

and  $[(\text{CH}_3)_2\text{PBH}_2]_3^4$  or  $[(\text{CH}_3)_2\text{NBH}_2]_2^{11}$  respectively.

**Registry No.**  $\text{B}_2\text{H}_6$ , 19287-45-7;  $\text{NaAs}(\text{CH}_3)_2$ , 13787-40-1;  $\text{Na}(\text{CH}_3)_2\text{As}(\text{BH}_3)_2 \cdot \frac{1}{2}\text{C}_4\text{H}_8\text{O}_2$ , 37956-01-7;  $[(\text{CH}_3)_3\text{NH}]\text{Cl}$ , 593-81-7;  $(\text{CH}_3)_3\text{NBH}_2\text{As}(\text{CH}_3)_2\text{BH}_3$ , 37954-24-8.

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### Far-Infrared Spectra of Some Nickel(II) and -(IV) Complexes of 2,6-Diacetylpyridine Dioxime

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Several recent studies have dealt with the effect of oxidation state changes on the far-infrared spectra of transition metal complexes.<sup>1-3</sup> These studies have dealt with the numerous low formal oxidation states stabilized by 2,2'-bipyridine and 1,10-phenanthroline.

Recently, Baucom and Drago have reported the synthesis and characterization of Ni(II) and Ni(IV) complexes derived from 2,6-diacetylpyridine dioxime (DAPDH<sub>2</sub>) shown in Figure 1.<sup>4</sup> The ligand forms a bis chelate and is bonded through the iminoxy and pyridine nitrogens as indicated. The Ni(IV) complex appears to be one of the few authentic examples of Ni in this high oxidation state. We report in this paper a far-infrared spectroscopic investigation of  $[\text{Ni}(\text{DAPDH}_2)_2](\text{ClO}_4)_2$ ,  $\text{Na}_2[\text{Ni}(\text{DAPD})_2]$ , and  $[\text{Ni}(\text{DAPD})_2]$ . Due to the complicated nature of the spectra in the 600-100-cm<sup>-1</sup> region, the metal isotope technique was used to identify the metal-ligand stretching vibrations.<sup>5-7</sup> The Ni-N<sub>1</sub> and Ni-N<sub>2</sub> stretches (see Figure 1 for subscripts) were found to be sensitive to both the charge on the ligand and the oxidation state of Ni.

### Experimental Section

The ligand 2,6-diacetylpyridine dioxime and the natural-abundance Ni complexes  $[\text{Ni}(\text{DAPDH}_2)_2](\text{ClO}_4)_2$ ,  $\text{Na}_2[\text{Ni}(\text{DAPD})_2]$ , and  $[\text{Ni}(\text{DAPD})_2]$  were prepared as described by Baucom and Drago.<sup>4</sup> All of the solvents used in the preparation of  $\text{Na}_2[\text{Ni}(\text{DAPD})_2]$  were anhydrous and deoxygenated, and the reactions were carried out in a nitrogen atmosphere.  $[\text{Ni}(\text{DAPD})_2]$  was prepared both by method A, which consists of the oxidation of  $[\text{Ni}(\text{DAPD})_2]^{2-}$  by  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  in aqueous  $\text{NH}_3$ -acetone solution, and by method B, which consists of the oxidation of  $[\text{Ni}(\text{DAPDH}_2)_2](\text{ClO}_4)_2$  by addition of bromine

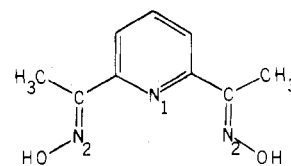


Figure 1. Structure of 2,6-diacetylpyridine dioxime.

and pyridine to the perchlorate salt dissolved in methanol-acetonitrile. Both methods gave products whose ir spectra were identical.

