Oxygenation of Cobalt Tetraphenylporphine as Investigated by ESR Spectroscopy

The reversible one-electron oxidation of cobalt phthalocyanine by O_2, and related oxidation catalytic action have already been reported (*1*). Further studies of biological interest have been carried out on the oxygenation of cobalt(II) tetraphenylporphine (Co-TPP), further coordinated with ligands in solutions. Special attention has been paid to the electronic effect exerted by these other ligands.

The Co-TPP was synthesized according to Ref. (*2*) and allowed to dissolve in $CHCl_3$ containing excess amounts of further ligands *in vacuo*. The ligands used were tetrahydrofuran, triphenylphosphine, piperidine, quinoline, pyridine, 4-cyanopyridine, 4-aminopyridine, 4-methylpyridine, benzimidazole, and imidazole. The concentration of Co-TPP in $CHCl_3$ was ranged from 1.42×10^{-3} to 1.42×10^{-2} *M*, and oxygenation was carried out at room temperature usually for about 10 min. ESR spectra of the complex were measured before and after exposure to O_2, respectively, at 77°K by a JEOL-P-10 (X-band) spectrometer with 100-kcps field modulation.

All of the Co-TPP complex coordinated with further ligands gave rise to ESR spectra characterized with 8 *hf* lines familiar to the cobalt(II) complexes (*3*). Some of them yielded, in addition, 3 *shf* lines due to ligand-nitrogen ($I = 1$) or 2 *shf* lines due to ligand-phosphorus ($I = \frac{1}{2}$). The presence of these *shf* lines suggests that the cobalt complex is coordinated with a *single* ligand molecule such as pyridine or triphenylphosphine, unlike Mn(II)-TPP or Fe(II)-TPP in which two ligand molecules (pyridine or imidazole) are bound to one metal atom (*4*), perhaps along the *Z* direction in accord with Eq. (1).

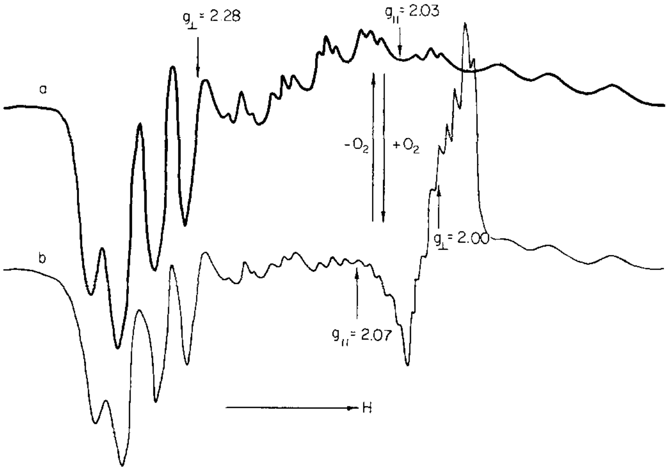

FIG. 1. ESR spectra of cobalt–tetraphenylporphine–pyridine complex in chloroform–pyridine solution measured at 77°K: (a) evacuated; (b) exposed to O_2 for 10 min at room temperature.

$$\text{Co-TPP} + n\text{L} \rightleftarrows \text{Co-TPP-L} + (n-1)\text{L}. \quad (1)$$

A typical ESR spectrum for Co-TPP-pyridine is illustrated in Fig. 1a.

When the Co-TPP-L was exposed to 1 atm O_2, the original signal due to Co(II)

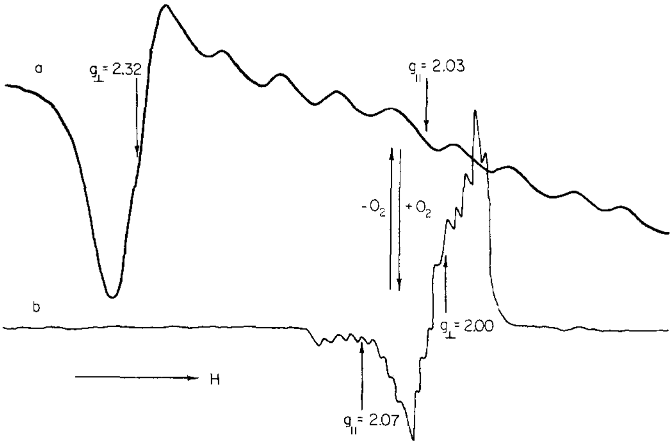

FIG. 2. ESR spectra of cobalt–tetraphenylporphine–4-aminopyridine complex in chloroform–4-aminopyridine solution measured at 77°K: (a) evacuated; (b) exposed to O_2 for 10 min at room temperature.

more or less decayed depending on the kind of further ligand while a new signal developed in the vicinity of $g \sim 2.0$. Evacuation of O_2 restored the original spectrum. Thus, the spectral change was reversible with respect to O_2 exposure. In Fig. 1 is shown such a spectral change for Co-TPP-pyridine. The change in the spectrum was rather similar to that of the oxygenation of cobalt phthalocyanine (*1*) or Vitamin B_{12r} (*5*). It should be noted however that for the Co-TPP coordinated with benzimidazole or imidazole the oxygenation took place in an irreversible manner giving rise to no ESR signal.

