Electron Spin Resonance Study of the Autoxidation of Hydrazine, Hydroxylamine, and Cysteine catalysed by the Cobalt(II) Chelate Complex of 3,10,17,24-Tetrasulphophthalocyanine

By **David J. Cookson** and **Thomas D. Smith,*** Chemistry Department, Monash University, Clayton, Victoria, Australia 3168
John F. Boas, Peter R. Hicks, and **John R. Pilbrow,** Physics Department, Monash University, Clayton, Victoria, Australia 3168

The title complex [Co^{II}(tspc)] is an efficient catalyst for the oxidation of hydrazine, hydroxylamine, or cysteine in aqueous solution by molecular oxygen. E.s.r. measurements have been made on frozen aqueous solutions containing the complexes of [Co^{II}(tspc)] with dioxygen, hydrazine, and hydroxylamine as a precursor to similar measurements on aqueous solutions containing the [Co^{II}(tspc)] substrate complexes exposed to molecular oxygen. The oxidation of hydrazine and hydroxylamine involves the initial formation of a 1 : 1 adduct between [Co^{II}(tspc)] and the substrate which reacts with molecular oxygen to yield the oxidation products and [Co^{II}(tspc)]. In the case of cysteine the oxidation process involves an electron-transfer reaction resulting in the formation of [Co^{I}(tspc)]$^-$ and cystine.

STUDIES of 3,10,17,24-tetrasulphophthalocyanine (H_2tspc) complexes have indicated that their catalytic activity is remarkably dependent on the nature of the central metal ion and its ability to bind extraplanar ligands.[1] Thus it might be expected that [Co^{II}(tspc)], which readily binds extraplanar ligands, would possess catalytic activity. For example, [Co^{II}(tspc)] was found to catalyse the autoxidation of hydrazine at pH >12.[2,3] Addition of hydrazine to an alkaline solution of [Co^{II}(tspc)] resulted in the formation of a green solution which became yellow at pH >12. This change has been interpreted as arising from the formation of a 1 : 1 [Co^{II}(tspc)]–N_2H_4 adduct,[2] although other workers have assigned the resulting change as reduction to [Co^{I}(tspc)]$^-$.[4-6] Since both oxygen and hydrazine form adducts with Co^{II} reversibly, the reactive intermediate involved in the autoxidation reaction was considered to be a ternary complex of [Co^{II}(tspc)] containing hydrazine and oxygen.

Wagnerova *et al.*[7] showed that the autoxidation of hydroxylamine is also catalysed by [Co^{II}(tspc)] and results in the formation of nitrogen, dinitrogen oxide, and nitrite. The oxidation reaction was shown to proceed only at pH >10 and, as in the case of hydrazine, the mechanism of the reaction was explained by the formation of a ternary complex (substrate–catalyst–oxidant) in whose co-ordination sphere the electron-transfer process occurred. At pH 11.6 the reaction was very slow, while at pH <10 the reaction rate was practically zero. It was assumed by these workers that a prerequisite for the reactivity of [Co^{II}(tspc)] is dissociation of a very weakly acidic hydrogen atom, probably from the pyrrole nitrogen of the phthalocyanine.

The catalytic processes involved in the oxidation of cysteine to cystine by [Co^{II}(tspc)] have been studied by Kundo and Keier.[8] In contrast to the reactions involving hydrazine and hydroxylamine, the existence of a reduced form of the catalyst was postulated. The reaction of cysteine with [Co^{II}(tspc)] caused reduction of the latter to [Co^{I}(tspc)]$^-$ and this process was compared with similar reactions involving other reducing agents including hydrazine.

It is apparent from these investigations that confusion exists as to the nature of the intermediates formed during the catalytic process, particularly with respect to the oxidation state of the cobalt ion. E.s.r. spectroscopy is a powerful tool in the study of changes occurring as a result of redox reactions, and in the present investigation can be used to delineate the presence of the various oxidation states of [Co^{II}(tspc)] and any binary or ternary adducts formed. Before the role of [Co^{II}(tspc)] in any catalytic process can be investigated, the nature of the cobalt(II) species present in solution under comparable conditions to that under which the catalytic process takes place must be known. The ability of [Co^{II}(tspc)] to bind molecular oxygen reversibly, a property which has been shown to play a vital role in the catalytic activity of the complex, needs to be known as well. It has been postulated that [Co^{II}(tspc)] shows its highest catalytic activity in solution in the range pH 8.5—10.0.[9] However, this conflicts with the observations of Veprek-Siska *et al.*[10] for catalytic processes involving both hydrazine and hydroxylamine, and also calls into question the role of molecular oxygen as it has been shown that the oxygen adduct of [Co^{II}(tspc)] is only formed to a large extent in alkaline solutions, *i.e.* 0.1—1.0 mol dm^{-3} Na[OH], while a monomer–dimer equilibrium prevails at neutral pH.[4]

