Formation of a Co–O_2 Complex by the Co-ordination of Free Superoxide Ion

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Summary The Co^{III} complex aquocobalamin (vitamin B_{12a}) reacts with solutions of O_2^- in dimethylformamide to give superoxocobalamin.

BOTH the bond-lengths and bond-angles of the Co–O_2 group as shown by X-ray analysis,[1] and the low values of the cobalt coupling constants of the e.s.r. spectra[2] indicate that the mononuclear complexes[3] formed by the reaction of Co^{II} complexes with O_2 are better formulated as Co^{III} complexes with a superoxide (O_2^-) ligand. This formulation suggests that one should also be able to prepare these complexes by simple ligand substitution reactions of the Co^{III} complex involving the co-ordination of free O_2^-. We have, therefore, studied the reaction of O_2^- with aquocobalamin (vitamin B_{12a}) which, unlike most other Co^{III} complexes, can undergo rapid ligand substitution in the axial positions.[4] Superoxocobalamin is, of course, formed by the usual reaction of O_2 with the Co^{II} complex, vitamin B_{12r}, at low temperature.[5]

Solutions of superoxide in dimethylformamide (DMF) were prepared by the electrochemical reduction of dissolved O_2.[6] The DMF was distilled from K_2CO_3, stored over molecular sieve type 5A, and Bu_4NBF_4 added to give a 0·1M-solution of electrolyte. A stream of dry air was bubbled through 25—40 ml portions of the solution in a cell containing a Hg pool cathode, a Pt wire anode (separated by a frit), and a standard calomel reference electrode (separated by a bridge); reduction continued for *ca.* 4 h at 0·7—0·8 V and *ca.* 5 mA. The resultant yellowish solution gave an e.s.r. signal at −170 °C with *g*-values of 1·999, 2·004, and 2·032, which are typical of the superoxide anion.[6,7] 0·5 ml samples of the solution held at −50 °C were treated with a small quantity (*ca.* 15 mg) of solid vitamin B_{12a}, stirred until the solid dissolved, transferred to an e.s.r. tube, and frozen to −170 °C (all within *ca.* 30 s). The e.s.r. spectra of these solutions (g 1·999, A_{Co} 11·8 G) were identical with that of a solution of the Co–O_2 adduct prepared by the standard method of passing O_2 into a solution of aquocobalamin in DMF reduced to the Co^{II} complex with a small quantity of $NaBH_4$ (g 1·998, A_{Co} 11·7 G).

$$Co^{II} + O_2 \rightleftharpoons [Co^{III}O_2^-] \rightleftharpoons Co^{III} + O_2^-$$

The same complex can, therefore, be formed by the two different routes shown schematically above; we do not yet know the degree of reversibility of the second reaction. As far as we are aware, this reaction provides the first example of the co-ordination of free superoxide ion to give a detectable complex, not only by a Co^{III} ion, but by any transition-metal ion, with the possible exception of certain metal-containing enzymes.[8] Its occurrence also provides a direct check on the validity of formulating these O_2-adducts as Co^{III} superoxide complexes.

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