Configurational and Conformational Effects on Electron Transfer Rates[1]

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Electron transfer rate constants of the cage complexes Λ, Δ, *fac, mer*-$[Co\{(NH_3)_2, Me_3sar\}]^{5+/4+}$ [where $\{(NH_3)_2, Me_3sar\}$ = (4*R*,12*R*,17*R*) or (4*R*,11*R*,17*R*)-trimethyl-3,6,10,13,16,19-hexa-azabicyclo[6.6.6]icosane-1,8-diamine or the catoptric (*S*) forms] show $>10^3$-fold differences for these very similar diastereoisomeric ions which are ascribed primarily to *lel–ob* conformational changes and their effect on the redox potentials of the couples as well as on the electron transfer rates.

Two of the salient features of the $[Co(sepulchrate)]^{3+/2+}$ chemistry were the unusual chiral inertness of the encapsulated Co^{II} complex and the substantial enhancement of the electron transfer rate [$\sim10^5$] between the two oxidation states relative to the $[Co(en)_3]^{3+/2+}$ (en = ethane-1,2-diamine) couple.[2,3] This has been ascribed to the tightness of ligand binding in both oxidation states and to the strain engendered in both ground states. These factors help the cages reach the configurations required for the activated complex. Essentially, the cavity size is a little too small for Co^{II} and a little too large for Co^{III} for these ligands[4] and the related carbon capped analogues of the sarcophagine type.[5]

The cage complexes also have a rich stereochemistry and quite a lot is known about the configurations around the metal ions and the N centres.[2,5,6] However, there is less certainty about the conformational characteristics of the cages in solution and their influence on the electron transfer rates and redox potentials. The current study was therefore carried out to stabilize the lel_3 and ob_3 conformations in the resulting cage complexes by choosing appropriate synthetic templates in advance. The obvious choices were the stable ob_3 and lel_3 forms of tris(*trans*-cyclohexane-1,2-diamine)cobalt(III) ions but while the lel_3 form can be capped[7] we have not yet succeeded in either removing the metal ion from the resulting cage or capping the ob_3 complex.[7] Another choice was to cap the ob_3 and lel_3 forms of the tris-(*R*)- or -(*S*)-propane-1,2-diamine)cobalt(III) ions[8,9] $\{[Co(pn)_3]^{3+}\}$. Here the requirement for the methyl group to remain equatorial in the chelate rings leads to stabilization of *fac*- and *mer*-lel_3-Λ(*S*)-and-Δ(*R*)-$[Co(pn)_3]^{3+}$ configurations.[9]

The formaldehyde/nitromethane/base strategy developed for capping the $[Co(en)_3]^{3+}$ ion[5] was successful in encapsulating the *fac*- and *mer*-lel_3-$[Co(pn)_3]^{3+}$ complexes to give the analogous $[Co\{(NO_2)_2, Me_3sar\}]^{3+}$ complexes {*fac* form = 1,8-dinitro-(4*R*,12*R*,17*R*)trimethyl-3,6,10,13,16,19-hexa-azabicyclo[6.6.6]icosane.} Unfortunately, the ob_3 isomers did not succumb to the same treatment. The Δ- and Λ-ob_3 cages were produced, however, by an indirect route. The lel_3 dinitro-complexes above were reduced to the Co^{II} diamine complexes and Co^{II} was then extruded with CN^- ion. The free ligand $\{(NH_2)_2, Me_3sar\}$ was isolated after ion-exchange chromotography.[8] Co^{III} was then reinstated in the cage using the *trans*-$[Co(pyridine)_4Cl_2]Cl$ reagent in 2-methoxyethanol. This procedure led to a mixture of lel_3 (95%) and ob_3 (5%) forms which were readily separated by ion exchange chromatography.[8] In this way, the eight diastereoisomeric complexes were isolated and characterised as *fac* (Figure 1) and *mer* isomers of Λ(*S*)- and Δ(*R*)-lel_3-, and Λ(*R*)- and Δ(*S*)-ob_3-$[Co\{(NH_2)_2, Me_3sar\}]Cl_3$. The u.v./visible spectra of the orange lel_3 [ε_{max} (480 nm) 151; ε_{max} (345 nm) 137; ε_{max} (247 nm) 19 900 $dm^3\ mol^{-1}\ cm^{-1}$] and yellow ob_3 forms [ε_{max} (450 nm) 85; ε_{max} (332 nm) 95; ε_{max} (323 nm) 19 200 $dm^3\ mol^{-1}\ cm^{-1}$] as trifluoromethanesulphonate salts in 0.1 M CF_3SO_3H are markedly different. However the respective *fac*- and *mer*-isomers gave virtually identical spectra. Clearly the ob_3 isomers absorb at appreciably higher energies and this could reflect a stronger ligand field for the cage in the ob_3 conformation.

