of the metal-ligand bond distance in going from $[Ni(DAPDH_2)_2]^{2+}$ to $[Ni(DAPD)_2]$.[16]

Baucom and Drago also pointed out that the primary mode of bonding that stabilizes the Ni(IV) complex is σ bonding and that π bonding is not expected to be a factor in stabilizing the $Ni-N_1$ or $Ni-N_2$ bonds.[4] In systems where π bonding is a significant factor, the metal-ligand stretches appear to show little sensitivity to the oxidation state of the metal.[1-3] As stated previously, it is difficult to separate the two contributing factors to the shift to higher frequency of both $Ni-N_1$ and $Ni-N_2$ stretches upon oxidation of $[Ni(DAPD)_2]^{2-}$ to $[Ni(DAPD)_2]$. However, the large shift is consistent with a negligible π contribution.

Registry No. $[Ni(DAPDH_2)_2](ClO_4)_2$, 38188-04-4; $Na_2[Ni(DAPD)_2]$, 38188-05-5; $[Ni(DAPD)_2]$, 38188-08-8.

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

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Aquation of Chloropentaamminecobalt(III) Perchlorate in Aqueous Media

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The aquation of $Co(NH_3)_5Cl^{2+}$ in aqueous media has been studied by Garrick,[1] by Laurie and Monk,[2] and by Langford and Muir.[3] Burnett[4] has reinterpreted the data of Langford and Muir. Using ^{36}Cl tracer Laurie and Monk[2] found that the observed aquation rate of 0.004 M $[Co(NH_3)_5Cl]Cl_2$ was independent of added NaCl concentration within experimental error over the range $0.0 \leqslant [NaCl] \leqslant 0.10\,M$ in 0.01 M perchloric acid. Langford and Muir[3] studied the aquation over the concentration range of $0.0 \leqslant [NaCl] \leqslant 0.6\,M$ 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_d mechanism[5] proceeding through the ion pair $Co(NH_3)_5OH_2^{3+},Cl^-$. Burnett[4] reinterpreted the data of Langford and Muir assuming three parallel I_d paths, namely

$$MOH_2^{3+},Cl^- \xrightarrow{k_1} MCl^{2+} + H_2O \tag{1}$$

$$MOH_2^{3+},Cl^- + Cl^- \xrightarrow{k_2} MCl^{2+},Cl^- + H_2O \tag{2}$$

$$MOH_2^{3+},ClO_4^- + Cl^- \xrightarrow{k_3} MCl^{2+},ClO_4^- + H_2O \tag{3}$$

where M stands for the pentaamminecobalt(III) group. Since reactions 1 and 2 contributed comparably at Cl^- concentrations of 0.5 M in Burnett's treatment, increasing the 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 Cl^- concentration much more pronounced. Consequently we have studied the aquation rate over a larger range of Cl^- concentration.

Furthermore, since the contribution of reaction 3 is equal to or greater than the contribution of reaction 1 at low Cl^- concentrations and large ClO_4^- concentrations according to the interpretation of Burnett,[4] 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 ± 0.1° in a thermostated cell compartment of a Beckman DU spectrophotometer for various concentrations of added NaCl in the range $0.0 \leqslant [NaCl] \leqslant 0.9\,M$. Reaction mixtures were maintained at unit ionic strength with $NaClO_4$, $Al(ClO_4)_3$, $NaBF_4$, or $Na(CF_3SO_3)$. The $NaBF_4$ was twice recrystallized from water. The $Na(CF_3SO_3)$ was prepared from the barium salt by ion exchange. The $Al(ClO_4)_3$ was analyzed gravimetrically with 8-hydroxyquinoline. All rates were determined at 380, 532, and 550 nm.

Equilibrium concentration ratios, $[MCl^{2+}]/[MOH_2^{3+}]_t$, where the subscript t means the total concentration of all forms of the aquopentaamminecobalt(III) ions, were obtained at the same temperature, NaCl concentrations, and wavelengths.

Results and Discussion

At the three wavelengths employed the molar absorptivities of MOH_2^{3+} and of the ion pairs such as MOH_2^{3+},Cl^- were equal within the absorbance experimental error over the concentration range $0.0 \leqslant [NaCl] \leqslant 0.90\,M$ of added sodium chloride. Hence at these three wavelengths the total, $[MOH_2^{3+}]_t$, of the concentrations of the free ion and of the ion pairs can be measured simultaneously with the concentration of MCl^{2+}. If it is assumed that the inner-sphere complex, MCl^{2+}, and the outer-sphere complex, MOH_2^{3+},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 MOH_2^{3+},ClO_4^- is not important, then the ratio $[MCl^{2+}]/[MOH_2^{3+}]_t[Cl^-]$, which can be determined experimentally, is given by

