Oxidation of Co-ordinated Thiol to Co-ordinated Disulphide *via* Induced Electron Transfer

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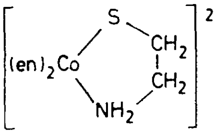
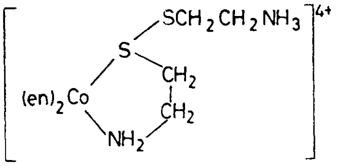
Summary The reaction of an excess of [(2-mercaptoethylamine)-*N,S*]bis(ethylenediamine)cobalt(III) with the one-equivalent oxidant Np^{VI} (or $[Co_{aq}]^{3+}$) in aqueous $HClO_4$ gives [(2-aminoethyl 2-ammonioethyl disulphide-*N,S*]-bis(ethylenediamine)cobalt(III) *via* induced electron transfer and a presumed radical ion dimer intermediate.

The following observations define the oxidation of [(2-mercaptoethylamine)-*N,S*]bis(ethylenediamine)cobalt(III)[1] (I) by the one-equivalent oxidants Np^{VI} and $[Co_{aq}]^{3+}$; the product of the reaction is shown to be (II), the first cobalt(III) disulphide complex to be reported.



(I)

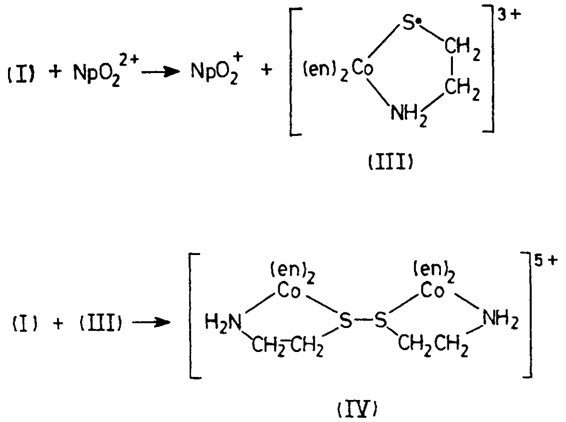


(II)

Compound (I) is oxidized by Np^{VI} (equation 1) within the time of manual syringe mixing;§ conditions: $[I]_{initial}$ = *ca.* 0·05 M, $([I]/[Np^{VI}])_{initial}$ = 6·0. The products were separated by ion-exchange chromatography. Therefore

$$2(I) + NpO_2^{2+} + 5H^+ \rightarrow (II) + Co_{aq}^{2+} + NpO_2^{+} + 2enH_2^{2+} \qquad (1)$$

(II) results from (I) by a two-equivalent oxidation, one equivalent arising from Np^{VI} and the other from a molecule of (I) which is in turn converted into $[Co_{aq}]^{2+}$. The elution characteristics of (II) are consistent with a 4+ charge. The reaction of (I) with $[Co_{aq}]^{3+}$ is similar. The u.v. and visible spectra of (I) and (II) are similar,¶ indicating that on going from (I) to (II) there is no drastic change in the spectrochemical environment about cobalt(III). Elemental analysis of a red-orange, hygroscopic solid precipitated (with ethanol) from a 6M HCl ion-exchange eluant containing (II) supports its proposed formulation. The proposed structure of (II) as a complex containing co-ordinated cystamine receives further support from the observation that it is quantitatively reduced to (I) by Sn^{II} in 6M HCl. An excess of cysteamine in 6M HCl also effects this reduction.



(III)

(IV)

Scheme

The oxidation of free thiols, RSH, by hydroxyl radicals proceeds *via* consecutive formation of RS• and RSSR$^-$.[2] By analogy, the reaction of (I) with a one equiv. oxidant could take place as shown in the Scheme. The cobalt(III) radical ion dimer (IV) presumably then decays by internal electron transfer, the resultant labile cobalt(II) escaping to solution as $[Co_{aq}]^{2+}$ and leaving the newly formed S–S bond (equation 2).

$$(IV) + 5H^+ \rightarrow (II) + Co_{aq}^{2+} + 2enH_2^{2+} \qquad (2)$$

This mode of metal-thiol interaction is not inherently limited to systems containing the Co^{II}–Co^{III} couple, but may also function in systems of biological importance which contain the Fe^{II}–Fe^{III} and Cu^{I}–Cu^{II} couples.

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§ Our original report (C. J. Weschler, J. C. Sullivan, and E. Deutsch, *Inorg. Chem.*, 1974, **13**, 2360) that 'no Np^{V} can be detected even after several hours' in the reaction of Np^{VI} with (I) was based on an erroneous interpretation of spectra of the reaction mixtures.

¶ For (I), λ_{max} = 482 (ϵ 140 l mol^{-1} cm^{-1}) and 282 (ϵ 14,000) nm; for (II), λ_{max} = 492 (ϵ 175) and 275 (ϵ 8300) nm.

[1] (a) L. E. Asher and E. Deutsch, *Inorg. Chem.*, 1973, **12**, 1774; (b) R. C. Elder, L. R. Florian, R. E. Lake, and A. M. Yacynych, *ibid.*, p. 2690.

[2] (a) G. E. Adams, G. S. McNaughton, and B. D. Michael, 'The Chemistry of Ionization and Excitation,' eds. G. R. A. Johnson and G. Scholes, Taylor and Francis, London, 1967, pp. 281—293; (b) G. E. Adams, G. S. McNaughton, and B. D. Michael, *Trans. Faraday Soc.*, 1968, **64**, 902; (c) M. Z. Hoffman and E. Hayon, *J. Phys. Chem.*, 1973, **77**, 990.