}]\text{PF}_6$  (mp  $170^\circ$ ; conductivity in nitrobenzene  $22.8 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ) has been obtained in 79% yield. This high yield suggests the reaction is not a disproportionation reaction of the tris compound and implies that this initial compound may be a tetrakisphosphine complex, although we cannot discount the possibility that there is free methoxydiphenylphosphine present in the material. Because of the air sensitivity of the material we have been unable to obtain useful conductivity data but it appears unlikely that compound **2** is  $(\text{POMePh}_2)_4\text{Rh}^+\text{Cl}^-$  because the chloro group remains coordinated after protonation with trifluoroacetic acid.

We have been unable to isolate the corresponding complex from *n*-butoxydiphenylphosphine, but since the addition of trifluoroacetic acid to a solution of the compound obtained from chlorodicarbonylrhodium(I) and the phosphine ligand shows a high-field  $^1\text{H}$  nmr spectrum virtually identical with that found for compound **1**, it is likely that the compound exists in solution.

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### Acid-Base Properties of the Systems $\text{AlCl}_3\text{-MCl}$ ( $\text{M} = \text{Li, Na, K, Cs}$ )

BY G. TORSI<sup>1</sup> AND G. MAMANTOV\*

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We have recently reported<sup>2</sup> the values of the equilibrium constant for the dissociation  $2\text{AlCl}_4^- \rightleftharpoons \text{Cl}^- + \text{Al}_2\text{Cl}_7^-$  in molten  $\text{AlCl}_3\text{-NaCl}$  in the temperature range  $175\text{-}400^\circ$ . We now have extended these potentiometric measurements to other  $\text{AlCl}_3\text{-MCl}$  ( $\text{M} = \text{Li, K, Cs}$ ) systems and report the results in this note.

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### Experimental Section

The experimental procedures have been described previously.<sup>2</sup> The  $\text{Cl}^-$  concentration at the equivalence point of a potentiometric titration curve for a slightly basic  $\text{AlCl}_3\text{-MCl}$  melt ( $\text{M} = \text{Li, K, Cs}$ ) with  $\text{AlCl}_3$  was calculated as in ref 2. With this information, the desired equilibrium constant can be readily calculated. Only a narrow composition region near the equivalence point was studied. The electrochemical cells were made from quartz except for the Pyrex membrane separating the reference electrode compartment from the bulk melt. Reagent grade KCl was recrystallized twice from water (deionized and distilled). KCl, LiCl (Baker Analyzed reagent grade), and CsCl (99.9% pure from Alfa Inorganics) were dried in quartz tubes under reduced pressure ( $\sim 2 \times 10^{-2}$  Torr) at  $\sim 400^\circ$  for several hours; the tubes were then sealed and stored in the drybox.

In the measurements, particular care was taken to make sure that the asymmetry potential<sup>2</sup> was constant with time and temperature. In order to obtain equilibrium between the Pyrex membrane and the melts, the cell was kept at a constant temperature until there was no change in the measured voltage; this was followed by several temperature excursions until the potentials were reproducible to  $\pm 3$  mV. At the end of each run, the asymmetry potentials were evaluated and corrected for by using saturated solutions of MCl in both compartments.

### Results and Discussion

$\text{p}K$  (where  $K = X_{\text{Cl}^-}X_{\text{AlCl}_4^-}/X_{\text{AlCl}_4^-}$ ) values at several temperatures are given in Table I. Data for

Temp, $^\circ\text{C}$	Li <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Cs <sup>+</sup>
175	4.3	7.1		
250	4.0	6.3		
275			7.5	
300	3.9	5.7	7.1	
350	3.8	5.3	6.4	
400	3.8	5.0	5.8	7.4
450				6.8

the  $\text{AlCl}_3\text{-NaCl}$  system were reported previously.<sup>2</sup> It is obvious that the nature of the cation plays an important role in determining the  $\text{p}K$  value. The greater the polarizing power of the cation, the smaller is the  $\text{p}K$  at a given temperature. Plots of  $\text{p}K$  vs. either  $1/r$  (where  $r$  is the cationic radius) or the cationic size ( $r^3$ ) were, however, not linear. It is interesting to note that good linearity was obtained for the plot of  $\text{p}K$  vs.  $d^2$  (where  $d$  is the sum of the radii of  $\text{M}^+$  and  $\text{AlCl}_4^-$ ). At this time it appears that no theoretical significance may be attached to this correlation.

