Strain Affected Electron Transfer: The $[Co(tmen)_3]^{2+/3+}$ Couple (tmen = Tetramethylethylenediamine)

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The title compound, a methylated analogue of $[Co(en)_3]^{3+}$ (en = ethylenediamine), has many properties radically different from $[Co(en)_3]^{3+}$; in particular the estimated electron self-exchange rate constant is three orders of magnitude smaller than for $[Co(en)_3]^{3+}$.

The inner shell contributions to the activation energy for the electron transfer process involving a $ML_6^{n+/(n-1)+}$ couple depend on the force constants for the breathing mode and on the difference of the metal–ligand distances in the two oxidation states (Δr).[1] Substitution at the carbon backbone of organic ligands generally does not greatly affect the properties of the resulting complex ion, *e.g.* the Co^{III} tris complexes of ethylenediamine (en) and 2,3-diaminobutane[2] show very similar physical properties. We have observed significant changes, however, when the methylene protons are replaced by methyl groups, producing 2,3-dimethyl-2,3-diaminobutane or tetramethylethylenediamine (tmen).[3]

$[Co(tmen)_3]^{3+}$ is prepared by adding an excess of tmen to a methanolic solution of *trans*-$[Co(tmen)_2(H_2O)_2]Cl_3$.[4] The tris complex has been isolated as the chloride, tosylate (p-$MeC_6H_4SO_3$), and triflate ($CF_3SO_3^-$) salts whose elemental analyses confirm the expected stoicheiometry. In contrast with the vast majority of cobalt(III) amine complexes with an octahedral or pseudo-octahedral CoN_6 core, $[Co(tmen)_3]^{3+}$ is not yellow but pink. The corresponding red shift of about 2000 cm^{-1} for the ligand field bands is attributed to a lengthening of the Co–N bonds with respect to the parent $[Co(en)_3]^{3+}$, to be confirmed by a crystal structure analysis in progress. The approximate doubling of the extinction coefficient is attributed to a stronger trigonal twist owing to the steric interaction of the twelve peripheral methyl groups. The larger cavity of the ligand frame is also manifested in the considerable shift of the reduction potential; $[Co(tmen)_3]^{3+}$ is significantly more easily reduced than $[Co(en)_3]^{3+}$ (Table 1).

Differences of many orders of magnitude between the en and the tmen complexes are observed in the reactivity patterns, *e.g.* for base hydrolysis and base catalysed racemization (Table 1). For the $[Co(tmen)_3]^{3+}$ complex, both reactions obey a rate law of the form: $V = k[Co(tmen)_3{}^{3+}][OH^-]$. The reactions most likely proceed *via* the D(CB) mechanism. Owing to the high substitution lability of the tmen complex in basic solution the rate of racemization approach[5] for a direct measurement of the self-exchange rate for the $[Co(tmen)_3]^{2+/3+}$ couple could not be applied. An estimate of the self-exchange rate may be gained, however, by application of the Marcus cross-relationship.[6] We have therefore measured the kinetics of reduction of $[Co(tmen)_3]^{3+}$ by $[Ru(H_2O)_6]^{2+}$ and $[Cr(H_2O)_6]^{2+}$ at 25 °C, $[H^+] = 0.1$ M and at unit ionic strength ($NaCF_3SO_3$).

Table 1. A comparison of selected properties of $[Co(en)_3]^{3+}$ and $[Co(tmen)_3]^{3+}$.

Property	$[Co(en)_3]^{3+}$	$[Co(tmen)_3]^{3+}$
Colour	Yellow	Red
λ_{max}/nm (ε)	338(85), 464(93)	362(177), 504(177)
Δ, *B*/cm^{-1} [a]	32 170, 587	21 300, 568
Reduction potential/V *vs.* n.h.e.[b]	−0.12[b]	+0.28
Estimated half-life for hydrolysis[c]	3.2 yrs[c]	13.6 s
Estimated half-life for racemization[c]	>3.2 yrs[c]	1.0 ms
First c.d. maximum/nm	489	495
Electron self-exchange rate constant/ dm^3 mol^{-1} s^{-1}	8×10^{-5} [d]	10^{-7} [e]
^{59}Co Chemical shift/p.p.m.	+ 7088[a]	+ 8151

