

An Electron Spin Resonance Study of Monomeric Oxygen Adduct of Cobalt(II) Schiff-Base Complex

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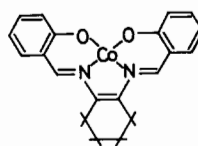
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Received January 28, 1982

In contrast to (N,N'-disalicylideneethylenediaminato)cobalt(II) [Co(II)salen] which forms a dioxygen complex in solid state or in solution, cobalt(II) complexes of N,N'-disalicylidene-1,2-ethenediamine derivatives do not undergo coordination with dioxygen in solid state and in solution at ambient temperature [1].

Stynes and Ibers have pointed that the nature of equatorial ligands is important in determining the stability of dioxygen complexes by referring to thermodynamic parameters for complex formation [2]. In addition, the cobalt(II) complexes of Schiff-bases bind molecular oxygen at temperatures higher than those for cobalt(II) porphyrins [3–6]. The cobalt atom in porphyrin complexes is coordinated to four nitrogen atoms which take part of a highly conjugated tetrapyrrole system, while that in Schiff-base complexes is coordinated to two oxygen and two nitrogen atoms which in turn take part of a less conjugated system relative to the former. Thus, the dinegative charge is less delocalized in Schiff-base complexes than that of porphyrins, and hence a higher electron density on the cobalt atom is expected for the former relative to the latter. As the electron density on the cobalt atom increases, the strength of the Co–O₂ bond is expected to increase; a cobalt-oxygen bond is stronger in Schiff-base complexes than in porphyrin complexes. Therefore, the extent of π -conjugation in equatorial ligands is considered to be a critical factor for manipulating the stability of dioxygen complexes.

In the present work, we employed one of the cobalt(II) complexes of N,N'-disalicylidene-1,2-ethenediamine derivatives: (N,N'-disalicylidene-1-cyclohexene-1,2-diaminato)cobalt(II) [abbreviated as Co(II)salcn] which has a conjugated system higher than Co(II)salen. We examined the nature of the in-plane ligand and the effect of axial base-ligands on



Co(II)salcn

the ESR behavior of the 1:1 dioxygen Co(II)salcn adduct. The strength of the cobalt-oxygen bond may reflect the extent of π -back donation from the filled 3d_{xz} (or 3d_{yz}) orbital of the cobalt atom into the half-empty π^* orbital of the coordinated dioxygen as pointed out by Basolo et al. [7].

Experimental

Preparation of Complexes

The preparative procedure for Co(II)salcn has been reported previously [1].

Physical Measurements

ESR spectra were obtained with a JEOL JES-ME-1 X-band spectrometer equipped with a 100-kHz field modulation unit. All samples were measured in N,N-dimethylformamide (DMF) at 77 K, concentrations being maintained in the 10⁻² ~ 10⁻³ M range. The manganese ion diffused into magnesium oxide was used to obtain reference signals for the measurements. DMF used for ESR spectroscopy was distilled *in vacuo* after being dried over a molecular sieve (4A, 1/16; Wako Pure Chemical Industries, Ltd.) and kept over the molecular sieve. Pyridine (Py), 2-methyl-(2-MePy) and 4-methylpyridine (4-MePy) were fractionally distilled after refluxing with potassium hydroxide, and 4-cyano-(4-CNPy) and 4-aminopyridine (4-NH₂Py) were recrystallized from aqueous ethanol and benzene, respectively.

Results and Discussion

The ESR spectrum of the dioxygen complex of Co(II)salcn observed in DMF in the presence of O₂ and 4-MePy at 77 K is shown in Fig. 1 as an example. A set of eight hyperfine lines due to the cobalt nucleus were observed on the parallel component of g -tensor (g_{\parallel}) at lower field, while such hyperfine splittings were not so clearly identified on the perpendicular component of g -tensor (g_{\perp}) as on the former component. The spin Hamiltonian parameters obtained in this work are comparable to those for Co(II)salen-Py-O₂, as shown in Table I [8]. The hyperfine splitting constant (A -tensor) is much smaller in magnitude than those observed for

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TABLE I. Spin Hamiltonian Parameters for the Monomeric Oxygen Adducts of Cobalt(II) Complexes.^a