From the linear plots of  $\text{p}K$  vs.  $1/T$  for  $\text{AlCl}_3\text{-LiCl}$  (the lowest three temperatures),  $\text{AlCl}_3\text{-NaCl}$ , and  $\text{AlCl}_3\text{-KCl}$ , the  $\Delta H$ 's were calculated to be 4.0, 13.6, and 22.9 kcal/mol, respectively.

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### Raman Intensity Measurements on and Boron-Halogen Bond Polarizability Derivatives for the Boron Trihalides

BY R. J. H. CLARK\* AND P. D. MITCHELL

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The observed intensity of a Raman band is given by the expression

$$I_i = \frac{KM(\nu_0 - \nu_i)^4}{\nu_i[1 - \exp(-hc\nu_i/kT)]} [45(\bar{\alpha}')^2] \frac{3(1 + \rho_i)}{3 - 4\rho_i}$$

where  $K$  is a constant (depending, among other factors, on the intensity of the incident beam),  $\nu_0$  is the frequency of the exciting line,  $\nu_i$  is the vibrational frequency of the  $i$ th normal mode,  $Q_i$ , of the molecule,  $\bar{\alpha}'$  is the mean molecular polarizability derivative (with respect to  $Q_i$ ), and  $\rho_i$  is the depolarization ratio of the band for a polarized exciting line. For planar  $\text{MX}_3$  and tetrahedral  $\text{MX}_4$  molecules, there is in each case only a single normal mode belonging to the  $a_1$  species, and consequently the transformation from mean molecular polarizability derivatives to the corresponding bond polarizability derivatives is made simply by way of the appropriate  $G$  matrix element. Thus<sup>1</sup> for  $\text{MX}_4$  molecules

$$\bar{\alpha}' = (4/m_X)^{1/2} \bar{\alpha}'_{\text{MX}}$$

and for  $\text{MX}_3$  molecules

$$\bar{\alpha}' = (3/m_X)^{1/2} \bar{\alpha}'_{\text{MX}}$$

where  $m_X$  is the atomic weight of the halogen atom X.

A relationship between MX bond polarizability derivatives and the degree of covalent character of the MX bonds has been established in the case of group IV tetrahalides.<sup>2-4</sup> With the view of investigating this relationship further and, in particular, of testing the Long and Plane equation<sup>5</sup> for the calculation of bond polarizability derivatives, we have measured the molar intensities and the depolarization ratios of the  $a_1$  bands of the boron trihalides. In each case the  $806\text{-cm}^{-1}$  band of cyclohexane was used as internal standard, and the  $\bar{\alpha}'_{\text{BX}}$  values obtained were related to the value  $2.04 \text{ \AA}^2$  for  $\bar{\alpha}'_{\text{CCl}_4}$  of carbon tetrachloride.<sup>3</sup>

Boron trifluoride proved to be insufficiently soluble in any solvent to allow any intensity measurements to be carried out.

### Experimental Section

**Preparation of Samples.**—Boron trichloride, boron tribromide (both British Drug Houses Ltd.), and boron triiodide (Alpha Inorganics Ltd.) were purified by vacuum distillation or sublimation. Cyclohexane (British Drug Houses Ltd., spectroscopic grade) was stored over calcium hydride to remove residual water. The samples were made up for the intensity measurements by distillation of the trihalide and the cyclohexane into a small Pyrex cell fitted with a "Rotaflo" vacuum tap. The bottom of the cell had been blown flat, although not necessarily optically flat. The molarities of the solutions studied (three for each halide) were such that the intensity of the  $a_1$  band of each halide and the  $806\text{-cm}^{-1}$  reference band of cyclohexane were of the same order of magnitude. The molar intensities were independent of concentration. In order to minimize its decomposition, boron triiodide solutions were held at  $<0^\circ$  and (except when under study) in the dark.

**Instrumental Work.**—The Raman spectra were recorded using a Spex 1401 spectrometer fitted with Coherent Radiation Ar<sup>+</sup> and Kr<sup>+</sup> laser sources. The arrangement was similar to that used previously.<sup>4</sup> The intensities of the 4880-, 5145-,

5682-, and 6471-Å exciting lines were approximately 1 (w), 1.5 (w), 300 (mw), and 750 (mw), respectively, although it was frequently found necessary to attenuate the power. The peak areas were determined by use of a counter (Ekco Electronics Ltd. Automatic Scaler Type N530F) as described previously.<sup>4</sup> Both sample peak and reference peak were counted at least ten times for each solution using a bracketing procedure. All apparent intensity ratios were converted to true intensity ratios by use of a spectral response curve for the spectrometer. Spectra were normally run with slit widths  $100/150/100 \mu$ , slit height 50 mm, and scanning speed  $40 \text{ cm}^{-1}/\text{min}$ .

