planes are virtually identical (1.466 and 1.476 Å), and the metal is approximately equidistant from the facial boron and carbon atoms although the Co–C distances are slightly shorter than the Co–B vectors [mean values 2.046 (2) and 2.097 (2) Å, respectively]. The difference of 0.05 Å correlates well with the larger covalent radius of boron vs. carbon (0.82 vs. 0.77 Å).

The two $C_2B_9H_{11}^{2-}$ ligands are mutally rotated by 37°, as measured by the dihedral angle subtended by the two planes through cobalt and bisecting the C(1)–C(2) and C(1′)–C(2′) bonds. This produces a staggered orientation of the carborane cages with the two C–C edges in close proximity, the molecule having overall approximate (not crystallographic) C_2 symmetry. The ligand orientation in this species is very similar to that previously found[4] in the isoelectronic nickel(IV) complex $Ni(1,2\text{-}C_2B_9H_{11})_2$, in which the mutual rotation of the ligands away from an eclipsed position is 36°. In contrast, the electron-rich sandwich complex $Ni^{III}(1,2\text{-}C_2B_9H_{11})_2^-$ exhibits a trans orientation with respect to the carbons in the two ligands.[11]

As noted above, the earlier X-ray study of $Cs^+[Co(1,2\text{-}C_2B_9H_{11})_2]^-$ did not locate the carbon atoms and hence the ligand orientation could not be determined. However, in the bis(8,9,12-tribromo) derivative of this ion[12] the cages adopt a trans arrangement with the facial carbon atoms on opposite sides of cobalt, undoubtedly because of steric repulsion involving bromine substituent on the cages. In both $Co(C_2B_9H_{11})_2^-$ and $Ni(C_2B_9H_{11})_2$, each 12-vertex polyhedron is a closo 26-electron ($2n + 2$) system and the metals satisfy the 18-electron rule; this is reflected in the normal metal–carbon, metal–boron, carbon–carbon, and carbon–boron bond distances and in the absence of any significant distortion from regular 12-vertex closo geometry. These systems can be contrasted with the slip-distorted sandwich complexes of 1,2- and 1,7-$C_2B_9H_{11}^{2-}$, referred to above, which usually incorporate d^n metal ions where $n > 6$. Such species have been extensively discussed elsewhere.[1,13]

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Registry No. $(C_2H_5)_3NH^+[Co(1,2\text{-}C_2B_9H_{11})_2]^-$, 80584-07-2.

Supplementary Material Available: Listings of observed and calculated structure factors, anisotropic thermal parameters, and least-squares planes (13 pages). Ordering information is given on any current masthead page.

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Pressure and Temperature Dependencies of the Mercury-Catalyzed Aquation of *mer*-$RhCl_3(OH_2)_3$ in Acidic Aqueous Solution

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The kinetics and stereochemistry of aquation and chloride anation of the series of complexes $RhCl_x(OH_2)_{6-x}^{(3-x)+}$ where $x = 0\text{–}6$, in acidic aqueous solutions have been studied in detail[2-6] and shown to be dominated by the trans effect of coordinated chloride.[6] Water exchange[7] with $Rh(OH_2)_6^{3+}$ and chloride exchange[4] with $RhCl_6^{3-}$ have been interpreted in terms of a dissociative mechanism. Consequently, the remaining reactions within the sequence may be safely assumed to conform to this assignment. In order to explain the steric course of these reactions, it was necessary to refine the mechanism further to include a tetragonal-pyramidal intermediate.[6]

A high-pressure kinetic study[8] of the reactions involving the $RhCl_6^{3-}$, $RhCl_5(OH_2)^{2-}$, and *cis*-$RhCl_4(OH)_2)_2^-$ complex ions indicated that the large positive ΔV^* values observed were also directly compatible with a D mechanism.