Ligand	Axial base	g_{\parallel}	g_{\perp}	$A_{\parallel}^{\text{Co}} \times 10^4$ cm^{-1}	$A_{\perp}^{\text{Co}} \times 10^4$ cm^{-1}	$\bar{A}^{\text{Co}} \times 10^4$ ^b cm^{-1}	$\Delta A \times 10^4$ ^c cm^{-1}	$\text{pK}_a(\text{BH}^+)$ ^d	Ref.
Salcen	DMF	2.089	2.001	26.3	14.8	18.6	7.7		
	4-CNPy	2.082	2.001	17.0	10.7	12.8	4.2	1.90	
	Py	2.082	2.000	16.2	10.5	12.4	3.8	5.19	
	2-MePy	2.085	2.001	17.3	11.5	13.4	3.9	5.97	
	4-MePy	2.083	2.001	15.8	9.7	11.7	4.1	6.02	
	4-NH ₂ Py	2.083	2.001	15.3	9.6	11.5	3.8	9.11	
Salen	Py	2.079	2.028	17.0	13.1	14.4	2.6	5.19	8
			1.999						

^aMaximum possible errors: g , ± 0.005 ; $A_{\parallel}^{\text{Co}}$, $\pm 0.5 \times 10^{-4} \text{ cm}^{-1}$; A_{\perp}^{Co} , $\pm 0.5 \times 10^{-4} \text{ cm}^{-1}$. ^bCalculated from $\bar{A}^{\text{Co}} = (2A_{\perp}^{\text{Co}} + A_{\parallel}^{\text{Co}})/3$. ^cCalculated from $\Delta A = A_{\parallel}^{\text{Co}} - \bar{A}^{\text{Co}}$. ^dCited from 'Handbook of Biochemistry and Molecular Biology. Physical and Chemical Data', vol. 1, 3rd edn., ed. by G. D. Fasman, CRC Press, Inc., Cleveland, Ohio (1976).

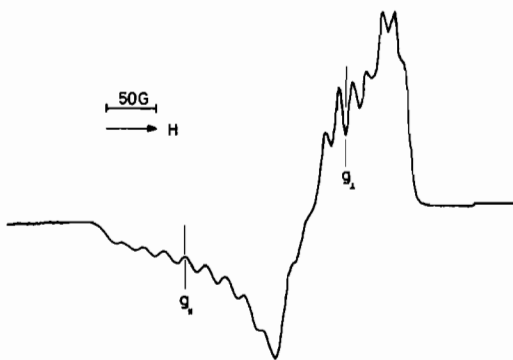


Fig. 1. ESR spectrum of cobalt(II) salcen complex in DMF containing 4-MePy and O₂ at 77 K.

the low-spin cobalt(II) Schiff-base complexes [7, 9]. This suggests that the unpaired electron spends much less time on the Co atom than on the π^* -levels of O₂ molecules. A correlation, $g_{\parallel} > g_{\perp}$, holds for all the present complexes and the g values are close to 2.0. The ESR spectral pattern for all the complexes are consistent with the formation of monomeric dioxygen-Co(II) salcen complexes of a 1:1 molar ratio. A similar spectral behavior has also been observed for Co(II)-acacen^{*1}-Py-O₂ [7, 9], for Co(II)-salen-Py-O₂ [10, 11], and for Co(II)P^{*2}-Im^{*3}-O₂ [12]. The g values of these cobalt-dioxygen complexes described above are not affected by the nature of equatorial ligands, as seen in Table I. The

^{*1}acacen, N,N'-bis[1-methyl-3-oxobutylene]ethylenediamine.

^{*2}P, 13,17-bis[2-(methoxycarbonyl)ethyl]-3,8-divinyl-2,7,12,18-tetramethylporphine.

^{*3}Im, imidazole.

superhyperfine splitting, due to magnetic interaction between an unpaired electron in Co(II) and nitrogen nuclei ($I = 1$), was not observed in the cobalt dioxygen complex. This seems to indicate that the unpaired d-electron has a significantly large population on dioxygen rather than the pyridyl nitrogen placed at the axial site, due to the back donation effect.