**Anal.** Calcd for  $[\text{Ni}(\text{DAPDH}_2)_2](\text{ClO}_4)_2$ : C, 33.57; H, 3.45; N, 13.04. Found: C, 33.49; H, 3.27; N, 12.99. Calcd for  $[\text{Ni}(\text{DAPD})_2]$ : C, 49.05; H, 4.12; N, 19.03. Found: C, 48.87; H, 4.07; N, 18.91.

Isotopically pure (minimum isotopic purity >98%) complexes were prepared from <sup>58</sup>Ni and <sup>62</sup>Ni metal (Oak Ridge National Laboratory). Weighed amounts of the respective metal isotopes (≈10 mg) were dissolved in minimum volumes of 70%  $\text{HClO}_4$ . The resulting solutions were evaporated to dryness, small volumes of water (<1 ml) added and again evaporated to dryness. The resulting  $[\text{Ni}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$  and  $[\text{Ni}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$  were dissolved in minimum volumes of acetone and DAPDH<sub>2</sub> added in 2:1 mole ratios;  $[\text{Ni}(\text{DAPDH}_2)_2](\text{ClO}_4)_2$  and the <sup>62</sup>Ni analog were isolated as previously described for the natural-abundance complexes. Portions of isotopic  $[\text{Ni}(\text{DAPDH}_2)_2](\text{ClO}_4)_2$  were converted to  $\text{Na}_2[\text{Ni}(\text{DAPD})_2]$  and  $[\text{Ni}(\text{DAPD})_2]$ ; the Ni(IV) complex ( $[\text{Ni}(\text{DAPD})_2]$ ) was prepared by method B. In all cases, the spectra of the isotopically substituted complexes were checked against the spectra of the natural-abundance complexes.

The infrared spectra were recorded on Beckman IR-12 (600-400 cm<sup>-1</sup>) and Hitachi-Perkin Elmer FIS-3 (400-100 cm<sup>-1</sup>) spectrophotometers. The spectra were recorded as Nujol mulls on CsI and polyethylene plates at scanning speeds of 1-2 cm<sup>-1</sup>/min. The reproducibility was checked by multiple scans over the frequency range of interest: the average error in frequency was ±0.5 cm<sup>-1</sup>.

### Results and Discussion

Far-infrared spectra (600-100 cm<sup>-1</sup>) for  $[\text{Ni}(\text{DAPDH}_2)_2](\text{ClO}_4)_2$ ,  $\text{Na}_2[\text{Ni}(\text{DAPD})_2]$ , and  $[\text{Ni}(\text{DAPD})_2]$  are shown in Figure 2. Observed frequencies and isotopic shifts for  $[\text{Ni}(\text{DAPDH}_2)_2](\text{ClO}_4)_2$ ,  $\text{Na}_2[\text{Ni}(\text{DAPD})_2]$ ,  $[\text{Ni}(\text{DAPD})_2]$ , and their respective <sup>62</sup>Ni analogs are listed in Table I.

Although three ir-active stretching bands (2 B<sub>2</sub> + E) are expected from the symmetry (*D*<sub>2d</sub>) of the cation, the only isotope-sensitive bands observed for  $[\text{Ni}(\text{DAPDH}_2)_2](\text{ClO}_4)_2$  are at 235 and 229 cm<sup>-1</sup> (Table I). It is not possible to identify the Ni-N<sub>1</sub> and Ni-N<sub>2</sub> stretching vibrations on the basis of available data. However, the spectral evidence does indicate that the Ni-N<sub>1</sub> and Ni-N<sub>2</sub> bonds are quite similar as evidenced by the narrow frequency range. The observed frequencies for Ni-N<sub>1</sub> and Ni-N<sub>2</sub> stretches are in the general range previously assigned for Ni-N(pyridine) type stretches. For example, Clark and Williams assigned the Ni-N(pyridine) stretches at 236 and 233 cm<sup>-1</sup> in *trans*-Ni(py)<sub>4</sub>Cl<sub>2</sub> and *trans*-Ni(py)<sub>4</sub>(NCS)<sub>2</sub>, respectively.<sup>8,9</sup>

