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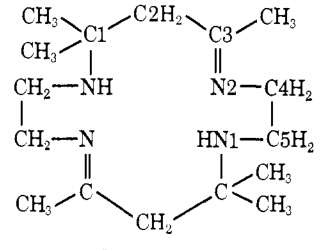
Structural Evidence for Franck–Condon Barrier to Electron Transfer between Low-Spin Cobalt(II) and Cobalt(III)[1]

Sir:

Although electron transfer reactions between coordination complexes have been extensively investigated[2] and although sophisticated theoretical treatments of these reactions have been developed,[3,4] some rather glaring fundamental problems remain. Among these must be counted the approximately 10^{15}-fold difference in the rate of the self-exchange reactions for the $Co(NH_3)_6^{3+}$–$Co(NH_3)_6^{2+}$ [5,6] and the $Ru(NH_3)_6^{3+}$–$Ru(NH_3)_6^{2+}$ [7,8] couples. The extraordinarily slow rate for the cobalt(III)–cobalt(II) couple has been variously attributed to a spin multiplicity restriction[9] (the cobalt(II) complex is high spin in this case) and to the large ligand reorganizational barriers which must accompany the transfer of electron density between metal centered antibonding orbitals.[9,10] The early discussions of the magnitude of the reorganizational barrier were based on a 0.3 Å difference in the cobalt–nitrogen distance reported for $Co(NH_3)_6^{3+}$ and $Co(NH_3)_6^{2+}$.[11] More recently Ibers and coworkers[12] have determined structural parameters in $Co(NH_3)_6Cl_2$ and $Co(NH_3)_6I_3$ and have inferred a reorganizational barrier of about 7 kcal/mol, too small to account for the slow self-exchange rate, but consistent with a kinetically significant spin multiplicity restriction.

On the other hand, very recent work has indicated that intramolecular changes in spin multiplicity (*i.e.*, intersystem crossing rate constants) in transition metal complexes are probably too fast to be rate determining in most intermolecular electron transfer processes.[13] Furthermore, the self-exchange rate for the $Co([14]dieneN_4)(OH_2)_2^{3+}$–$Co([14]dieneN_4)(OH_2)_2^{2+}$ [14,15] couple has been shown to be comparable in magnitude to that for the $Co(NH_3)_6^{3+}$–$Co(NH_3)_6^{2+}$ couple, despite the fact that $Co([14]dieneN_4)(OH_2)_2^{2+}$ is low spin.[15,16]



$[14]dieneN_4$

We are now able to report structural results for $[Co([14]dieneN_4)(OH_2)_2](BF_4)_2$ and for $[Co([14]dieneN_4)(NH_3)_2](ClO_4)_3$ and an estimated reorganizational barrier based on these results. Although one would prefer the identical axial ligands of both members of the redox couple, we could only obtain crystals suitable for X-ray analysis for the compounds indicated. Both compounds possess crystallographic inversion centers (C_i-$\bar{1}$) such that the cobalt ions and four nitrogen atoms are necessarily coplanar. Comparison of the macrocyclic ligands revealed no significant differences between them and the expected distance and angle patterns.[17] Bond distances and angles for the ligands and the coordination spheres about the metal centers are given in Table I.

Table I. Selected Bond Distances (Å) and Angles (deg)

	Co(II)	Co(III)
N1′–Cl	1.506 (8)	1.517 (10)
N1–C5	1.469 (8)	1.474 (10)
N2═C3	1.285 (8)	1.277 (10)
N2–C4	1.485 (8)	1.478 (10)
C1–C2	1.545 (9)	1.516 (11)
C2–C3	1.495 (10)	1.500 (12)
Co–N1	1.968 (6)	1.986 (6)
Co–N2	1.936 (5)	1.916 (7)
Co–NH_3		1.954 (6)
Co–OH_2	2.482 (5)	
C5′–N1′–Cl	114.0 (5)	115.5 (6)
N1′–C1–C2	105.6 (5)	106.3 (7)
C1–C2–C3	118.1 (5)	118.6 (8)
C2–C3═N2	120.7 (6)	121.4 (8)
C3═N2–C4	119.2 (6)	119.4 (7)
N2–C4–C5	105.6 (5)	107.5 (6)
C4–C5–N1	106.4 (5)	105.3 (7)
N1′–Co–N2	94.6 (2)	94.2 (3)
N2–Co–N1	85.4 (2)	85.8 (3)
N1–Co–NH_3		87.0 (3)
N1–Co–OH_2	83.1 (2)	
N2–Co–NH_3		91.6 (3)
N_2–Co–OH_2	92.5 (2)	

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[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] For recent reviews see (a) R. G. Linck, "MTP International Review of Science, Inorganic Chemistry," Vol. 9, Ser. 1, M. L. Tobe, Ed., University Park Press, Baltimore, Md., 1971, p 303. (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.

