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Polarography of Cobaloximes

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The reduction of bis(dimethylglyoximato)cobalt (III) complexes, or cobaloximes, has been investigated polarographically by a number of workers[1-4]. Since the initial report by Maki[1], however, interest has centred largely on alkyl derivatives of these complexes. We have had reason to investigate a series of cationic and neutral cobaloximes with axial nitrogen- and sulphur-donor ligands.

In aqueous solution, three one-electron half-waves are observed in most cases, corresponding to stepwise reduction of the Co ion from Co(III) to Co(0) (see Table I). Only the first of these is reversible, a plot of E *vs.* log $i/i_d - i$ yielding a straight line of gradient in the range 55 - 65 mV. When the axial ligands are N-donors, there is a clear correlation between the first half-wave potential and the basicity of the ligands, with the apparent exception of cyclohexylamine. Although several factors are probably involved, this is consistent with the raising in energy of the lowest anti-bonding orbital with increasing σ-donor strength of the ligands, and is in agreement with the results of Hohokabe and Yamazaki[2], although the process under consideration is somewhat different. However, no such correlation exists for the second half-wave; if the reaction involved no change in the coordination shell, as proposed by Maki[1], then the second redox potential should follow the same trend as the first. However, the constancy of the Co^I–Co^0 potential suggests to us that the species being reduced is the same in all cases.

TABLE I. Half-wave Potentials for Cobaloximes (Volts *vs.* S.C.E.)[a]

A. Complexes of the type $[Co(DH)_2L_2]^+$

L	$Co^{III} \rightarrow Co^{II}$	$Co^{II} \rightarrow Co^{I}$	$Co^{I} \rightarrow Co^{0}$
$EtNH_2$	−0.63	−0.99	−1.18
NH_3	−0.61	−0.99	−1.19
Cyclohexylamine	−0.50	−1.01	−1.19[b]
3,5-Lutidine	−0.36	−0.93	−1.18
Pyridine (py)	−0.26	−0.89	~−1.19[c]
Aniline	−0.22	−0.97	−1.17
Thiourea	>0	−0.95	~−1.22[c]
Thioacetamide (Thac)	>0	−0.92	−1.17

B. Complexes of the type $[Co(DH)_2LX]$

L	X	$Co^{III} \rightarrow Co^{II}$	$Co^{II} \rightarrow Co^{I}$	$Co^{I} \rightarrow Co^{0}$
NH_3	Cl	−0.12	−1.01	1.18
Py	Cl	>0	−0.94	~−1.18[c]
Me_2S	Cl	>0	−1.03	−1.20
Thac	Cl	>0	−0.96	~−1.2 [d]
NH_3	Br	>0	−1.01	1.18[b]

[a] 10^{-4} to 10^{-3} *M* in 0.1 *M* aq. KCl, containing approx. 0.002% Triton X-100. T = 25.0 ± .2 °C. [b] Not well defined. [c] Maximum wave. [d] Inflection only.

Schrauzer has proposed that the cobaloximes(I) are 5-coordinate in solution, and has produced convincing spectroscopic evidence for this structure[4]; π-acceptor ligands are expected to be bound more strongly in the apical position than strong σ-donors. In fact, the results (presented in reference 3) of polarographic investigation in acetonitrile show that here also the third half-wave is constant, except in the cases where trialkylphosphine or CN^- are bound to Co. We deduce, therefore, that in all the examples we have studied, cleavage of the bonds between Co(I) and both the axial ligands is rapid. Thus assuming a 5-coordinate structure for the complex the second half-wave corresponds *either* to the process

$$[Co^{II}(DH)_2L_2] \xrightarrow[+H_2O]{} [Co^{I}(DH)_2(OH_2)]^- + 2L$$

or to the reaction

$$[Co^{II}(DH)_2L_2] \rightarrow [Co^{I}(DH)_2L]^- + L$$

which is then followed by the rapid displacement of L by H_2O in solution. Hence the third half-wave in all cases corresponds to the reduction of $[Co^{I}(DH)_2(OH_2)]^-$.

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References

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