Electron-transfer Reactions of Cobaloximes. Part II.[1] The Transition from Outer- to Inner-sphere Mechanisms with Vanadium(II): a Non-linear Free-energy Relation

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The reduction of a series of cationic cobaloximes of the form $[Co(Hdmg)_2L_2]^+$ by V^{2+}(aq) has been investigated [Hdmg = dimethylglyoximato(1−); L = $EtNH_2$, $PhNH_2$, py, or 3,5-Me_2py]. Rate constants and activation parameters at 25 °C are reported. A plot of $\Delta G^{\ddagger}$ for these reactions against $E_{\frac{1}{2}}$ for the polarographic reduction is used to illustrate the progression from inner- to outer-sphere mechanism as the base strength of the axial ligands is lowered.

In Part I we presented evidence to suggest that *trans*-amminechlorobis(dimethylglyoximato)cobalt(III) and the corresponding bromo-complex are reduced by V^{2+}(aq) by an outer-sphere mechanism, while the bis(ammine) complex reacts by a substitution-controlled inner-sphere process.[1] If we consider that in each case there is competition between the two possible paths, then it is clear that the outer-sphere path for the bis(ammine) complex

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[1] Part I, R. H. Prince and M. G. Segal, *J.C.S. Dalton*, 1975, 330.

must be considerably slower than the observed inner-sphere one and therefore very much slower than the reduction of the amminehalogeno-complexes. Three factors might be expected to contribute to the change in reactivity: (*a*) the charge on the complex; (*b*) the Franck–Condon, or ligand-reorganisation, barrier; and (*c*) the electrode potential of the oxidant. For an outer-sphere reaction these may be related elegantly to the observed free energy of activation, $\Delta G^{\ddagger}$, by the relative Marcus theory [2] which reduces in the simplest form to $\Delta G^{\ddagger} \approx 0{\cdot}5\ \Delta G^{\ominus} + 0{\cdot}5\lambda_{Co} + \text{const.}$, where λ_{Co} is the ligand-reorganisation term that may be deduced from the self-exchange rates of the oxidant complexes. It has been found in several cases that the correlation with $\Delta G^{\ominus}$ is accurately predicted by this equation, whereas there is no such simple correlation with the self-exchange reaction rates.[3,4] In other cases a linear free-energy relation holds with rather different coefficients.[5,6]

We have investigated a number of cobaloximes polarographically; [7] there is a difference of 0·5 V between the first half-wave potentials of $[Co(Hdmg)_2(NH_3)_2]^+$ and $[Co(Hdmg)_2(NH_3)Cl]$ [Hdmg = dimethylglyoximato-(1−)], enough to account for a difference in reaction rate of several orders of magnitude if the quoted free-energy relation is applicable. We have therefore studied the kinetics of reduction by $V^{2+}(aq)$ of a number of cobaloximes for which the Co^{III}–Co^{II} half-wave potential lies in this range.

RESULTS AND DISCUSSION

Four complexes of the type $[Co(Hdmg)_2L_2]^+$ were studied [L = pyridine (py), aniline, 3,5-Me_2py, and ethylamine]. The results are presented in Table 1. As in the case of the bis(ammine) complex,[1] the low solubility of the perchlorate salts prevented a study of the acid dependence of the reactions in a medium of this anion; a few experiments were carried out in 1M-chloride media,[*] otherwise the medium used was $I = 0{\cdot}1$M maintained with sodium perchlorate.

The observed dependences on $[H^+]$ are not very conclusive. We have indicated previously that a positive dependence is expected when the rate-determining step is the electron-transfer process,[1,8] while in a substitution-controlled reaction the reverse might be expected. The latter holds in the case of L = $EtNH_2$, where the complex reacted at a rate similar to that when L = NH_3; [1] the activation parameters (Table 2) are also strikingly similar, indicating that the same inner-sphere mechanism operates. When L = $PhNH_2$, the positive $[H^+]$ dependence suggests a different mechanism, although the rate of reaction was not high enough to preclude an inner-sphere mechanism; the virtual absence of any dependence on acidity when L = py remains inexplicable.