Chan and Harris[9] recently investigated the mercury-catalyzed aquation of the species *fac*-$RhCl_3(OH_2)_3$, *cis*-$RhCl_2(OH_2)_4^+$, and $RhCl(OH_2)_5^{2+}$. These species are virtually immune to aquation in acidic solution, presumably due to the greater trans effect of the chloride ligands with respect to the aquo ones. From the relative magnitudes of the formation constants of the respective precursor complexes $HgRhCl_x(OH_2)_{6-x}^{(5-x)+}$, they[9] proposed that an electrostatic interaction was responsible for their formation.

It was our hope that a knowledge of the volume changes associated with precursor formation and its subsequent decomposition would shed more light on the nature of the interactions involved.

Experimental Section

The *fac*-$RhCl_3(OH_2)_3$ and *mer*-$RhCl_3(OH_2)_3$ isomers were prepared in solution from $K_2[RhCl_5(OH_2)]$ and separated on a mixed-bed, ion-exchange column containing equal parts of Lewatit S1080 (H^+ form) and Lewatit M5080 (Cl^- form) by the method of Palmer and Harris.[6] These solutions were then shaken with a weak basic anion-exchange resin (Lewatit MP7080) in the ClO_4^- form to remove traces of free chloride ion.

The *fac* isomer was characterized by absorption maxima at 376 and 473 nm with the ratio of the respective extinction coefficients being 1.26, which compares very favorably with the value of 1.27 for ϵ(376 nm)/ϵ(473 nm) recorded previously[6] but differs from a more recent[9] value of 1.11 for $\epsilon(376)/\epsilon(474)$. Absorption maxima for the *mer* species were found at 370 and 469 nm with a resulting extinction coefficient ratio of 0.89 (cf. $\epsilon(370)/\epsilon(469) = 0.84$).[6]

It should be mentioned that we were unsuccessful in our attempts to separate these two isomers using the above mentioned resins in the H^+ and ClO_4^- forms. Furthermore, the ratio of the extinction coefficients reported by Chan and Harris[9] for the *fac* isomer may indicate the presence of some *mer* isomer in their sample. Apart from an immediate spectral change, which occurred when mixing solutions of *fac*-$RhCl_3(OH_2)_3$ and $Hg(ClO_4)_2$, only a very small change took place subsequently—presumably due to the catalyzed aquation reaction—such that we were unable to study this reaction.

Solutions of mercury(II) perchlorate were prepared and analyzed as described previously.[9] Water used to make up these solutions was purified with a commercial ion-exchange column and a double-distillation assembly.

The ionic strength and acidity were kept constant at 2.0 M by the addition of $HClO_4$. The complex concentration was maintained at 2.5×10^{-4} M.

The spectra were recorded on a Zeiss PMA 10 spectrophotometer whereas the kinetics were investigated on a Zeiss PMQ II adapted to accommodate a "split-beam" differential amplifier and a high-pressure vessel.[10] The quartz cell seated inside the vessel was con-

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Table I. Temperature Dependence of the Rate Constants for the Catalyzed Aquation of *mer*-$RhCl_3(OH_2)_3$

T, °C	$10^3 \times [Hg^{2+}]$, M	$10^3 \times k_{obsd}$, s^{-1}	10^3k, s^{-1}	K, M^{-1}
19.0	5.00	0.47	0.60 ± 0.03	758 ± 63
	2.50	0.41		
	2.00	0.35		
	1.25	0.29		
	1.00	0.26		
23.0	5.00	0.91	1.11 ± 0.04	788 ± 43
	2.50	0.73		
	2.00	0.67		
	1.25	0.54		
	1.00	0.50		
26.0	5.00	1.15	1.50 ± 0.07	771 ± 55
	2.50	1.03		
	2.00	0.92		
	1.25	0.74		
	1.00	0.65		
29.0	5.00	1.81	2.21 ± 0.10	848 ± 67
	2.50	1.54		
	2.00	1.33		
	1.25	1.14		
	1.00	1.02		
33.0	5.00	2.75	3.55 ± 0.21	845 ± 85
	2.50	2.56		
	2.00	2.24		
	1.25	1.80		
	1.00	1.63		

structed of two interfitting cylindrical tubes each sealed with a quartz window and has an average path length of 18 mm at atmospheric pressure.[11] The temperature inside the vessel was maintained to an accuracy of ±0.1 °C. The reaction was monitored at 235 nm.