Previous investigations on the effect of deprotonation upon metal-nitrogen stretching vibrations have been made by Watt and coworkers. They have shown that small shifts to higher frequency generally accompany deprotonation. For example, deprotonation of Ni(gly)<sub>2</sub> to  $[\text{Ni}(\text{gly-H})_2]^{2-}$  results in a shift of ≈50 cm<sup>-1</sup> in the Ni-N(glycine) stretch;<sup>10</sup> this shift is, however, unusually large. Typically, deprotonation results in much smaller shifts; e.g., deprotonation of Ni-(β-ala)<sub>2</sub> results in a shift of only ≈15 cm<sup>-1</sup>.<sup>10</sup> Other systems show similar small shifts (0-10 cm<sup>-1</sup>) to higher frequency upon deprotonation.<sup>11,12</sup> These results would indicate that

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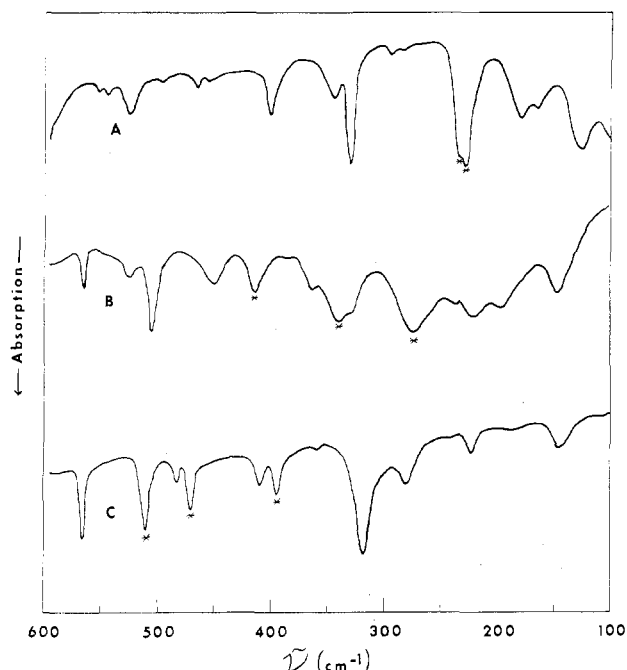


Figure 2. Far-infrared spectra of  $[\text{Ni}(\text{DAPDH}_2)_2](\text{ClO}_4)_2$  (A),  $\text{Na}_2[\text{Ni}(\text{DAPD})_2]$  (B), and  $[\text{Ni}(\text{DAPD})_2]$  (C) in the 600–100- $\text{cm}^{-1}$  region; isotope-sensitive bands are indicated with an asterisk.

Table I. Far-Infrared Spectra of  $[\text{Ni}(\text{DAPDH}_2)_2](\text{ClO}_4)_2$ ,  $\text{Na}_2[\text{Ni}(\text{DAPD})_2]$ , and  $[\text{Ni}(\text{DAPD})_2]$  in the 600–100  $\text{cm}^{-1}$  Region