[3] For reviews see (a) R. A. Marcus, *Annu. Rev. Phys. Chem.*, **15**, 155 (1964); (b) W. L. Reynolds and R. W. Lumry, "Mechanisms of Electron Transfer," Ronald Press, New York, N. Y., 1966.

[4] P. P. Schmidt, *Aust. J. Chem.*, **22**, 673 (1969); *J. Phys. Chem.*, **77**, 488 (1973); *J. Chem. Phys.*, **56**, 2775 (1972); **57**, 3749 (1972).

[5] k_{exch} estimated[6] as 10^{-2} M^{-1} sec^{-1} at 25° using the data of N. S. Biradar and D. R. Stranks, *Trans. Faraday. Soc.*, 58, 2421 (1963).

[6] J. F. Endicott and H. Taube, *J. Amer. Chem. Soc.*, **86**, 1686 (1964).

[7] k_{exch} estimated as about 10^3 M^{-1} sec^{-1} at 25°.[8]

[8] (a) T. J. Meyer and H. Taube, *Inorg. Chem.*, **7**, 2369 (1968); (b) G. Navon and D. Meyerstein, *J. Phys. Chem.*, **74**, 4067 (1970).

[9] L. E. Orgel, Reports of the 10th Solvay Conference on Chemistry, Brussels, 1956, p 329.

[10] R. A. Marcus, *Discuss. Faraday Soc.*, **29**, 21 (1960); *J. Phys. Chem.*, **67**, 853 (1963).

[11] D. R. Stranks, *Discuss. Faraday Soc.*, **29**, 73 (1960).

[12] H. C. Stynes and J. A. Ibers, *Inorg. Chem.*, **10**, 2304 (1971).

[13] (a) J. T. Yardley and J. K. Beattie, *J. Amer. Chem. Soc.*, **94**, 8925 (1972); (b) J. K. Beattie, N. Sutin, D. H. Turner, and G. W. Flynn, *ibid.*, **95**, 2052 (1973).

[14] Abbreviations: $[14]dieneN_4$ = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene.

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

[16] In aqueous solution at 25°, μ_{eff} = 1.85 BM.[15b]

[17] See also (a) R. R. Ryand, B. T. Kolbourne, and J. Dunitz, *J. Chem. Soc. A*, 2407 (1969); (b) M. F. Bailey and I. E. Maxwell, *Chem. Commun.*, 883 (1966); (c) D. R. Ireland and W. T. Robinson, *J. Chem. Soc. A*, 663 (1970).

For this discussion the small differences between the equatorial Co–N distances may be ignored. We shall thus only be concerned with the axial metal ligand distances. The Co(III)–NH_3 distance of 1.96 Å may be used to derive *via* covalent radii a Co(III)–O distance of $\sim$1.94 Å (r_{III}). The Co(II)–O distance of 2.48 Å provides a value for r_{II}. The large difference is, of course, a consequence of Jahn–Teller distortion in the Co(II) system, an effect which is surely static as a consequence of the well-defined size of the N_4 girdle.

These structural results indicate that the Co([14]-dieneN$_4$)(OH$_2$)$_2^{2+}$ and Co([14]dieneN$_4$)(OH$_2$)$_2^{3+}$ complexes are unique models for the study of intermolecular electron transfer processes since changes in bond lengths (and therefore inner sphere reorganizational barriers) are confined to one molecular axis. This is also the first known example of an essentially forbidden self-exchange reaction ($k_{exch} = 2 \times 10^{-7}$ M^{-1} sec^{-1} at 70°)[15] between low-spin cobalt(II) and cobalt(III) complexes. Stranks' method[18] may be used to estimate the activation barrier which results from compressing the cobalt(II)–OH_2 bonds and stretching the cobalt(III)–OH_2 bonds until they are dimensionally equivalent. We find this bond distance in the activated complex to be $r^{\ddagger} = 2.10$ Å;[19,20] the corresponding reorganizational barrier[21] is approximately 21 kcal/mol. A reorganizational barrier of this magnitude is certainly compatible with the small self-exchange rate.

If one takes these cyclic complexes as models of "spin-allowed" intermolecular electron transfer between cobalt(III) and cobalt(II) complexes, then it appears that any "spin" constraint manifested in the $Co(NH_3)_6^{3+}$–$Co(NH_3)_6^{2+}$ self-exchange reaction may be attributed to the reorganizational barrier which results from the Jahn–Teller distortion accompanying the localization of electron density in a d_{z^2} orbital in the low-spin cobalt(II) intermediate.