$$\frac{[MCl^{2+}]}{[MOH_2^{3+}]_t[Cl^-]} = \frac{Q_c}{1 + Q_o[Cl^-]} \tag{4}$$

where Q_c is the concentration equilibrium quotient for the formation of MCl^{2+} from the free ions MOH_2^{3+} and Cl^- at the ionic strength used and Q_o is the concentration equilibrium quotient for the formation of the outer-sphere complex MOH_2^{3+},Cl^- from the free ions. A plot of the inverse of the left-hand side of eq 4 *vs.* Cl^- ion concentration is shown in Figure 1. For sodium perchlorate media the intercept gave a value of Q_c of $2.57 \pm 0.17\,M^{-1}$ and the ratio slope/intercept gave a value of Q_o of $1.35 \pm 0.15\,M^{-1}$ which was in satisfactory agreement with the value of $1.21 \pm 0.13\,M^{-1}$ obtained from kinetic measurements. For aluminum perchlorate media the values of Q_c and Q_o were $Q_c = 2.46 \pm 0.2\,M^{-1}$ and $Q_o = 1.24 \pm 0.2\,M^{-1}$, 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 MOH_2^{3+} ions by forming fewer MOH_2^{3+},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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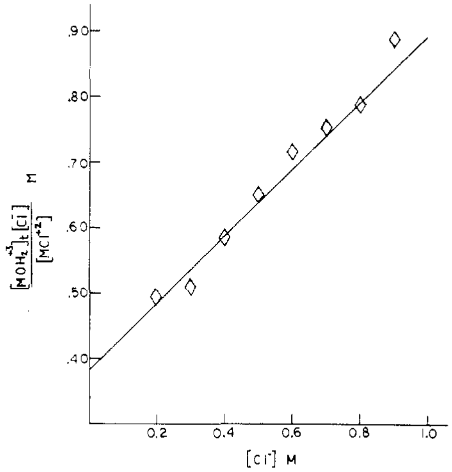

Figure 1. Plot of the inverse of the concentration quotient $[MCl^{2+}]/[MOH_2^{3+}]_t[Cl^-]$ *vs.* chloride concentration at 1 *M* ionic strength and 45°.

excellent agreement with the values reported by Langford and Muir[3] for Cl^- concentrations up to approximately 0.4 *M*; for Cl^- concentrations greater than this the calculated values are greater than the values reported by Langford and Muir.[3] Since our measurements cover a larger range of Cl^- concentrations, we believe they are more reliable at the higher Cl^- concentrations.

The rate of approach to equilibrium was given by

$$\ln (A - A_e) = \ln (A_o - A_e) - (k_{aq} + k_{an})t \qquad (5)$$

where A_o, A, and A_e were the corrected absorbances at zero time, time t, and equilibrium, respectively, and k_{aq} and k_{an} were the observed first-order aquation and anation rate constants for a given concentration of added NaCl. The two rate constants were related by

$$k_{an} = \frac{[MCl^{2+}]_e}{[MOH_2^{3+}]_{t,e}} k_{aq} \qquad (6)$$

Since the value of the concentration ratio at equilibrium, $[MCl^{2+}]_e/[MOH_2^{3+}]_{t,e}$, was known for a given Cl^- concentration, both k_{aq} and k_{an} were obtained for 10 different Cl^- concentrations in the range $0 \leqslant [NaCl] \leqslant 0.9$ *M*. The results are shown in Figure 2.

It was found that k_{aq} was constant within experimental error over the range of added Cl^- concentration and equal to $(1.80 \pm 0.14) \times 10^{-5}$ sec^{-1}. The rather large experimental error arose because the total change in absorbance at any one wavelength in a given experiment decreased markedly with increasing Cl^- concentration as a result of increasing amounts of MCl^{2+} left at equilibrium and because of the error in the measurement of the concentration ratio in eq 6. Our result differs from that of Langford and Muir,[3] who found that k_{aq} decreased with decreasing Cl^- concentration at a constant ionic strength of 1 *M*.

The values of k_{aq} obtained at zero added Cl^- concentration for several different reaction media at 1 *M* ionic strength are listed in Table I. The values are not significantly different from each other or from the value of $(1.80 \pm 0.14) \times 10^{-5}$ sec^{-1} obtained for all Cl^- concentrations. These values are in fair agreement with a value of 1.95×10^{-5} sec^{-1} for 45° interpolated from the values listed for different temperatures by Laurie and Monk.[2]

The rate equations of Burnett[4] show that if aquation proceeded by the reverse of reactions 2 and 3, as well as by the reverse of reaction 1, then k_{aq} would be dependent on Cl^- concentration and on ClO_4^- concentration. Furthermore the dependence on Cl^- concentration should be readily observable over the concentration range 0.5–0.9 *M* for the following reason. At a Cl^- concentration of approximately 0.5 *M*, reactions 1 and 2 were comparable in their contributions to the anation process.[4] Because of the principle of microscopic reversibility, the reverse reactions of 1 and 2 must also be comparable in their contributions to the aquation process at the same Cl^- concentration. At Cl^- concentrations between 0.5 and 0.9 *M*, the relative contribution of the reverse of reaction 2 should increase markedly and be experimentally verifiable. However, k_{aq} was essentially unchanged over the range from zero to 0.9 *M* added Cl^- and it was concluded that the values obtained for k_{aq} do not support the postulate that the reverse of reaction 2 makes an important contribution for the media used.