The activation parameters (Table 2) present a much clearer picture. The two types of reaction mechanism are very distinct: inner-sphere reactions, with similar parameters to those observed in many other such reactions,[1] and outer-sphere reactions where $\Delta S^{\ddagger}$ is nearly constant at *ca.* −31 cal K^{-1} mol^{-1} but $\Delta H^{\ddagger}$ varies considerably. We have outlined in some detail the assignment of mechanisms to V^{2+} reductions of the bis(ammine) and the two amminehalogeno-complexes,[1] and similar arguments apply here. The data for L = NH_3 and $EtNH_2$

TABLE 1

Reactions of $[Co(Hdmg)_2L_2]^+$ with $V^{2+}(aq)$ at $I = 0{\cdot}1$M ($NaClO_4$)

L	θ_c/°C	$10^4[V^{2+}]$/M	$10^2[H^+]$/M	k_2/ l mol^{-1} s^{-1}
$EtNH_2$ [a]	25·0	9·25	4·73	0·450
	25·0	23·1	4·73	0·428
	25·0	46·3	4·73	0·397
	25·0	46·3	4·73 [b]	1·05
	25·0	46·3	91·8 [b]	0·749
	15·1	46·3	4·73	0·180
	19·9	46·3	4·73	0·298
	32·0	46·3	4·73	0·882
	39·7	46·3	4·73	1·53
Py [c]	25·0	4·62	3·80	3·74
	25·0	9·25	3·80	3·92
	25·0	18·5	3·80	3·89
	25·0	9·25	0·945 [b]	8·29
	25·0	9·25	97·6 [b]	7·98
	13·2	9·25	0·945	2·16
	19·0	9·25	0·945	2·94
	31·1	9·25	0·945	5·03
	38·6	9·25	0·945	6·89
$PhNH_2$	25·0	9·25	0·945	5·30
	25·0	4·63	0·945	5·32
	25·0	18·5	0·945	5·23
	25·0	9·25	0·945 [b]	15·1
	25·0	9·25	98·9 [b]	21·4
	13·0	9·25	0·945	2·93
	19·6	9·25	0·945	4·23
	31·7	9·25	0·945	7·15
	39·7	9·25	0·945	9·66
3,5-Me_2py [e]	12·7	38·6	3·27	0·534
	19·8	37·0	3·78	0·711
	25·0	38·6	3·27	0·982
	30·6	37·0	3·78	1·42
	35·4	37·0	3·78	1·75
	40·3	37·0	3·78	2·44

[a] λ = 290 nm, $[Co^{III}] \approx 5{\cdot}0 \times 10^{-5}$M. [b] $I = 1{\cdot}0$M (NaCl). [c] λ = 285 nm, $[Co^{III}] \approx 2{\cdot}5 \times 10^{-5}$M. [d] λ = 325 nm, $[Co^{III}] \approx 2{\cdot}5 \times 10^{-5}$M. [e] λ = 290 nm, $[Co^{III}] \approx 1{\cdot}3 \times 10^{-5}$M.

TABLE 2

Activation parameters for reduction by $V^{2+}(aq)$

Oxidant	$\Delta H^{\ddagger}$/ kcal mol^{-1}	$\Delta S^{\ddagger}$/ cal K^{-1} mol^{-1}	Proposed mechanism
$[Co(Hdmg)_2(NH_3)Cl]$	5·40 ± 0·13	−32·9 ± 0·4	O.s.*
$[Co(Hdmg)_2(NH_3)Br]$	5·67 ± 0·13	−31·0 ± 0·4	O.s.*
$[Co(Hdmg)_2(py)_2]^+$	7·53 ± 0·14	−30·6 ± 0·5	O.s.
$[Co(Hdmg)_2(NH_2Ph)_2]^+$	7·03 ± 0·17	−31·6 ± 0·6	O.s.
$[Co(Hdmg)_2(NH_3)_2]^+$	14·5 ± 0·1	−11·0 ± 0·4	I.s.*
$[Co(Hdmg)_2(NH_2Et)_2]^+$	14·73 ± 0·42	−10·7 ± 1·4	I.s.
$[Co(Hdmg)_2(3,5\text{-}Me_2py)_2]^+$	9·85 ± 0·44	−25·5 ± 1·5	Both

