Autoxidation Pathways of Co^{II}-Complexes of Pyridyl-containing Pentamines involving Dioxygen Complexes as Intermediates

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Because of the lack of a low energy pathway for the extension of conjugation in the dioxygen adduct of the cobalt(II) complex of the pentamine, 2,6-bis[2-(3,6-diazahexyl)]pyridine, its autoxidation reaction involves displacement of peroxide and is thus fundamentally different from the dehydrogenation reactions of analogous cobalt dioxygen complexes formed from the pentamine ligands 1,9-bis(2-pyridyl)-2,5,8-triazanonane and 1,11-bis(2-pyridyl)-2,6,10-triazaundecane.

It has now been found that the conformation of the aromatic and aliphatic amino groups in the co-ordination sphere of peroxo-bridged binuclear cobalt dioxygen complexes (formed with pyridyl-containing pentadentate polyamines as ligands) has a profound effect on the reaction pathway and mechanism of redox rearrangement of such complexes. These reactions may be classified as metal-centred oxidations or ligand-centred oxidations with the co-ordinated dioxygen serving as an electron sink. Metal-centred oxidations produce cobalt(III) complexes and hydrogen peroxide, whereas ligand-centred oxidations frequently involve dehydrogenation of saturated polyamine ligands to the corresponding imines. Oxidative dehydrogenation of co-ordinated ligands has recently been recognized for polyamine complexes of copper[1] and cobalt,[2] that are postulated or known to form oxygen adducts. An additional Co^{II}-catalysed dehydrogenation of a co-ordinated polyamine recently reported[3] also seems to involve the formation of a dioxygen complex as an intermediate. The relative inertness of the formal Co^{III} oxidation state in cobalt dioxygen complexes makes investigation of reaction rates and oxidation products possible at moderate temperatures in aqueous solution. Because of their inherent lability, analogous dioxygen complex intermediates in the autoxidation of complexes of other first row transition metals (*e.g.* Cu^{II}, Fe^{III}), are more difficult to observe.

Autoxidation reactions of Co^{II} complexes of the polyamines

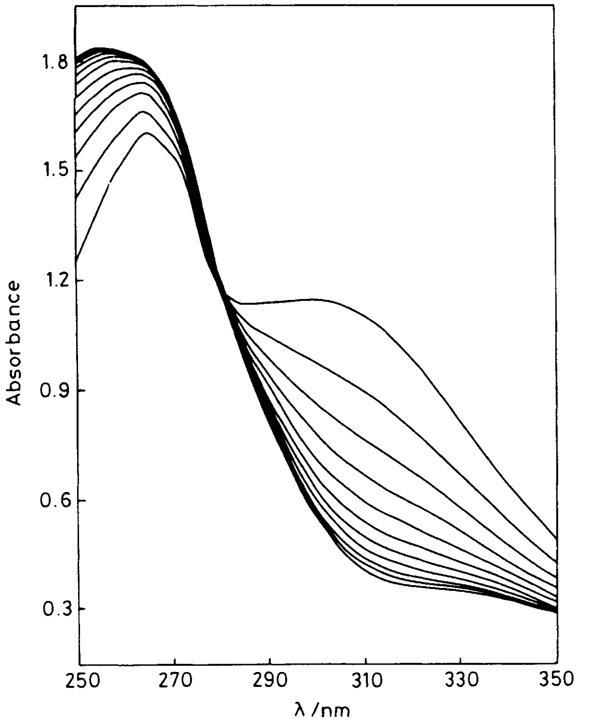
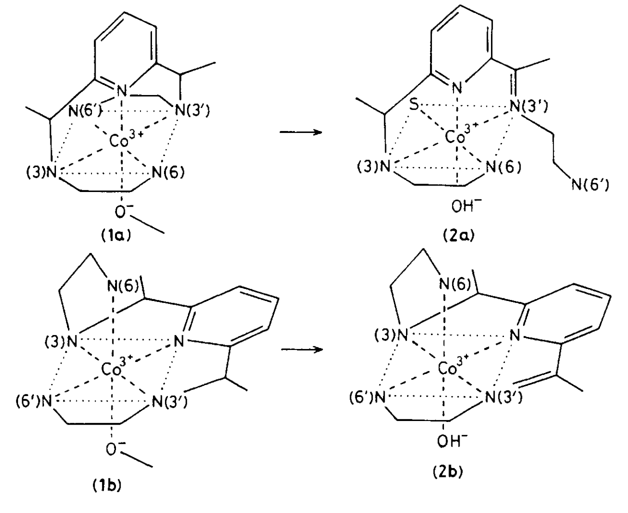