Since Co(II)salcen in chloroform in the absence of bases showed no appreciable change in the ESR pattern upon introducing oxygen, the presence of bases such as Py is required for the formation of the oxygen complex. A pyridine base must be coordinated to the cobalt atom at the axial site *trans* to dioxygen on the basis of the discussion given below. In order to investigate the systematic correlation between basicity of the axial ligands and ESR A -tensor, we used various pyridine derivatives, such as 4-CNPy, 4-MePy, 2-MePy, and 4-NH₂Py, as axial ligands. As seen in Table I, all those of g_{\parallel} and g_{\perp} values for the present complexes remain nearly at identical values regardless of the nature of axial bases, even though their basicities (pK_a) change from 1.90 to 9.11. On the contrary, the A -tensor is very sensitive to the basicity change. Even though both 4-MePy and 2-MePy have similar pK_a values (6.02 and 5.97, respectively), the 2-MePy complex shows greater $A_{\parallel}^{\text{Co}}$ and A_{\perp}^{Co} values relative to those observed for the 4-MePy complex. This may be attributed to the steric repulsion between the in-plane ligand of Co(II)salcen and the 2-methyl group of 2-MePy at the axial site. There exists a linear relationship between ESR A -tensor and the basicities (Fig. 2), except for 2-MePy as stated above. The decreasing order of A -tensor is parallel to the increasing order of the basicity of the axial ligands. This trend is analogous to the correlation between the stability of oxygen complexes (K_{O_2}) and the basicity of porphyrin ligands (pK_a) [13]. Apparently, there exists no systematic correlation between $\Delta A =$

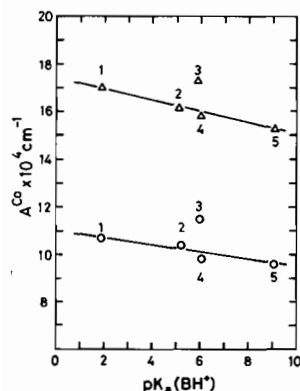


Fig. 2. Correlation between ^{59}Co hyperfine splitting constant ($A^{\text{Co}} \times 10^4 \text{ cm}^{-1}$) and amine basicity. ^{59}Co hyperfine splitting constant: Δ , $A_{\parallel}^{\text{Co}} \times 10^4 \text{ cm}^{-1}$; \circ , $A_{\perp}^{\text{Co}} \times 10^4 \text{ cm}^{-1}$. Amines: 1) 4-CNPy; 2) Py; 3) 2-MePy; 4) 4-MePy; 5) 4-NH₂-Py.

($A_{\parallel}^{\text{Co}} - \bar{A}^{\text{Co}}$), anisotropic parameter, and pK_a (Table 1). The ΔA values are much smaller in magnitude than the corresponding isotropic parameters (A s).

The isotropic ^{59}Co hyperfine splitting constant (\bar{A}^{Co}) is directly proportional to the spin density on the cobalt nucleus. As for the equatorial ligand effect on \bar{A}^{Co} , salen provides a smaller \bar{A}^{Co} value than salen with an identical axial base (Py), as seen in Table I. This means that the electron density on the cobalt nucleus is subjected to change by varying the extent of π -conjugation in an equatorial ligand and tends to decrease as the π -conjugation is increased. There exists a systematic correlation between \bar{A}^{Co} and the axial ligand basicity as shown in Fig. 3, where \bar{A}^{Co} decreases in the following order as pK_a increases; 4-CNPy > Py > 4-MePy > 4-NH₂Py. The exception is 2-MePy which exerts a steric repulsion with the equatorial ligand in the coordination process. It is generally expected that \bar{A}^{Co} tends to increase as the pK_a of an axial ligand increases.

In the present case, however, an antiparalleled correlation was observed as maintained above with pyridine bases as axial ligands. This seems to indicate that the π -back donation from Co to the coordinated dioxygen becomes more effective as the basicity of pyridine ligand becomes greater, and the Co-O₂ bond is more polarized (Co=O₂^{δ-}). In other words, such π -back donation is assisted by a pyri-

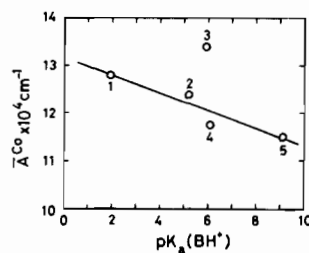


Fig. 3. Correlation between isotropic ^{59}Co hyperfine splitting constant ($\bar{A}^{\text{Co}} \times 10^4 \text{ cm}^{-1}$) calculated from $\bar{A}^{\text{Co}} = (2A_{\perp}^{\text{Co}} + A_{\parallel}^{\text{Co}})/3$ and amine basicity. Amines: 1) 4-CNPy; 2) Py; 3) 2-MePy; 4) 4-MePy; 5) 4-NH₂Py.

dine ligand through π -back interaction between nitrogen donor and cobalt atoms.

Acknowledgements

The authors wish to express their thanks to Professor Y. Murakami and Dr. Y. Matsuda, Kyushu University, for their helpful discussions.

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