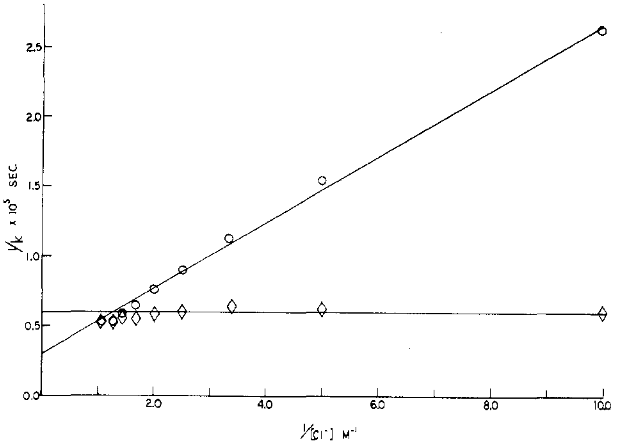

Figure 2. Plots of the inverse of k_{aq} and k_{an} *vs.* inverse of chloride ion concentration at 1 *M* ionic strength and 45°: ◇, k_{aq}; ○, k_{an}.

Table I. Aquation Rate Constants in the Absence of Added Chloride Ion (1.0 *M* ionic strength; 45.0°)

Supporting electrolyte	$10^5 k_{aq}$, sec^{-1}	No. of trials
$NaClO_4$	1.64 ± 0.09	9
$Al(ClO_4)_3$	1.78 ± 0.06	6
$NaBF_4$	1.63 ± 0.06	6
$NaCF_3SO_3$	1.57 ± 0.05	6

Because the values of k_{aq} showed so little dependence on the ClO_4^- concentration, or even on the presence or absence of ClO_4^-, it was concluded that the results for k_{aq} do not support the postulate that the reverse of reaction 3 makes an important contribution in the ClO_4^- media used. On the other hand it is possible that the effects of ClO_4^-, BF_4^-, and $CF_3SO_3^-$ are so similar that the rates of aquation by the reverse of reaction 3 are essentially the same for these three ions. However there are two observations which make this possibility less attractive. First, the value of k_{aq} was not significantly changed in the absence of added Cl^- by changing ClO_4^- concentration from 1 to 0.5 *M* upon substitution of $Al(ClO_4)_3$ for $NaClO_4$ at constant ionic strength. Second, the value of k_{aq} remains unchanged (or is decreased by about 15% at most if the value of 1.95×10^{-5} sec^{-1} interpolated from results listed by Laurie and Monk[2] is correct) when the ClO_4^- concentration is increased from 0.01 to 1 *M* whereas an increase in k_{aq} would be expected.[4] An increase would be expected because at 1 *M* ClO_4^- the apparent second-order anation rate constant for the reaction of MOH_2^{3+} and Cl^- through the MOH_2^{3+},ClO_4^- ion pair is greater than the apparent second-order anation rate constant for the reac-

Table II. Values of the Pseudo-First-Order Anation Rate Constant, k_{an}, at Various Cl^- Ion Concentrations (1.0 *M* Ionic Strength; 45.0°; $NaClO_4$ and NaCl Variable)

$[Cl^-]$, *M*	$10^5 k_{an}$, sec^{-1} Ref 3[a]	This work[b]	Ref 4
0.1	0.34	0.38	0.35
0.2	0.80	0.65	0.70
0.3	1.09	0.85	1.06
0.4	1.31	1.11	1.41
0.5	1.45	1.32	1.76
0.6	1.56	1.56	2.11
0.7		1.70	
0.8		1.90	
0.9		1.85	

[a] 0.001 *M* $HClO_4$. [b] 0.100 *M* $HClO_4$.

tion through the $MOH_2{}^{3+},Cl^-$ ion pair[4] and, by the principle of microscopic reversibility, the apparent first-order aquation rate constant for MCl^{2+} through the $MOH_2{}^{3+},ClO_4{}^-$ ion pair must be greater than the first-order aquation rate constant for the direct aquation of MCl^{2+}.