$[\text{Ni}(\text{DAPDH}_2)_2](\text{ClO}_4)_2$		$\text{Na}_2[\text{Ni}(\text{DAPD})_2]$		$[\text{Ni}(\text{DAPD})_2]$	
$^{58}\text{Ni}$	$\Delta\bar{\nu}$ - ( $^{58}\text{Ni}$ - $^{62}\text{Ni}$ )	$^{58}\text{Ni}$	$\Delta\bar{\nu}$ - ( $^{58}\text{Ni}$ - $^{62}\text{Ni}$ )	$^{58}\text{Ni}$	$\Delta\bar{\nu}$ - ( $^{58}\text{Ni}$ - $^{62}\text{Ni}$ )
551.0 w	-0.2	566.0 m	0.0	564.0 s	-0.2
544.8 w	0.2	524.0 w	0.0	509.8 <sup>d</sup> s	3.8
524.5 m	0.2	504.2 s	-0.1	482.0 m	0.6
495.0 w	0.0	449.0 m	-0.7	472.0 <sup>d</sup> s	4.5
466.2 w	0.0	416.3 <sup>d</sup> m	1.8	410.3 m	0.4
456.1 w	0.5	364.8 m	-0.4	394.8 <sup>d</sup> m	2.2
400.1 m	0.4	341.2 <sup>d</sup> m	1.6	359 vw	$\approx 0^a$
345.8 w	0.8	328 sh	$\approx 0^b$	318.1 s	-0.1
329.9 m	0.0	275.7 <sup>d</sup> s	2.5	279.5 m	0.2
296.0 w	-0.5	237 vw	$\approx 0^a$	222.3 m	0.0
285 vw	$\approx 0^a$	219 m, br	... <sup>c</sup>	147.0 m	-0.2
235 <sup>d</sup> sh	$\approx 5^b$	198 w, br	... <sup>c</sup>		
229.1 <sup>d</sup> s	3.4	151.0 m	0.0		
179.0 m	0.2				
165.8 w	0.5				
126.0 s	-0.4				
100.0 m	0.0				

<sup>a</sup> Too weak to obtain accurate shift data. <sup>b</sup> Exact shift not determined due to overlapping bands. <sup>c</sup> Band too broad to determine exact band maxima; shift <1.0. <sup>d</sup> Frequencies assigned to Ni-N stretches.

the charge is highly localized on the nitrogen atom with only slight interaction with the metal atom. Also, in these systems the charge is generated on the nitrogen bound directly to the central metal atom.

Deprotonation of  $[\text{Ni}(\text{DAPDH}_2)_2]^{2+}$  results in the creation of a charge in the position  $\beta$  to the Ni atom. However, substantial changes are observed in the far-infrared spectra upon deprotonation as can be seen from Figure 2. The isotope-sensitive bands at 341.2 and 416.3  $\text{cm}^{-1}$  in the spectra of  $[\text{Ni}(\text{DAPD})_2]^{2+}$  are assigned to the Ni-N<sub>2</sub> stretching vibrations. Since  $[\text{Ni}(\text{DAPDH}_2)_2]^{2+}$  shows the Ni-N<sub>2</sub> stretch in the 230- $\text{cm}^{-1}$  region, these results suggest that considerable interaction occurs between the charge created

by deprotonation of the oxime moiety and the Ni atom. Furthermore, this interaction results in a strengthened Ni-N<sub>2</sub> bond. The relatively large shift to higher frequencies in the Ni-N<sub>2</sub> stretch upon deprotonation is also consistent with the changes found in the electronic spectra. The effect of deprotonation is to produce an exceedingly strong ligand ( $[\text{Ni}(\text{DAPD})_2]^{2-}$ ,  $Dq = 1580 \text{ cm}^{-1}$ ;  $[\text{Ni}(\text{DAPDH}_2)_2]^{2+}$ ,  $Dq = 1214 \text{ cm}^{-1}$ ).<sup>4</sup> The Ni-N<sub>1</sub> stretch is assigned to the isotope-sensitive band at 275.7  $\text{cm}^{-1}$ . This smaller shift indicates the Ni-N<sub>1</sub> bond is less perturbed by deprotonation than the Ni-N<sub>2</sub> bond. This is reasonable since the charge can affect the Ni-N<sub>1</sub> bond only indirectly through changes in the Ni-N<sub>2</sub> bonds. Even so, this shift to higher frequency indicates some strengthening of the Ni-N<sub>1</sub> bond as compared to  $[\text{Ni}(\text{DAPDH}_2)_2]^{2+}$ . These results are in excellent agreement with the bonding changes predicted from the extended Huckel molecular orbital calculations of Baucom and Drago.<sup>4</sup> Their calculations show that converting  $[\text{Ni}(\text{DAPDH}_2)_2]^{2+}$  to  $[\text{Ni}(\text{DAPD})_2]^{2-}$  leads to greatly increased Ni-imine nitrogen (Ni-N<sub>2</sub>) interaction through  $\sigma$ -type bonding molecular orbitals. They also postulated that this Ni-N<sub>2</sub> interaction could lead to an increased Ni-N<sub>1</sub> interaction.

