Electron Spin Resonance Studies of 1:1 Cobalt–Oxygen Adducts

By DAMON DIEMENTE, BRIAN M. HOFFMAN,* and FRED BASOLO
(*Northwestern University, Evanston, Illinois,* 60201)

Summary. The e.s.r. of the known 1 : 1 molecular oxygen adduct with Co(3-methoxysalen) and a newly discovered, reversible 1 : 1 oxygen adduct with Co(salen) have been observed.

REVERSIBLY-FORMED molecular oxygen adducts of planar cobalt(II) complexes in solution have been objects of recent interest.[1] A series of 1 : 1 adducts of the Schiff's base complex Co(acacen),† of the form Co(acacen)B(O_2) where B is a σ-donor ligand, has been isolated[1a] and studied by e.s.r.[1b] Other stable 1 : 1 adducts have also been reported.[1c,d]

Several oxygen adducts of Co(salen)† and some ring-substituted salen derivatives have been studied,[1e] but only the 3-methoxy derivative was found to form a stable 1 : 1 adduct, *viz.* Co(3-methoxysalen)py(O_2).† In all other cases, only 2 : 1 complexes of the well known μ-peroxo-type[2] were isolated.[1e] In particular, the bridged compound [Co(salen)py]$_2O_2$ is known.[1e,3]

We now report e.s.r. observations confirming the formation of the 1 : 1 molecular oxygen adduct with Co(3-methoxysalen).‡ We have further discovered a new 1 : 1 adduct prepared from Co(salen), Co(salen)py(O_2) has been observed by e.s.r. both as a solid and in fluid and frozen solution.

The 1 : 1 adduct Co(3-methoxysalen)py(O_2) was prepared by a slight modification of the procedure reported by Floriani and Calderazzo,[1e] we found it expedient to maintain the solution in the temperature range 0 to −20°. E.s.r. spectra of the oxygen adduct were taken from both frozen solution at 77°K and fluid solution at −44°. The parameters are listed in the Table. The spectra exhibit hyperfine lines from a *single* ^{59}Co nucleus and are quite similar to those published previously for 1 : 1 oxygen adducts of square-planar cobalt(II) complexes,[1b,c] except for the poorer resolution of the signal from frozen solution. The product of this oxygenation then is indeed a 1 : 1 adduct of a cobalt(II) Schiff's base complex with molecular oxygen, as reported by Floriani and Calderazzo.[1e]

Modifying the procedure of Bailes and Calvin,[3] we prepared [Co(salen)py]$_2O_2$ by exposing to oxygen an anhydrous solution of Co(salen) in pyridine at room temperature. Within about one half hour precipitation began and was completed overnight. The product was collected by filtration, washed with pyridine, and dried *in vacuo*. It was

---

† Abbreviations: acacen = [$CH_3C(O^-){=}CHC(CH_3)NCH_2$-]$_2$, salen = *NN′*-ethylenebis(salicylideneiminate), see also ref. 1e.

‡ It has been brought to our attention that similar observations have been recently and independently made in the laboratory of Dr. E. Perrotti.

identified as the 2 : 1 species by i.r. spectrum[1e] and elemental analysis.

E.s.r. parameters for some cobalt complexes[e]

Compound	$g_{\perp}$	$g_{\parallel}$[a]	g_{iso}[b]	Co $A_{\parallel}$, G[a]	Co a_{iso}, G[b]	N $A_{\parallel}$, G[a]
Co(3-methoxysalen)py_2	2·33[a,c]	2·038		78·0		12·5
Co(salen)py_x	2·32[a,c]	2·038[c]		75·1[c]		
Co(3-methoxysalen)py(O_2)	1·997[d]	2·079	2·024	17·3	12·6	
Co(salen)py(O_2)	1·997[d]	2·080	2·024	17·9	12·9	

[a] Measured from frozen pyridine solutions at 77°K.
[b] Measured from fluid pyridine solutions at −46°.
[c] Approximate value.
[d] Calculated from $g_{\perp} = \frac{1}{2}(3g_{\mathrm{iso}} - g_{\parallel})$.
[e] Estimated errors, unless noted: g values, ±0·005; hyperfine splittings, ±0·5.

However, the solution from which this dinuclear adduct precipitated gave an e.s.r. signal characteristic of a 1 : 1 molecular oxygen adduct which must be Co(salen)py(O_2). The e.s.r. parameters are listed in the Table. If the solution is stored at room temperature for some weeks, the signal from the 1 : 1 adduct weakens and ultimately disappears, and our observations preclude the existence of an equilibrium between Co(salen)py(O_2) and $[\mathrm{Co(salen)py}]_2O_2$.