---

[1] P. Waldmeir and H. Sigel, *Chimia* (*Switz.*), 1970, **24**, 195.
[2] D. M. Wagnerova, E. Schwertnerova, and J. Veprek-Siska, *Coll. Czech. Chem. Comm.*, 1973, **38**, 756.
[3] E. Schwertnerova, D. M. Wagnerova, and J. Veprek-Siska, *Z. Chem.*, 1974, **14**, 311.
[4] L. C. Gruen and R. J. Blagrove, *Austral. J. Chem.*, 1973, **26**, 319.
[5] D. H. Busch, J. H. Weber, D. H. Williams, and N. J. Rose, *J. Amer. Chem. Soc.*, 1964, **86**, 5161.
[6] P. Day, H. A. O. Hill, and M. G. Price, *J. Chem. Soc.* (*A*), 1968, 90.
[7] D. M. Wagnerova, E. Schwertnerova, and J. Veprek-Siska, *Coll. Czech. Chem. Comm.*, 1974, **39**, 3036.
[8] N. N. Kundo and N. P. Keier, *Russ. J. Phys. Chem.*, 1968, **42**, 707.
[9] N. N. Kundo, N. P. Keier, G. V. Glazneva, and E. K. Mamaeva, *Kinetika i Kataliz*, 1967, **8**, 1325.
[10] J. Veprek-Siska, E. Schwertnerova, and D. M. Wagnerova, *Chimia* (*Switz.*), 1972, **26**, 75.

Consequently, the present investigation has been carried out under both acidic and alkaline conditions in order to shed some light on these contradictions.

RESULTS AND DISCUSSION

Oxygenation of [Co^{II}(tspc)].—A 1.0×10^{-3} mol dm^{-3} aqueous solution of [Co^{II}(tspc)] at pH 7.0 did not give an e.s.r. spectrum due to aggregation of the cobalt(II) chelate. However, addition of 10% v/v of *NN*-dimethylformamide (dmf) resulted in the disaggregation of the chelate and provided ideal circumstances for the observation of an e.s.r. spectrum due to the monomeric form of [Co^{II}(tspc)].[11] A decrease in the pH of this solution resulted in a decrease in signal intensity, presumably due to reformation of the aggregate. When the pH was increased above 10.0 and the solution exposed to air, a signal attributed to an oxygen adduct of the type [Co^{III}(tspc)(O_2)] was observed at −140 °C.[12]

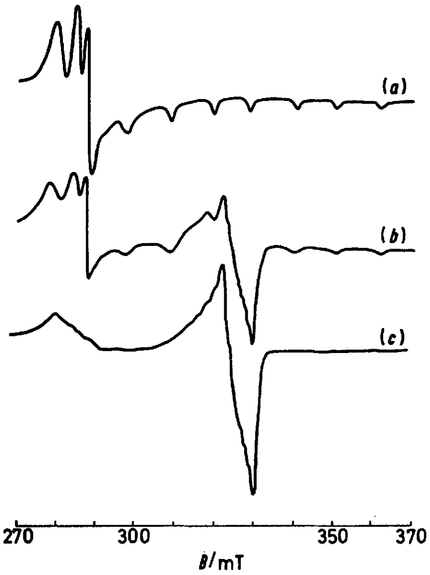

FIGURE 1 *X*-Band e.s.r. spectra at −140 °C due to a 10% dmf–water solution of [Co^{II}(tspc)] at pH 7.0—9.6 (*a*), 10.2—11.5 (*b*), and 1.20—13.0 (*c*) [Curve (*a*) is identical to the spectrum shown in ref. 11, Figure 2]

The intensity of this signal increased with pH, reaching a maximum in the range pH 12.0—13.0. At the same time, the signal at −140 °C due to [Co^{II}(tspc)] decreased in intensity, so that only a weak signal was observed at pH 13 at 2 800 G (Figure 1).[*]

At high pH the intensity of the oxygen signal could be increased by bubbling oxygen through the solution. On the other hand, decreasing the pH from 12 or bubbling nitrogen through the solution resulted in a decrease in intensity of the oxygen signal and a regeneration of the signal due to the cobalt(II) species. Prolonged standing in air, however, resulted in a loss of signal intensity due to irreversible oxidation to a cobalt(III) complex.