Oxidation of  $[\text{Ni}(\text{DAPD})_2]^{2-}$  gives the diamagnetic complex  $[\text{Ni}(\text{DAPD})_2]$  which has Ni in a 4+ formal oxidation state. Two factors are expected to influence the Ni-N stretches upon oxidation: (1) the removal of the electrons occupying the  $e_g$  orbitals (an  $O_h$  model assumed for simplicity) and (2) an increased electrostatic attraction due to the change in oxidation state. Both factors should lead to shifts to higher frequency for the Ni-N<sub>1</sub> and Ni-N<sub>2</sub> stretching vibrations. In the series of  $[\text{M}(\text{bipy})_3]^{2+}$  complexes (M = first-row transition metals, bipy = 2,2'-bipyridine), the M-N(bipy) stretches are highly dependent on the electronic configuration of the central metal atom.<sup>2</sup> For example,  $[\text{Cr}(\text{bipy})_3]^{2+}$  (low-spin  $d^4$ ) and  $[\text{Fe}(\text{bipy})_3]^{2+}$  (low-spin  $d^6$ ) show Cr-N and Fe-N stretches at 351, 343 and 386, 376  $\text{cm}^{-1}$ , respectively, whereas the Mn-N (high-spin  $d^5$ ) stretch in  $[\text{Mn}(\text{bipy})_3]^{2+}$  occurs at 224 and 191  $\text{cm}^{-1}$ . In metal-halide systems, increasing the oxidation state generally results in increasing the metal-halide stretching frequency.<sup>13,14</sup> Separating the role of oxidation state vs. that of electronic configurational change is not possible from this study. However, the combined effect of the two can be seen in the case of  $[\text{Co}(\text{NH}_3)_6]^{3+}$  (low-spin  $d^6$ ) vs.  $[\text{Co}(\text{NH}_3)_6]^{2+}$  (high-spin  $d^7$ ); both oxidation states are "normal" for cobalt. The Co-N stretches are found at 499, 476, and 449  $\text{cm}^{-1}$  in  $[\text{Co}(\text{NH}_3)_6]^{3+}$  and 327  $\text{cm}^{-1}$  for  $[\text{Co}(\text{NH}_3)_6]^{2+}$ .<sup>15</sup> As can be seen from Figure 2 and Table I, both Ni-N<sub>1</sub> and Ni-N<sub>2</sub> stretches are shifted to higher frequency for the Ni(II)-Ni(IV) oxidation state change. The Ni-N<sub>2</sub> stretches are assigned to the isotope-sensitive bands at 509.8 and 472.0  $\text{cm}^{-1}$  and the Ni-N<sub>1</sub> stretch at 394.8  $\text{cm}^{-1}$ . The Ni-N<sub>1</sub> stretch is similar in frequency to the Fe-N stretch in the isoelectronic low-spin  $d^6$   $[\text{Fe}(\text{bipy})_3]^{2+}$  complex (386, 376  $\text{cm}^{-1}$ ). These results are consistent with the proposed oxidation of Ni(II) to Ni(IV). It is also interesting to note that both the Ni-N<sub>1</sub> and the average of Ni-N<sub>2</sub> stretches are shifted to higher frequency by 110–120  $\text{cm}^{-1}$ . Thus the oxidation state change would appear to have approximately the same effect on both the Ni-N<sub>1</sub> and Ni-N<sub>2</sub> bonds. These shifts are also consistent with a recently reported shortening

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of the metal-ligand bond distance in going from  $[\text{Ni}(\text{DAPDH}_2)_2]^{2+}$  to  $[\text{Ni}(\text{DAPD})_2]$ .<sup>16</sup>