Figure 1. U.v. visible absorption spectra illustrating conversion of EPYDEN cobalt dioxygen complex (λ_{max} = 308 nm) to aquo EPYDEN-Co^{III} complex (λ_{max} = *ca.* 266 nm), at 20 min intervals; [Co] = [EPYDEN] = 1.63×10^{-3}; [KCl] = 1.00; $-\log[H^+]$ = 11.00; T = 35.0 °C.

1,9-bis(2-pyridyl)-2,5,8-triazanonane (PYDIEN), or 1,11-bis(2-pyridyl)-2,6,10-triazaundecane (PYDPT), form intermediate binuclear dioxygen complexes, having two formal Co^{III} centres with a bridging peroxo group. The high oxygenation constants of these complexes have been reported.[4] These co-ordinated polyamines are now found to undergo dehydrogenation in the autoxidation process to form bis-imines with the double bonds conjugated to the pyridine rings. The reaction products are identified by their characteristic infrared absorption bands at *ca.* 1630 cm^{-1} and by t.l.c. analysis of derivatives of the corresponding aldehydes formed by hydrolysis.[5] Hydrogen peroxide is not formed in either case.

Parallel studies of the autoxidation of the Co^{II} complex of 2,6-bis[2-(3,6-diazahexyl)pyridine (EPYDEN) indicate that metal-centred oxidation and not oxidative dehydrogenation takes place under the same reaction conditions. First, iodometric methods of analysis demonstrate that H_2O_2 is a reaction product; second the redox potential of the Co^{III}/Co^{II}-ligand is not changed by the autoxidation reaction, demonstrating that the co-ordinated ligand is not changed; and third, an isosbestic point is found in the absorption spectra obtained by monitoring the disappearance of the ligand to metal charge transfer ($\pi^*O_2 \rightarrow d_{z^2}$) transition at 308 nm of the intermediate cobalt complex (Figure 1). The absorption spectrum of the final product is identified as that of 2,6-bis[2-(3,6-diazahexyl)]pyridine cobalt(III) chloride, which has been reported in an earlier spectrophotometric study.[6] The spectral data in Figure 1 reveal that a simple first order substitution occurs with a rate constant of $2.7 \times 10^{-4} s^{-1}$, having a correlation coefficient of 1.000.

The reaction pathway in the autoxidation of EPYDEN Co^{II} is in sharp contrast to those of analogous complexes of PYDIEN, PYDPT, and other polyamine ligands that undergo facile oxidative dehydrogenation. A probable rationale for this unusual behaviour may be seen in considering the possible conformations of the dioxygen complex intermediate in the autoxidation process, formulae (**1a**) and (**1b**). The aliphatic nitrogens 3,3′ would be expected to be approximately coplanar with the pyridine nitrogen, with the terminal nitrogens 6,6′ either *cis* or *trans* to each other. Complex (**1b**) has the lower energy dehydrogenation pathway through the formation of a conjugated imine (**2b**), because it does not require that the co-ordinate bonds be broken upon oxidative dehydrogenation. On the other hand, formation of complex (**2a**) would result in the breaking of a terminal amine-Co^{III} bond in the oxidative dehydrogenation process, because of the steric restraints of the trigonal imine nitrogen thus formed. The cobalt dioxygen complexes containing PYDIEN or PYDPT as ligands do have low energy pathways for oxidative dehydrogenation as can be seen in the crystal structures of these complexes,[7] which show each co-ordinated ligand to have a terminal pyridine nitrogen and two adjacent aliphatic nitrogens in a nearly planar arrangement. The results reported here for autoxidation of the Co^{II}-EPYDEN complex imply that formula (**1a**) most closely represents the conformation of the complex that meets the requirements of the experimental results. Further work on this interesting complex system is in progress, including preparation of crystalline solids for *X*-ray structure determination.



S = solvent

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