The values obtained for k_{an} fit the equation for the I_d mechanism with the ion pair $MOH_2{}^{3+},Cl^-$ as intermediate; thus

$$\frac{1}{k_{an}} = \frac{1}{k} + \frac{1}{kQ_o}\frac{1}{[Cl^-]} \qquad (7)$$

where *k* is the rate constant for the interchange of Cl^- for H_2O in reaction 1. The value obtained for *k* from the inverse of the intercept was $(3.48 \pm 0.35) \times 10^{-5}$ sec^{-1}. The value of the ratio of the intercept-to-slope was 1.21 ± 0.13 M^{-1}, in good agreement with the value obtained from equilibrium measurements.

The values of k_{an} obtained by us are listed in Table II where they can be compared with the values of k_{an} obtained by Langford and Muir[3] and with the values of k_{an} calculated by Burnett.[4] The values of k_{an} obtained by Langford and Muir at Cl^- concentrations from 0.1 to 0.4 *M* are larger than those obtained by us because Langford and Muir found *decreasing* values of k_{aq} with *decreasing* Cl^- concentration whereas we found k_{aq} to be independent of Cl^- concentration. Consequently, for a given value of $(k_{aq} + k_{an})$ in eq 5 at 1 *M* ionic strength, the value of k_{aq} from ref 2 is smaller and the value of k_{an} is larger than our values for k_{aq} and k_{an}, respectively. Furthermore, because the k_{an} values in ref 3 at the lower Cl^- concentrations were too large, the plot of k_{an} *vs.* Cl^- concentration must show a larger "bend-over" effect as the Cl^- concentration reaches the region where k_{aq} becomes constant than is the case for our k_{an} values; at Cl^- concentrations above 0.6 *M* k_{an} as predicted by the results of Langford and Muir[3] will not increase as much as observed by us.

The values of k_{an} given by Burnett[4] for 0.5 and 0.6 *M* Cl^- distinctly show the effect of the squared term for the Cl^- concentration in the expression for k_{an} and the calculated values of k_{an} are greater than the values of Langford and Muir being fit by Burnett. The relative importance of this squared term increases approximately twofold as the Cl^- concentration increases from 0.5 to 0.9 *M*. Since the expected increase was not found and k_{an} became essentially constant at 0.8–0.9 *M* Cl^-, it was concluded that the values obtained for k_{an} did not support the postulate that reaction 2 made an important contribution to the anation process in the media used.

Registry No. Chloropentaamminecobalt(III) perchlorate, 15156-18-0.

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Inner-Orbital Binding-Energy Shifts of Antimony and Bismuth Compounds

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Two previous reports[1,2] have described inner-orbital binding-energy shifts for related compounds based on members of the group Va and IVa family of elements. In our first study[1] analogous nitrogen, phosphorus, and arsenic chemical environments were compared both experimentally and theoretically, with the aid of atomic SCF calculations, to determine the relative chemical shifts. The other investigation[2] compared identical compounds of carbon, silicon, germanium, tin, and lead. In each case the chemical shift effects for these compounds were observed to decrease with increasing atomic size, and although part of this effect could be attributed to the increasing atomic radii, the additional decreases were thought to arise from a charge equalization through π bonding. The present work in X-ray photoelectron spectroscopy completes the comparison of the group Va compounds by extending the investigations to include antimony and bismuth compounds. Atomic SCF calculations are presented for the entire series of group Va elements and the experimental data for antimony and bismuth are compared with the previously reported nitrogen, phosphorus, and arsenic measurements.

Experimental Section

Two independent X-ray photoelectron spectrometers of the electrostatic-analyzer type[3] manufactured by Varian were used to collect the binding-energy data reported herein. The description, operation, sample preparation techniques, and reproducibility of the Varian IEE-15 spectrometer have previously been discussed.[1,2,4,5] The corrected binding-energy measurements were referenced to the thin layer of adsorbed hydrocarbon contaminant assuming a value[6] of 285.0 eV for the resulting C "1s" line. The high reproducibility of the Varian spectrometer yielded a standard deviation of *ca.* ±0.3 eV for the binding-energy data obtained from those compounds upon which several replicate measurements were taken. The antimony and bismuth compounds used in this study were commercially available samples of high purity.

Atomic SCF calculations[7] were completed for nitrogen, phosphorus, arsenic, antimony, and bismuth as neutral atoms (with outer electron configuration s^2p^3), 1+ ions (s^2p^2), and 2+ ions (s^2p^1) in the lowest Hund's-rule energy states. The results of these calculations agreed, where such comparisons were possible, with near-limit[8] Hartree–Fock calculations.

Results and Discussion

The Sb "$3d_{3/2}$," "$3d_{5/2}$," and "4d" binding energies are reported in Table I for a series of 15 antimony compounds. The relative area ratio of the Sb "$3d_{3/2}$"-"$3d_{5/2}$" doublet

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