Formation and Degradation of an Oxalato and Peroxo Bridged Dicobalt Bisdien† Dioxygen Complex: A Binuclear Complex as Host for the Activation of Two Co-ordinated Guests

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The dioxygen complex of the dicobalt bisdien complex co-ordinates with and oxidizes a bridging oxalato group, thus providing the first example of a redox reaction between two co-ordinated ligands within the cavity of a binuclear macrocyclic complex.

It has been reported previously that binuclear complexes of the macrocyclic ligand bisdien (**1**)† combine with bridging secondary donor groups to form dinuclear complexes. In fact this hexa-amine ligand has a tendency to form mononuclear rather than binuclear complexes, probably because of the flexibility of the macrocyclic ring and lack of sufficient pre-organization needed to keep the diethylenetriamine moieties separated from each other. Thus the binuclear copper(II) complex combines with a bridging imidazole[1,3] to form a complex represented by (**2**), where X–Y = the imidazole anion.[1] We have now found that oxalate (ox) also binds to the binuclear bisdien (L) cobalt(II) complex as bringing anion, to form the complex $Co_2(ox)L^{2+}$, as does ethylenediamine (en),[1] which forms $Co_2(en)L^{4+}$. Another bridging group that effectively organizes the dicobalt(II) complex of the bisdien macrocycle is dioxygen, which forms the binuclear μ-peroxo-μ-hydroxo-dicobalt-bisdien complex (**3**).[1] It had also been noted[1] that complex (**3**) undergoes two successive hydrolysis steps to form complexes containing two and three co-ordinated hydroxide ions (only one of which probably occupies a bridging position), $Co_2O_2(OH)_2L^{2+}$ (**4**) and $Co_2O_2(OH)_3L^{+}$ (**5**), resulting in strong 6-co-ordination of the formally Co^{III} centres. It is apparent, therefore that the dioxygen complex initially formed, (**3**), has two aquated co-ordination sites that may be occupied by an appropriate bidentate bridging ligand. It is now reported that the oxalate

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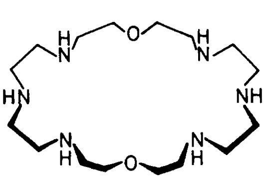
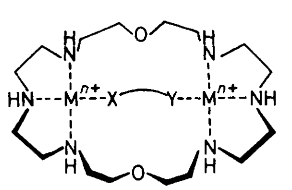
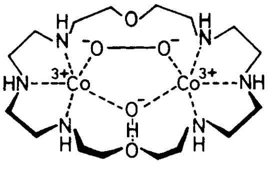
† Bisdien = 1,13-dioxa-4,7,10,16,19,22-hexa-azacyclotetracosane, [24]N_6O_2.



(**1**) bisdien base



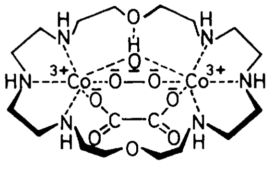
(**2**) Binuclear bridged bisdien chelate $M_2(X\text{-}Y)L^{2+}$ (X-Y = bidentate ligand)



(**3**) μ-Hydroxo-μ-peroxo-dicobalt bisdien chelate

$Co_2O_2(OH)_2L^{2+}$

(**4**)



(**6**) μ-Hydroxo-μ-oxalato-μ-peroxo-dicobalt bisdien chelate

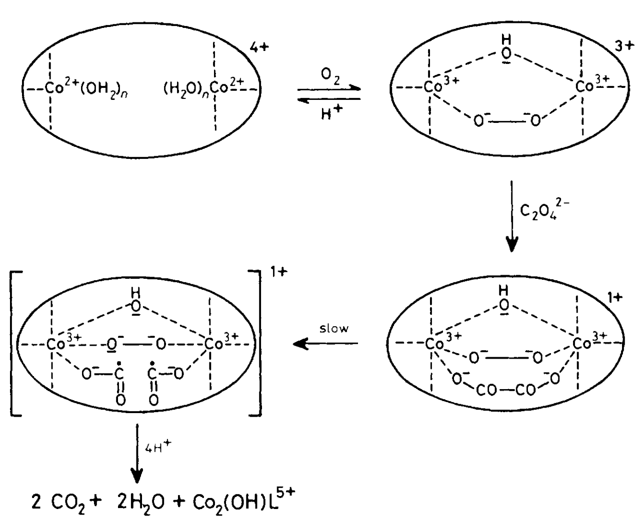
$Co_2O_2(OH)_3L^{+}$

(**5**)

