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Attribution of Water-Exchange Mechanisms of Transition-Metal Hexaaqua Ions Using Quantum Chemical Methods^{a)}

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Abstract. The mechanism for the water-exchange reaction with the transition-metal aqua ions from Sc^{III} through Zn^{II} has been investigated. The exchange mechanisms are analyzed on a model that involves the metal ion with six or seven water molecules. The structures of the reactants/products, transition states, and penta- or heptacoordinated intermediates have been computed with *Hartree-Fock* or CAS-SCF methods. Each type of mechanism, associative, concerted, or dissociative, proceeds *via* a characteristic transition state. The calculated activation energies agree with the experimental ΔG^\ddagger_{298} or ΔH^\ddagger_{298} values, and the computed structural changes indicate whether an expansion or compression takes place during the transformation of the reactant into the transition state. These changes are in perfect agreement with the changes deduced from the experimental volumes of activation. The dissociative mechanism is always feasible, but it is the only possible pathway for high-spin d⁸, d⁹, and d¹⁰ systems. In contrast, the associative mechanism requires that the transition-metal ion does not have more than seven 3d electrons. Thus, Sc^{III}, Ti^{III}, and V^{III} react *via* the A, Ni^{II}, Cu^{II}, and Zn^{II} *via* the D (or I_d) mechanism, whereas all pathways are feasible for the elements in the middle of the periodic table.

Introduction

In 1965, Langford and Gray [1] proposed a classification for of the substitution reactions into associative (A), concerted (I_a, I_d), and dissociative (D) mechanisms. The A and D pathways proceed in two steps and involve a hepta- or a pentacoordinated intermediate, respectively. In contrast, the concerted mechanisms are one-step processes. For these mechanisms, I_a or I_d, respectively, either bond formation or bond breaking is more pronounced in the transition state. Since the intermediates are very short-lived and therefore in most cases inaccessible experimentally, it is in general impossible to distinguish an A from an I_a or a D from an I_d mechanism. For this reason, the usefulness of this classification has been questioned [2].

A recent review [3] summarizes the experimental data on the water- and solvent-exchange reactions involving metal ions. The volumes of activation cover a wide range, and this can be taken as an indication for the existence of quite disparate substitution mechanisms. For the thoroughly investigated first-row transition metals [3], the most negative value has been found for Ti^{III} [4], and the most positive one for Ni^{II} [5].

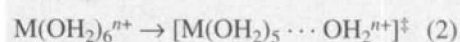
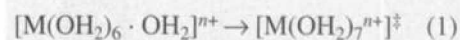
All the quantum chemical calculations on reaction mechanisms involving mononuclear transition-metal complexes have been reviewed recently by Bray *et al.* [6]. Most of these studies deal with reactions of uncharged organometallic compounds, but a few investigations on the water exchange of (charged) transition-metal aqua complexes are also available [7–9].

In the following section, the mechanism of water exchange of the di- and trivalent aqua ions of the first-row transition metals will be discussed in more detail.

Computational Results

The structures and energies of the transition states and intermediates arising in the water exchange of all the di- and trivalent first-row transition-metal aqua ions except Co(OH₂)₆³⁺ have been computed using *ab initio* methods, since the latter allow the treatment of any electronic state. A minimum of seven water molecules is required to describe the exchange reaction proceeding *via* the A, I_a, or I_d mechanisms (*Reaction 1*), whereas six molecules are involved in the D mechanism (*Reaction 2*) [9]. The structures of reactants, transition

states, and intermediates as well as the structural and energetic changes for *Reactions 1* and *2* have been computed at the *Hartree-Fock* or CAS-SCF level.



Reaction 1 is applicable to all mechanisms, whereas *Reaction 2* can only be used for the D mechanism. [9] The substitution mechanisms have been assigned based on the structures of their respective transition states and, for the A and D mechanisms, also those of their intermediates. The structural changes computed for *Reactions 1* and/or *2* and the imaginary vibrational mode serve as an additional criterion [9][10]. In the following, each exchange pathway will be illustrated by an example.

For the hexaaqua ion of Co^{II}, the dissociative pathway has been calculated using *Reaction 2*. The structure of the corresponding transition state and pentacoordinated intermediate are shown in *Fig. 1*. Although the associative pathway is energetically less favorable, and hence does not occur, it can also be computed. The pertinent transition state and heptacoordinated intermediate are shown in *Fig. 2*.

