

## Volume of Activation and Reactivity of the Conjugate Base of Cobalt(III) Amine Complexes

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A model inferred from features of the ammoniation of cobalt(III) haloamines is extended to base hydrolysis in aqueous solution. This model connects the reactivity of the conjugate base to a large volume increase on passing to the transition state in a limiting dissociative mode. A comparison with experimental results shows good agreement for the compounds  $\text{Co}(\text{NH}_3)_5\text{X}^{n+}$ , with  $\text{X} = \text{F}, \text{Cl}, \text{NO}_3, \text{PO}_4, \text{or } \text{SO}_4$ , whereas compounds with  $\text{X} = \text{N}_3$  and  $\text{NCS}$  do not comply and the compound with  $\text{X} = \text{Br}$  is ambiguous. The relation between the change in structure of the second coordination sphere on activation and the specific properties of the electrostatic field of the  $\text{Co}^{3+}$  ion is examined.

Although the general outline of the conjugate-base (CB) mechanism operative in octahedral amine complexes of chromium(III), cobalt(III), rhodium(III), and iridium(III) is at present universally agreed upon,<sup>1-3</sup> a more detailed understanding of the component parts of the postulated mechanism, such as acid dissociation constants of the rapid preequilibrium, labilizing effect of the coordinated amido residue, and shape and reactivity of the supposed five-coordinated intermediate,<sup>2,4</sup> is still largely unclarified and remains the object of investigation.<sup>5-8</sup> Evidence has accumulated<sup>9</sup> for an essentially D (dissociative) type mechanism. A detailed mechanistic understanding of the reaction is hampered by the fact that in aqueous solution the acid dissociation constants ( $K_a$ ) of the reactive amine complexes are too small to be determined experimentally ( $\text{p}K_a > 15$ ).<sup>3</sup>

Fortunately the higher acidic strength in some nonaqueous solvents such as dimethyl sulfoxide<sup>10</sup> and liquid ammonia<sup>7,8,11</sup> opens the way to a separate determination of the relevant  $K_a$  values. In our laboratory we have succeeded in doing this for liquid ammonia solutions by a combination of kinetic and pH-metric measurements for the complexes  $[\text{Co}(\text{NH}_3)_5\text{Cl}](\text{ClO}_4)_2$  and  $[\text{Co}(\text{NH}_3)_5\text{Br}](\text{ClO}_4)_2$  and the series<sup>12</sup> of *cis*- and *trans*- $[\text{Co}(\text{en})_2\text{Cl}_2]\text{ClO}_4$  and  $[\text{Co}(\text{en})_2\text{NH}_3\text{Cl}](\text{ClO}_4)_2$ . This has led to a number of mechanistic inferences.<sup>7,8,12</sup> The CB mechanism in aqueous solution is characterized by very high values of the entropy of activation.<sup>2,13</sup> This feature is maintained in the results for the rate-determining step in liquid ammonia. A comparison between aquation and ammoniation parameters for the aminocobalt(III) complexes has led to the conclusion<sup>7,8,12</sup> that not a lowering of  $\Delta H^\ddagger$  but the very favorable  $\Delta S^\ddagger$  is the rate-enhancing factor. The location of this entropy effect can be limited to the second coordination sphere, because there is no correlation between steric course and entropy of activation for the base-catalyzed ammoniation of the bis(ethylenediamines) mentioned above,<sup>12</sup> to the extent that the *cis*- $[\text{Co}(\text{en})_2\text{NH}_3\text{Cl}]^{2+}$  complex that also shows a large  $\Delta S^\ddagger$  value reacts with retention of configuration.<sup>8</sup>

The mechanistic significance of the entropy change is not straightforward.<sup>14,15</sup> A much more readily visualized quantity is the volume of activation  $\Delta V^\ddagger$ , which regrettably is not easily accessible in liquid ammonia. A way out of this dilemma is offered by the recent proposal<sup>16</sup> of an experimental linear relation between  $\Delta S^\ddagger$  and  $\Delta V^\ddagger$  valid for both A and D activation.

$$\Delta V^\ddagger (\text{cm}^3 \text{mol}^{-1}) = 0.25\Delta S^\ddagger (\text{J K}^{-1} \text{mol}^{-1}) - 4.4 \quad (1)$$