Results and Discussion

The observed pseudo-first-order rate constant, k_{obsd}, for the aquation of *mer*-$RhCl_3(OH_2)_3$ was studied as a function of Hg^{2+} concentration at five temperatures, and these data are presented in Table I. The suggested reaction mechanism consists of reactions 1 and 2. As reported earlier,[9] k_{obsd} is

$$mer\text{-}RhCl_3(OH_2)_3 + Hg^{2+} \overset{K}{\rightleftharpoons} \{RhCl_3(OH_2)_3Hg\}^{2+} \qquad (1)$$

$$[RhCl_3(OH_2)_3Hg]^{2+} + H_2O \xrightarrow{k} RhCl_2(OH_2)_4{}^{+} + HgCl^{+} \qquad (2)$$

not a linear function of $[Hg^{2+}]$ but rather conforms to eq 3

$$k_{obsd} = kK[Hg^{2+}]/(1 + K[Hg^{2+}]) \qquad (3)$$

so that a double-reciprocal plot of $1/k_{obsd}$ vs. $1/[Hg^{2+}]$ gives the values of K and k, corresponding to eq 1 and 2, respectively. These values (also listed in Table I) and their uncertainties were derived from a linear least-squares treatment.

It is immediately apparent that K at 19 °C is considerably larger than the value reported[9] for the *fac*-$RhCl_3(OH_2)_3$ complex (20 °C and μ = 3 M) of 137 ± 5 M^{-1}. This is difficult to reconcile with the concept of a Coulombic interaction being mainly responsible for the association. The original concept considered the Hg^{2+} interaction to be influenced by the adjacent chloride ligands with the net result that the effective negative charge of the three chlorides in *fac*-$RhCl_3(OH_2)_3$ amounted to ca. 2−. The *mer* isomer would therefore be expected to interact more weakly, possibly with a net charge of 1− as seen by the Hg^{2+} ion. Due to this apparent disparity, we prefer to consider that coordinate bonds, Rh–Cl–Hg, exist in the intermediate complex. Moreover, the unique product of reaction 2 is *cis*-$RhCl_2(OH_2)_4{}^+$, which implies that only two chloride ligands in the *mer* complex are labile with respect to Hg^{2+}, whereas all three are equivalent in the *fac* isomer. Thus, there is an additional factor of 1.5 to be applied when comparing K_{mer} with K_{fac}, emphasizing the difference further. However, the difference is qualitatively as expected on the basis of Grinberg's electrostatic theory of the trans effect. In other words, the trans effect of the two trans oriented chloride ligands in *mer*-$RhCl_3(OH_2)_3$ may be sufficient to ensure an enhanced electronegativity of one of them at any point in time to give rise to a stronger bridging bond than in the *fac* analogue.

Table II. Pressure Dependence of the Rate Constants for the Catalyzed Aquation of *mer*-$RhCl_3(OH_2)_3$ at 23.0 °C

P, bar	$10^3 \times [Hg^{2+}]$, M	$10^2 \times k_{obsd}$, s^{-1}	10^3k, s^{-1}	K, M^{-1}
10	5.00	9.1	1.11 ± 0.04	788 ± 43
	2.50	7.3		
	2.00	6.7		
	1.25	5.4		
	1.00	5.0		
250	5.00	8.5	1.04 ± 0.06	790 ± 66
	2.50	6.8		
	2.00	6.4		
	1.25	5.0		
	1.00	4.7		
500	5.00	7.7	0.99 ± 0.02	759 ± 31
	2.50	6.5		
	2.00	6.0		
	1.25	4.75		
	1.00	4.3		
750	5.00	7.0	0.90 ± 0.03	721 ± 36
	2.50	5.8		
	2.00	5.4		
	1.25	4.2		
	1.00	3.8		
1000	5.00	6.3	0.81 ± 0.04	713 ± 47
	2.50	5.3		
	2.00	4.6		
	1.25	3.9		
	1.00	3.35		
1250	5.00	5.6	0.75 ± 0.03	699 ± 42
	2.50	4.9		
	2.00	4.4		
	1.25	3.45		
	1.00	3.05		
1500	5.00	5.3	0.68 ± 0.02	670 ± 29
	2.50	4.3		
	2.00	3.85		
	1.25	3.1		
	1.00	2.8		