* Ref. 1. O.s. = outer sphere, I.s. = inner sphere.

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[*] 1M = 1 mol dm^{-3}, 1 cal = 4·184 J, 1 eV ≈ $1{\cdot}60 \times 10^{-19}$ J.

[2] R. A. Marcus, *Ann. Rev. Phys. Chem.*, 1964, **15**, 155; *J. Phys. Chem.*, 1968, **72**, 891.

[3] D. P. Rillema, J. F. Endicott, and R. C. Patel, *J. Amer. Chem. Soc.*, 1972, **94**, 394.

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[5] P. R. Guenther and R. G. Linck, *J. Amer. Chem. Soc.*, 1969, **91**, 3769.

[6] D. R. Rosseinsky, *J.C.S. Chem. Comm.*, 1972, 225.

[7] R. H. Prince and M. G. Segal, *Inorg. Chim. Acta*, 1974, **11**, L35.

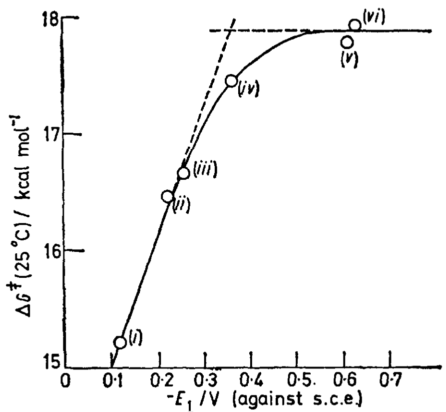
[8] R. H. Prince and M. G. Segal, *Nature*, 1974, **249**, 246.

imply a substitution limit of *ca.* 0·5 l mol^{-1} s^{-1} for inner-sphere reactions of complexes of this type; thus all the reactions with rate constants greater than this must proceed, at least in part, by outer-sphere mechanisms. Inner-sphere reactions with electron transfer as the rate-determining step can only be slower than the substitution limit. Assignment of mechanisms on the basis of activation parameters is well established for V^{2+}(aq); for a comparison of the data in Table 2 with other reactions of V^{2+} see, for example, refs. 1, 9, or 10. One of the oxidants that we have studied, however, fits in neither class.

We set out deliberately to find a ligand which would give us a cobaloxime whose reduction potential was intermediate between those of the bis(ammine) and bis(pyridine) complexes. Since there is a correlation between the first $E_{\frac{1}{2}}$ observed polarographically and the pK_a of the axial ligands,[7] this required a ligand of rather stronger basicity than py hence the choice of 3,5-Me_2py. The activation parameters for this cobaloxime were in between those of the two groups and the rate constant at 25 °C was just twice that of those reactions we take to be inner sphere. Hence the data are consistent with a reaction in which both inner- and outer-sphere paths contribute to the observed reaction. Similar parallel inner- and outer-sphere reactions have been discussed elsewhere [11,12] and have in fact been observed in the reductions of two oxalato-complexes of cobalt(III).

