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# Reaction Volume for the $OH^-$ Addition to Hexafluoroacetylacetonate Ligand on $Co^{III}$ Complex

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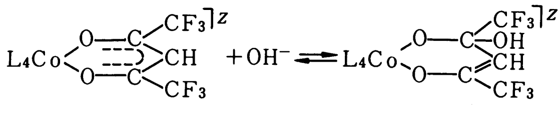
**Synopsis.** For the title reaction in water: $L_4Co(hfac)^z + OH^- = L_4Co(hfacOH)^{z-1}$, reaction volumes ($\Delta V^\circ$) at infinite dilution were obtained at 25 °C, where $A_4$ is $(NH_3)_4$, $(en)_2$, α-trien, β-trien, *f*(*N*)-*i*-dtma, α-edda, β-edda, and Hhfac stands for hexafluoroacetylacetone. The resulting $\Delta V^\circ$ values supported the addition of $OH^-$ to $CoA_4(hfac)^z$.

In our recent report, a unique character was clarified for the reaction between an $OH^-$ ion and a $Co^{III}$ complex containing a hfac ligand in water.[1] That is, the color of a $CoL_4(hfac)^z$ complex changes rapidly and reversibly upon a pH change of the solution.

This phenomenon can be explained by a shift in the following equilibrium:[1,2]



(1)

In another work, $\Delta V^\circ$ was obtained for 19 acid-base reactions of an octahedral complex:[3]

$$MA^z + OH^- = MB^{z-1} + H_2O \qquad (2)$$

In Reaction 2, $MA^z$ is an octahedral transition-metal ($Pt^{IV}$, $Rh^{III}$, $Co^{III}$) complex with ligand $A = H_2O$, $NH_3$, and $C_2O_4H^-$; $MB^{z-1}$ is the corresponding conjugate base complex with ligand $B = OH^-$, $NH_2^-$, and $C_2O_4^{2-}$, where the charge (*z*) on the reactant ranges from −2 to 4. The $\Delta V^\circ$'s at 25 °C for these reactions can be summarized as:

$$\Delta V^\circ = (-2.5 \pm 0.2)\Delta Z^2 + (14.5 \pm 0.8)\ \mathrm{cm^3\,mol^{-1}}, \qquad (3)$$

where $\Delta Z^2$=(charge of the product complex)$^2$−(charge of the reactant complex)$^2 = 1-2z$, and the first term in Eq. 3 corresponds to the electrostatic volume contribution due to the interaction with solvent and the second to the intrinsic volume of ions.

Interest has been developed here regarding whether the distinct difference between Reactions 1 and 2 is reflected in their reaction volumes. Thus, in the present work, $\Delta V^\circ$ of Reaction 1 has been obtained dilatometrically for seven $CoL_4(hfac)^z$ complexes. Their magnitudes are discussed in relation to Eq. 3.

## Experimental

The respective complex (perchlorate) was obtained and identified in a previous work.[1]

Dilatometry was carried out using a Carlsberg dilatometer as described before.[3] 15 cm$^3$ of an aqueous complex solution was mixed with 3 cm$^3$ of NaOH and the resulting volume change ($\Delta v_{\mathrm{exptl}}$) was observed. Generally, two runs were performed at one condition. The correction term ($\Delta v_{\mathrm{corr}}$) for the change in the ionic strength upon mixing was calculated as before.[3] $\Delta V^\circ$ has been calculated from $\Delta v_0 = \Delta v_{\mathrm{exptl}} - \Delta v_{\mathrm{corr}}$, where the degree of the completion of the neutralization process (*R*%) has been taken into account.

## Results and Discussion

The dilatometric results and the reaction volume obtained, therefrom, are summarized in Tables 1 and 2. The experimental $\Delta V^\circ$'s range from moderately positive to moderately negative. Thus, the main contribution to $\Delta V^\circ$ may be ascribed to the solvational change around the complex during Reaction 1.[4]

The $\Delta V(3)$ in Table 2 is the reaction volume calculated upon inserting the relevant value of $\Delta Z^2$ into Eq. 3. The value definitely differs from the corresponding experimental $\Delta V^\circ$. On the other hand, assuming that the difference in the electrostriction volume for $CoL_4(hfacOH)^{z-1}$ and $CoL_4(hfac)^z$ equals $(-2.5 \pm 0.2)\ \mathrm{cm^3\,mol^{-1}}$, the volume change of Reaction 1 can be predicted as follows by the use of

