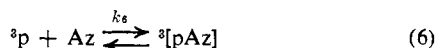


gaps are achieved in nearly planar transoid geometries. A detailed interpretation of the azulene effect would then involve eq 6-8, where brackets designate exciplexes



or encounter complexes.¹³ Accordingly, k'_{az} in eq 3 is replaced by the expression in eq 9, which reduces to

$$k'_{az} = \frac{k_6 K_7 (k_8/k_{-6})}{(k_8 K_7/k_{-6}) + k_8/k_{-7} + 1} \quad (9)$$

eq 10 assuming that k_6 , k_{-6} , and k_8 are diffusion con-

$$k'_{az} = k_{dif} K_7 / (1 + K_7) \quad (10)$$

trolled and that equilibration step 7 is faster than diffusional separation of the donor-acceptor pair. This mechanism accounts for the dependence of $k'_{az\tau}$ values on solvent viscosity,⁶ and, using $k_{dif} = 10^{10} M^{-1} sec^{-1}$, gives $K_7 \simeq 0.04$ in benzene at 30°.

The deactivation of stilbene triplets by oxygen to either ground state isomer suggests that the 22 kcal/mol energy gap required in eq 2, if ${}^1\Delta_g$ oxygen is produced, is achieved with nearly unit efficiency by torsional displacement toward either transoid or cisoid geometries. The larger energy gaps required for excitation transfer to azulene and other quenchers are apparently achieved only by torsional displacement toward transoid geometries.

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(13) For a related case see R. A. Caldwell, *J. Amer. Chem. Soc.*, **92**, 3229 (1970).

(14) Fellow of the Alfred P. Sloan Foundation, 1971-1973.

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Structural Evidence for Variations in the Franck-Condon Barrier to Electron Transfer between Low-Spin Cobalt(II) and Cobalt(III)¹

Sir:

We recently reported² the discovery of a 0.5 Å cobalt-axial ligand distortion in low spin Co([14]dieneN₄)(OH₂)₂²⁺, and we called attention to the fact that this distortion is of sufficient magnitude to account for the very small self-exchange rate constant of the Co([14]dieneN₄)(OH₂)₂³⁺-Co([14]dieneN₄)(OH₂)₂²⁺ couple ($k_{\text{exchange}} = 2 \times 10^{-7} M^{-1} sec^{-1}$ at 70°).^{3,4} In their related kinetic study, Rillema, *et al.*,⁴ found the self-

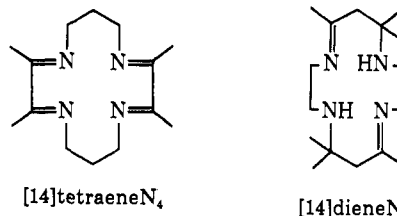
(1) Partial support of this research by the Public Health Service (Grant AM 14341) and the National Science Foundation (Grant GP-15070) is gratefully acknowledged.

(2) M. D. Glick, J. M. Kusza, and J. F. Endicott, *J. Amer. Chem. Soc.*, **95**, 5097 (1973).

(3) Abbreviations: [14]dieneN₄ = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene; [14]tetraeneN₄ = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene plus other abbreviations from ref 8 and 9.

(4) (a) D. P. Rillema, J. F. Endicott, and N. A. P. Kane-Maguire, *J. Chem. Soc., Chem. Commun.*, 495 (1972); (b) manuscript in preparation.

exchange rate for the Co([14]tetraeneN₄)(OH₂)₂³⁺-Co([14]tetraeneN₄)(OH₂)₂²⁺ couple to be at least 10⁶ larger than the comparable rate for the closely related couple with [14]dieneN₄ equatorial ligands, and these authors cited some limited spectroscopic evidence for stronger association of axial ligands in Co^{II}([14]tetraeneN₄)X₂ complexes than in Co^{II}([14]dieneN₄)X₂ complexes. Since both these cobalt(II) complexes are low spin,⁵ the two couples provide a unique opportunity to investigate directly the correlation of inner ligand reorganizational barriers with the magnitudes of self-exchange rates for electron transfer reactions.⁶



We are now able to report structural results for [Co([14]tetraeneN₄)(OH₂)₂](ClO₄)₂ and [Co([14]tetraeneN₄)(NH₃)₂Br₃] and can compare the reorganizational barrier based on these results to that inferred previously for the Co([14]dieneN₄)(OH₂)₂²⁺ couple. For the tetraene couple, the cobalt(II)-OH₂ bond distance is found to be 0.3 Å longer than the cobalt(III)-NH₃ distance. In both tetraene compounds all equatorial cobalt-N distances are equivalent indicating that the distortion is confined to the axial direction. Using Stranks' method,^{7,8} and appropriate estimates of force constants,⁸ we estimate an inner-sphere reorganizational energy of 7 ± 1 kcal/mol, significantly less than the similar barrier of 20 ± 1 kcal/mol estimated for the diene couple.² A difference of 14 kcal/mol is easily sufficient to account for the >10⁶-fold difference in self-exchange rates between the two couples. It has been noted⁹ that the neglect of zero point and thermal vibrational energies leads to a slight overestimate of the reorganizational energy barrier when the above procedure is used. However, the correction should be comparable in both the diene and tetraene couples and thus does not significantly affect the value of the difference.

Several conclusions can now be drawn. First, the unusually slow cobalt(II)-cobalt(III) self-exchange for the diene couple results from an unusually large difference in bond lengths between the oxidized and reduced complexes. Second, the contributions of inner-sphere reorganizational barriers to the observed chemical re-

(5) Determined at 35° in 1 M NaCl solutions, $\mu_{\text{eff}} = 1.82$ BM for ([14]tetraeneN₄)Co(II) and $\mu_{\text{eff}} = 1.86$ BM for ([14]dieneN₄)Co(II).

(6) For pertinent reviews see (a) R. G. Linck, *MTP (Med. Tech. Publ. Co.) Int. Rev. Sci., Inorg. Chem.*, **9** (1), 303 (1971); (b) A. G. Sykes, *Advan. Inorg. Chem. Radiochem.*, **10**, 153 (1967); (c) H. Taube, "Electron Transfer Reactions of Complex Ions in Solution," Academic Press, New York, N. Y., 1970; (d) N. Sutin, "Inorganic Biochemistry," Vol. 2, G. L. Eichhorn, Ed., Elsevier, New York, N. Y., 1973, Chapter 19, p 611; (e) R. A. Marcus, *Annu. Rev. Phys. Chem.*, **15**, 155 (1964); (f) W. L. Reynolds and R. W. Lumry, "Mechanisms of Electron Transfer," Ronald Press, New York, N. Y., 1965.

(7) D. R. Stranks, *Discuss. Faraday Soc.*, **29**, 116 (1960).

(8) For $r^\ddagger = (k_{IIrII} + k_{IIIrIII}) / (k_{II} + k_{III})$, in which k_{II} and k_{III} are force constants for the cobalt(II)-OH₂ and cobalt(III)-OH₂ stretching vibrations, respectively. In the actual calculation we use $k_{II} \simeq 0.7 \times 10^8$ dyn cm⁻¹ and $k_{III} \simeq 1.7 \times 10^8$ dyn cm⁻¹ which are values for the respective cobalt-NH₃ vibrations and find $r^\ddagger = 2.05$ Å. The total energy may then be derived from $E_{\text{total}} = k_{II}(r_{II} - r^\ddagger)^2 + k_{III}(r_{III} - r^\ddagger)^2$.

(9) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," Wiley, 2nd ed, 1967, p 458.