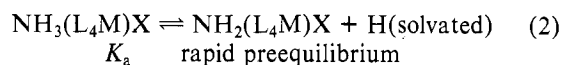
Reinforcement of the argument comes from earlier observations that volume and entropy changes parallel one another for complex formation in aqueous solution<sup>17</sup> and that theoretically for ionization reactions  $\Delta V^\ddagger$  should be proportional to  $\Delta S^\ddagger$ , as confirmed by experiment.<sup>18</sup> Adoption of a similar relation for reactions in liquid ammonia or even the assumption

of a rough general correlation between  $\Delta V^\ddagger$  and  $\Delta S^\ddagger$ , as already hinted at by Swaddle,<sup>19</sup> means that the extraordinary rate enhancement for the base-catalyzed reaction is related to the volume increase in the rate-determining step.

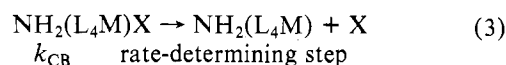
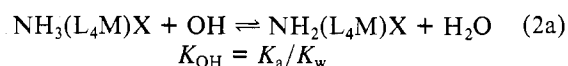
It is tempting to associate this volume increase with a greater freedom of motion<sup>16</sup> of the leaving group in the second coordination sphere. The idea of a (large) volume increase on going to the activated state for a D-type reaction is of course not new.<sup>20,21,22</sup> In aqueous solution too, base-catalyzed hydrolysis of the complexes in question is characterized by a large value of the entropy of activation for the overall reaction.<sup>2</sup> This fact seems to suggest the possibility of extending the scheme thought to be operative in liquid ammonia to aqueous solutions.

This study examines whether the proposed model is relevant for the interpretation of the CB mechanism in aqueous solution, for which the available experimental information is more extensive than for liquid ammonia. The object is to test whether a significant part of the high reactivity of the N conjugate base in aqueous solution may be derived from a relatively large entropy gain on passing to the activated state and whether this gain can be mechanistically associated with a substantial volume increase of the second coordination sphere.

**Description of the Outer-Sphere Model for Aqueous Solutions.** The CB mechanism involves the following two steps in the route to the five-coordinated intermediate (charges will be omitted):



or



The extreme lability of the conjugate base  $\text{NH}_2(\text{L}_4\text{M})\text{X}$  arises from the presence of the coordinated  $\text{NH}_2^-$  residue,<sup>23</sup> effecting a labilization of the ground state due to the strong basicity of the group<sup>24</sup> and/or a stabilization of the transition state.<sup>6</sup> An overwhelming amount of evidence<sup>9</sup> is now available to the effect that the mechanism of the rate-determining step is essentially D (dissociative). It has been early recognized that the fact that the intermediate  $\text{NH}_2(\text{L}_4\text{M})$  has properties independent of the leaving group X means that the five-coordinated intermediate is stable enough to survive a few molecular collisions, as Basolo and Pearson<sup>25</sup> have argued. As a consequence X will have left the second coordination sphere when the free energy saddle point due to the intermediate is reached. This argument does not apply to the transition state of reaction 3, for which the general argument of Swaddle<sup>19</sup>

holds that the second coordination sphere must be taken as permanent for the single molecular vibration which takes the complex to the transition state that in this case consequently still contains X. The essence of the present presupposition is that the entropy increase associated with the liberation of the leaving group into the second sphere (and the resulting greater freedom of motion) is responsible for a large part of the reactivity of the conjugate base. This presentation of the outer-sphere entropy effect does not diminish the essential role of the conjugated  $\text{NH}_2^-$  residue. However, attention must be drawn to the fact that for the compounds  $[\text{Co}(\text{NH}_3)_5\text{Cl}](\text{ClO}_4)_2$ ,  $[\text{Co}(\text{NH}_3)_5\text{Br}](\text{ClO}_4)_2$ , *cis*- and *trans*- $[\text{Co}(\text{en})_2\text{NH}_3\text{Cl}](\text{ClO}_4)_2$ , and *cis*- $[\text{Co}(\text{en})_2\text{Cl}_2]\text{ClO}_4$ , for which the activation enthalpy of reaction 3 is separately available for liquid ammonia as solvent, the value of this parameter is not substantially lower than the value for the corresponding spontaneous aquation. In addition the composite  $\Delta H^\ddagger$  values for reactions 2 and 3—obtained from the temperature dependence of the product  $k_{\text{CB}}/K_a$ —for the limited number of cases studied show a nearly constant difference between ammonia and water of which the numerical value is very close to the difference between ammoniation and hydration enthalpy of the proton,<sup>7,8,12,26</sup> suggesting that also for aqueous solutions no significant lowering of  $\Delta H^\ddagger$  for the rate-determining step (3) ought to be assumed.<sup>7</sup>

