Synthesis and Characterization of the Diamagnetic Co^{III}–O$_2$ Complex with a Salen Analogue containing a Pendant Phenolic Group

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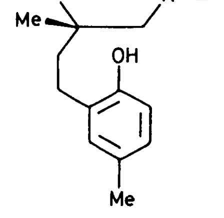
The diamagnetic Co^{III}–O$_2$ complex with a salen analogue containing a pendant phenolic group capable of axial co-ordination with the Co atom has been isolated and characterized by means of its elemental analysis and i.r. and Raman spectra.

N,*N*′-Ethylenebis(salicylideneaminato)cobalt(II) [Co(salen)] and its congeners are known to bind molecular oxygen reversibly[1] and hence are regarded as models for haemoglobin and myoglobin. To bind O_2 these cobalt(II) complexes need a base to act as the fifth ligand, a property inherent in new salen analogues with an attached group capable of axial co-ordination.[2] We have prepared such a compound, *N*,*N*′-disalicylidene-2-methyl-4-(2-hydroxy-5-methylphenyl)butane-1,2-diamine [(**1**), H_2(sal-Hpen)], with an attached phenol group. We report here the reaction of Co(sal-Hpen) with molecular oxygen and the isolation and characterization of the diamagnetic Co^{III}–O_2 complex Co(sal-pen)O_2.

When a dichloromethane solution of Co(sal-Hpen) was exposed to air, the colour of the solution changed from orange to brown and finally to deep purple without addition of base. The partly oxidized, brown solution exhibited a typical e.s.r. signal for a superoxo-cobalt(III) complex, suggesting the formation of Co(sal-Hpen)O_2 as an intermediate in the oxidation, in which the phenolic oxygen probably acts as the fifth ligating atom. The purple solution was, though, e.s.r. silent.



(1)

The reaction of Co(sal-Hpen) with molecular oxygen was followed spectroscopically (Figure 1). The visible spectrum of the reaction solution had isosbestic points at 327 and 431 nm, and exhibited a strong absorption (ϵ = *ca.* 7000 dm^3 mol^{-1} cm^{-1}) at 560 nm.

The purple solution, when concentrated, gave diamagnetic black–purple prismatic crystals. The elemental analysis of these suggested the formation of a new O_2 adduct of the composition Co(sal-pen)O_2. Deprotonation of the phenolic hydroxy group in the sal-pen ligand was shown by the absence

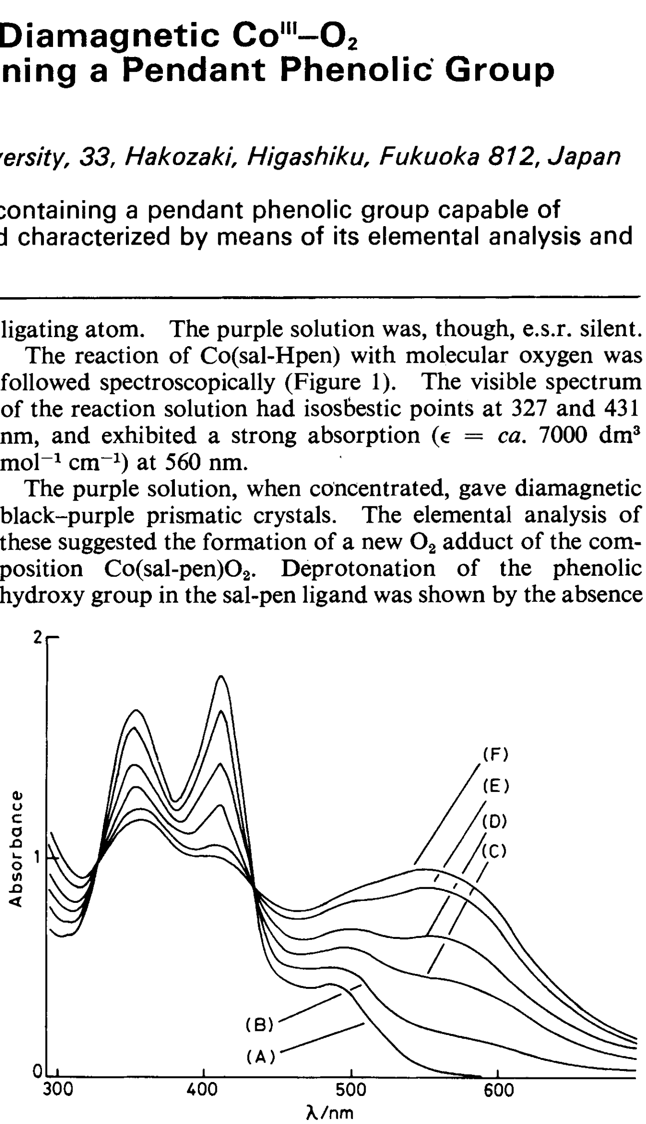
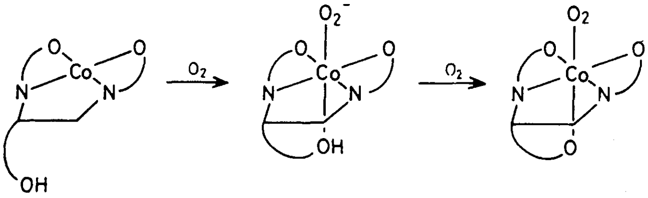


