

Formation of a 1:1 Oxygen Adduct with the Cobalt(II)-Tetrasulphophthalocyanine Complex

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Summary The reversible formation of a 1:1 molecular oxygen adduct with cobalt(II)-tetrasulphophthalocyanine has been demonstrated by e.s.r. spectroscopy.

THERE has recently been considerable interest in the reactions of oxygen with cobalt(II) complexes. Mononuclear oxygen adducts have been reported with cobalt(II) complexes containing various Schiff bases,¹ corrin,² porphyrins,³ and bis-dimethylglyoxime.⁴ Adducts with the phthalocyanines, which show many similarities to the porphyrins, have not been reported though it is notable that an e.s.r. signal was observed in the reaction of cobalt(II)-phthalocyanine with oxygen, which was ascribed to a one-electron oxidation product of the phthalocyanine ligand.⁵ We report here the detection, by e.s.r. spectroscopy, of the formation of a mononuclear adduct of oxygen with cobalt(II)-tetrasulphophthalocyanine [Co(II)-TsPc hereafter] at low temperatures.

Solutions of Co(II)-TsPc⁶ in deoxygenated methanol showed an e.s.r. signal (see Table). Passage of gaseous ammonia for 2–3 s at –84 °C gave an extremely air-sensitive solution, from which we were unable to obtain accurate e.s.r. data for the simple cobalt(II) complex, owing to overlap with another signal. Oxygenation of this solution at –84 °C for 2–3 s caused complete conversion into this new complex with the new e.s.r. signal (see Figure and Table). The spectra show eight hyperfine lines due to a single ⁵⁹Co nucleus ($I = 7/2$), and the parameters are analogous to those of other 1:1 oxygen adducts with cobalt(II) complexes.^{1–4} We conclude that this is a 1:1 adduct of oxygen with Co-TsPc which, like the other

oxygen adducts, is best described¹ as a paramagnetic cobalt(III) complex with the superoxide anion (O_2^-) as a

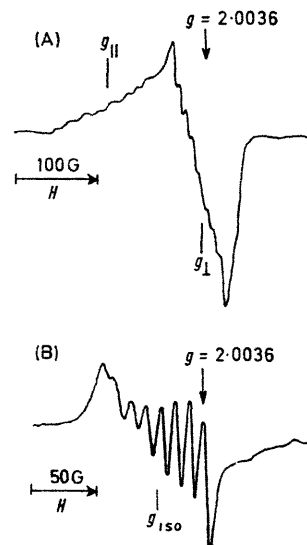


FIGURE. E.s.r. spectra of Co-TsPc(O₂): (A) frozen solution at –175 °C, (B) fluid solution at –100 °C.

ligand. The lack of nitrogen superhyperfine structure implies that either ammonia is not co-ordinated, or that the coupling constant is very small.

The oxygenation of solutions of Co(II)-TsPc in 90—95% aqueous methanol in the absence of ammonia caused both in the presence and absence of ammonia is reversible (at least three cycles of oxygenation and deoxygenation).

TABLE. *E.s.r. parameters at X-band for phthalocyanine complexes^a*

Compound	Solvent	g_{\perp}^d	g_{\parallel}^d	g_{iso}^e	$a_{\text{iso}}^{b,e}$	$A_{\parallel}(\text{Co})^{b,d}$	$A_{\perp}(\text{Co})^{b,d}$
Co(II)-TsPc	MeOH	2.27 ^c	2.068			107	c
Co-TsPc(O ₂)	MeOH + trace NH ₃	2.004	2.075	2.025	9.9	14.9	7.9

^a Errors: g_{iso} and $g_{\perp} \pm 0.001$; $g_{\parallel} \pm 0.002$; hyperfine splittings ± 0.5 .

^b $\times 10^4 \text{ cm}^{-1}$.

^c Approximate value [see T. Vännngard and R. Aasa in 'Proceedings of the First International Conference on Paramagnetic Resonance,' Jerusalem, 1962, Vol. 2 (ed. W. Low), Academic Press, New York, 1963, p. 517].

^d Measured from frozen solution at -175°C .

^e Measured from fluid solution at -100°C .

15—20% conversion into a species with $g_{\perp} = 2.005$ and $A_{\perp}(\text{Co}) = 9.2 \times 10^{-4} \text{ cm}^{-1}$ [g_{\parallel} is obscured by overlap with the signal of the simple cobalt(II) complex], *i.e.* a cobalt-oxygen adduct can be formed even in the absence of a nitrogenous base. The formation of the oxygen adducts

These results show that Co(II)-TsPc resembles the cobalt(II) corrinoids and porphyrins in the ability to form an oxygen adduct reversibly at low temperature, and that like the cobalt(II) corrinoids,² it can do this even in the absence of a nitrogenous base in the second axial position.

(Received, March 15th, 1971; Com. 274.)

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⁶ J. H. Weber and D. H. Busch, *Inorg. Chem.*, 1965, **4**, 469.