Additions and Corrections

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D. Paul Rillema and John F. Endicott: Outer-Sphere Reductions of Cobalt(III) Complexes Containing Macrocyclic Ligands. A Further Examination of Free Energy Correlations and Anomalous Reorganizational Barriers.

Page 2361. In correcting $E_{1/2}$ values we inadvertently added rather than subtracted a calibration correction of 0.08 V, based on $Cd(NO_3)_2$. In Table IV the correct values are Co(teta)$(NH_3)_2{}^{3+}$ ($E_{1/2} = -0.06$ V; $E° = 0.18$ V), Co(*trans*[14] diene)$(NH_3)_2{}^{3+}$ (−0.09; 0.15), Co(DIM)$(NH_3)_2{}^{3+}$ (−0.14; 0.10) and Co(TIM)$(NH_3)_2{}^{3+}$ (−0.24; 0.00). These changes of potential alter the values of various rate constants computed in Table VI; correct values are indicated in the table below (no correction was required for $Co(NH_3)_6{}^{3+}$ or the *trans*-diaquo complexes). In addition, the last entry in the last column of Table IV should read "−1.74". These corrections do not significantly alter most of the points raised in the Discussion. Two exceptions are in section A the reactivity ranges are about the same for each reducing agent rather than opposite to the Guenther and Linck prediction of a contracted range for Cr^{2+}; and in section C the k_i values for aquo and ammine complexes are about the same (within a factor of 10) rather than opposite to a predicted greater reactivity of ammine complexes.

Comparison of Intrinsic Electron-Transfer Rate Constants ($\Delta G_{12}° = 0$) and Apparent Cobalt Self-Exchange Parameters for Reductions of $Co(N_4)(NH_3)_2{}^{3+}$ and $Co(N_4)(OH_2)^{3+}$ Complexes

Reducing agent	N_4	$k_{12}, M^{-1}\ sec^{-1}$ ($\mu = 1.0$)	$K_{12}{}^{1/2}$	$(k_{11}k_{22}f_{12})^{1/2}$, $M^{-1}\ sec^{-1}$	k_i,[a] $M^{-1}\ sec^{-1}$	log k_e[b]
$Ru(NH_3)_6{}^{2+}$	teta	8.4	4.7	1.8	1.8	−2.5
	trans[14] diene	2.9	2.6	1.1	1.1	−2.9
	DIM	6.0	1.0	6.1	6.1	−1.4
	TIM	3.7	0.14	26	31	0.0
V^{2+}	teta	2.3	5.2×10^3	4.4×10^{-4}	7.0×10^{-4}	−3.3
	trans[14] diene	2.3	2.9×10^3	4.8×10^{-4}	7.2×10^{-4}	−3.3
	DIM	3.1	1.1×10^3	2.8×10^{-3}	4.0×10^{-3}	−1.8
	TIM	5.7	1.6×10^2	3.6×10^{-2}	4.4×10^{-2}	0.3
Cr^{2+}	teta	3.4×10^{-2}	9.7×10^4	3.5×10^{-7}	5.0×10^{-8}	−8.6
	trans[14] diene	1.5×10^{-2}	5.4×10^4	2.8×10^{-7}	7.6×10^{-7}	−6.2
	TIM	0.18	2.9×10^9	6.2×10^{-5}	1.0×10^{-4}	−2

[a] $k_i = k_{12}/K_{12}{}^{1/2}f_{12}{}^{1/2}$. In estimating f_{12} we have assumed $10^{-9}\ M^{-1}\ sec^{-1}$ for self-exchange rates of teta and *trans*[14] diene complexes, $10^{-2}\ M^{-1}\ sec^{-1}$ for DIM complexes, and $10\ M^{-1}\ sec^{-1}$ for TIM complexes. [b] $k_e = k_i{}^2/k_{11}\ M^{-1}\ sec^{-1}$.

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