The singlet and quintet electronic states of Co(OH₂)₆³⁺ lie quite close [11]. For this reason, electronic singlet, triplet, and quintet states of transition states and intermediates arising from this water-exchange reaction have to be investigated. This work is currently in progress [12], and the most favorable pathway is not yet known. As an example, the structure of the transition state with a singlet electronic state corresponding to the I_a mechanism is depicted in *Fig. 3*. The entering and leaving ligands are indistinguishable and have each a Co–O bond length of 2.74 Å. In contrast to the aqua ions of V^{II} and Cr^{III}, which react also *via* the I_a mechanism [9][10], the exchanging water molecules are not in *cis*-position to each other.

The M–O bond lengths together with the imaginary vibrational mode in the transition state are characteristic for a given

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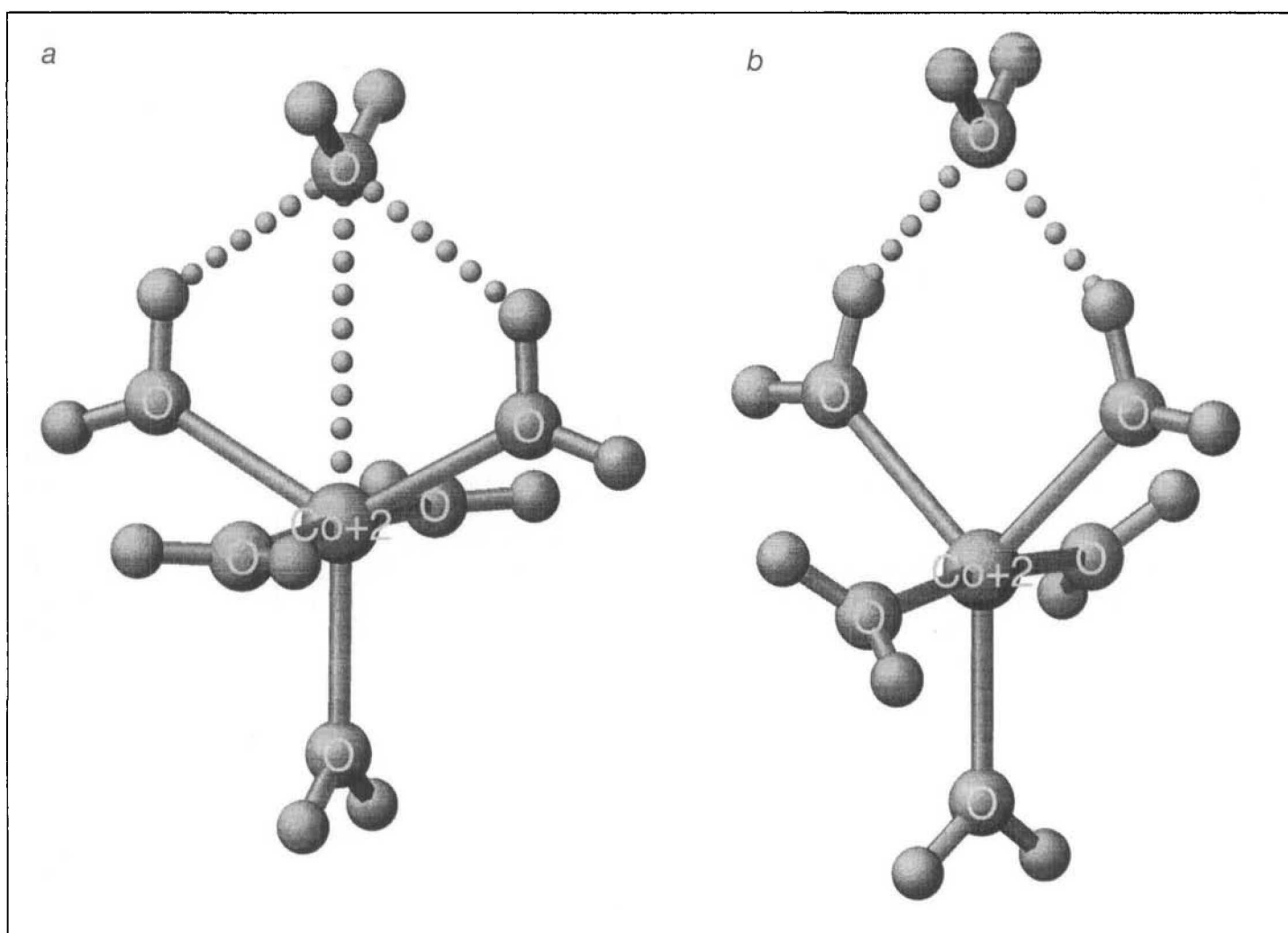