Table 1. Dilatometric results at 25 °C

| Complex[a] | $C$[b]/mM | NaOH/mM | $\Delta v_{\mathrm{exptl}}/\mu l$ | $\Delta v_{\mathrm{corr}}/\mu l$ | *R*% |
|---|---|---|---|---|---|
| $[Co(NH_3)_4hfac](ClO_4)_2$ | 10 | 50 | 1.55, 1.63 | −0.14 | 100 |
| | | 100 | 1.39 | −0.20 | 100 |
| $[Co(en)_2hfac](ClO_4)_2$ | 10 | 50 | 1.44, 1.50 | −0.14 | 100 |
| | | 100 | 1.41, 1.42 | −0.20 | 100 |
| α-$[Co(trien)hfac](ClO_4)_2$ | 10 | 50 | 1.14, 1.25 | −0.14 | 100 |
| β-$[Co(trien)hfac](ClO_4)_2$ | 9.5 | 47.5 | 1.49, 1.42 | −0.13 | 100 |
| *f*(*N*)-$[Co(i\text{-}dtma)hfac](ClO_4)$ | 7.5 | 37.5 | 0.20, 0.09 | −0.04 | 100 |
| α-Co(edda)hfac | 4.0 | 20 | −0.53, −0.43 | −0.01 | 94 |
| β-Co(edda)hfac | 3.0 | 15 | −0.19, −0.17 | −0.01 | 98 |

a) Trien = triethylenetetramine, *i*-dtma = *N*,*N*-bis(2-aminoethyl)glycinate, edda = ethylenediamine-*N*,*N*′-diacetate.
b) Complex concentration.

Table 2. Volume change ($cm^3\,mol^{-1}$) for the reaction of $CoL_4(hfac)^z$ with $OH^-$ ion in water at 25 °C

| Complex | $\Delta Z^2$ | Experimental | Calculated | |
|---|---|---|---|---|
| | | $\Delta V°$ | $\Delta V(3)$ | $\Delta V(4)$ |
| $Co(NH_3)_4hfac^{2+}$ | −3 | 11.2±0.4 | 22.0±1.4 | 6.1±2.6 |
| $Co(en)_2hfac^{2+}$ | −3 | 10.7±0.1 | 22.0±1.4 | 6.1±2.6 |
| α-Co(trien)$hfac^{2+}$ | −3 | 8.9±0.4 | 22.0±1.4 | 6.1±2.6 |
| β-Co(trien)$hfac^{2+}$ | −3 | 11.1±0.3 | 22.0±1.4 | 6.1±2.6 |
| *f*(*N*)-Co(*i*-dtma)$hfac^+$ | −1 | 1.6±0.5 | 17.0±1.0 | 1.1±2.2 |
| α-Co(edda)hfac | 1 | −8.3±0.9 | 12.0±1.0 | −3.9±2.2 |
| β-Co(edda)hfac | 1 | −3.9±0.3 | 12.0±1.0 | −3.9±2.2 |

$\bar{V}(OH^-)=1.4\pm 2\ cm^3\,mol^{-1}$;[5]

$$\Delta V° = (-2.5\pm 0.2)\Delta Z^2 - (1.4\pm 2)\ cm^3\,mol^{-1} \qquad (4)$$

The experimental $\Delta V°$'s agree fairly well with those $\Delta V(4)$ calculated using Eq. 4. Thus, the magnitudes of the experimental $\Delta V°$'s reinforce the suggestion that the origin of the rapid and reversible color change of the $CoL_4(hfac)^z$ solution is not a deprotonation from $CoL_4(hfac)^z$ but an addition of $OH^-$ to $CoL_4(hfac)^z$. It should be noted that measurements regarding the reaction volume could, thus, become relevant tools for discriminating a reaction type.

Alternatively, a linear correlation between the experimental $\Delta V°$ and the $\Delta Z^2$ can be obtained by a least-squares method:

$$\Delta V° = (-4.2\pm 0.4)\Delta Z^2 - (2.1\pm 0.8)\ cm^3\,mol^{-1} \qquad (5)$$

The intercepts of Eqs. 4 and 5 coincide well, whereas the $\Delta Z^2$ coefficients somewhat differ. According to the Drude-Nernst equation regarding electrostriction, the $\Delta Z^2$ coefficient is inversely proportional to the assumed common ionic radius ($r$) of the reactant and the product.[6] Since a $\Delta Z^2$ coefficient of $-2.5\ cm^3\,mol^{-1}$ corresponds to $r$=1.7 Å, that ($-4.2\ cm^3\,mol^{-1}$) of Eq. 5 corresponds to $r$=1.0 Å.[3] Although small, the thus-derived $r$ is not so far from reality since the coordination bond lengths are 2.0—2.5 Å. Also, the effective charge may be fairly concentrated towards the center of the complex ion.[3] Consequently, the charge dependence of $\Delta V°$ can be consistently understood by using the Drude-Nernst equation regarding electrostriction.

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