On the other hand the mechanism of the spontaneous aquation is supposed to involve solvent assistance. In the anation reaction the entering group must be present in a position close to the coordination site to be vacated by the leaving water molecule.<sup>27</sup>

The microscopic reversibility argument will then fix the leaving group in the transition state of the aquation, so that some probably electrostatic energy interaction between substrate and leaving group remains on activation. This is no longer possible in the proposed mechanism for the base hydrolysis where the leaving group is completely separated from the metal in the transition state and even a comparatively stable five-coordinated intermediate is subsequently formed, as generally agreed upon (see above).

As a consequence it follows that the labilizing effect of the  $\text{NH}_2^-$  group is needed to compensate for the loss of solvent assistance. Introduction of the leaving group into the second sphere will be associated with a large volume increase that can tentatively be related to the entropy change via the empirical formula (1) proposed by Twigg.<sup>16</sup> For the moment it is assumed that this will be the only contribution to the entropy of activation. Although unfortunately only a few experimental  $\Delta V^\ddagger$  values are found in the literature, these will nevertheless provide a test for the model presented.

**Comparison with Experimental Results.**  $\Delta V_0^\ddagger$  values for the overall reaction, (2a) + (3), have been published for  $\text{Co}(\text{NH}_3)_5\text{X}^{n+}$ , with X = Br  $8.5 \text{ cm}^3 \text{ mol}^{-1}$  ( $I = 0.0004 \text{ M}$ ,  $t = 30^\circ \text{C}$ ),<sup>28</sup> X =  $\text{SO}_4$   $19.5 \text{ cm}^3 \text{ mol}^{-1}$  ( $I = 0.5 \text{ M}$ ,  $t = 55^\circ \text{C}$ ),<sup>20</sup> X =  $\text{PO}_4$   $28.9 \text{ cm}^3 \text{ mol}^{-1}$  ( $I = 0.5 \text{ M}$ ,  $t = 55^\circ \text{C}$ ),<sup>20</sup> and X = Cl  $33.4 \text{ cm}^3 \text{ mol}^{-1}$  ( $I = 0.06 \text{ M}$ ,  $t = 35^\circ \text{C}$ ).<sup>21</sup>  $\Delta V^\circ$  for the preequilibrium reaction (2a) cannot be determined separately for aqueous solutions as no appreciable acid dissociation of normal cobalt(III) ammine complexes is observed. Application of the Born equation<sup>29</sup> or taking the acid dissociation of the aquo ligand of the  $\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+}$  ion as a model<sup>21,29</sup> gives for  $\Delta V^\circ$  of reaction 2a a value of  $20\text{--}22 \text{ cm}^3 \text{ mol}^{-1}$ . This value yields rather low values for  $\Delta V^\ddagger$  of reaction 3, thus destroying the picture presented here:  $\Delta V^\ddagger = -12 \text{ cm}^3 \text{ mol}^{-1}$  (Br),  $-1 \text{ cm}^3 \text{ mol}^{-1}$  ( $\text{SO}_4$ ),  $9 \text{ cm}^3 \text{ mol}^{-1}$  ( $\text{PO}_4$ ),  $13 \text{ cm}^3 \text{ mol}^{-1}$  (Cl).

In view of the uncertainty of the  $\Delta V^\circ$  estimate another approach will be presented here consisting of the construction of volume profile diagrams<sup>30</sup> for the CB reactions. In the following  $\bar{V}^\circ$  values for simple anions and cations will be taken

from the tables of conventional molar volumes<sup>18</sup> at  $25^\circ \text{C}$ , with  $\bar{V}^\circ(\text{H}^+) = -4.5 \text{ cm}^3 \text{ mol}^{-1}$ .<sup>30</sup> For cobalt(III) ammine complexes  $\bar{V}$  values come from ref 30, unless otherwise stated.