The visible and ultraviolet spectra of the halides were determined by use of a Cary 14 spectrometer in conjunction with evacuable silica cells.

### Results and Discussion

The relative molar intensities of the Raman bands are given by the expression

$$\frac{I_2 M_1}{I_1 M_2} = \left( \frac{\nu_0 - \nu_2}{\nu_0 - \nu_1} \right)^4 \left( \frac{\nu_1}{\nu_2} \right) \left[ \frac{1 - \exp(-hc\nu_1/kT)}{1 - \exp(-hc\nu_2/kT)} \right] \times \left( \frac{1 + \rho_2}{1 + \rho_1} \right) \left( \frac{3 - 4\rho_1}{3 - 4\rho_2} \right) \left( \frac{\bar{\alpha}'_2}{\bar{\alpha}'_1} \right)^2$$

where the subscript 2 refers to the  $a_1$  band of the boron trihalide and the subscript 1 refers to the  $806\text{-cm}^{-1}$  band of cyclohexane. The values obtained for  $I_2 M_1/I_1 M_2$  of each halide at each of the four exciting frequencies used are given in Table I. This table also includes the

TABLE I  
RELATIVE MOLAR INTENSITIES OF THE  $a_1$  MODES AND  
BOND POLARIZABILITY DERIVATIVES OF THE BORON  
TRIHALIDES AT FOUR EXCITING FREQUENCIES

Halide <sup>a</sup>	$\rho$	4880 Å			5145 Å		
		$I_2 M_1/I_1 M_2$ relative to 806 cm <sup>-1</sup> 459 cm <sup>-1</sup>			$I_2 M_1/I_1 M_2$ relative to 806 cm <sup>-1</sup> 459 cm <sup>-1</sup>		
		C <sub>6</sub> H <sub>12</sub>	CCl <sub>4</sub>	$\bar{\alpha}'_{\text{BX}}$	C <sub>6</sub> H <sub>12</sub>	CCl <sub>4</sub>	$\bar{\alpha}'_{\text{BX}}$
BCl <sub>3</sub>	0.022	1.199	0.653	1.89	1.132	0.638	1.87
BBr <sub>3</sub>	0.031	2.075	1.130	2.53	2.087	1.176	2.58
BI <sub>3</sub>	0.041	5.898	3.211	3.95	5.425	3.056	3.85
CCl <sub>4</sub> <sup>b</sup>	0	1.837	1.000	2.04	1.775	1.000	2.04

  

Halide <sup>a</sup>	$\rho$	5682 Å			6471 Å		
		$I_2 M_1/I_1 M_2$ relative to 806 cm <sup>-1</sup> 459 cm <sup>-1</sup>			$I_2 M_1/I_1 M_2$ relative to 806 cm <sup>-1</sup> 459 cm <sup>-1</sup>		
		C <sub>6</sub> H <sub>12</sub>	CCl <sub>4</sub>	$\bar{\alpha}'_{\text{BX}}$	C <sub>6</sub> H <sub>12</sub>	CCl <sub>4</sub>	$\bar{\alpha}'_{\text{BX}}$
BCl <sub>3</sub>		1.106	0.654	1.89	1.080	0.671	1.91
BBr <sub>3</sub>		1.960	1.160	2.56	1.966	1.221	2.61
BI <sub>3</sub>		4.932	2.918	3.75	4.933	3.064	3.82
CCl <sub>4</sub> <sup>b</sup>		1.69	1.00	2.04	1.61	1.00	2.04

<sup>a</sup> The frequencies of the  $a_1$  bands of boron trichloride, boron tribromide, and boron triiodide in cyclohexane are 472.7, 278.8, and  $192 \text{ cm}^{-1}$ , respectively. <sup>b</sup> Values taken from ref 4.

