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The *trans*-Effect in the Monomeric Dioxygen Adduct of the Dipyrido[14]annulene–Cobalt(II) Complex

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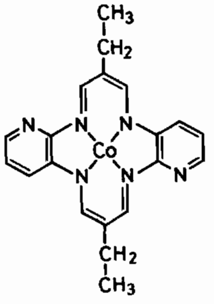
The reaction of dioxygen with cobalt(II) complexes is known to form both binuclear peroxocobalt derivatives ($Co:O_2 = 2:1$) and mononuclear complexes ($Co:O_2 = 1:1$) [1]. The latter is paramagnetic and its ESR spectrum reveals a characteristic which suggests that the unpaired electron is located chiefly on the dioxygen moiety. That is to say, the chelate is best mentioned as a cobalt(III) species coordinated to a superoxide anion. There is no systematic study for the effect of changing the axial base ligand on the spin Hamiltonian parameters of cobalt dioxygen complexes containing unsaturated N_4-macrocycles.

We prepared the dipyrido[14]annulene–cobalt(II) complex, 7,16-diethyl-(*E*)-dipyrido[b,i][1,4,8,11]-tetraazacyclotetradecinato)cobalt(II) (**Co(1-E)**) and discovered the fact that **Co(1-E)** becomes the superoxo complex in the presence of pyridine and dioxygen at 77 K [2]. We have been interested in the effect of changing the axial base on the ESR parameters and report here an ESR research on changing the axial base to the monomeric dioxygen adduct of **Co(1-E)**.



Co(1-E)

Experimental

General Information

ESR spectra were carried out with a Jeol JES-ME-1 X-band spectrometer equipped with a 100 kHz field modulation unit. All samples were run in benzene–toluene (2:3 *v*/*v*) at 77 K, the concentration of the cobalt(II) complex being maintained in the 10^{-2} mol dm^{-3} range. Manganese ion diffused thermally into magnesium oxide was employed in order to establish the standard reference signals for measurements. Benzene and toluene for ESR spectroscopy were distilled after being dried over a molecular sieve (4 A, 1/16; Wako Pure Chemical Industries Ltd.) and preserved over the molecular sieve. 2-Methylpyridine, 4-methylpyridine and pyridine were fractionally distilled after refluxing with potassium hydroxide, and 4-aminopyridine and 4-cyanopyridine were recrystallized from benzene and ethanol, respectively.

Preparation of the Macrocyclic Complex

(7,16-Diethyl-(E)-dipyrido[b,i][1,4,8,11]tetraazacyclotetradecinato)cobalt(II) (Co(1-E))

Preparation of **Co(1-E)** employed in this work has been described in our previous paper [2].

Results and Discussion

In order to observe the effect of various changes in the basicity of the axial base ligand, five kinds of pyridine as an axial base were used for the ESR investigation of the monomeric dioxygen adduct of the dipyrido[14]annulene–cobalt(II) complex (**Co(1-E)**). The ESR spectrum for the monomeric dioxygen adduct of **Co(1-E)** observed in benzene–toluene in the presence of dioxygen and 4-methylpyridine at 77 K is shown in Fig. 1A. The spin Hamiltonian parameters in this study are compiled in Table I. The spectral feature is consistent with that reported by us previously [2] and reveals the formation of the monomeric dioxygen adduct of **Co(1-E)**.

The tabulated results show that the $g_{\parallel}$ and $g_{\perp}$ values are insensitive to the changes in the basicity of the axial base ligand, where the axial pyridine base is changed from 4-cyanopyridine to 4-aminopyridine, but the $A^{Co}{}_{\parallel}$ and $A^{Co}{}_{\perp}$ values are very sensitive to the basicity variation. The examination has shown that there apparently exists a definite trend in the ^{59}Co coupling constants as seen in Table I. $A^{Co}{}_{\parallel}$ and $A^{Co}{}_{\perp}$ values reduce in the following order, except for 2-methylpyridine and 4-aminopyridine: 4-cyanopyridine > pyridine > 4-methylpyridine. The reason for excluding 2-methylpyridine and 4-aminopyridine is as follows. 4-Methylpyridine and 2-methylpyridine indicate analogous pK_a values, but the latter chelate has greater $A^{Co}{}_{\parallel}$ and $A^{Co}{}_{\perp}$ values relative to those obtained for the former chelate. This may be correlated to a steric repulsion in the coordination process between the equatorial dipyrido[14]annulene of the cobalt complex and the 2-methyl group of 2-methyl-

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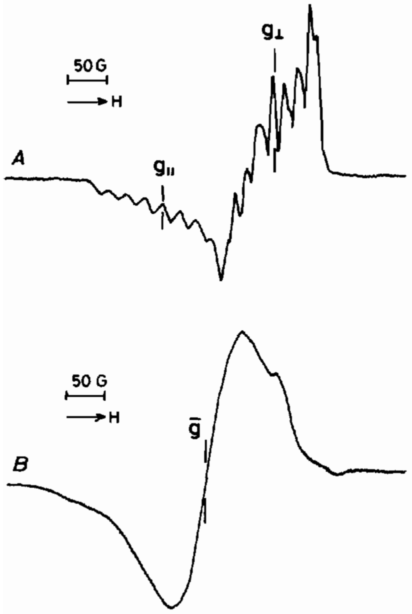

Fig. 1. ESR spectra of the dipyrido[14]annulene–cobalt(II) complex in benzene–toluene (2:3 v/v) at 77 K: A, containing 4-methylpyridine and O_2; B, containing 4-aminopyridine and O_2.

