Co-ordination Stabilization of Reactive Molecules: Preparation of ***trans***-$[(en)_2Co(OH_2)(S_3O_3)]^+$, a Cobalt(III) Complex containing Disulphane Monosulphonate

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Summary *cis*-$[(en)_2Co(S_2O_3)_2]^-$ is oxidized by aqueous iodine to yield free sulphate and *trans*-$[(en)_2Co(OH_2)(S_3O_3)]^+$, a moderately stable complex containing the very reactive ligand, disulphane monosulphonate.

RECENT research has shown that unstable sulphur-containing molecules such as sulphenic acids and sulphenyl iodides are stabilized by co-ordination to cobalt(III).[1-3] Thus, the sulphenato complex,[1] $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$ (en = ethylenediamine), and the sulphenyl iodide complex,[3] $\{[(en)_2Co(SCH_2CH_2NH_2)]_2I\}^{5+}$, have sufficient stability to permit crystallization and characterization by single crystal *X*-ray analysis, whereas non-co-ordinated sulphenic acids and sulphenyl iodides are extremely reactive species which are often postulated as reaction intermediates.[4,5] While attempting to prepare, by iodine oxidation of *cis*-$[(en)_2Co(S_2O_3)_2]^-$, a complex containing co-ordinated tetrathionate, we have encountered an unusual example of co-ordination stabilization of a reactive molecule. The following evidence leads us to conclude that, while the desired tetrathionate complex may be formed initially, it is unstable and decomposes with S–S and Co–S bond fission to yield a moderately stable complex, formulated *trans*-$[(en)_2Co(OH_2)(S_3O_3)]^+$.

The reaction of aqueous iodine with a slight excess of *cis*-$[(en)_2Co(S_2O_3)_2]^-$ leads to the release of one mole of sulphate, 1·7 mole of H^+ and 0·85 mole of the principal cobalt(III) product per mole of I_2 consumed. The mole of sulphate is the two-equivalent oxidation product of one thiosulphate ligand and accounts for the two equivalents of oxidizing power consumed in the reaction The principal cobalt(III) product, purified by ion exchange chromatography and isolated as a chloride derivative, has a S/Co ratio of 3 and an elemental analysis† consistent with the formulation, $[(en)_2Co(Cl)(S_3O_3)]$

The cationic reaction product exhibits properties characteristic of cobalt(III) complexes containing a moderately labile water ligand, *e g* , *trans*-$[(en)_2Co(OH_2)(SO_3)]^+$[6] and *trans*-$[(en)_2Co(OH_2)(S_2O_3)]^+$[7] Thus, in dilute aqueous solutions *trans*-$[(en)_2Co(OH_2)(S_3O_3)]^+$ is yellow-brown, but the isolated chloride derivative is dark green suggesting co-ordination of the chloride anion in the solid state, dissolution of the dark green solid, *trans*-$[(en)_2Co(Cl)(S_3O_3)]$, regenerates the yellow-brown aquo derivative *trans*-$[(en)_2Co(OH_2)(S_3O_3)]^+$ Likewise, addition of NO_2^- or SCN^- to solutions of *trans*-$[(en)_2Co(OH_2)(S_3O_3)]^+$ rapidly yields products of zero formal charge, presumably *trans*-$[(en)_2Co(NO_2)(S_3O_3)]^0$ and *trans*-$[(en)_2Co(NCS)(S_3O_3)]^0$ Since sulphur-donating ligands are known to induce kinetic *trans* effects in cobalt(III) complexes,[6–8] the yellow-brown reaction product is taken to have a water ligand situated *trans* to a co-ordinated sulphur atom

The i r spectrum of the solid chloride derivative contains bands characteristic of the *trans*-bis(ethylenediamine)-cobalt(III) group as well as bands attributable to the $-SO_3$ group However, some of these latter bands are shifted relative to those observed in *trans*- and *cis*-$[(en)_2Co(S_2O_3)_2]^-$ salts indicating that the $-SO_3$ group of *trans*-$[(en)_2Co(Cl)(S_3O_3)]$ is in a somewhat modified environment

All *trans*-$[(en)_2Co(L)(S_2O_3)]^{n+}$ complexes exhibit an intense band in the 360—380 nm region, $\lambda_{max} = 367$, 375, and 363 nm for L = H_2O, NO_2^-, and NCS^-, respectively ‡ Intense charge-transfer bands between 350 and 370 nm have been shown to be characteristic of the Co–S(O)–R bonding array,[1] and thus it is likely that the *trans*-$[(en)_2Co(L)(S_3O_3)]^{n+}$ complexes contain a Co–S(S)–SO_3 bonding array

In either perchlorate or chloride media *trans*-$[(en)_2Co(OH_2)(S_3O_3)]^+$ decomposes overnight at ambient temperature depositing elemental sulphur and producing higher charged cationic cobalt(III) species Likewise, silver(I), mercury(I), and mercury(II) react over several hours with *trans*-$[(en)_2Co(OH_2)(S_3O_3)]^+$ to deposit mixed sulphides These qualitative observations are consistent with the chemistry expected for the Co–S(S)–SO_3 bonding array, and with the chemistry of non-co-ordinated disulphane monosulphonate[9]

Free disulphane monosulphonate reacts readily with water,[9] but this ligand appears to acquire considerable thermal stability when co-ordinated to cobalt(III) The *trans*-$[(en)_2Co(OH_2)(S_3O_3)]^+$ is, however, quite photosensitive, ordinary laboratory fluorescent lighting causing *ca* 50% decrease in the intensity of the 367 nm band of a 10^{-4} mol l^{-1} solution in *ca* 60 min

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† Satisfactory elemental analytical data were obtained for this compound

‡ Visible-u v spectrophotometric parameters for *trans* $[(en)_2Co(OH_2)(S_3O_3)]^+$ λ in nm and ϵ, given in parentheses, in l mol^{-1} cm^{-1} 600sh(73), 520(97), 367(9,000), 212(14 000)

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