The Free-energy Relation.—The relation between $\Delta G^\ddagger$ and $E_{\frac{1}{2}}$ is illustrated in the Figure. The half-waves are reversible [7] and so the values of $E_{\frac{1}{2}}$ differ from $E^\ominus$ of reaction only by a constant;[13] thus such a plot illustrates the applicability or otherwise of the relative Marcus theory. The theoretical curve shown was calculated on the basis of contributions to the total rate constant from both inner- and outer-sphere paths. The inner-sphere contribution was taken as constant, equal to the mean of the two observed inner-sphere reactions; the outer-sphere contribution was calculated on the basis that a linear free-energy relation is applicable to this system, inasmuch as $\Delta G^\ddagger = \alpha\Delta G^\ominus + \beta$. The three reactions which are thought to be outer sphere, and have measurable half-wave potentials, do lie very close to a straight line {the first half-wave for [Co(Hdmg)$_2$(NH_3)Br] is $\geqslant 0$ (ref. 7)}. From a least-squares fit through the points (*i*)—(*iii*), we obtain $\alpha = 10{\cdot}7 \pm 1{\cdot}1$ kcal mol^{-1} eV^{-1} and $\beta = 14{\cdot}0 \pm 0{\cdot}2$ kcal mol^{-1}. The value of α, converted to a dimensionless number, is $0{\cdot}46 \pm 0{\cdot}05$. This is in good agreement with the value of 0·5 predicted by the Marcus theory; this indicates that neither the change in charge, nor any possible change in the ligand-reorganisation barriers of the cobaloximes, have any significant effect. Clearly the test of this theoretical curve is that a point other than those used in its calculations should lie on it. The fact that point (*iv*) lies so close to the curve, in the region where the free-energy relation is non-linear, must be regarded as confirming the validity of our interpretation regarding the mechanisms involved.

The Inner-sphere Mechanism.—The precise mechanism of the inner-sphere processes is of interest. The only possible binding site for the reductant in these species is at one, or more likely two, of the oxime oxygen atoms. Binuclear complexes in which two metal ions are doubly linked through the N and O atoms of oxime ligands have been postulated for other cobaloxime derivatives, such as [{Co(Hdmg)$_2$L}$_2$] (L = Me [14] or neutral bases [15]). Such binuclear species are well established for Cu^{II}, notably [{Cu(Hdmg)$_2$}$_2$].[16] In these cases, the six-membered ring containing two metal, nitrogen, and oxygen atoms is not planar but in the chair configuration. In one case, however, with another chelating oxime ligand a Cu^{II} dimer has been found in which the metal ions and bridging NO bonds are coplanar.[17]



Free-energy relation for the V^{2+}(aq) reduction of cobaloximes: (*i*) [Co(Hdmg)$_2$(NH_3)Cl]; (*ii*)—(*vi*), [Co(Hdmg)$_2$L$_2$]$^+$ where L = PhNH_2 (*ii*), py (*iii*), 3,5-Me_2py (*iv*), NH_3 (*v*), and EtNH_2 (*vi*). The theoretical curve was calculated on the basis of contributions from inner- and outer-sphere paths (broken lines)

An inner-sphere electron-transfer reaction through a bridging unit greater than a single atom has not previously been observed except where there is formal conjugation between the two metal binding sites.[18] However, although no such conjugation exists here, one might expect considerable π delocalisation over the NO bond in an oxime. Moreover, it has been shown that in the planar Cu^{II} dimer superexchange occurs between the metal ions at room temperature:[17] the complex is virtually diamagnetic. It seems reasonable to suggest that, if magnetic interaction of this kind can occur through such

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[18] Examples of this type of reaction are discussed by, for example, H. Taube and E. S. Gould, *Accounts Chem. Res.*, 1969, **2**, 321.

a bridging unit, then there is a path for electron transfer to take place.

In our initial examination of the Cr^{2+}(aq) reduction of $[Co(Hdmg)_2(NH_3)_2]^+$ we were unable to find any direct evidence for such an inner-sphere process.[8] We have re-examined this reaction, however, on a larger scale and can now report that ligand transfer does indeed take place between cobaloxime and reductant. By separating the products of this reaction on an ion-exchange column we were able to isolate a fraction in which dimethylglyoxime was eluted together with Cr^{III} and was therefore bound to it. Unfortunately, we cannot as yet state whether the ligand : metal ratio is 1 : 1 or 2 : 1, as the fraction contains a certain amount of free Cr^{3+}(aq), but the amount of free H_2dmg isolable suggests a 1 : 1 ratio in the Cr^{III} complex. The inner-sphere mechanism, however, is clearly proven for this reaction.