pyridine. Figure 1B exhibits the ESR spectrum for the monomeric dioxygen adduct of **Co(1-E)** in benzene–toluene containing dioxygen and 4-aminopyridine at 77 K. A hyperfine splitting structure was not observed in Fig. 1B. The explanation may be a pseudo-segregation of the cobalt(II) complex from the solvent by 4-aminopyridine solute segregation from the solution in solution crystallization [4, 5]. There is a linear relationship between the A value and the basicity of an axial pyridine derivative. The decreasing order of $A^{Co}{}_\parallel$ and $A^{Co}{}_\perp$ values is parallel to the increasing order of the basicity of the axial base ligand. This suggests that the A values provide useful information on the ground state *trans*-effects of the axial base ligands.

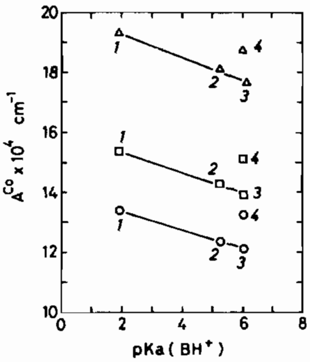

Fig. 2. Correlation between ^{59}Co hyperfine splitting constant and pyridine basicity. ^{59}Co hyperfine splitting constant: △, $A^{Co}{}_\parallel \times 10^4$ cm^{-1}; ○, $A^{Co}{}_\perp \times 10^4$ cm^{-1}; □, $\bar{A}^{Co} \times 10^4$ cm^{-1}. Pyridines: 1, 4-CNPy; 2, Py; 3, 4-MePy; 4, 2-MePy (see Table I for abbreviations).

The isotropic ^{59}Co coupling constant ($\bar{A}^{Co}$) is in proportion to the spin density on the cobalt nucleus. There is a systematic relation between the $\bar{A}^{Co}$ value and the axial pyridine basicity as shown in Fig. 2, where the $\bar{A}^{Co}$ value decreases in the following order as the pK_a value of the axial pyridine derivative increases: 4-cyanopyridine > pyridine > 4-methylpyridine.

The inverse correlation was observed as described above with pyridine derivatives as axial bases. The results suggest that the π back donation from a cobalt to the coordinated dioxygen is more effective as the basicity of the axial pyridine derivative gets greater, and the bond of $Co-O_2$ is more polarized. That is to say, the π back donation is aided by the axial pyridine base through π back interaction between a nitrogen donor of the pyridine base and a cobalt atom.

In conclusion, there exists a systematic correlation between the $\bar{A}^{Co}$ value and the pK_a value of the axial pyridine derivative for the dipyrido[14]annulene–cobalt superoxo complex. The decreasing order of the $\bar{A}^{Co}$ value is parallel to the increasing order of the basicity of the axial pyridine base ligands, except for 2-methylpyridine and 4-aminopyridine.

TABLE I. Spin Hamiltonian Parameters for the Monomeric Dioxygen Adduct of the Dipyrido[14]annulene–Cobalt(II) Complex[a]

Pyridine base[b]	$\bar{g}$	$g_\parallel$	$g_\perp$	$A^{Co}{}_\parallel \times 10^4$ (cm^{-1})	$A^{Co}{}_\perp \times 10^4$ (cm^{-1})	$\bar{A}^{Co} \times 10^4$[c] (cm^{-1})	pK_a[d] (BH$^+$)	Reference
4-CNPy		2.073	1.999	19.3	13.4	15.4	1.90	this work
Py		2.076	1.999	18.1	12.4	14.3	5.19	2
4-MePy		2.076	1.999	17.6	12.1	13.9	6.02	this work
2-MePy		2.076	1.999	18.8	13.2	15.1	5.97	this work
4-NH_2Py	2.024						9.11	this work

[a] Maximum possible errors: g, ±0.005; $A^{Co}{}_\parallel$, ±0.5 × 10^{-4} cm^{-1}; $A^{Co}{}_\perp$, ±0.5 × 10^{-4} cm^{-1}. [b] Py, pyridine; 4-CNPy, 4-cyanopyridine; 4-MePy, 4-methylpyridine; 4-NH_2Py, 4-aminopyridine; 2-MePy, 2-methylpyridine. [c] Calculated from $\bar{A}^{Co} = (2A^{Co}{}_\perp + A^{Co}{}_\parallel)/3$. [d] Cited from ref. 3.

References

1 (a) G. McLendon and A. E. Martell, *Coord. Chem. Rev., 19,* 1 (1976); (b) R. D. Jones, D. A. Summerville and F. Basolo, *Chem. Rev., 79,* 139 (1979); (c) E. C. Niederhoffer, J. H. Timmons and A. E. Martell, *Chem. Rev., 84,* 137 (1984).

2 K. Sakata, Y. Hayashida, M. Hashimoto, K. Terada and Y. Kato, *Inorg. Chim. Acta, 105,* L25 (1985).

3 G. D. Fasman (ed.), 'Handbook of Biochemistry and Molecular Biology. Physical and Chemical Data', Vol. 1, 3rd edn., CRC Press, Cleveland, Ohio, 1976.

4 E. Tsuchida, E. Hasegawa and T. Kanayama, *Macromolecules, 11,* 947 (1978).

5 E. Hasegawa, T. Kanayama and E. Tsuchida, *Biopolymers, 17,* 651 (1978).