# An Electron Spin Resonance Study of the Interaction of Sulphur Dioxide with Tetraphenylporphyrincobalt(II)

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*Summary* Sulphur dioxide interacts reversibly with tetraphenylporphyrincobalt(II) to form an adduct in which $SO_2$ functions as a donor, while oxygen forms a superoxide complex.

TETRAPHENYLPORPHYRINCOBALT(II) [Co(tpp)], and related low spin $Co^{II}$ complexes can function as one electron donors or two electron acceptors.[1,2] We report that while oxygen interacts with Co(tpp) and Co(tpp)B (B = MeCN, py) to form co-ordinated superoxide complexes, $SO_2$ functions as a donor toward Co(tpp) and there is no evidence for any $SO_2^-$ species, or oxidation of $Co^{II}$.

Frozen toluene solutions of Co(tpp) with $SO_2$ have e.s.r. spectra that indicate formation of a near axially symmetric complex (Figure, Table). This adduct formation is found to be completely reversible. The e.s.r. spectrum of the $SO_2$ adduct is similar to that for free Co(tpp) except that the $^{59}Co$ coupling constants are reduced and the $g$ values shifted. In contrast with the $O_2$ complex, the $SO_2$ adduct clearly contains $Co^{II}$. The $g$ value ordereing ($g_\perp > g_\parallel$) for Co(tpp) and the $SO_2$ adduct are most consistent with a $(d_{xz}, d_{yz}, d_{xy})^6 (d_{z^2})^1$ ground configuration. Reductions in $g_\perp$ and the $^{59}Co$ coupling constants for Co(tpp)$SO_2$ compared to the values for Co(tpp), are characteristic of donor adduct formation and primarily result from an increase in the $d_{xz,yz} \rightarrow d_{z^2}$ energy separation ($g_\perp = 2{\cdot}00 - 6\, \lambda_{eff}/\Delta E_{xz,yz \rightarrow z^2}$).[3] Both $\sigma$-donor and $\pi$-acceptor properties of $SO_2$ can contribute to the increased $d_{xz,yz} \rightarrow d_{z^2}$ energy separation. Comparison of the e.s.r. parameters

TABLE

*E.s.r. parameters for* Co(tpp) *and adducts with* CO, $O_2$, *and* $SO_2$ *in frozen toluene* (100 K)

| | $g_\parallel$ | $A(^{59}Co),G$ | $g_\perp$ | $B(^{59}Co),G$ |
|---|---|---|---|---|
| Co(tpp) .. .. .. | 1·97 | 161 | 2·80 | 153 |
| Co(tpp)$SO_2$ .. .. | 2·025 | 109 | 2·465 | 66 |
| Co(tpp)CO[a] .. .. | 2·017 | 78 | 2·217 | 33 |
| Co(tpp)MeCN[a] .. .. | 2·028 | 92 | 2·364 | 23 |
| Co(tpp)$O_2$ .. .. | *ca.* 2·05 | — | 1·993 | 31 |
| Co(tpp)MeCN($O_2$) .. | 2·068 | 13 | 2·003 | 18 |

[a] ref. 1.

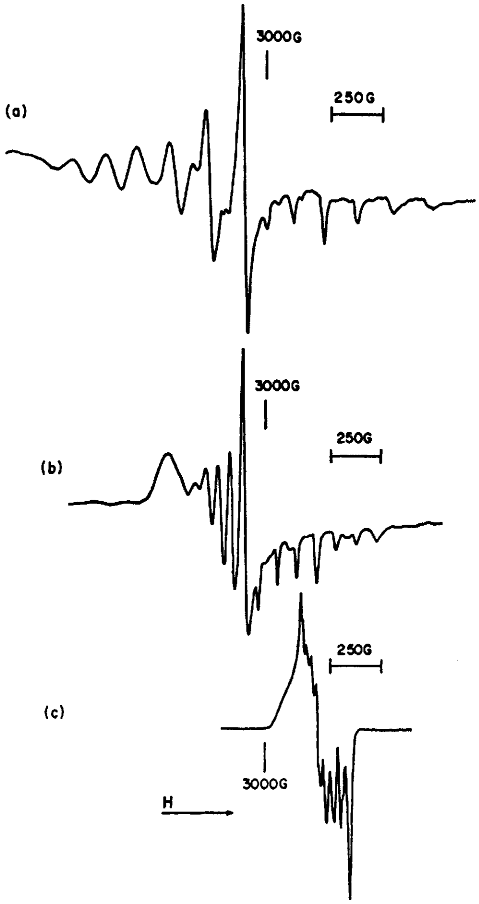

FIGURE. *E.s.r. spectra for frozen toluene solutions* (100 K. ($\nu$ = 9·154 GHz), (*a*) Co(tpp), (*b*) Co(tpp)$SO_2$, (*c*) Co(tpp)$O_2$.

suggests that $SO_2$ is substantially less effective than CO, MeCN, or pyridine in these combined effects. The most important result is that there is no evidence for an $SO_2^-$ species or any oxidation of $Co^{II}$ which can be contrasted with oxygen interacting with Co(tpp)B (B = MeCN, py) to form superoxide complexes of $Co^{III}$.[2] We have also found that oxygen co-ordinates Co(tpp) even in the absence of a donor to form a superoxide complex, (Table, Figure).

Presence of a donor molecule in the fifth co-ordination site is considered to facilitate oxidative addition reactions of $Co^{II}$ including oxygen adduct formation.[2] Mono base adducts of Co(tpp) with py and MeCN were studied with $SO_2$ in order to evaluate the influence of the co-ordinated donor on $SO_2$ complex formation. Addition of $SO_2$ to a toluene solution of Co(tpp)B (B = MeCN or py) did not result in an $SO_2$ complex. There is no indication of ligand displacement, six co-ordinate adduct, $SO_2^-$ species, or oxidation of $Co^{II}$ in this system. This is in marked contrast with the oxygen system where added donor such as pyridine enhances $O_2$ complex formation.[2] This is particularly interesting, for $SO_2$ has a higher electron affinity and is in general a better acceptor than $O_2$.[4] The electron affinity of the ligand is clearly not the exclusive factor in determining the charge and spin distribution in the complex. Covalent bonding of oxygen to Co(tpp) must be responsible for producing an adduct resembling co-ordinated superoxide. $[Co(CN)_5]^{3-}$ is known to react with $SO_2$ to give a diamagnetic oxidative addition product formulated as $\{[(NC)_5Co]_2SO_2\}^{6-}$.[5] The absence of any related oxidative addition products in the Co(tpp) or Co(tpp) donor system with $SO_2$ may result in part from the relatively large steric requirements of this porphyrin complex.

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