**Calculated Volume Profile Diagrams.** The apparent overall  $\Delta V_0^\ddagger$  value for the combined reactions (2a) and (3) represents the transition from the ground state,  $\text{Co}(\text{NH}_3)_5\text{X} + \text{OH}^-$ , to the activated complex,  $\text{Co}(\text{NH}_3)_4\text{NH}_2\cdots\text{X} + (\text{H}_2\text{O})$ .  $\Delta V_0^\ddagger$  will then be given by (omitting charges)

$$\Delta V_0^\ddagger = \bar{V}^\ddagger + \bar{V}(\text{H}_2\text{O}) - \bar{V}(\text{OH}^-) - \bar{V}(\text{Co}(\text{NH}_3)_5\text{X}) \quad (4)$$

in which  $\bar{V}$  represents a partial molar volume.

$\bar{V}^\ddagger$  referring to the transition state can be split into structural and solvent-dependent components<sup>31</sup>

$$\bar{V}^\ddagger = \bar{V}_1^\ddagger + \bar{V}_2^\ddagger + \bar{V}_X^\ddagger \quad (5)$$

in which  $\bar{V}_1^\ddagger$  represents the intrinsic volume of the first coordination sphere of the five-coordinated complex,  $\bar{V}_2^\ddagger$  the second-sphere contribution from electrostrictive effects from the cation, and  $\bar{V}_X^\ddagger$  the change introduced by bringing X into the second sphere. Transfer of X from the first to the second sphere is not expected to influence  $\bar{V}_2^\ddagger$ , as follows from the absence of a charge separation effect in the electrostrictive volume on bringing  $\text{SO}_4^{2-}$  from the first to the second sphere.<sup>17</sup>

$\bar{V}_1^\ddagger$  and  $\bar{V}_2^\ddagger$  can readily be estimated. A change in the inner sphere on reducing the coordination number from 6 to 5 is expected to be very small or zero,<sup>20,21,29</sup> which makes  $\text{Co}(\text{NH}_3)_5\text{NH}_2^{2+}$  a good "model" for  $\text{Co}(\text{NH}_3)_4\text{NH}_2^{2+}$ , referring to both  $\bar{V}_1^\ddagger$  and  $\bar{V}_2^\ddagger$ . Pursuing this argument,  $\text{Co}(\text{NH}_3)_6^{3+}$  will also be a good model as to molar volume for  $\text{Co}(\text{NH}_3)_5\text{NH}_2^{2+}$ , as the substitution of small, strongly solvated strong bases as  $\text{OH}^-$  or  $\text{F}^-$  for  $\text{NH}_3$  into the hexaammine leaves the partial molar volume of the complex nearly constant. Compare:  $\bar{V}^\circ(\text{Co}(\text{NH}_3)_6) = 55$ ;  $\bar{V}^\circ(\text{Co}(\text{NH}_3)_5\text{OH}) = 56$  (from the data of ref 17),  $\bar{V}^\circ(\text{Co}(\text{NH}_3)_5\text{F}) = 57.9 \text{ cm}^3 \text{ mol}^{-1}$ . Whether the volume constancy is due to a strong local solvation of the coordinated  $\text{F}^-$  and  $\text{OH}^-$  or must be explained from dielectric saturation, as put forward in this respect,<sup>17,32</sup> is difficult to determine. In any case, the conclusion is safe that  $\text{NH}_2^-$  fits in the series  $\text{F}^-$ ,  $\text{OH}^-$ , and  $\text{NH}_2^-$ , so the molar volume of the  $\text{Co}(\text{NH}_3)_5\text{NH}_2^{2+}$  is close to that of the hexaammine, which, combined with the earlier argument, gives  $\bar{V}_1^\ddagger + \bar{V}_2^\ddagger \approx \bar{V}^\circ(\text{Co}(\text{NH}_3)_6) = 55 \text{ cm}^3 \text{ mol}^{-1}$  as a good estimate. Equation 4 then becomes

$$\Delta V_0^\ddagger = \bar{V}(\text{Co}(\text{NH}_3)_6) + \bar{V}_X^\ddagger - \bar{V}(\text{Co}(\text{NH}_3)_5\text{X}) + \bar{V}(\text{H}_2\text{O}) - \bar{V}(\text{OH}^-) \quad (6)$$