The lel_3/ob_3 difference is also reflected in the reduction potentials and electron transfer rates between the isomers, Table 1. The more negative reduction potentials of the ob_3 isomers imply that the ob_3 conformation has a somewhat smaller natural cavity size. It fits the Co^{III} ion better than the lel_3 conformer and *vice versa* for the larger Co^{II} ion. The ob_3 isomers also have 30-fold larger self-exchange rate constants than the lel_3 isomers in keeping with the predictions of molecular mechanics calculations.[8,10]

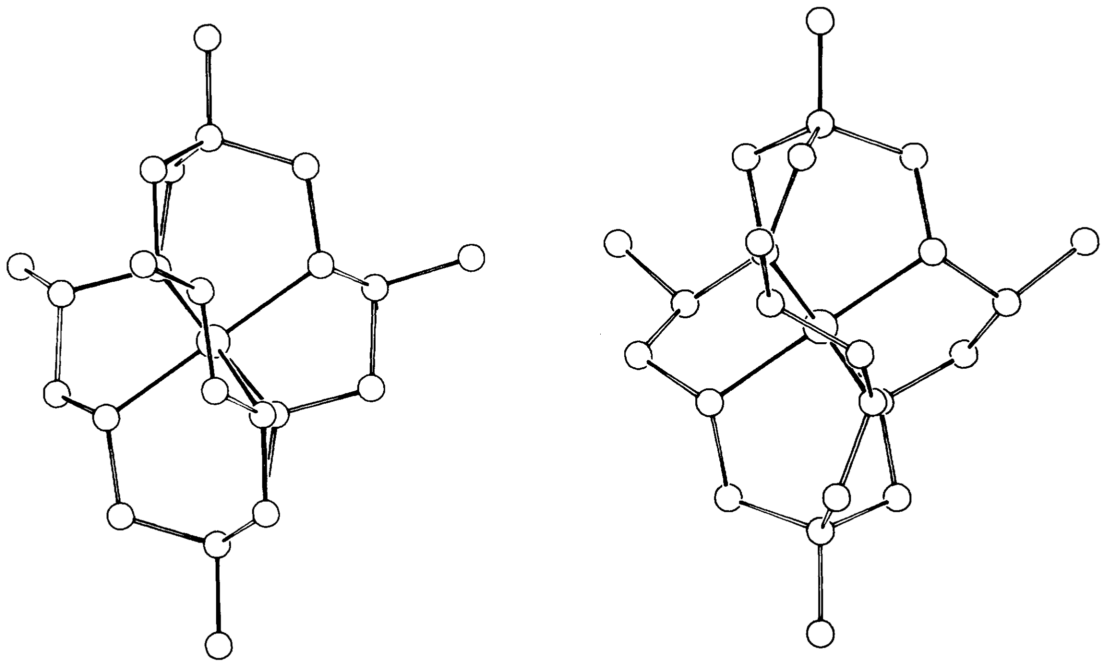
Much of the variation in the cross-reaction rate constants (Table 1) can be accommodated by the Marcus–Hush theories.[11,12] Eight doubly degenerate cross-reactions are accessible from the eight chiral pairs and it can be seen from Table 1 that the calculated and observed rate constants agree within the limits expected for this theoretical framework. Under the acidic conditions used the exo-amine groups are protonated so that essentially the electron exchange is taking place between 5^+ and 4^+ partners. The most notable result is

Table 1. Rate constants and redox potentials for stereo- and diastereo-isomers of $[Co\{(NH_3)_3, Me_3sar\}]^{5+/4+}$ ions at 25 °C.

Stereoisomeric pairs	$k_{1,1}$(obs)[a] /$dm^3\ mol^{-1}\ s^{-1}$	E'/V *vs.* n.h.e.[b]
Fac-lel_3	0.031(1)	0.015
Mer-lel_3	0.033(1)	0.015
Fac-ob_3	0.97(1)	-0.29_5
Mer-ob_3	1.00(1)	-0.32_5
$[Co\{(NH_3)_2sar\}]^{5+/4+}$	0.025[16]	0.02

Diastereoisomeric pairs	$k_{1,1}$/$dm^3\ mol^{-1}\ s^{-1}$ obs.[a]	calc.[c]	E'/V *vs.* n.h.e.[b]
Mer-Λ-lel_3 + *Fac*-Δ-ob_3	54	89	0.34
Mer-Δ-lel_3 + *Fac*-Δ-ob_3	45		
Fac-Δ-lel_3 + *Fac*-Δ-ob_3	40		0.34
Fac-Λ-lel_3 + *Fac*-Δ-ob_3	32		
Mer-Δ-lel_3 + *Mer*-Δ-ob_3	17		0.31
Mer-Λ-lel_3 + *Mer*-Δ-ob_3	14		
Fac-Λ-lel_3 + *Mer*-Δ-ob_3	13		0.31
Fac-Δ-lel_3 + *Mer*-Δ-ob_3	10	53	

[a] Conditions 25 ± 0.1 °C in 0.1 M CF_3SO_3H/0.1 M CF_3SO_3Na. Rates determined polarimetrically by mixing Δ and Λ isomers or by stopped-flow spectrophotometric measurements for diastereoisomers. [b] n.h.e. = normal hydrogen electrode. Measured by cyclic voltammetry at a hanging mercury drop electrode under the same conditions as for electron transfer. [c] Calculated from the Marcus cross reaction relationship: $k_{1,2} = (k_{1,1}k_{2,2}K_{1,2}f_{1,2})^{0.5}$.