Table III. Rate Parameters for the Mercury-Catalyzed Aquation of *mer*-$RhCl_3(OH_2)_3$ at 23 °C

K, M^{-1}	788 ± 43	10^3k, s^{-1}	1.11 ± 0.04
ΔH, kJ mol^{-1}	6.3 ± 0.2	$\Delta H^{\ddagger}$, kJ mol^{-1}	90 ± 3
ΔS, J K^{-1} mol^{-1}	76 ± 7	$\Delta S^{\ddagger}$, J K^{-1} mol^{-1}	4 ± 10
ΔV, cm^3 mol^{-1}	2.8 ± 0.3	$\Delta V^{\ddagger}$, cm^3 mol^{-1}	8.1 ± 0.4

Furthermore, the instantaneous spectral change, which extends through the visible spectrum, observed upon mixing solutions of *mer*-$RhCl_3(OH_2)_3$ and Hg^{2+} indicates the formation of a new species rather than being a charge-transfer effect.

The pressure dependence of k_{obsd} was studied at 23 °C, and these results are shown in Table II together with the calculated values of k and K. Plots of the natural logarithm of these values vs. pressure proved to be linear within experimental error. The associated volume data and other parameters are summarized in Table III.

The large ΔS value, which is almost solely responsible for the large K value, must be associated with the bonding changes, but primarily with the release of a water molecule from the coordination sphere of the Hg^{2+} ion. Similarly, ΔV

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is a composite quantity of bonding and solvation effects where the negative contribution of Hg–Cl bond formation is more than compensated by the positive effects of Rh–Cl bond stretching and H_2O release. In addition, a "dilution of the 2+ charge" over the entire bridged complex would cause a reduction in electrostriction and consequently a small positive contribution to ΔS and ΔV.

The dissociation of the precursor complex, eq 2, exhibits a lower ΔH^* value than for the uncatalyzed reaction (cf. $\Delta H^* = 137 \pm 3$ kJ mol^{-1} and $\Delta S^* = -80 \pm 9$ J K^{-1} mol^{-1})[6] presumably due to a weakening of the Rh–Cl bond in the bridged species and also it shows a higher ΔS^* value because no new charge is created during the process. The large ΔH^* and a ΔS^* of almost 0 tend to favor a dissociative mechanism involving only Rh–Cl bond breaking. The positive ΔV^* value is also consistent with this mechanism, particularly as the corresponding values for the aquation of $RhCl_6^{3-}$ and $RhCl_5(OH_2)^{2-}$ are 21.5 ± 1.6 and 14.3 ± 0.5 cm^3 mol^{-1} (20 °C and $\mu = 4$ M).[8]

The $HgCl^+$ cation has catalytic activity almost identical with that of Hg^{2+} so that its increasing presence during the reaction should not affect the kinetics adversely. Indeed, the close similarity in activity helps to maintain pseudo-first-order conditions throughout the reaction even at the lowest Hg^{2+} concentrations. As may be expected, $HgCl_2$ exhibits only a slight catalytic effect with $k_{obsd} = 5 \times 10^{-5}$ s^{-1} at $[HgCl_2] = 5 \times 10^{-2}$ M at 28 °C.