Substituting the experimental values for  $\Delta V_0^\ddagger$  (X = Br, Cl,  $\text{SO}_4$ ) for which  $\bar{V}(\text{Co}(\text{NH}_3)_5\text{X})$  has been determined<sup>30</sup> into eq 6 and using  $\bar{V}^\circ(\text{X})$  values for  $\bar{V}(\text{X})$  as stated above give  $\bar{V}_X^\ddagger = 31.0$  (106%) for X = Br;  $46.7$  (210%) for X = Cl; and  $43.5 \text{ cm}^3 \text{ mol}^{-1}$  (190%) for X =  $\text{SO}_4$ . The numbers in parentheses express  $\bar{V}_X^\ddagger$  as percentages of  $\bar{V}(\text{X})$ . The larger volume of the anion in the second sphere compared to the bulk is not surprising in view of the volume increase on bringing the sulfate ion from the bulk to the second sphere, discussed above. Apparently X = Br presents an exception. The other two cases may be interpreted as meaning that  $\bar{V}_X^\ddagger = \text{constant}$  ( $45 \text{ cm}^3 \text{ mol}^{-1}$  in average) or that  $\bar{V}_X^\ddagger = 2\bar{V}(\text{X})$  (as the average of 190% and 210% of  $\bar{V}(\text{X})$ ). Two possible equations for  $\Delta V_0^\ddagger$  follow:

$$\Delta V_0^\ddagger = 72.5 + 2\bar{V}(\text{X}) - \bar{V}(\text{Co}(\text{NH}_3)_5\text{X}) \quad (\bar{V}_X^\ddagger = 2\bar{V}(\text{X})) \quad (7)$$

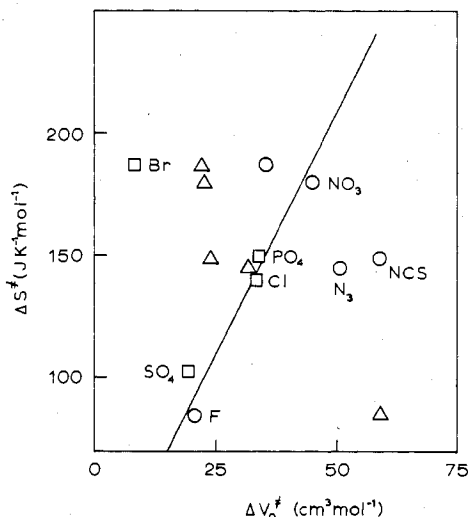
$$\Delta V_0^\ddagger = 117.5 - \bar{V}(\text{Co}(\text{NH}_3)_5\text{X}) \quad (\bar{V}_X^\ddagger = \text{constant}) \quad (8)$$

Starting from eq 7 and 8  $\Delta V_0^\ddagger$  values were calculated for the cases for which  $\bar{V}(\text{Co}(\text{NH}_3)_5\text{X})$  values are known.<sup>30</sup> The results are in Table I.

**Table I.**<sup>a</sup> Partial Molar Volumes and Overall Entropy and Volume of Activation for the Base-Hydrolysis Reaction of  $\text{Co}(\text{NH}_3)_5\text{X}^{n+}$  Complexes

X	$\bar{V}(\text{Co}(\text{NH}_3)_5\text{X})$	$\bar{V}(\text{X})$	$\Delta V_0^\ddagger(\text{calcd})^b$	$\Delta V_0^\ddagger(\text{calcd})^c$	$\Delta V_0^\ddagger(\text{exptl})^d$	$\Delta S^\ddagger$
F	57.9	3.3	21.2	59.6		85
Cl	85.8	22.3	31.3	31.7	33.4 (21)	140
Br	95.0	29.2	35.9	22.5	8.5 (28)	187
$\text{N}_3^-$	85.3	31.8	50.8	32.2		145
$-\text{NCS}$	93.8	40.2	59.1	23.7		149
$\text{SO}_4^{2-}$	96.5	23.0	22.0	21.0	19.5 (20)	103
$\text{PO}_4^{3-}$					28.9 (20)	150
$\text{NO}_3^-$	94.5	33.5	45.0	23.0		180

<sup>a</sup> Volume in units  $\text{cm}^3 \text{mol}^{-1}$ ; entropy in units  $\text{J K}^{-1} \text{mol}^{-1}$ . <sup>b</sup> Calculated from eq 7. <sup>c</sup> Calculated from eq 8. <sup>d</sup> In parentheses the reference from which the volume of activation has been copied.