Oxygenation of a solution of Co(salen) in pyridine in the temperature range −40° to −10° enabled us to prepare and observe the e.s.r. spectra of the 1 : 1 cobalt–oxygen adduct in both frozen and fluid solution without precipitation of the solid 2 : 1 species (Figure). This formation of Co(salen)py(O_2) at low temperature is reversible over several oxygenation–deoxygenation cycles.

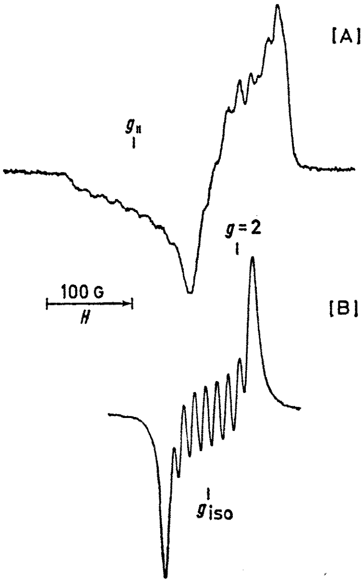
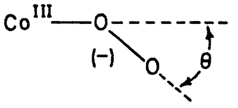


FIGURE. *E.s.r. spectra of* Co(salen)py(O_2). [A] *Frozen pyridine solution at* 77°K. [B] *Fluid pyridine solution at* −46°.

A dark-brown solid can be precipitated from these cold solutions by addition of heptane–toluene (4 : 1) with vigorous shaking, washed with cold pyridine, and dried *in vacuo* at −10°. This solid, cooled to 77°K, gives a strong but poorly resolved e.s.r. spectrum characteristic of a mononuclear or 1 : 1 adduct, together with a weaker signal due to unoxygenated Co(salen)py_x, where x is as yet undetermined. No signal due to unsolvated Co(salen) is observed. These results indicate that the solid material precipitated from cold solution is Co(salen)pyO_2, which, although impure, is here isolated for the first time.

The detection of a reasonably stable 1 : 1 oxygen adduct of Co(salen), suggested to us that residual paramagnetism of $[\mathrm{Co(salen)py}]_2O_2$ might be due to the presence of this adduct. The bridged dinuclear adduct does in fact exhibit a fairly strong e.s.r. signal in the solid state at 77°K, the interpretation of which is consistent with its being a superposition of two signals, one due to Co(salen)py(O_2), as expected, and a weaker one from Co(salen)py_x.

The strong resemblance of the e.s.r. spectra of the various 1 : 1 oxygen adducts of Co(acacen)B with those of Co(3-methoxysalen)B and Co(salen)B suggests that all of them have similar structures. On the basis of both i.r.[1a] and e.s.r.[1b] data, we have assigned the following structure to the Co–O–O fragment of Co(acacen)B(O_2):



This geometry for the salen adducts is contrary to the conclusion of Floriani and Calderazzo,[1e] which they drew from i.r. data alone, that Co(3-methoxysalen)py(O_2) contains a symmetrically disposed oxygen molecule, as in the case of $\mathrm{IrXCO(PPh_3)_2O_2}$, where X = Cl or I.[4]

This work was supported by the Advanced Research Projects Agency of the Department of Defense through the Northwestern University Materials Research Center and by the National Institutes of Health.

(*Received, February 18th,* 1970; *Com.* 236.)

---

[1] (a) A. L. Crumbliss and F. Basolo, *J. Amer. Chem. Soc.*, 1970, **92**, 55; (b) B. M. Hoffman, D. Diemente, and F. Basolo, *ibid.*, p. 61; (c) J. H. Bayston, N. King, F. D. Looney, and E. M. Winfield, *ibid.*, 1969, **91**, 2775; (d) H. Kon and N. Sharpless, *Spectroscopy Letters*, 1969, **1**, 45; (e) C. Floriani and F. Calderazzo, *J. Chem. Soc.* (*A*), 1969, 946.

[2] A. G. Sykes and J. A. Weil, *Progr. Inorg. Chem.*, in the press.

[3] R. H Bailes and M. Calvin, *J. Amer. Chem. Soc.*, 1947, **69**, 1886.

[4] S. J. LaPlaca and J. A. Ibers, *J. Amer. Chem. Soc.*, 1965, **87**, 2581; J. A. McGinnety, R. J. Doedens, and J. A. Ibers, *Science*, 1967, **155**, 709.