Conclusions.—The outer-sphere reductions of cobaloximes by V^{2+}(aq) obey a linear free-energy relation; the coefficient relating $\Delta G^{\ddagger}$ to $\Delta G^{\ominus}$ agrees closely with that predicted by the Marcus theory. A non-linear free-energy relation is observed over a wide range of electrode potentials when we include the region in which inner-sphere reaction dominates. This form of relation can, in fact, be predicted for reactions of V^{2+}(aq) with any series of oxidants provided this covers a sufficient range of measurable $E^{\ominus}$ values without altering the fundamental nature of the oxidants; these cobaloximes comprise the first such system to be studied. We can even envisage a more complex relation, for if a less efficient bridging ligand is used the inner-sphere reactions might fall below the substitution limit and then produce a second, linear, rising portion of the plot of $\Delta G^{\ddagger}$ *versus* $\Delta G^{\ominus}$. A free-energy relation covering such slower, inner-sphere, reactions has been observed in penta-aminecobalt(III) carboxylates.[19]

It has been suggested [11] that when V^{2+} is used to reduce a number of azidocobalt(III) complexes a change in mechanism from inner to outer sphere occurs with changes in the non-bridging ligands. (The data for the supposed outer-sphere reaction are extremely limited.) The authors assign this change only to an undefined ' non-bridging-ligand perturbation '. As in the case of penta-amminehalogenocobalt(III) complexes,[10] electrode-potential data are unavailable, but it is tempting to suggest that in both cases the changes in mechanism may be brought about simply by the effect of these potentials on the outer-sphere path.

EXPERIMENTAL

Full details of the experimental methods used for the kinetic studies have been published elsewhere.[1] The cobaloximes were synthesised from $CoCl_2 \cdot 6OH_2$, dimethylglyoxime (H_2dmg), and excess of ligand, oxidised by air in EtOH, and converted to perchlorate salts by double decomposition. Other reagents were prepared and analysed as described.[1]

Chromium(II) *Reduction of* $[Co(Hdmg)_2(NH_3)_2]^+$.—The nitrate salt (0·32 g) of the cobaloxime was dissolved in deaerated water (50 cm^3) in a flask (100 cm^3) which was flushed with N_2 and sealed with a serum cap. A solution of Cr^{2+}(aq) (7·5 cm^3), made by reducing 0·1M-$Cr[ClO_4]_3$ in 0·16M-$HClO_4$ on zinc amalgam, was injected followed by 4N-$HClO_4$ (3 cm^3) after 2 min. The solution was allowed to stand for 20 min, filtered to remove unreacted cobaloxime perchlorate, and then extracted with diethyl ether (4 × 50 cm^3). The ether solution was dried on $CaCl_2$ and then evaporated to dryness. The residue was shown to be H_2dmg, with a slight trace of biacetyl monoxime, by t.l.c. on silica (10% MeOH–$CHCl_3$) and by its i.r. spectrum (yield 53 mg or 42% based on the amount of cobaloxime reacted). The aqueous solution was absorbed onto a column of Dowex 50 W X8 cation-exchange resin (*ca.* 5 × 1 cm diameter) and eluted successively with water, 1N- and 3N-$HClO_4$. Only Co^{2+}(aq) appeared in the second fraction; a dark green, rather broad, band was eluted by the stronger acid. U.v. and visible spectra of this fraction showed peaks similar to Cr^{3+}(aq) and to aqueous H_2dmg; when treated with NaOH, the u.v. absorption shifted to that characteristic of the $Hdmg^-$ ion in aqueous solution.

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