**Figure 1.** Relation between entropy of activation and experimental ( $\square$ ) and calculated ( $\circ$  from eq 7 and  $\Delta$  from eq 8) volumes of activation for base hydrolysis of  $\text{Co}(\text{NH}_3)_5\text{X}^{n+}$ . The nature of the group X is indicated in the graph.

To test the model presented the overall  $\Delta S^\ddagger$ , obtained from Table 8 of ref 5 (taking the values at zero ionic strength, except for  $\text{SO}_4^{2-}$  and  $\text{PO}_4^{3-}$ ;  $I = 1.0 \text{ M}$ ), was plotted as a function of  $\Delta V_0^\ddagger(\text{calcd})$ .  $\Delta S^\ddagger$  as a function of  $\Delta V_0^\ddagger$ , calculated from eq 8, only shows scattering, whereas the plot of  $\Delta S^\ddagger$  against  $\Delta V_0^\ddagger$ , calculated from eq 7, gives a good linear relation for  $\text{X} = \text{F}, \text{Cl}, \text{SO}_4, \text{PO}_4$ , or  $\text{NO}_3$  (Figure 1). Even the value calculated for  $\text{X} = \text{Br}$  lies close to the regression line. A least-squares analysis of  $\Delta V_0^\ddagger(\text{exptl})$  for  $\text{X} = \text{Cl}, \text{SO}_4$ , or  $\text{PO}_4$  and  $\Delta V_0^\ddagger(\text{calcd})$  for  $\text{X} = \text{F}$  or  $\text{NO}_3$  on the basis of the relation

$$\Delta V_0^\ddagger (\text{cm}^3 \text{mol}^{-1}) = A + B\Delta S^\ddagger (\text{J K}^{-1} \text{mol}^{-1}) \quad (9)$$

gives  $A = -3.5 \pm 4.5$  and  $B = 0.25 \pm 0.06$ .

The value found for  $B$  is in excellent agreement with eq 1, although in the present CB case an overall reaction is considered. This result seems to give good support to the assumptions involved in deriving eq 7. In particular the small volume increase associated with reaction 2a inherent in the present model is a necessary condition for eq 9 to hold. A further check on the reliability of the combination of eq 1 and 7 was performed by fitting the  $\Delta S^\ddagger(\text{X})$  values involved in eq 9 ( $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{SO}_4, \text{NO}_3$ ) to the parametrized equation

$$\Delta S^\ddagger(\text{X}) = a_0 + a_1\bar{V}(\text{X}) + a_2\bar{V}(\text{Co}(\text{NH}_3)_5\text{X}) \quad (10)$$

A computerized least-squares fit gave  $a_1 = 7.3 \pm 2.5$  (8.0) and  $a_2 = -3.0 \pm 1.8$  (-4). In parentheses are the values expected from the combination of the eq 1 and 7. The agreement is surprisingly good. Equations 7 and 10 have been applied here to a combination of mono-, di-, and trivalent anions X. For a simple neutral group like  $\text{NH}_3$  these equations appear not

to apply. Application of eq 6 to  $\text{NH}_3$  loss of  $\text{Co}(\text{NH}_3)_6^{3+}$ <sup>33</sup> and  $\text{Co}(\text{NH}_3)_5\text{OH}^{2+}$ <sup>34</sup> gives  $\bar{V}_X^\ddagger = 8.8$  or  $15.8 \text{ cm}^3 \text{mol}^{-1}$ , respectively, compared to  $\bar{V}^\circ(\text{NH}_3) = 25 \text{ cm}^3 \text{mol}^{-1}$ .<sup>35</sup>

### Conclusion

In a tentative formulation it may be concluded that base hydrolysis as well as base-catalyzed ammoniation derive at least part of the relatively large rate of the reaction from the associative elimination of the anion into the second coordination sphere. Caution must be exercised as general rules like the one presented in eq 1 will know many exceptions. Already the systems that show a deviation from the line expressed by eq 9 in Figure 1 prove that also other factors are at stake. Especially cases where special solvation effects operate or steric hindrance is involved<sup>22</sup> are expected to be at variance with the simple model presented.