The Co-TPP coordinated with 4-aminopyridine revealed an *intermediary* behavior for the complexing of O_2; the signal due to Co entirely diminished on adding O_2 while the signal near $g \sim 2.0$ developed and remained stable for a while (Fig. 2b) although prolonged contact with O_2 overnight resulted in disappearance of the signal. The O_2 uptake was largely reversible at the initial stage of O_2 exposure but not after prolonged contact where no ESR signal was detectable. The reversible change of the spectrum is illustrated in Fig. 2. As shown in Fig. 2b, the $g \sim 2.0$ signal newly developed was anisotropic and furthermore it was characterized with two sets of 8 *hf* lines having a rather small coupling constant (14.2–18.3 G). A similar *hf* structure was reported recently by Winfield *et al.* (*5*) with respect to an oxygenated Vitamin B_{12r} and also by Misono and Koda (*6*) with 1:1 adducts of bissalicylaldehyde–imine–cobalt(II) complexes with O_2. The presence of 8 *hf* lines would suggest that the newly developed signal on exposure to O_2 is ascribable to an oxygen radical combined to cobalt atom.

The oxygenation of Co-TPP-L can be considered to occur via replacing a weakly coordinated $CHCl_3$ molecule by O_2, resulting in the formation of a hexacoordinated complex (O_2-Co-TPP-L). Since the amount of O_2 taken up by the Co-TPP-L was, at most, less than 0.5 mole of O_2/mole of cobalt,* the oxygenation may probably be represented by the successive reactions:

$$O_2 + \text{Co-TPP-L} \rightleftarrows O_2\text{-Co-TPP-L}, \quad (2)$$

$$\text{L-TPP-Co} + O_2\text{-Co-TPP-L} \rightarrow \text{L-TPP-Co-}O_2\text{-Co-TPP-L}. \quad (3)$$

The $3d_{z^2}$ orbital energy of Co-TPP-L is expected to rise up when L is strongly coordinated just as in the case of $Co(CN)_5^{3-}$ (*7*) so that the unpaired electron of Co(II) may readily be transferred to the oxygenated complex resulting in a diamagnetic, binuclear cobalt (*8*) as shown by Eq. (3), where the complexing of O_2 is no longer

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* The amount of O_2 taken up was not the same for each ligand investigated; the Co-TPP coordinated with benzimidazole or imidazole took up O_2 to the greatest extent.

reversible. The role of benzimidazole or imidazole in the complexing of O_2 could be explained in such a way. On the other hand, the Co-TPP complexes coordinated with the other ligands (tetrahydrofuran, quinoline, and some of the pyridine derivatives) took up O_2 weakly and reversibly according to Eq. (2). Inspection of ESR spectra at 10 min after O_2 addition led us to suggest that the degree of O_2 complexing is approximately given by the sequence:

tetrahydrofuran ∼ quinoline < 4-cyanopyridine
< 4-methylpyridine < triphenylphosphine
∼ pyridine < piperidine < 4-aminopyridine
< benzimidazole < imidazole.

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Crystalline Structures of USb_3O_{10} and $USbO_5$ in Acrylonitrile Catalysts*

In an earlier publication (*1*) the existence of two new U–Sb-oxide crystalline phases was reported and their importance in the catalytic synthesis of acrylonitrile from propylene, ammonia, and air was illustrated. Additional study of these crystalline compounds leads to the conclusion that Phase I, reported earlier as $(UO_2)Sb_3O_7$, is better described as USb_3O_{10} and Phase II as $USbO_5$, instead of $Sb_3U_3O_{14}$.

Pure Phase I was prepared by dissolving the excess antimony oxide with HCl from a U–Sb-oxide composition having a high antimony content ($U/Sb = 1:9.2$). Pure Phase II was prepared by thermal decomposition of Phase I at 1090°C. The heavy atom ratio of the compounds was assessed by wet test methods (*2*) and X-ray fluorescence analysis.

The crystal structure of Phase I was determined from powder diffraction data and by analogy to the single crystal work of Chevalier and Gasperin (*3*) on the UNb_3O_{10} and related systems. As shown in Table 1, the USb_3O_{10} compound (in which the d calculations come from our lattice constants and the intensity calculations come from the x,y,z and B's of Chevalier and Gasperin (*3*) for UNb_3O_{10}) has orthorhombic symmetry and belongs to the *Fddd* space group. All of the previously observed lines (*1*) could be assigned, and more importantly the fit between calculated

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