anion satisfies the requirement for such a ligand, to form the complex which is schematically represented by (**6**). Equilibrium analysis by potentiometric pH measurements similar to the procedures employed previously with the ligand bisdien[1] and the tris(aminoethyl)amine analogue bistren[4] showed that between pH 8.0 and 9.6 this complex is the predominant species (>70%) in aqueous solution saturated with dioxygen, containing a 2:1:1 molar ratio of cobalt(III), bisdien, and oxalate, respectively. It is formed in this pH range at the expense of (**3**) and (**4**), which become relatively minor species in the presence of oxalate.

Measurement of the rate of metal-centred degradation of (**3**) showed it to be a relatively robust dioxygen complex [compared to dioxygen adducts of other cobalt(II)–polyamine complexes] with a first-order rate constant of $1.0 \times 10^{-3}\,s^{-1}$ at 90 °C, and pH 7.28 (to give the binuclear Co^{III}–bisdien complex and H_2O_2). The oxalato-bridged dioxygen complex (**6**), on the other hand, undergoes relatively rapid degradation to give the dicobalt(III)–bisdien complex and CO_2, with a first-order rate constant of $4.0 \times 10^{-4}\,s^{-1}$ at 45 °C. The carbon dioxide was determined quantitatively (*ca.* 95%) by acidification of the final reaction mixture and measurement of the carbon dioxide released to the inert atmosphere (purified nitrogen) by gas chromatography. The strong activation of dioxygen towards oxalate oxidation is considered to be due to simultaneous co-ordination of the oxidant and reductant to the cobalt centres. Homolytic scission of the oxalato C–C bond, with concomittant electron transfer through the metal ions to co-ordinated peroxide, results in the formation of CO_2, H_2O, and the dicobalt(III)–bisdien complex, $Co_2(OH)L^{5+}$, indicated in outline form by Scheme 1. The alternative possibility of direct reaction in the macrocyclic complex between co-ordinated peroxide and oxalate is dismissed in view of the fact that mutual coulombic repulsions would make direct contact energetically improbable. Also, the possibility of direct reaction between free unco-ordinated oxalate in solution and the dioxygen complex (**3**) has been eliminated by the fact that doubling the concentration of free oxalate has no effect on the reaction rate.

This redox reaction is the first example of a reaction between co-ordinated dioxygen and a reducing substrate co-ordinated within the same binuclear complex. The intermediate (**6**) was present to the extent of 70% of the total macrocyclic complexes present in solution at the beginning of the reaction. The binuclear Cu^I complexes of analogous ligands have been reported by Nelson and co-workers,[5,6] wherein catechol[5] and hydrazobenzene[6] as bridging groups undergo dehydrogenation by reacting with molecular oxygen. The reactions in non-aqueous media were followed by measuring dioxygen uptake. Dioxygen complexes were postulated, but, if formed, were not present in sufficient concentration to be detected. The redox reaction reported in this communication differs in two respects: the intermediate containing both dioxygen and substrate is formed in considerable concentration, and the four-electron reduction of oxygen to water is balanced by conversion of cobalt(II) to cobalt(III) and oxalate to carbon dioxide. Further work on this and related binuclear complexes is being directed toward obtaining more structural information and determining the conditions necessary to carry out these redox reactions in a catalytic mode.



Scheme 1. Proposed mechanism for oxalate oxidation by co-ordinated dioxygen in the binuclear bisdien cobalt(II) complex.

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