Additions and Corrections

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Mohamed S. A. Hamza, Carlos Dücker-Benfer, and Rudi van Eldik*: Ligand Substitution Behavior of a Simple Model for Coenzyme B_{12}

Page 3782. Equations 8 and 9 and the subsequent paragraph must be replaced by the following:

$$\textit{trans}\text{-}[Co(en)_2(Me)H_2O]^{2+} \rightleftharpoons [Co(en)_2(Me)]^{2+} + H_2O \qquad k_3, k_{-3}$$

$$[Co(en)_2(Me)]^{2+} + L \rightleftharpoons [Co(en)_2(Me)L]^{2+} \qquad k_4, k_{-4}$$

(8)

$$k_{obs} = \{k_3k_4[L] + k_{-3}k_{-4}\}/\{k_4[L] + k_{-3}\}$$

$$= k_3k_4[L]/k_{-3} + k_{-4} \qquad (9)$$

According to this rate law, $k_a = k_3k_4/k_{-3} = k_4K_3$, such that $\Delta V^{\ddagger}(k_a) = \Delta V^{\ddagger}(k_4) + \Delta V(K_3)$. In this case the volume changes associated with $\Delta V^{\ddagger}(k_4)$ and $\Delta V(K_3)$ are also expected to partially cancel each other, since $\Delta V(K_3)$ must be significantly positive, ca. 13 $cm^3\ mol^{-1}$ for the dissociation of a water molecule from an octahedral complex, and $\Delta V^{\ddagger}(k_4)$ must be negative for the binding of L.[28,41] Thus on the basis of the observed volumes of activation it is not possible to distinguish between an I_d and D mechanism in this particular case. We can only conclude that significant bond breakage must occur in the transition state, giving it a dissociative character. Weak bond formation with the entering nucleophile in the transition state cannot be ruled out.

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Martin Köckerling* and Enric Canadell*: Electronic Structures of $M_{21}S_8$ (M = Nb, Zr) and $(M,M')_{21}S_8$ (M, M′ = Hf, Ti; Nb, Ta) Phases and Reasons for Variations in the Metal Site Occupations.

Pages 4200−4205: All formulas $Nb_{6.9}Ta_{14.1}S_8$ throughout the article should read $Nb_{14.8}Ta_{6.2}S_8$. The results and discussion of the article correspond, however, to the correct formula.

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