[a] Calculated according to R. Bramley, M. Brorson, A. M. Sargeson, and C. E. Schäffer, *J. Am. Chem. Soc.*, 1985, **107**, 2780. [b] N.h.e. = normal hydrogen electrode; A. M. Bond, G. A. Lawrance, P. A. Lay, and A. M. Sargeson, *Inorg. Chem.*, 1983, **22**, 2010. [c] In 0.1 M OH^- at 25 °C; J. A. Friend and E. K. Nunn, *J. Chem. Soc.*, 1958, 1567; W. G. Gehman and W. C. Fernelius, *J. Inorg. Nucl. Chem.*, 1957, **9**, 71. [d] F. P. Dwyer and A. M. Sargeson, *J. Phys. Chem.*, 1961, **65**, 1892. [e] Estimated using the Marcus cross-relationship and data from the $[Ru(H_2O)_6]^{2+}$ reduction.

Reduction of the complex by $[Ru(H_2O)_6]^{2+}$ obeys the rate law: $V = k_1 [Co(tmen)_3{}^{3+}][Ru^{2+}]$, with a rate constant $k_1 = (5.6 \pm 0.5) \times 10^{-3}$ dm^3 mol^{-1} s^{-1}. The equilibrium constant for the reaction is only ~18 in favour of the $Ru^{3+}/Co(tmen)_3{}^{2+}$ side. Reduction of the complex by Cr^{2+} proceeds readily and obeys a two-term rate law of the form: $V = k_2 [Co(tmen)_3{}^{3+}][Cr^{2+}] + k_3[Co(tmen)_3{}^{3+}][Cr^{2+}][Cl^-]$. The rate constants were found to be $k_2 < 10^{-2}$ dm^3 mol^{-1} s^{-1}, and $k_3 = (5.0 \pm 0.5)$ dm^6 mol^{-2} s^{-1}.

Application of the Marcus cross-relationship[6] using the Cr data yields an estimate for the self-exchange rate constant k_{11} for $[Co(tmen)_3]^{2+/3+}$ of $< 10^{-9}$ dm^3 mol^{-1} s^{-1}. The Ru data, which are considered to be more reliable, yield an estimate of 10^{-7} dm^3 mol^{-1} s^{-1} for k_{11}. There are several reasons for attributing more significance to the ruthenium data, the main one being that the equilibrium constant for the reaction is very small, and another being that an accurate rate constant is available for the $[Ru(H_2O)_6]^{2+/3+}$ self exchange[7] whereas the same is not true for $[Cr(H_2O)_6]^{2+/3+}$. The Marcus relationship holds best when the difference in the reduction potentials of the two reactants is small, *i.e.* there is a small equilibrium constant for the cross-reaction.[1] Sutin and co-workers have found that cross-reactions with large driving forces generally underestimate the value of the self-exchange rate constant.[8]

This estimate of the self-exchange rate for the $[Co(tmen)_3]^{2+/3+}$ couple is almost three orders of magnitude less than the self-exchange rate constant for the parent $[Co(en)_3]^{2+/3+}$ couple. This corresponds to an increase in activation energy of ~15 kJ mol^{-1}. The elucidation of the various contributions to the activation energy for electron transfer will depend on a complete analysis of the nuclear and electronic factors. However, molecular mechanics calculations[9] on the $[Co(tmen)_3]^{3+}$ complex indicate that the energy required to deform the atomic co-ordinates from their equilibrium positions is much higher for $[Co(tmen)_3]^{3+}$ than for $[Co(en)_3]^{3+}$. Thus despite the probability that the longer Co–N bonds in $[Co(tmen)_3]^{3+}$ mean that the Δr value for $[Co(tmen)_3]^{2+/3+}$ will be less than for $[Co(en)_3]^{2+/3+}$, it appears that the energy needed to achieve the required deformation will be greater.

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