Baucom and Drago also pointed out that the primary mode of bonding that stabilizes the Ni(IV) complex is  $\sigma$  bonding and that  $\pi$  bonding is not expected to be a factor in stabilizing the Ni-N<sub>1</sub> or Ni-N<sub>2</sub> bonds.<sup>4</sup> In systems where  $\pi$  bonding is a significant factor, the metal-ligand stretches appear to show little sensitivity to the oxidation state of the metal.<sup>1-3</sup> As stated previously, it is difficult to separate the two contributing factors to the shift to higher frequency of both Ni-N<sub>1</sub> and Ni-N<sub>2</sub> stretches upon oxidation of  $[\text{Ni}(\text{DAPD})_2]^{2+}$  to  $[\text{Ni}(\text{DAPD})_2]$ . However, the large shift is consistent with a negligible  $\pi$  contribution.

**Registry No.**  $[\text{Ni}(\text{DAPDH}_2)_2](\text{ClO}_4)_2$ , 38188-04-4;  $\text{Na}_2-[\text{Ni}(\text{DAPD})_2]$ , 38188-05-5;  $[\text{Ni}(\text{DAPD})_2]$ , 38188-08-8.

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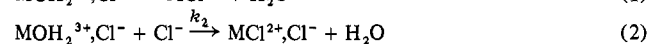
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### Aquation of Chloropentaamminecobalt(III) Perchlorate in Aqueous Media

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The aquation of  $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$  in aqueous media has been studied by Garrick,<sup>1</sup> by Laurie and Monk,<sup>2</sup> and by Langford and Muir.<sup>3</sup> Burnett<sup>4</sup> has reinterpreted the data of Langford and Muir. Using <sup>36</sup>Cl tracer Laurie and Monk<sup>2</sup> found that the observed aquation rate of 0.004 M  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  was independent of added NaCl concentration within experimental error over the range  $0.0 \leq [\text{NaCl}] \leq 0.10$  M in 0.01 M perchloric acid. Langford and Muir<sup>3</sup> studied the aquation over the concentration range of  $0.0 \leq [\text{NaCl}] \leq 0.6$  M in the absence of sodium perchlorate and in the presence of sodium perchlorate to maintain constant ionic strength. The latter authors interpreted their data in terms of an I<sub>d</sub> mechanism<sup>5</sup> proceeding through the ion pair  $\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+}, \text{Cl}^-$ . Burnett<sup>4</sup> reinterpreted the data of Langford and Muir assuming three parallel I<sub>d</sub> paths, namely



where M stands for the pentaamminecobalt(III) group. Since reactions 1 and 2 contributed comparably at  $\text{Cl}^-$  concentrations of 0.5 M in Burnett's treatment, increasing the

$\text{Cl}^-$  concentration to approximately 0.9 M would increase the relative contribution of reaction 2 and make the dependence of the rate on the square of the  $\text{Cl}^-$  concentration much more pronounced. Consequently we have studied the aquation rate over a larger range of  $\text{Cl}^-$  concentration.

Furthermore, since the contribution of reaction 3 is equal to or greater than the contribution of reaction 1 at low  $\text{Cl}^-$  concentrations and large  $\text{ClO}_4^-$  concentrations according to the interpretation of Burnett,<sup>4</sup> the dependence of the rate on perchlorate ion concentration should be measurable. Consequently we have studied the aquation rate for a change of perchlorate ion concentration at constant ionic strength and for the substitution of perchlorate by tetrafluoroborate and trifluoromethanesulfonate ions.