Fig. 1. Dissociative mechanism (D): perspective view of a) the transition state $\{[\text{Co}(\text{OH}_2)_5 \cdots \text{OH}_2]^{2+}\}^\ddagger$ (C_{2v} symmetry) and b) the pentacoordinated intermediate $[\text{Co}(\text{OH}_2)_5 \cdot \text{OH}_2]^{2+}$ (C_2 symmetry)

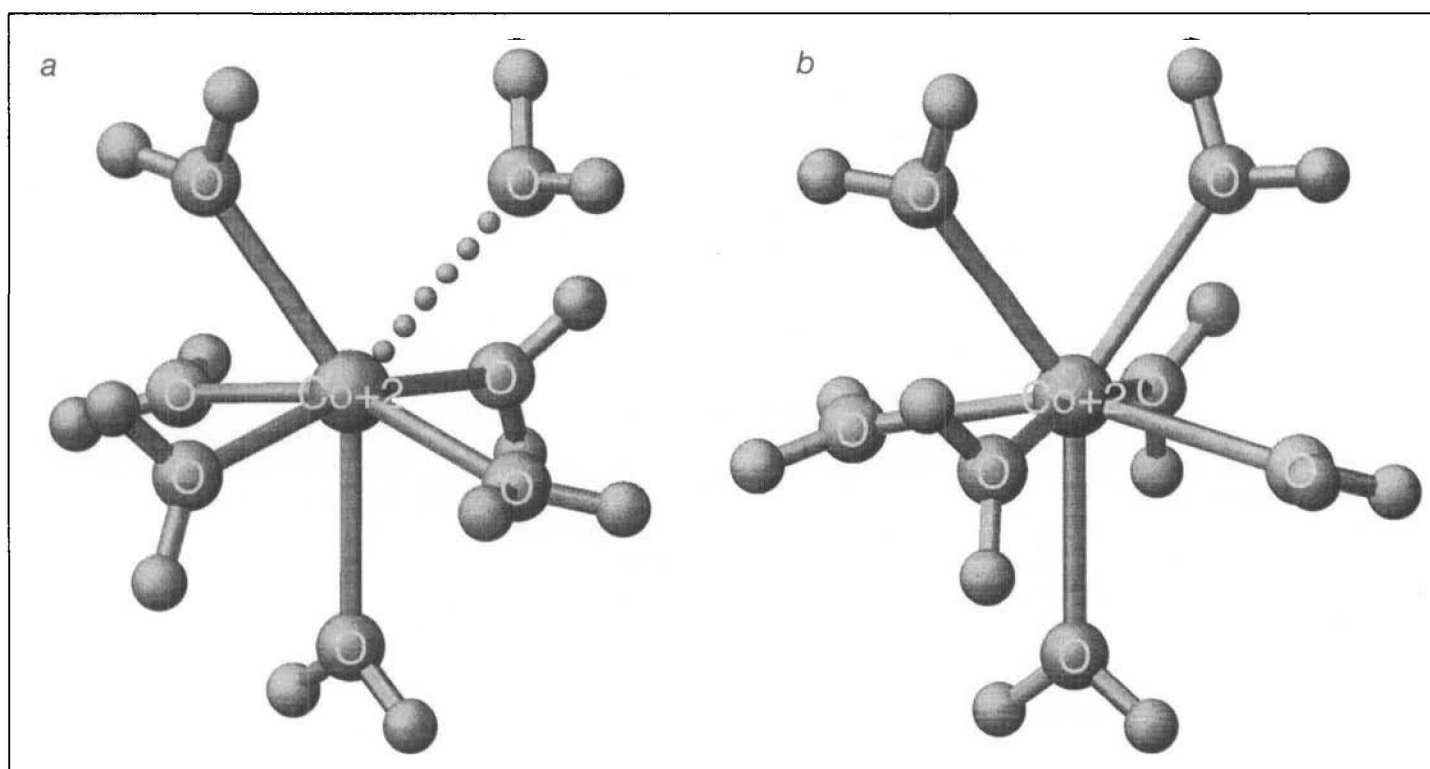


Fig. 2. Associative mechanism (A): perspective view of a) the transition state $\{[\text{Co}(\text{OH}_2)_6 \cdots \text{OH}_2]^{2+}\}^\ddagger$ (C_1 symmetry) and b) the heptacoordinated intermediate $\text{Co}(\text{OH}_2)_7^{2+}$ (C_2 symmetry)