molar intensities of the  $a_1$  bands of the boron trihalides relative to that of the  $a_1$  band of carbon tetrachloride, the conversion being carried out by means of data obtained previously.<sup>4</sup> From the second set of relative molar intensities together with the values for  $\nu_1$ ,  $\nu_2$ ,  $\rho_1$ ,  $\rho_2$ , and  $\nu_0$  in each case, is obtained a set of  $(\bar{\alpha}'_2/\bar{\alpha}'_1)$  values, from which the required bond polarizability derivatives  $\bar{\alpha}'_{\text{BX}}$  are obtained by way of the relationship

$$\bar{\alpha}'_{\text{BX}} = \bar{\alpha}'_{\text{CCl}_4} \left[ \left( \frac{4}{3} \right) \left( \frac{m_X}{35.453} \right) \right]^{1/2} \left( \frac{\bar{\alpha}'_2}{\bar{\alpha}'_1} \right)$$

In anticipation of a dependence of the  $\bar{\alpha}'_{\text{BX}}$  values on the frequency gap between the exciting frequency,  $\nu_0$ , and the frequency of the first allowed electronic transition of each halide in cyclohexane solution,  $\nu_e$ , the latter was determined in each case.  $\nu_e$  values are  $>50,000 \text{ cm}^{-1}$  for boron trichloride,  $38,995 \text{ cm}^{-1}$  for boron tribromide, and  $28,945 \text{ cm}^{-1}$  for boron triiodide. However, contrary to the behavior of the group IV tetra-

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(5) The equation reduces to the expression  $\bar{\alpha}'_{\text{MX}}(\text{calcd}) = 2/3(\chi^{1/2} p / Z_{\text{eff}})(1/m)^{1/2}$ , where  $\chi$  and  $Z_{\text{eff}}$  are the geometric means of the electronegativities and effective nuclear charges, respectively, of M and X,  $Z_{\text{eff}}$  in each case being taken to be the atomic number of the atom minus the number of inner-shell electrons,  $a_0$  is the Bohr radius,  $p$  is the Pauling fractional covalent character,  $1/m$  is the MX bond order, and  $r$  is the equilibrium MX internuclear distance.

halides,<sup>4</sup> there is no resonance enhancement to the  $a_1$  bands of boron trichloride and boron tribromide and only very slight enhancement to that of boron triiodide. The average values for  $\bar{\alpha}'_{\text{BCl}}$  and  $\bar{\alpha}'_{\text{BBr}}$  are 1.89 and 2.57 Å<sup>2</sup>, respectively, and the value for  $\bar{\alpha}'_{\text{BI}}$  found by extrapolation of the plot of  $\bar{\alpha}'_{\text{BI}}$  at each exciting frequency against the frequency function of Shorygin,<sup>6</sup>  $[1 + (\nu_0/\nu_e)^2]/[1 - (\nu_0/\nu_e)^2]^2$ , is 3.75 Å<sup>2</sup>.

The experimental values of  $\bar{\alpha}'_{\text{BX}}$  for each halide are compared in Table II with the values calculated on the

TABLE II  
BOND POLARIZABILITY DERIVATIVES  $\bar{\alpha}'_{\text{BX}}$   
(Å<sup>2</sup>) FOR THE BORON TRIHALIDES

Halide <sup>a</sup>	100 <i>p</i> <sup>a</sup>	<i>r</i> <sub>0</sub> <sup>b</sup> Å	$\bar{\alpha}'_{\text{BX}}$ (calcd) <sup>c</sup>	$\bar{\alpha}'_{\text{BX}}$ (exptl)
BF <sub>3</sub>	39.0	1.295	0.39	...
BCl <sub>3</sub>	73.1	1.75	1.72	1.89
BBr <sub>3</sub>	80.9	1.87	2.28	2.57
BI <sub>3</sub>	90.8	2.10	3.53	3.75

<sup>a</sup> The fractional covalent character, *p*, is defined as  $p = \exp(-1/4(\chi_{\text{M}} - \chi_{\text{X}})^2)$ . <sup>b</sup> Values taken from *Chem. Soc., Spec. Publ.*, No. 11 (1958); No. 18 (1965). The *r* value for boron triiodide is taken from M. A. Ring, J. D. H. Donnay, and W. S. Koski, *Inorg. Chem.*, 1, 109 (1962). <sup>c</sup> Calculated according to the equation given in ref 3 and 5.

