An ESR Study of 1:1 Adducts of Bis-salicylaldehyde-imine-cobalt(II) Complexes with Oxygen in Solutions

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The present authors have already reported[1] that oxygen coordinates reversibly in the ratio of 1 : 1 with bis-salicylaldehyde-imine-cobalt complexes supported on poly-4-vinylpyridine. In the present communication, they wish to report on the observation of the ESR spectra of 1 : 1 adducts of bis-salicylaldehyde-imine-cobalt(II) complexes with oxygen, which may exist equilibrially in solutions.

When a pyridine solution of *N,N'*-ethylene-bis(3-methoxysalicylideneiminato)cobalt(II) (Co 3-MeOsalen) was exposed to oxygen, there appeared an ESR signal in which hf structures caused by a cobalt nucleus were observed (eight lines, I (^{59}Co)$=7/2$). This signal decreased when the solution was exposed to nitrogen and increased again when the solution was again exposed to oxygen. Similar spectra could be observed in substituted pyridines, *N,N*-dimethylformamide, and dimethyl sulfoxide used as solvents. Moreover, *N,N'*-ethylene-bis-(salicylideneiminato)cobalt(II) (Co salen) showed a similar spectrum in pyridine under oxygen.

These observations prove that there may be some amounts of a 1 : 1 adduct of bis-salicylaldehyde-imine-cobalt(II) complexes with oxygen in some solutions. The observed ESR spectra may be caused by the 1 : 1 adducts, for the existence of eight resolved lines in the spectra clearly shows that the adducts intrinsically contain only one cobalt atom. In fact, the observed ESR spectra closely resemble those of superoxocobalamin ($Co/O_2=1/1$).[2] Moreover, recently the preparation of the adduct, (Co 3-MeOsalen)$\cdot$py$\cdot O_2$ has been reported.[3]

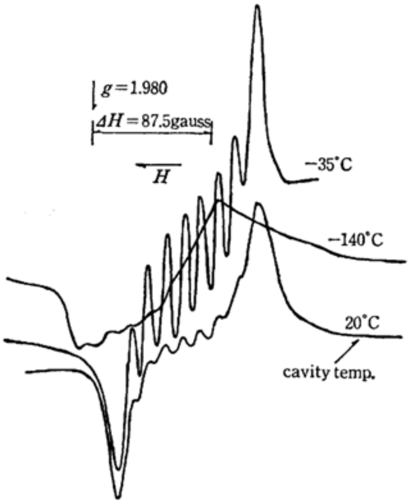

Fig. 1. ESR Spectra of Co 3-MeOsalen in pyridine under oxygen (1 atm).
complex concn.$=1.4\times10^{-2}$ mol/*l*

The small A_{Co} values (A_{Co} is the mean interval of two adjacent lines among the eight lines) may mean that little of the unpaired spin is at the cobalt atom; if so, the adducts can be regarded as essentially superoxide cobalt(III) complexes. The explanation of the solvent effect is difficult, but it is reasonable that a solvent molecule coordinates to a cobalt complex in the *trans* position against oxygen and affects the electron distribution on the coordinated oxygen molecule.

Table 1. ESR characters of the adducts

Complex	Solvent (complex concn., 10^{-2} mol/*l*)	*g*	A_{Co} (gauss)	Cavity temp. (°C)
Co 3-MeOsalen	Pyridine(1.4)	2.023	12.8	−35
Co 3-MeOsalen	Pyridine(1.8)	2.022*	—	20
Co 3-MeOsalen	4-Methylpyridine(1.7)	2.022*	13*	20
Co 3-MeOsalen	4-Ethylpyridine(1.7)	2.022	12.8	−10
Co 3-MeOsalen	DMF(1.4)	2.028	17.0	−15
Co 3-MeOsalen	DMSO(1.7)	2.028	17.3	20
Co 3-MeOsalen	DMF+Pyridine (1/1 vol)(0.9)	2.023	12.8	−10
Co salen	Pyridide(1.1)	2.022*	13*	20

* The spectrum is not well resolved. oxygen pressure = 1 atm

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[1] A. Misono, S. Koda and Y. Uchida, This Bulletin, **42**, 580 (1969); *ibid.*, No. 12 (1969).

[2] J. H. Bayston, N. K. King, F. D. Looney and M. E. Winfield, *J. Am. Chem. Soc.*, **91**, 2775 (1969)

[3] C. Floriani and F. Calderazzo, *J. Chem. Soc.*, *A* **1969**, 946.