substitution mechanism: for D, there are five normal M–O bonds and one elongated M···O bond (Fig. 1, a), for I_a, five normal M–O bonds and two elongated M···O bonds (Fig. 3), and for A, six normal M–O bonds and one elongated M···O bond (Fig. 2, a). Furthermore, the imaginary mode describes essentially the motion of the leaving or entering ligand for the D or A mechanisms, respectively, whereas for the I_a pathway, this mode represents mainly the concerted motions of the entering and leaving ligands.

The calculated activation energies [9] [10] agree with the experimental data [3], although the computations are based on a rather simple model [9] that neglects the second coordination sphere, bulk water, and the anions. The changes of the M–O bond lengths along Reactions 1 or 2 indicate whether a compression or expansion of the reactant takes place during the activation process. The sign of the changes of the sum of all the computed M–O bond lengths is the same as that of the corresponding volumes of activation. Because of the agreement between experiment and computations, the calculated structures of the transition states and intermediates are likely to be qualitatively correct in spite of the simplicity and limitations of the model.

The results of the calculations for the di- and trivalent transition-metal ions from Sc^{III} through Zn^{II} are summarized in Fig. 4. The elements on the left side of the periodic table react preferentially via the A and those on the right via the D mechanism, whereas for the metals in the middle all mechanisms are possible. In the absence of steric effects (strain or constraints in the ligand sphere), the occupation of the 3d orbitals determines the reaction mechanism [10]. It should be noted that the D mechanism is feasible for all metal ions in contrast to the A or I_a mechanisms which can, at least within the present model, only operate for high-spin 3d⁰–3d⁷ systems.

This simple model provides evidence for the existence of the A, I_a, and D mechanisms and supports the classification of substitution mechanisms proposed in 1965 by Langford and Gray [1]. All the attempts to compute transition states for the I_a mechanism failed [10]. It remains to be shown using an improved model involving for instance a second coordination sphere, whether it exists, and if so, which of the reactions to which the D mechanism has been attributed follows in fact the I_a one.

The calculations predict the exchange mechanism for the aqua ions of Sc^{III}, Mn^{III}, and Zn^{II} (Fig. 4), for which experimen-