The e.s.r. signal due to the [Co^{III}(tspc)(O_2)] adduct is shown in detail in Figure 2, together with a simulated spectrum computed using the parameters given in Table 1 and the computer-simulation techniques described previously.[11,13] The best fit to the experimental lineshape was obtained using a model in which the *g* and hyperfine tensors were non-coincident with the unpaired electron largely localized on the oxygen molecule. The spin Hamiltonian employed in the analysis of the results is as in (1) where the *z* and *Z* axes coincide but, in the *x*–*y* plane, the *x* and *X* axes differ in orientation by an angle α; otherwise the terms in the equation have their usual meanings. These considerations, which are identical to those discussed previously for the complex [Co^{III}(tpps)(O_2)] (tpps = tetraphenylporphyrintetrasulphonate),[13] suggest the model shown in Figure 3(*a*), with a Co–O–O angle of 100 ± 5°. The *g* values and hyperfine constants are similar to those found for other oxygenated planar cobalt(II) complexes.[13] It is particularly important to notice that, in order to obtain satisfactory agreement between experiment and theory, α must be non-zero, confirming the idea that the Co–O–O angle is neither 90 nor 180°. Figure 3(*b*) shows that, by suitable rearrangement of axes, the results could, alternatively, suggest a Co–O–O angle of 170°. As argued previously[13] the model in Figure 3(*a*) is believed to be the more likely.

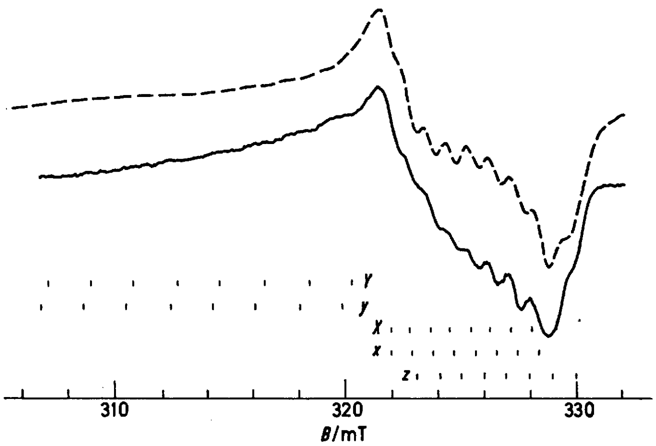

FIGURE 2 *X*-Band e.s.r. spectrum at −140 °C due to the oxygen complex of [Co^{II}(tspc)] at pH 12.0. The broken curve represents a computer simulation of the experimental spectrum using the parameters listed in Table 1

$$\mathscr{H} = \beta \sum_{i=x,y,z} g_i B_i S_i + \sum_{j=X,Y,Z} A_j S_j I_j (S = \tfrac{1}{2}, I = \tfrac{7}{2}) \quad (1)$$

TABLE 1

Spin-Hamiltonian parameters for oxygenated [Co^{II}(tspc)] [model in Figure 3(*a*)]

$g_x = 2.005 \pm 0.002$, $g_y = 2.084 \pm 0.002$, and $g_z = 2.001 \pm 0.002$
$A_X = (8.0 \pm 0.5) \times 10^{-4}$, $A_Y = (18.0 \pm 0.5) \times 10^{-4}$, and $A_Z = (9.0 \pm 0.5) \times 10^{-4}$ cm^{-1}, $\alpha = 10 \pm 5°$
Linewidths: $\sigma_x = 0.0006$, $\sigma_y = 0.0022$, and $\sigma_z = 0.0007$ cm^{-1}

---

[*] Throughout this paper: 1 G = 10^{-4} T.

[11] J. A. De Bolfo, T. D. Smith, J. F. Boas, and J. R. Pilbrow, *J.C.S. Faraday II*, 1976, 481.

[12] E. W. Abel, J. M. Pratt, and R. Whelan, *Chem. Comm.*, 1971, 449.

[13] J. A. De Bolfo, T. D. Smith, J. F. Boas, and J. R. Pilbrow, *J.C.S. Dalton*, 1976, 1495.