lel$_3$-*fac*-Λ-$[Co\{(NH_3)_2\text{-}(S)\text{-}Me_3sar\}]^{3+}$ *ob*$_3$-*fac*-Λ-$[Co\{(NH_3)_2\text{-}(R)\text{-}Me_3sar\}]^{3+}$

Figure 1. Facial isomers of $[Co^{III}\{(NH_3)_2, Me_3sar\}]^{5+}$.

that the *lel*$_3$ self-exchange rate is 1740-fold slower than the fastest rate for a cross reaction. This arises partly from the 0.32 V difference in redox potentials between *lel*$_3$ and *ob*$_3$ complexes and from the 30-fold difference in their self-exchange rates. What is surprising in a general sense is that there is more than three orders of magnitude difference in rate between electron transfer reactions of very similar isomer pairs.

Facial and meridional forms are not the major influence nor are the Δ and Λ configurations. It is the *lel, ob* conformational characteristic which has the dominant effect. However, once this factor is accounted for there is still an interesting observation which remains. By confining the reacting partners to *lel*$_3$–*ob*$_3$ interactions (Table 1), it can be seen that Δ and Λ interactions are not significant but that the meridional–facial combinations influence the rates, over a factor of five, in a regular way. By comparison the cross-reaction calculations only account for ~40% change in the rate. These results and the trend in the observed rate constants imply a stereoselectivity arising from the orientation of the methyl groups on the cage, presumably by influencing the manner in which the reacting pairs dock. Although the effect is not large, it is the largest seen to date in aqueous solution by comparison with other stereo-selective effects recorded for electron transfer reactions with co-ordination compounds.[13—15]

Finally, the different spectral, electrochemical, and electron transfer properties of these complexes allow an assessment of the conformations of the Co^{III}(sar) cage complexes in solution. For example in Table 1, the redox potential and self-exchange rate for the $[Co\{(NH_3)_2sar\}]^{5+/4+}$ couple[16] clearly match those for the *lel*$_3$-$[Co\{(NH_3)_2, Me_3sar\}]^{5+/4+}$ couple. Moreover the absorption maxima in the ligand field spectra (475 and 345 nm, 0.1 M CF_3SO_3H) indicate a *lel*$_3$ conformation for the Co^{III} ion in aqueous solution. Most of the sep and sar Co^{III} complexes to date also appear to be in this *lel*$_3$ conformation in aqueous solution as gauged by their spectral properties.

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References

1 For terminology used in this communication, see: IUPAC Commission on the Nomenclature of Inorganic Chemistry, *Inorg. Chem.*, 1970, **9**, 1; 1977, **16**, 233.
2 I. I. Creaser, J. M. Harrowfield, A. J. Herlt, A. M. Sargeson, J. Springborg, and R. J. Geue, *J. Am. Chem. Soc.*, 1977, **99**, 3181; 1982, **104**, 6016.
3 D. Geselowitz, *Inorg. Chem.*, 1981, **20**, 4457.
4 R. J. Geue, R. Pizer, and A. M. Sargeson, Abstracts 183rd ACS National Meeting Las Vegas, 1982, INOR 62, and unpublished work.
5 R. J. Geue, T. W. Hambley, J. M. Harrowfield, A. M. Sargeson, and M. R. Snow, *J. Am. Chem. Soc.*, 1984, **106**, 5478.
6 A. M. Sargeson, *Chem. Br.*, 1979, **15**, 23; *Pure Appl. Chem.*, 1984, **56**, 1603, and references therein.
7 R. J. Geue, M. G. McCarthy, and A. M. Sargeson, *J. Am. Chem. Soc.*, 1984, **106**, 8282.
8 A. J. Hendry, Ph.D. Thesis, Australian National University, 1986.
9 S. E. Harnung, S. Kallesøe, A. M. Sargeson, and C. E. Schäffer, *Acta Chem. Scand.*, 1974, **28**, 385, and references therein.
10 R. J. Geue, unpublished work.
11 R. A. Marcus, *Electrochim. Acta*, 1968, **13**, 997, and references therein.
12 N. S. Hush, *Trans. Faraday. Soc.*, 1961, **57**, 155, and references therein.
13 D. A. Geselowitz, A. Hammershøi, and H. Taube, *Inorg. Chem.*, 1987, **26**, 184, and references therein.
14 A. G. Lappin, R. A. Marusak, D. P. Martone, P. Osvath, and M. Kemper, *Inorg. Chem.*, 1989, in the press, and references therein.
15 A. G. Lappin, D. P. Martone, P. Osvath, and R. A. Marusak, *Inorg. Chem.*, 1983, **22**, 40.
16 I. I. Creaser, A. M. Sargeson, and A. W. Zanella, *Inorg. Chem.*, 1983, **22**, 4022.