Figure 1. Changes with time in the visible spectrum of Co(sal-Hpen) in dichloromethane (2.14 × 10^{-3} M) when the solution is exposed to air. (A), before exposure; (B), 10 h; (C), 1 day; (D), 2 days; (E), 5 days; (F), 10 days.



Scheme 1. Simplified illustration of the formation of the Co^{III}-(sal-pen)O_2 complex.

of an i.r. band in the 3300—3200 cm^{-1} region [Co(sal-Hpen) has an i.r. band at 3250 cm^{-1} attributable to the OH vibration]. The i.r. spectrum contained a band at 1240 cm^{-1}, which was not observed for Co(sal-Hpen).

The formation of the O_2 adduct was further confirmed by means of spin-label e.s.r. and resonance Raman spectroscopy. A solution of Co(sal-pen)O_2 and 2,2,6,6-tetramethylpiperidin-4-ol (TMPN) in dichloromethane did not show any e.s.r. signals. On adding a small amount of methanol to this mixture, the solution became orange and exhibited an e.s.r. signal (*g ca.* 2) with a three-lined hyperfine structure of line width *ca.* 16 G.† This can be attributed to the nitrosyl radical formed by the reaction of TMPN with singlet oxygen liberated from Co(sal-pen)O_2.

Resonance Raman spectra of Co(sal-pen)O_2 and Co(sal-Hpen) were measured in dichloromethane using excitations at 476.5 and 514.5 nm of an NEC GLG3200 Ar^+ laser. Co(sal-pen)O_2 was characterized by the new Raman bands at 1480, 1260, and 510 cm^{-1} the last two being enhanced by the excitation at 514.5 nm relative to that at 476.5 nm. These two bands must be related in origin to the 560 nm absorption band. The 1260 cm^{-1} Raman band corresponds well with the 1240 cm^{-1} i.r. band. Despite the lack of a resonance Raman experiment using $^{18}O_2$, the 1260 and 510 cm^{-1} bands can be attributed to ν(O–O) and ν(Co–O) vibrations, respectively, by comparison with the vibrational data of 1 : 1 Co–O_2 complexes.[3–5] The ν(O–O) frequency of Co(sal-pen)O_2 is considerably higher than those (1080—1180 cm^{-1}) of superoxocobalt(III) complexes with quadridentate Schiff bases.[3]

All these facts agree with the formation of a cobalt(III)–(singlet O_2) complex as shown in Scheme 1. The present O_2-complex is isoelectronic with oxyhaemoglobin and oxymyoglobin and hence is a new model for biological oxygen carriers.

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† 1 G = 10^{-4} T.