basis of the Long and Plane equation.<sup>3,5</sup> The agreement is certainly as good and probably considerably better than might have been expected bearing in mind the uncertainties associated with some of the parameters in the Long and Plane equation (in particular that associated with defining the value for  $Z_{\text{eff}}$ ). The experimental values are all somewhat higher than the calculated values, which suggests that  $1/2n > 1$ , *i.e.*, that the BX bond order is somewhat greater than one for boron trichloride, boron tribromide, and boron triiodide. Although not much weight can be put on this suggestion for the reasons given above, it is nevertheless in agreement with the results of nqr and other studies on these halides.<sup>7</sup> Thus the Long and Plane equation appears to be surprisingly good in its prediction of bond polarizability derivatives, not only for group IVb tetrahalides<sup>4</sup> but also for the boron trihalides.<sup>1</sup>

**Acknowledgment.**—P. D. M. thanks the Science Research Council for financial support.

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### Origin of Some Charge-Transfer Spectra. Oxo Compounds of Vanadium, Molybdenum, Tungsten, and Niobium Including Heteropoly Anions and Heteropoly Blues

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Since the original assignment of the lowest energy charge-transfer (LCT) bands to  ${}^2\text{B}_2 \rightarrow {}^2\text{E}(\text{II})$  ( $e_{\text{r}}^{\text{b}} \rightarrow$

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$b_2^n$ ) for  $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$  by Ballhausen and Gray<sup>2</sup> and for  $\text{CrOCl}_5^{2-}$  and  $\text{MoOCl}_5^{2-}$  by Gray and Hare,<sup>3</sup> there has been growing evidence that the LCT band originates in an electron transfer from an orbital on halogen to  $b_2^n$  (or  $b_2^*$  when it is treated as an antibonding orbital) on the metal ion for some oxyhalides.<sup>4-7</sup> We show here that some charge-transfer (CT) energies for oxo compounds of vanadium, molybdenum, tungsten, and niobium with zero or one d electron can be directly related to an optical electronegativity difference between the metal and ligand involved as found for the hexahalo-metalates,  $\text{MX}_6^{n-6,8,9}$ . We have also applied these electronegativities to a discussion of the spectra of heteropoly blues.

### Results and Discussion

Following Jørgensen,<sup>8,9</sup> the energy of the LCT band can be expressed as

$$E = x(\text{X}) - x(\text{M}) + q[\Delta x(\text{M}) + 4D/3] \quad (1)$$

where *x* is the electronegativity of ligand X or metal M, *q* is the number (0 or 1) of d electrons,  $\Delta x(\text{M})$  is the difference in electronegativities between  $d^0$  and  $d^1$  states of the metal, and *D* is the spin-pairing energy parameter.

By using the experimental data listed in Tables I

TABLE I  
OPTICAL SPECTRAL DATA FOR SOME  $d^0$  SYSTEMS

Compound	Band max, kK						Ref
	10.5	16.0	19.1	30.4	34.3	42.0	
$\text{VOCl}_4^-$							<i>a</i>
$\text{VOCl}_5^{2-}$		15.9	21.3	29.4			<i>b</i>
$\text{VOF}_3$	25.7	27.4	39.2				<i>c</i>
$\text{VOF}_5^{2-}$	30.1	38	40.8	46.3			<i>c</i>
$\text{VW}_5\text{O}_{13}^{3-}$	26.0	37.4					<i>d</i>
$\text{V}_2\text{W}_4\text{O}_{19}^{4-}$	25.3	40.0					<i>d</i>
$\text{MoOCl}_4$	14.4	20.8	37.2				<i>e</i>
$\text{Mo}_6\text{O}_{19}^{2-}$	30.8	39.1	45.0				<i>f</i>
$\text{PMo}_{12}\text{O}_{40}^{3-}$	32.3	47.2					<i>f</i>
$\text{P}_2\text{Mo}_{18}\text{O}_{62}^{6-}$	31	47					<i>g</i>
$\text{MoO}_2(\text{acac})_2$	31.6	38.0	48.1				<i>h</i>
$\text{WOB}_7^-$	21.6	26	36.3	43.1			<i>i</i>
$\text{WOC}_5^-$	22.9	28.4	35.2	37.0	43.5		<i>i</i>
$\text{PW}_{12}\text{O}_{40}^{3-}$	38	50					<i>j</i>
$\text{P}_2\text{W}_{18}\text{O}_{62}^{6-}$	34	39					<i>j</i>
$\text{NbOBr}_5^{2-}$	21.7	25.3	28.0	33.9			<i>k</i>
$\text{NbOCl}_5^{2-}$	29.8	36.4	43.5				<i>k</i>
$\text{Nb}_6\text{O}_{19}^{3-}$	43						<i>l</i>

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