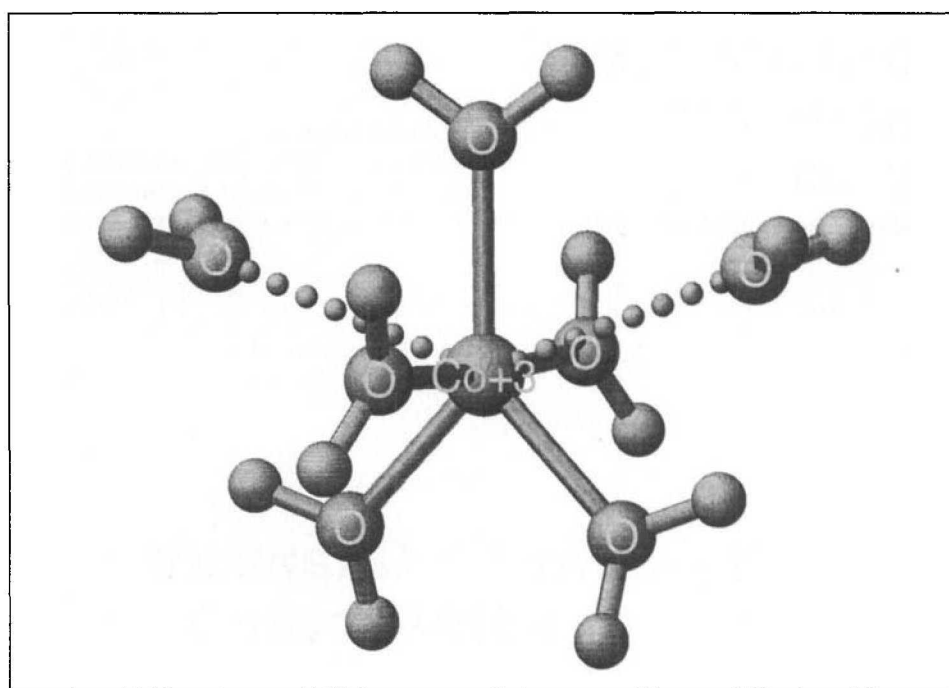


Fig. 3. Concerted mechanism (I_a): perspective view of the transition state $\{[Co(OH)_5 \cdots (OH)_2]^{3+}\}^\ddagger$ (C₂ symmetry)

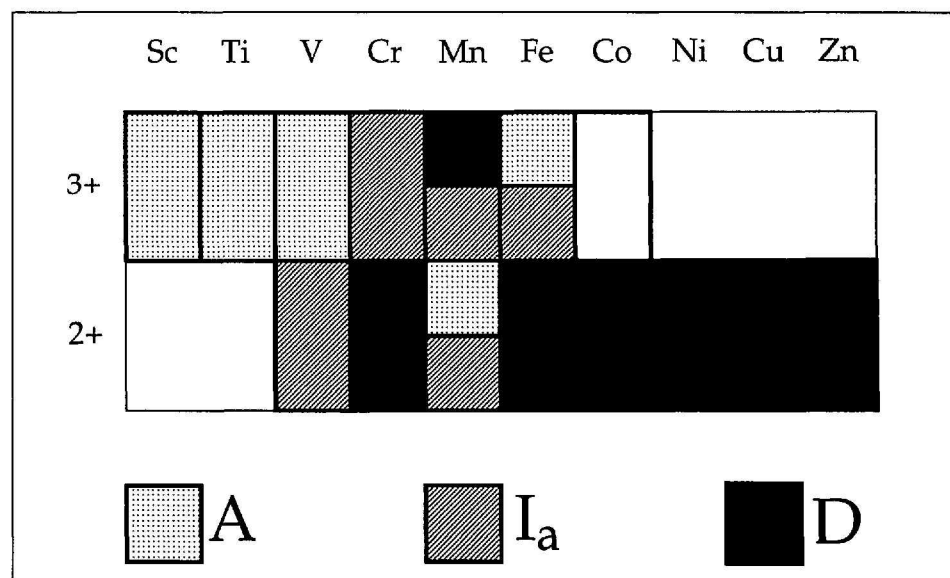


Fig. 4. Assignment of the water-exchange mechanism based on computations

tal activation volumes are not (yet) available.

To summarize, the computations offer a deeper insight into the course of the substitution reaction. In principle, it is possible to treat more complex reactions, for instance, those that lead to various stereoisomers. The detailed knowledge of their course should allow the development of systems giving rise to a high stereoselectivity.

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- [1] C.H. Langford, H.B. Gray, 'Ligand Substitution Dynamics', Benjamin, New York, 1965.
 [2] T.W. Swaddle, *Comments Inorg. Chem.* **1991**, *12*, 237.

- [3] S.F. Lincoln, A.E. Merbach, *Adv. Inorg. Chem.* **1995**, *42*, 1.
 [4] A.D. Hugi, L. Helm, A.E. Merbach, *Inorg. Chem.* **1987**, *26*, 1763.
 [5] Y. Ducommun, K.E. Newman, A.E. Merbach, *Inorg. Chem.* **1980**, *19*, 3696.
 [6] M.R. Bray, R.J. Deeth, V.J. Paget, *J. Prog. Reaction Kinetics* **1996**, *21*, 169.
 [7] R. Åkesson, L.G.M. Pettersson, M. Sandström, U. Wahlgren, *J. Am. Chem. Soc.* **1994**, *116*, 8705.
 [8] R.J. Deeth, L.I. Elding, *Inorg. Chem.* **1996**, *35*, 5019.
 [9] F.P. Rotzinger, *J. Am. Chem. Soc.* **1996**, *118*, 6760.
 [10] F.P. Rotzinger, submitted.
 [11] R. Åkesson, L.G.M. Pettersson, M. Sandström, U. Wahlgren, *J. Amer. Chem. Soc.* **1994**, *116*, 8691.
 [12] D.M. Benoit, F.P. Rotzinger, work in progress.