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STUDIES ON DIOXYGEN ADDUCTS OF COBALT(II) COMPLEXES WITH
SALEN-ANALOGS CONTAINING A PENDANT GROUP

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Abstract New cobalt(II) complexes ($[\text{Co}(\text{sal-P})]$) with pentadentate salen-analogs possessing a pendant group capable of axial coordination have been synthesized and discussed with respect to coordination behavior of the pendant groups.

Keywords: Salen-analogs, dioxygen adducts, axial coordination

INTRODUCTION

N,N' -Ethylenebis(salicylideneaminate)cobalt(II), $[\text{Co}(\text{salen})]$, has extensively been studied as a good model for the natural oxygen carriers because it reacts reversibly with dioxygen. Since the active sites of some metal enzymes are of square-pyramidal geometry, nine new cobalt(II) complexes with pentadentate salen-analogs ($[\text{Co}(\text{sal-P})]$) have been synthesized (Figure 1). The pendant group (P) which can coordinate to the axial position is phenolic hydroxy, ether, amino, or thioether; the donor atom is linked to the ethylene backbone of the salen-skeleton through a two-, three-, or four-carbon chain (Table I). In this study the nature of the cobalt(II) complexes and their oxygenation reactions were investigated with respect to the role of the pendant group.

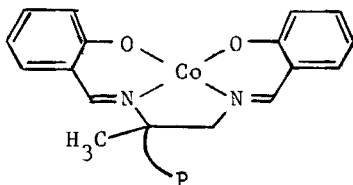
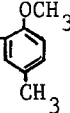

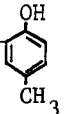


FIGURE 1 The chemical structure of $[\text{Co}(\text{sal-P})]$.

TABLE I Abbreviations of cobalt(II) complexes.

P	[Co(sal-P)]	P	[Co(sal-P)]
$-(\text{CH}_2)_2\text{OCH}_3$	[Co(sal-moen)]	$-(\text{CH}_2)_2\text{SCH}(\text{CH}_3)_2$	[Co(sal-ipsen)]
$-(\text{CH}_2)_3\text{OCH}_3$	[Co(sal-motn)]	$-(\text{CH}_2)_3\text{SCH}(\text{CH}_3)_2$	[Co(sal-ipstn)]
$-(\text{CH}_2)_2$ 	[Co(sal-mpen)]	$-(\text{CH}_2)_2\text{S}$ 	[Co(sal-bsen)]
$-(\text{CH}_2)_2$ 	[Co(sal-Hpen)]	$-(\text{CH}_2)_3\text{N}(\text{C}_2\text{H}_5)_2$	[Co(sal-eatn)]
		$-(\text{CH}_2)_3\text{N}(\text{C}_4\text{H}_9)_2$	[Co(sal-batn)]

SYNTHESES

The general synthetic procedure for [Co(sal-P)] is shown in Fig. 2. Ketones containing the P group at the carbonyl carbon were used as starting materials. They were converted into amino nitriles, which were then reduced with LiAlH_4 to diamines. The Schiff bases, $\text{H}_2(\text{sal-P})$, were obtained by condensing these amines and salicylaldehyde in the 1:2 molar ratio. The cobalt(II) complexes, [Co(sal-P)], were obtained by the reaction of the ligands with cobalt(II) acetate under a nitrogen atmosphere.¹

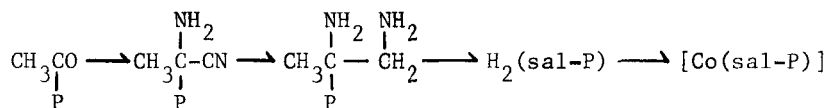


FIGURE 2 Representation of the synthetic procedure.

CHARACTERIZATION OF COBALT(II) COMPLEXES

All the cobalt(II) complexes showed a magnetic moment falling in the range 2.4-2.5 μ_B . Electronic spectra measured in dichloromethane at room temperature exhibited the absorption band near $8 \times 10^3 \text{ cm}^{-1}$ ($\epsilon \sim 20 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) which is characteristic of low spin, planar cobalt(II) complexes with salen-like Schiff bases. Evidently, no coordination of the pendant group to the metal occurs

at room temperature.