### Experimental Section

The aquation of chloropentaamminecobalt(III) perchlorate was studied at  $45.0 \pm 0.1^\circ$  in a thermostated cell compartment of a Beckman DU spectrophotometer for various concentrations of added NaCl in the range  $0.0 \leq [\text{NaCl}] \leq 0.9$  M. Reaction mixtures were maintained at unit ionic strength with  $\text{NaClO}_4$ ,  $\text{Al}(\text{ClO}_4)_3$ ,  $\text{NaBF}_4$ , or  $\text{Na}(\text{CF}_3\text{SO}_3)$ . The  $\text{NaBF}_4$  was twice recrystallized from water. The  $\text{Na}(\text{CF}_3\text{SO}_3)$  was prepared from the barium salt by ion exchange. The  $\text{Al}(\text{ClO}_4)_3$  was analyzed gravimetrically with 8-hydroxyquinoline. All rates were determined at 380, 532, and 550 nm.

Equilibrium concentration ratios,  $[\text{MCl}^{2+}] / [\text{MOH}_2^{3+}]_t$ , where the subscript t means the total concentration of all forms of the aquo-pentaamminecobalt(III) ions, were obtained at the same temperature, NaCl concentrations, and wavelengths.

### Results and Discussion

At the three wavelengths employed the molar absorptivities of  $\text{MOH}_2^{3+}$  and of the ion pairs such as  $\text{MOH}_2^{3+}, \text{Cl}^-$  were equal within the absorbance experimental error over the concentration range  $0.0 \leq [\text{NaCl}] \leq 0.90$  M of added sodium chloride. Hence at these three wavelengths the total,  $[\text{MOH}_2^{3+}]_t$ , of the concentrations of the free ion and of the ion pairs can be measured simultaneously with the concentration of  $\text{MCl}^{2+}$ . If it is assumed that the inner-sphere complex,  $\text{MCl}^{2+}$ , and the outer-sphere complex,  $\text{MOH}_2^{3+}, \text{Cl}^-$ , are the only important chloride-containing complexes and if it is assumed that the effect of perchlorate ion is only a general ionic strength effect and that specific ion-ion interaction forming  $\text{MOH}_2^{3+}, \text{ClO}_4^-$  is not important, then the ratio  $[\text{MCl}^{2+}] / [\text{MOH}_2^{3+}]_t [\text{Cl}^-]$ , which can be determined experimentally, is given by

$$\frac{[\text{MCl}^{2+}]}{[\text{MOH}_2^{3+}]_t [\text{Cl}^-]} = \frac{Q_c}{1 + Q_o [\text{Cl}^-]} \quad (4)$$

where  $Q_c$  is the concentration equilibrium quotient for the formation of  $\text{MCl}^{2+}$  from the free ions  $\text{MOH}_2^{3+}$  and  $\text{Cl}^-$  at the ionic strength used and  $Q_o$  is the concentration equilibrium quotient for the formation of the outer-sphere complex  $\text{MOH}_2^{3+}, \text{Cl}^-$  from the free ions. A plot of the inverse of the left-hand side of eq 4 vs.  $\text{Cl}^-$  ion concentration is shown in Figure 1. For sodium perchlorate media the intercept gave a value of  $Q_c$  of  $2.57 \pm 0.17$  M<sup>-1</sup> and the ratio slope/intercept gave a value of  $Q_o$  of  $1.35 \pm 0.15$  M<sup>-1</sup> which was in satisfactory agreement with the value of  $1.21 \pm 0.13$  M<sup>-1</sup> obtained from kinetic measurements. For aluminum perchlorate media the values of  $Q_c$  and  $Q_o$  were  $Q_c = 2.46 \pm 0.2$  M<sup>-1</sup> and  $Q_o = 1.24 \pm 0.2$  M<sup>-1</sup>, respectively, in good agreement with the values obtained in sodium perchlorate media. This result showed that decreasing the perchlorate ion concentration had little effect on increasing the activity of the  $\text{MOH}_2^{3+}$  ions by forming fewer  $\text{MOH}_2^{3+}, \text{ClO}_4^-$  ion pairs.

When the values obtained for  $Q_c$  and  $Q_o$  are used in eq 4, the values calculated for the left-hand side of eq 4 are in

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