Other factors too may influence the entropy of activation. In this respect it is difficult to say whether rearrangement in the inner sphere on forming the transition state will give an extra contribution to  $\Delta S^\ddagger$ . In any case, although this is often naively assumed, rearrangement does not per se augment the number of accessible independent eigen states necessary for an entropy increase.<sup>14</sup> It seems to be of interest to obtain more experimental volumes of activation for the CB reactions to test the extent of the second-sphere effect. In doing this care must be taken to obtain true  $\Delta V_0^\ddagger$  values, extrapolated to zero ionic strength, as this factor, together with the formation of ion pairs, has been shown to be very important in CB reactions.<sup>36</sup> Unfortunately no such  $\Delta V_0^\ddagger$  values, extrapolated to zero ionic strength, were available for the calculations presented here. This factor too could be a reason for the widely deviating experimental value for the bromo complex.

Present models of the second-sphere interaction are not detailed enough to fit in the proposed model, because there is not yet an adequate theoretical treatment for water.<sup>37</sup> Yet the general remark can be made that the apparently large increase in entropy (and volume) of the anion on passing from the first to the second sphere in the transition state seems to fit into the Frank-Wen picture of solvation.<sup>38</sup> This structural model sees the second sphere as an intermediate region of orientational disorder characterized by high energy and entropy compared to those of the bulk and the first-sphere solvent. Kinetic consequences of this model not directly related to the present case have been discussed.<sup>39</sup>

If the proposition of the volume effect in the transition state of the dissociative reaction (3) is accepted, one may speculate whether this effect is connected with the small radius of the  $\text{Co}^{3+}$  ion that has already been put forward as a cause of the prevailing dissociative character of substitution reactions at cobalt(III) centers.<sup>4</sup> The mechanism of action of this effect may be that the strong electrostatic field generated by the small and highly charged ion induces dielectric saturation<sup>17,32</sup> which will smooth out the change in electrostriction on altering the formal charge on the complex. Thus both the volume increase connected with the reduction of the effective charge

in equilibrium 2 and the volume decrease inherent in the charge separation effect of reaction 3 are diminished.

The first prediction is borne out by recent results of ion association<sup>40</sup> and acid dissociation<sup>41</sup> studies of hexammine-metal nitrates of the first-row transition elements in liquid ammonia. In this series  $\text{Co}(\text{NH}_3)_6^{3+}$  is exceptional in showing abnormally low  $\Delta S^\circ$  values for both reactions, if compared to the lower oxidation-state complex  $\text{Co}(\text{NH}_3)_6^{2+}$ . In addition in the strongly electrostricted second coordination sphere of the complexes, the necessary creation of freedom of motion and free volume<sup>42</sup> for the anion is expected to cause the large recorded volume increase. The smaller volume increase for a neutral group as  $\text{NH}_3$  can then be explained from a better fit of this group in the solvent structure of the second sphere.<sup>38</sup>

**Registry No.**  $\text{Co}(\text{NH}_3)_5\text{F}^{2+}$ , 15392-06-0;  $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ , 14970-14-0;  $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ , 14970-15-1;  $\text{Co}(\text{NH}_3)_5\text{N}_3^{2+}$ , 14403-83-9;  $\text{Co}(\text{NH}_3)_5\text{NCS}^{2+}$ , 14970-18-4;  $\text{Co}(\text{NH}_3)_5\text{SO}_4^+$ , 18661-07-9;  $\text{Co}(\text{NH}_3)_5\text{PO}_4$ , 15612-03-0;  $\text{Co}(\text{NH}_3)_5\text{NO}_3^{2+}$ , 15077-47-1.