ESR spectra of the cobalt(II) complexes were measured in frozen dichloromethane at liquid nitrogen temperature. The results are shown in Fig. 3. The spectra of [Co(sal-motn)], [Co(sal-mpen)], and [Co(sal-batn)], showed an ESR pattern typical of a low spin, planar Co(II) with the $(d_{yz})^1$ ground state. In contrast [Co(sal-ipsen)] exhibited a well-defined rhombic pattern which can be interpreted in terms of the $(d_z^2)^1$ electronic configuration typical of a five-coordinate Co(II) complex with a base at the apical site.² The ESR spectra of [Co(sal-

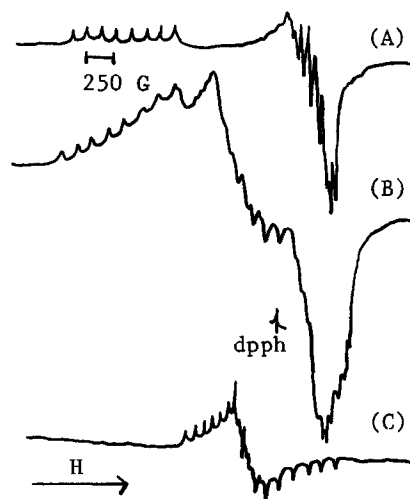


FIGURE 3 ESR spectra:
 (A) [Co(sal-mpen)];
 (B) [Co(sal-moen)];
 (C) [Co(sal-ipsen)].

eatn)], [Co(sal-moen)], [Co(sal-ipstn)], and [Co(sal-bsen)], on the other hand, showed complicated patterns with three signals. These spectra suggest that the four-coordinate and five-coordinate species coexist in frozen solutions. These complexes prefer five-coordination probably at lower temperatures with the pendant donor atom at the axial site, but the axial coordination is not complete in the frozen solution. From ESR spectra it was found that the axial coordination of ether oxygen occurs in [Co(sal-moen)] but not in [Co(sal-motn)]; the axial coordination was complete in [Co(sal-ipsen)] but incomplete in [Co(sal-ipstn)]. These results suggest that if the donor atom is the same, the pendant tail is sterically favorable for axial coordination when connected to the salen-skeleton through two methylene groups.

RESONANCE RAMAN SPECTRA

All the complexes showed ESR signals near $g \sim 2.02$ which are typical

of 1:1 Co-O₂ adduct at 78 K in an open atmosphere. In order to make detailed investigations on the oxygenated species, the resonance Raman spectra of several [Co(sal-P)] complexes were measured in dichloromethane under 4 atm O₂ pressure (Table II). The bands near 1145 cm⁻¹ are assigned to the O-O vibration of the "base-bound", six-coordinate Co(II)-O₂ adduct.³ On the other hand, [Co(sal-Hpen)] and [Co(salen)] showed the Raman bands near 1095 cm⁻¹. These bands are assigned to the O-O vibration of the "base-free", five-coordinate O₂ adduct.³ The phenol pendant group of [Co(sal-Hpen)]O₂, therefore, does not coordinate to the metal. Further, the 821 cm⁻¹ band of [Co(sal-ipsen)] is the O-O vibration of the 2:1 Co-O₂ adduct.² Thus, the structures of the dioxygen adducts have been determined through the O-O vibration.

TABLE II Resonance Raman spectral data.

samples	$\Delta\nu / \text{cm}^{-1}$	
	¹⁶ O ₂	¹⁸ O ₂
[Co(sal-mpen)]	1148	1087
[Co(sal-bsen)]	1145	1080
[Co(sal-ipsen)]	1142, 821	1077, 772
[Co(sal-Hpen)]	1095	1033
[Co(salen)]	1097	—

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