Self-exchange Reactions of Cobalt Complexes and Implications concerning Redox Reactivity of Vitamin B₁₂

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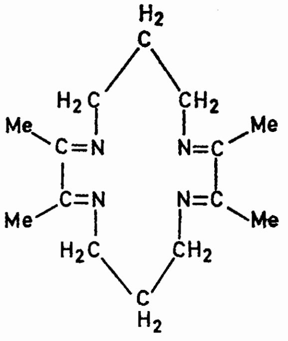
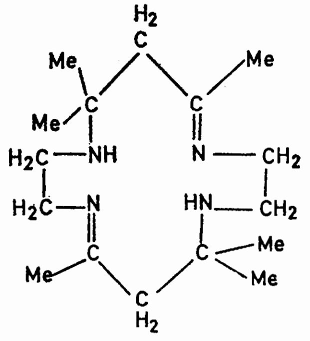
Summary The self-exchange rates of $Co(N_4)(OH_2)_2^{3+,2+}$ complexes, where (N_4) is a tetradentate macrocyclic ligand, have been found to vary by a factor of 10^{10}; the large reactivity range cannot be related to "spin effects", but is likely a reflection of ligand reorganizational barriers; the vitamin B_{12a}–B_{12r} couple is at the high end of this range—a feature which has significance in the redox mechanisms of B_{12} and related systems.

We have extended our studies of the oxidation–reduction behaviour of complexes containing macrocyclic tetradentate ligands[1–4] to include determinations of the self-exchange rates between $Co(N_4)(OH_2)_2^{3+}$ and $Co(N_4)(OH_2)_2^{2+}$ complexes; N_4 = 2,3,9,10-tetramethyl-1,4,8,11-tetra-azacyclotetradeca-1,3,8,10-tetraene (tmtat) and 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene (hmtad).

In the case of the *trans*-Co(hmtad)$(OH_2)_2^{3+,2+}$ couples we have used cobalt-60 labelled *trans*-Co(hmtad)$(OH_2)_2^{3+}$ and determined the rate at which the label appeared in Co(hmtad)$^{2+}$. Reactions were run at 1·0M ionic strength ($NaClO_4$), 70°, pH 1, and were quenched by cooling to room temperature; reaction products were separated under nitrogen using Dowex 50WX12 cation exchange resin.

The (hmtad)cobalt(II) species in solution appear to be nearly four-co-ordinate with little evidence for interaction with axial ligands.[4,5] In fact, solution spectra of all Co(hmtad)$^{2+}$ are insensitive to the counter ions (λ_{max} 420 nm, ϵ_{max} 120) and are qualitatively similar (*i.e.*, same peak maxima) as the transmittance spectra of solid low spin (μ = 2·31 B.M. at 25°) Co(hmtad)$(ClO_4)_2$. Further, dilute (1×10^{-3}M) solutions containing (hmtad)cobalt(II) have typical, intense, low-spin cobalt(II) e.s.r. spectra. Owing to the magnitude of the self-exchange rate constant for the Co(tmtat)$(OH_2)_2^{3+,2+}$ couple, to the great reactivity of these complexes [in concentrated solution Co(tmtat)$(OH_2)_2^{3+}$ oxidizes water at temperatures above 70°], and


tmtat


hmtad

to the fact that the methyl group ^1H n.m.r. resonance is a triplet (*J* 2·6 Hz, at 60°; apparently due to homoallylic coupling to methylene groups), we had to use a ^1H n.m.r. method using methyl deuteriated $Co(tmtat)(OH_2)_2^{3+}$ to determine this self-exchange rate. A sample of $[Co(tmtat)(OH_2)_2](ClO_4)_3$[2] was equilibrated with D_2O at pD 8 for 12 h, then recrystallized. Solutions of $Co([^2H_{12}]\text{-tmtat})(OD_2)_2^{3+}$-(pD 1—2) were mixed anaerobically with $Co(tmtat)(OD_2)_2^{2+}$ (solutions from the perchlorate salt) in the sample tube and the growth of the methyl resonance was observed at timed intervals. Our results are summarized in the Table.