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## Coordinated Nitrosyl Hydride: Structural and Spectroscopic Study of $\text{OsCl}_2(\text{CO})(\text{HNO})(\text{P}(\text{C}_6\text{H}_5)_3)_2$

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That  $\text{OsCl}(\text{CO})(\text{NO})(\text{PPh}_3)_2$  (Ph = phenyl =  $\text{C}_6\text{H}_5$ ) reacts with HCl to form  $\text{OsCl}_2(\text{CO})(\text{HNO})(\text{PPh}_3)_2$  is confirmed by a structural and spectroscopic study of the product. The octahedrally coordinated Os(II) ion possesses trans phosphine ligands, cis chloro ligands, a carbonyl group, and a HNO molecule coordinated through the N atom. Important metrical details for this coordination are Os-N = 1.915 (6) Å, N-O = 1.193 (7) Å, N-H = 0.94 (11) Å, Os-N-O = 136.9 (6)°, Os-N-H = 123 (7)°, and O-N-H = 99 (7)°. These results have been derived from a three-dimensional X-ray study of  $\text{OsCl}_2(\text{CO})(\text{HNO})(\text{PPh}_3)_2 \cdot 1/2 \text{CH}_2\text{Cl}_2$ , based on 185 variables and 5563 significant observations. The material crystallizes with four molecules in space group  $C_{2h}^5-P2_1/n$  of the monoclinic system in a cell of dimensions  $a = 10.849$  (2) Å,  $b = 33.272$  (7) Å,  $c = 10.036$  (3) Å, and  $\beta = 104.56$  (1)°. The N-O stretching frequency has been identified at 1410  $\text{cm}^{-1}$  from the spectra of the unlabeled and  $^{15}\text{N}$ -labeled species. Coordination of HNO in solution has been established from the  $^1\text{H}$  NMR spectra of  $\text{OsCl}_2(\text{CO})(\text{H}^{14}\text{NO})(\text{PPh}_3)_2$  and the corresponding  $^{15}\text{N}$  derivative, which show the chemical shift of the unique proton at  $\delta = 21.2$ . Consistent with the solid-state study, the  $^1\text{H}$ - $^{15}\text{N}$  coupling constant of 75 Hz implies that the ligand is HNO rather than HON. Reaction of a noncoordinating acid,  $\text{HBF}_4$ , with  $\text{OsCl}(\text{CO})(\text{NO})(\text{PPh}_3)_2$  yields a variety of products, including  $[\text{OsCl}_2(\text{CO})(\text{NO})(\text{PPh}_3)_2][\text{BF}_4]$  whose identity was established by crystallographic methods.

### Introduction

Both nucleophilic and electrophilic attack of metal-coordinated nitric oxide have been reported. Typical of the nucleophilic attack, which occurs on linearly coordinated nitrosyls, is the reaction of  $\text{RuCl}(\text{NO})(\text{bpy})_2^{2+}$  (bpy = 2,2'-bipyridine) with base to form  $\text{RuCl}(\text{NO}_2)(\text{bpy})_2$ .<sup>1</sup> Typical of electrophilic attack, which occurs apparently on bent nitrosyls, is reaction with acid to convert the coordinated nitric oxide to coordinated nitrosyl hydride, HNO. Grundy, Reed, and Roper<sup>2</sup> provided the first example of such a reaction, namely,  $\text{OsCl}(\text{CO})(\text{NO})(\text{PPh}_3)_2$  with HCl to form  $\text{OsCl}_2(\text{CO})(\text{HNO})(\text{PPh}_3)_2$ , but other examples<sup>3,4</sup> have now been proposed. In none of these instances is there direct, unequivocal evidence

for the formation of coordinated HNO. The possibility of the alternative connectivity, NOH, cannot be discounted, as suggested for  $[\text{Fe}(\text{CN})_5(\text{NOH})]^{2-}$ <sup>5,6</sup> and  $\text{RhCl}_3(\text{NOH})(\text{PPh}_3)_2$ ,<sup>7</sup> although other formulations for these species have been suggested.<sup>8,9</sup>

In this paper we present structural and spectroscopic evidence that definitively establishes the presence in the solid state and in solution of the N-coordinated HNO molecule in the prototype example,  $\text{OsCl}_2(\text{CO})(\text{HNO})(\text{PPh}_3)_2$ .

### Experimental Procedure

Infrared spectra (4000–600  $\text{cm}^{-1}$ ) were measured in Nujol mulls and dichloromethane solutions using Perkin-Elmer 727-B and IR 283