The Role of Thiourea Ligands in Electron-transfer Reactions of Cobalt(III)

By Reg H. Prince and Michael G. Segal
(*University Chemical Laboratory, Lensfield Road, Cambridge* CB2 1EW)

Summary Kinetic studies show that the reaction of bis(dimethylglyoximato)bis(thiourea)cobalt(III) with V^{2+} proceeds by an outer-sphere mechanism, whereas that with Cr^{2+} probably proceeds by an inner-sphere mechanism *via* an intermediate with a simple Cr–S–Co bridge.

The presence of sulphur-donor ligands in transition-metal complexes has been shown in several cases to have a marked effect on the rates of electron-transfer reactions, either as bridging[1] or non-bridging[2] ligands in inner-sphere processes. Since many of the metal-containing proteins which undergo electron-transfer reactions *in vivo* contain metal-bound sulphur atoms at the active site,[3] the role of such ligands in these reactions is of great interest. We have investigated the role played by thiourea (thu) ligands in the reduction of $[Co(dmgH)_2(thu)_2]^+$, where $dmgH^-$ is the mono-anion of dimethylglyoxime; this is one of only very few Co^{III} complexes in which a C=S group is known to bind to the metal in the inner co-ordination sphere.[4]

The results of the kinetic study of the reduction of this complex by V^{2+} and Cr^{2+} are given in the Table. Since at least three forms of the complex are possible in solution, depending on pH,[5,6] the effects of varying the acidity were not investigated. Under the dilute acid conditions used, however, only the mono-cation is likely to be present in any significant concentration.

With V^{2+} as reductant, the temperature dependence of the reaction yields activation parameters of 5·02 kcal mol^{-1} for $\Delta H^{\ddagger}$ and $-30{\cdot}7$ cal mol^{-1} K^{-1} for $\Delta S^{\ddagger}$. These values are typical of those for an outer-sphere process.[7] Furthermore, the mean second-order rate constant of 255 l mol^{-1}

Table

Second-order rate constants for the reduction of $[Co(dmgH)_2(thu)_2]^{+}$[a]

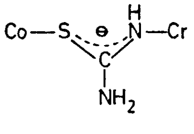
Reductant	Reductant concentrations /10^{-3} M	T/°C	k_2/l mol^{-1} s^{-1}
V^{2+}[b]	5·79	25·0	$2{\cdot}56 \times 10^2$
V^{2+}	2·90	25·0	$2{\cdot}46 \times 10^2$
V^{2+}	1·45	25·0	$2{\cdot}65 \times 10^2$
V^{2+}	2·90	17·0	$1{\cdot}93 \times 10^2$
V^{2+}	2·90	31·7	$3{\cdot}09 \times 10^2$
V^{2+}	2·90	39·5	$3{\cdot}88 \times 10^2$
Cr^{2+}[c]	2·30	25·0	$1{\cdot}21 \times 10^4$
Cr^{2+}	3·42	25·0	$1{\cdot}23 \times 10^4$
Cr^{2+}	4·15	25·0	$1{\cdot}18 \times 10^4$

[a] $[Co^{III}]$ = *ca.* 1×10^{-4} M; $\mu = 0{\cdot}10$ M ($NaClO_4$). All runs obeyed pseudo-first order kinetics up to at least three half-lives. The constancy of the observed k_2 values at 25 °C implies a simple second-order rate law at constant $[H^+]$ for both reductants.
[b] $[H^+] = 4{\cdot}90 \times 10^{-2}$ M; reactions were followed at 325 nm.
[c] $[H^+] = 1{\cdot}25 \times 10^{-2}$ M; reactions were followed at 300 nm.

s^{-1} at 25 °C is well above the substitution limit for V^{2+}, and so an outer-sphere mechanism is again indicated. We have already shown[7] that the rates of V^{2+} reduction of other cobaloximes were related to their polarographic half-wave potentials; extrapolation of this relation shows that the rate constant observed here is predicted for a complex with a half-wave potential of almost exactly zero relative to the S.C.E. Since the first reduction wave of this complex has been found to be $\geqslant 0$,[8] this is consistent with the thiourea complex obeying the free-energy relation observed previously.

The reaction with Cr^{2+} proceeds by a different mechanism. The rate of reduction is much greater than that observed when other cobaloximes with N-donor axial ligands react with this reductant; the mechanism of those reactions is thought to be inner-sphere, with the oxime groups acting as bridging ligands.[7,9] After separating the products of this reaction by ion-exchange, we have identified the major Cr^{III} product as a 1 : 1 complex with thiourea. Thus the reaction probably proceeds *via* an inner-sphere mechanism, in which a thiourea ligand bridges the two metal ions.

The bound thiourea has two possible sites for co-ordination of the reductant in the intermediate, binuclear complex required for such a mechanism: the S atom, already bound to the cobalt ion, or one of the N atoms. If we consider this ligand to be analogous to an amide in structure, then we would expect the N-bound intermediate to be reactive only if deprotonated, as in structure (A), since inner-sphere reaction through a bridge of this type has been observed with amide complexes only when deprotonated.[10] Since the ligand protons are quite acidic in the cobaloxime,[6] and would become much more so on binding of the nitrogen to another cation, this deprotonated intermediate could possibly exist even in the dilute acid conditions used.



(A)

As a test for this mechanism, we performed the same reaction on the cobaloxime with tetramethylthiourea as the axial ligands. The Cr^{III} product, isolated in solution by ion exchange, is very similar in its electronic spectra and chemical reactions to that obtained with the unsubstituted thiourea. Thus, it seems that the same form of product appears in both reactions, implying the same intermediate. Since the tetramethylthiourea complex cannot lose a proton, this suggests that the intermediate contains a simple metal–sulphur–metal bridge rather than the bridge in structure (A). With thiolate-type ligands[1] this sort of bridge is known to be very efficient; the rate of the reaction studied here shows that the sulphur atom in thiourea is also an effective mediator for the conduction of an electron between metal ions.

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[1] C. Shea and A. Haim, *J. Amer. Chem. Soc.*, 1971, **93**, 3055; R. H. Lane and C. E. Bennett, *ibid.*, 1970, **92**, 1089.

[2] J. H.Worrell and T. A. Jackman, *J. Amer. Chem. Soc.*, 1971, **93**, 1044; J. H. Worrell, R. A. Goddard, E. M. Gupton, and T. A. Jackman, *Inorg. Chem.*, 1972, **11**, 2734.

[3] See, for example, L. E. Bennett, *Progr. Inorg. Chem.*, 1973, **18**, 1.

[4] A. V. Ablov, N. N. Proskina, A. P. Sadovskii, L. N. Mazalov, and L. I. Nasonova, *Russ. J. Inorg. Chem.*, 1972, **17**, 1494.

[5] A. L. Crumbliss, J. T. Bowman, P. L. Gaus, and A. T. McPhail, *J.C.S. Chem. Comm.*, 1973, 415; R. D. Gillard and G. Wilkinson, *J. Chem. Soc.*, 1963, 6041.

[6] A. V. Ablov, B. A. Bovykin, and N. H. Samus', *Russ. J. Inorg. Chem.*, 1966, **11**, 31.

[7] R. H. Prince and M. G. Segal, *J.C.S. Dalton*, 1975, 1245.

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

[9] M. G. Segal, Ph.D. Thesis, Cambridge, 1975.

[10] R. J. Balahura and L. Hutley, *Canad. J. Chem.*, 1973, **51**, 3712; E. S. Gould, *J. Amer. Chem. Soc.*, 1968, **90**, 1740.