All X-ray intensity data were collected on a card-controlled Picker four-circle diffractometer with Zr-filtered Mo Kα radiation. The θ–2θ scan technique was used with a scan speed of 2°/min and a minimum scan width of 2° plus allowance for spectral dispersion. Those data with $I \geq 2.5\ \sigma(I)$ were used for the solution and refinement of the structure. The space groups and lattice constants are as follows: [Co[(14]dieneN$_4$)-(OH$_2$)$_2$](BF$_4$)$_2$ $P2_1/c$, a = 7.893 (7) Å, b = 9.518 (7) Å, c = 16.813 (13) Å, β = 107.16 (2)°; [Co([14]dieneN$_4$)-(NH$_3$)$_2$](ClO$_4$)$_3$ $A2/a$, a = 9.596 (9) Å, b = 18.829 (16) Å, c = 15.550 (14) Å, β = 86.09 (2)°.

The structures were solved by a combination of Patterson and Fourier techniques and were refined by full-matrix least-squares with anisotropic thermal parameters for all atoms other than hydrogen atoms. The discrepancy factors for the Co(II) complex are $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.068$ and $wR = [\Sigma w(F_o - F_c)^2/\Sigma w(F_o)^2]^{1/2} = 0.074$ for 1442 data with sin $(\theta/\lambda) < 0.628$. The structure of the Co(III) complex involves a statistical disordering of one of the ClO_4^- groups about a twofold axis. The refinement in the centrosymmetric space group has resulted in discrepancy factors of R = 0.066 and wR = 0.082 for 1533 data with sin $(\theta/\lambda) < 0.596$. We are presently working on improved models for the disordered ClO_4^- counterion.

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[18] D. R. Stranks, *Discuss. Faraday Soc.*, **29**, 116 (1960).

[19] For $r^{\ddagger} = (k_{II}r_{II} + k_{III}r_{III})/(k_{II} + k_{III})$, in which k_{II} and k_{III} are force constants for the cobalt(II)–OH_2 and cobalt(III)–OH_2 stretching vibrations, respectively. In the actual calculation we used $k_{II} \simeq 0.7 \times 10^5$ dyn cm^{-1} and $k_{III} \simeq 1.7 \times 10^5$ dyn cm^{-1} which are values for the respective cobalt–NH_3 vibrations. Cobalt–water force constants would be expected to be somewhat larger than cobalt–ammine force constants.[20]

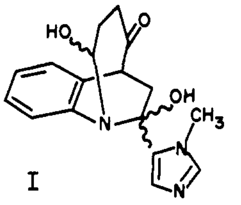
[20] K. Nakamoto, "Infrared Spectra of Coordination Compounds," Wiley, New York, N. Y., 1963.

[21] Estimated from $E_{total} = 2(E_{II} + E_{III})$ where $E_N = k_N(\Delta r)^2$.

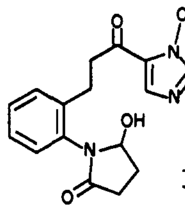
Synthesis and Revised Structure of Isolongistrobine[1]

Sir:

Our recent synthesis[1] of dehydroisolongistrobine cast doubt on the structure of a congeneric alkaloid, isolongistrobine. The latter alkaloid was assigned structure I by Arndt, *et al.*, who reported the isolation of these alkaloids in 1969.[2] Isolongistrobine exhibited no optical activity. Its uv spectrum suggested the presence of an acylimidazole. In accordance with our revised structure for dehydroisolongistrobine, we postulated structure II for isolongistrobine.[1]

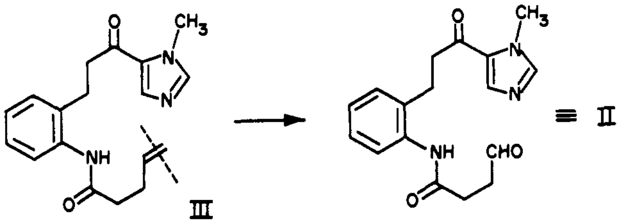


I



II

We planned to generate the proposed carbinol lactam of isolongistrobine (II) by oxidative cleavage of the vinyl group of a 4-pentenoamide (III) by ozone or its equivalent. Synthesis of III followed a sequence similar to that used in the preparation of the β-carbomethoxypropionamide[1] corresponding to 4-pentenoamide (III).



Acylation of amino alcohol IV[1] was effected by adding 4-pentenoyl chloride[3] to an equimolar mixture of IV and pyridine in dry methylene chloride at 0°. Plate chromatography on silica gel (9:1 CH_3CN–CH_3OH eluent) gave rise to amido alcohol V, a white

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[1] Imidazole Alkaloids. II. Part I: M. A. Wuonola and R. B. Woodward, *J. Amer. Chem. Soc.*, **95**, 284 (1973).

[2] R. R. Arndt, S. H. Eggers, and A. Jordaan, *Tetrahedron*, **25**, 2767 (1969).

[3] Prepared from 4-pentenoic acid and thionyl chloride, bp 103–122°, 73.7%. *Cf.* L. Henry and C. Aschmann, *Chem. Zentralbl.*, **69** (II), 663 (1898); H. Wohlgemuth, *Ann. Chim. (Paris)*, **2** (9), 329 (1914).