Summary of self-exchange rates observed for trans-$Co^{III,II}(N_4)X_2$ *couples*

Exchanging couple	k, M^{-1} s^{-1}	$T°$	Ionic strength	pH	Method
$Co(hmtad)(OH_2)_2^{3+,2+}$	2×10^{-7}	70	1·0	1	^{60}Co[a]
$Co(tmtat)(OH_2)_2^{3+,2+}$	0·9	35	0·1[b]	2	($[^2H_{12}]$-tmtat)
	10^{2+1}	25	1[c]		
Vitamin B_{12a}, B_{12r}	$1·5 \times 10^3$	35	0·1[b,d]	0·4	^1H n.m.r. line broadening
	$2·5 \times 10^3$	35	0·1[b,d]	5·2	
	$2·3 \times 10^3$	35	0·1[b,d]	7·5	
	$2·0 \times 10^3$	35	0·1[b]	1	

[a] Standard isotopic labelling. [b] Owing to problems of complex insolubility and ^1H n.m.r. sensitivity no inert electrolyte could be added. [c] Extrapolated to unit ionic strength. This rate was estimated from the $Co(tmtat)(OH_2)_2^{3+}$ catalysis of ammine hydrolysis in $Co(tmtat)(NH_3)_2^{3+}$ and correcting the rate constant for the free energy of reaction: ref. 2. [d] Chloride present; $[Cl^-] = 2[\text{total Cobalt}]$.

The observed difference in self-exchange rates for $Co(hmtad)(OH_2)_2^{3+,2+}$ and $Co(tmtat)(OH_2)^{3+,2+}$ couples amounts to more than 14 kcal mol^{-1} in free energy of activation. This difference in intrinsic redox reactivity clearly cannot be attributed to spin multiplicity restrictions such as have been invoked to account for the slow $Co(NH_3)_6^{3+,2+}$ self-exchange rate,[4-6] but is qualitatively consistent with very different ligand reorganizational barriers. The equilibrated Co^{II}(hmtad) complexes in solution involve only very weak interaction with axial ligands[1,3] while the spectral characteristics of Co^{II}(tmtat) solutions suggest relatively strong co-ordination of axial ligand (or ligands).

Except for a difference in charge the tmtat ligand is similar to dimethylglyoximate. The dimethylglyoximate complexes of cobalt have been suggested as model systems of vitamin B_{12} and it would seem that the metal–corrin ligand bonds in the B_{12} complexes should also give rise to rapidly self-exchanging species.[7] We have therefore examined the B_{12a}–B_{12r} self-exchange using a straightforward line broadening technique. Aquo-cobalamin was prepared from hydroxy-cobalamin obtained from Sigma Chemicals, St. Louis, Missouri, and reduced to B_{12r} catalytically with H_2 over PtO. Line widths were measured at several B_{12r} concentrations and the self-exchange rate was calculated (see Table).†

It appears that the B_{12a}–B_{12r} self-exchange rate is the fastest yet reported for a cobalt(III)–cobalt(II) couple. This intrinsic redox reactivity has significance in the chemistry of the B_{12} compounds and suggested model compounds. For example, the ease of preparation of Co^{III}(tmat)–alkyl complexes[8] may be contrasted to the difficulty in preparing Co^{III}(hmtad)–alkyl complexes.[2,8]

The present study suggests that such contrasts arise from the kinetic instability of Co^{II}(tmtat), B_{12r}, *etc.*, to oxidation rather than to an unusually great ligand field strength of the equatorial (N_4) ligands[9] or to the ability of some other factor to stabilize Co^{III}–alkyl bonds.[10]

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† $k_{exch} = 1/[Co^{II}]\{1/T(2Co^{III}, Co^{II}) - 1/T(2Co^{III})\}$ from H. M. McConnell and S. B. Berger, *J. Chem. Phys.*, 1958, **27**, 230. The effects of collisional line broadening were determined to be relatively insignificant since the methyl resonance of $N(CH_3)_4^+$ was found to be broadened less than 0·02 Hz in the presence of 0·025M-B_{12r}. The B_{12a} resonances were broadened up to 10 Hz depending on the concentration of B_{12r}.

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[9] For example, see p. 75 in ref. 8.
[10] For example, see p. 98 in ref. 7c.