Table I. Comparison of Observed and Calculated Rate Parameters for the $Co(terpy)_2^{2+}$–$Co(bpy)_3^{3+}$ and $Fe(phen)_3^{2+}$–$Fe(phen)_3^{3+}$ Systems in Water

parameter	$Co(terpy)_2^{2+}$– $Co(bpy)_3^{3+}$	$Fe(phen)_3^{2+}$– $Fe(phen)_3^{3+}$
$\bar{r}$, Å	14	14
ΔG^*_i, kcal/mol	7.9	3.2
ΔG^*_o, kcal/mol	3.3	3.3
k_{calcd}, $M^{-1}\ s^{-1}$	32	6×10^7
k_{obsd}, $M^{-1}\ s^{-1}$	64[a]	3.3×10^8 [b]

[a] Reported at 0 °C in ref 2. [b] Reported at 25 °C in ref 7.

$$\lambda_o = (\Delta Z)^2 e^2 (1/2r_1 + 1/2r_2 - 1/\bar{r})(1/D_{op} - 1/D) \qquad (9)$$

so that each component can be estimated. All terms in eq 9 have their usual meaning. A direct estimate of λ_i requires knowledge of force constants and bond lengths of these cobalt reactants in water which are unavailable. However, using reactant radii of 7 Å[6] with an $\bar{r}$ value of 14 Å allows λ_o to be estimated from which λ_i can be obtained by using eq 8. The values for the inner-sphere ($\lambda_i/4$) and outer-sphere ($\lambda_o/4$) reorganization energies are 7.9 and 3.3 kcal/mol, respectively. A comparison of these results with the $Fe(phen)_3^{2+,3+}$ system is made in Table I where a k_{obsd} of 3.3×10^8 $M^{-1}\ s^{-1}$ has been reported for the redox rate constant.[7] The comparison shows that although the outer-sphere reorganization energies are similar, large differences exist in the inner-sphere reorganization energy where the cobalt system is larger by about 4.7 kcal/mol. A large inner-sphere reorganization energy has been proposed by Sutin[8] for these type systems of cobalt since the electron being transferred is removed from an e_g orbital of the reductant where the increased electron density on the metal ion cannot be removed via a M→L π-bonding path as in $Fe(phen)_3^{2+}$. Moreover, e_g electrons are more intimately involved in σ bonding between the central metal ion and the coordinated ligands so that larger changes in the metal–ligand bonding are expected compared to the transfer of an t_{2g} electron. The large difference in the inner-sphere reorganization energies may simply reflect this and could be responsible for the relatively slow redox rate observed in these cobalt systems. Unlike the $Co(NH_3)_6^{2+,3+}$ self-exchange where the slowness has been attributed to energy differences between the spin states of the reactants,[9] both cobalt complexes are low spin.[10] The possibility of some nonadiabaticity brought about by weak interactions between reactants cannot be ruled out as one factor which could contribute to the slowness of the redox rate. Under these conditions, the outer-sphere rate constant would be given by $k = pZ \exp(-\Delta G^*/RT)$ with p being the probability of electron transfer in the activated complex. However, similar arguments would be applicable to the self-exchange reactions of the reactants, and if all reactions are uniformly nonadiabatic, i.e., $p_{12}^2 = p_{11}p_{22}$, the Marcus rate equations would still predict well as observed.

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Registry No. $Co(terpy)_2^{2+}$, 18308-16-2; $Co(bpy)_3^{3+}$, 19052-39-2; $Fe(phen)_3^{2+}$, 14708-99-7; $Fe(phen)_3^{3+}$, 13479-49-7.

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Additions and Corrections

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Eric A. Maatta, Barry L. Haymore,* and R. A. D. Wentworth*: Syntheses of $Mo(NC_6H_5)X_2(S_2CN(C_2H_5)_2)_2$ (X = Cl, Br) and the Structure of $Mo(NC_6H_5)Cl_2(S_2CN(C_2H_5)_2)_2 \cdot CHCl_3$.

Page 1057. In Table II, the *x* coordinate for atom C(10) should 0.4884 (6).

Page 1058. In Table V, Mo–Cl(1) should be 2.469 (1) Å and Mo–Cl(2) should be 2.467 (1) Å.—Barry L. Haymore