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B 1s Binding Energies in $MBPh_4$, Where M Is Na, K, Rb, Cs, and NH_4

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The purpose of this note is to describe the results of an X-ray photoelectron spectroscopy (XPS) study of the B 1s binding energy (BE) shifts in a series of tetraphenylborates, $MBPh_4$ where M is Na, K, Rb, Cs, and NH_4, which are isostructural.[1-5] It was anticipated that progressively increasing BE shifts would be observed on going from Na to Cs, as has been observed in similar studies.[6]

Samples of each compound were obtained as crystals, which were then ground to a fine powder and examined in a Vacuum Generators ESCA 3 photoelectron spectrometer. Several different support materials were tried (gold mesh, indium foil, silver paint, and adhesive tape), and each method gave essentially identical binding energies. Some sample discoloration after X-irradiation (300 W, 1 h) was noted for $NaBPh_4$ and NH_4BPh_4 and correlated with the appearance of a small shoulder on the high-BE side of the Na 1s, B 1s, and N 1s peaks. The samples were apparently stable to ultra-high vacuum in the absence of X-irradiation.

Table I. BE[a] Results and Selected Cation Properties[b] for $MBPh_4$

compd	B 1s, eV	C 1s, V	Δ, eV	cation ionic radius, Å	cation electronegativity
$NaBPh_4$	187.4	284.7	97.3	0.95	0.9
$KBPh_4$	186.7	283.0	96.5	1.33	0.8
$RbBPh_4$	186.5	283.2	96.5	1.48	0.8
$CsBPh_4$	189.6	285.5	96.5	1.69	0.7
NH_4BPh_4	187.9	284.4	95.9	1.43	

[a] Reproducibility for three determinations was ±0.15 eV.
[b] Obtained from "Handbook of Chemistry and Physics", 51st ed., Chemical Rubber Co., Cleveland, OH, 1970.

Average BE values for the C 1s and B 1s are given in Table I. The data were treated in terms of the relative shift of C 1s to B 1s, $\Delta = BE_{C\,1s} - BE_{B\,1s}$, which is independent of charging effects. Because the series of compounds $MBPh_4$ is isostructural, crystal field effects should be limited to those caused by the changing cation. The fairly large spacing between the B atom and the cations makes the choice of the boron atom as an internal reference a reasonable one. The size of the BPh_4 anion precludes large-scale model calculations on the $MBPh_4$ system, especially considering the rather narrow range of BE shifts observed. Thus an interpretation of trends in the data in terms of empirical parameters was considered.

The point-charge approximation for XPS chemical shifts,[7] in terms of Δ defined above, may be written: $\delta\Delta = k\delta q + \delta V + \delta R$, where k is a constant, q is the charge on the host atom, V the external (crystal) potential energy, and R the relaxation energy, which may be considered as a sum of intra- and extraatomic terms. In general, δq and δV, where the change δ here is relative to $NaBPh_4$, have opposite sign for a given atom, but for the $MBPh_4$ series, δV should be dominated by changes in cation and be small compared to δq. The relaxation contribution, δR, should have the same sign as δq since it describes the adiabatic collapse of electronic charge toward the core hole following photoionization. Although this term cannot be evaluated directly, the relative contribution of δR to $\delta\Delta$ should approximate that of δq.

Overall, therefore, it is expected that Δ should decrease as cation size increases. Table I illustrates that this is, in general, the observed result. It had been expected that the relative shift for $RbBPh_4$ should lie between that of $KBPh_4$ and $CsBPh_4$. Cation size and empirical electronegativity values, listed in Table I, show a reasonable correlation with Δ, suggesting a decrease in anion–cation charge transfer as cation size is increased. This decrease implies a decrease in δq from Na to Cs and probably a decrease in δR, which should also be strongly influenced by the ability of the cation to neutralize a core hole, although this might be offset somewhat by the varying energy of the core hole on going from Na to Cs. Although these results are basically in agreement with what might be expected on the basis of simple parameters such as electronegativity and ionic size, the relatively small shifts observed preclude detailed examination at this stage. One further note is that the coincidence of Δ values for the Rb, NH_4, and K salts may be interpreted as indicating similar charge transfer in $MBPh_4$ from the anion to the cation for these cations. However, the lack of discrimination of XPS in this case may also mask changes in δR that effectively compensate for the anticipated trend in q on going from Na to K, Rb, Cs, and NH_4.

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