Carter *et al.*,[14] in studies of the reversible oxygen uptake of several cobalt(II) complexes of the type [Co(L)B] (L = a quadridentate ligand and B = an axial ligand), concluded that the better the π-electron donating ability of B the more electron density there would be on the cobalt atom and hence the better the π-bonding electron flow from cobalt to oxygen, giving a greater ease of formation of the oxygen adduct. The relative effect of the π-donating ability of the two nitrogen bases imidazole and pyridine was compared by Rollman and Chan,[15] who noted that the imidazole derivative of [Co^{II}(tspc)] reacted rapidly with oxygen in solution whereas the pyridine derivative did not. In the present instance, a consideration of the pH dependence of the oxygenation of [Co^{II}(tspc)] in aqueous solution suggests that the mechanism involves the replacement of a solvent molecule in [Co^{II}(tspc)] by a hydroxyl group at higher pH, thereby increasing the oxygen-carrying ability of [Co^{II}(tspc)].

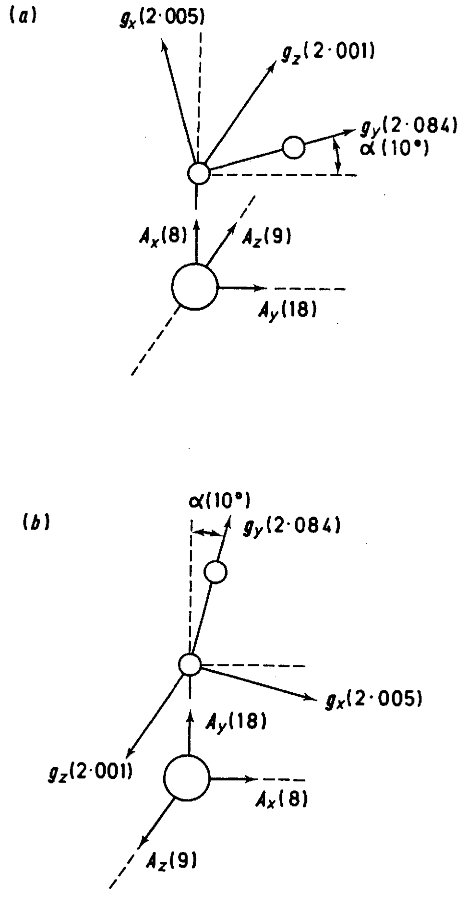

FIGURE 3 Arrangement of principal axes for two possible models of the [Co^{III}(tspc)(O$_2$)] complex

Catalytic Autoxidation of Hydrazine.—Addition of hydrazine (5—10% v/v) to the intensely blue aqueous solution of [Co^{II}(tspc)] gave a green solution, which, when frozen to −140 °C, gave the e.s.r. spectrum shown in Figure 4. At high spectrometer gain, splitting of the lines in the ' parallel ' region of the spectrum was apparent, and is attributed to formation of a 1 : 1 adduct between [Co^{II}(tspc)] and hydrazine. The magnetic parameters of the spectrum in Figure 4, attributed to low-spin Co^{II} in a d_{z^2} ground state, were determined by computer simulation of the lineshape using the methods described previously [11] and are given in Table 2. The spin Hamiltonian (2) used to explain the results was based on an axial model, where $S = \frac{1}{2}$, $I = \frac{7}{2}$, and

$$\mathscr{H} = \beta[g_{\parallel}B_zS_z + g_{\perp}(B_xS_x + B_yS_y)] + A_{\parallel}S_zI_z + A_{\perp}(S_xI_x + S_yI_y) + A_{\parallel}{}^{N}S_zI^{N} + A_{\perp}{}^{N}(S_xI_x{}^{N} + S_yI_y{}^{N}) \quad (2)$$

$I^N = 1$. Here $A_{\parallel}{}^N$ and $A_{\perp}{}^N$ refer to nitrogen hyperfine structure due to a single nitrogen nucleus of either hydrazine or hydroxylamine in an axial position. The possible influence of a quadrupole term, including ' forbidden ' $\Delta m = \pm 1$ and ± 2 lines, $P[I_{z^2} - \frac{1}{3}I(I + 1)]$, was investigated, but the best results were found for $P = 0$, consistent with previous work on phthalocyanines.[11] Improvement in the overall fit in the ' parallel ' region of the spectrum, *viz.* 300—361 mT, was achieved through the linewidth variation (3) where

$$\sigma_{\parallel} = a + bm_I{}^2 \quad (3)$$

$m_I = I, I - 1 \ldots - I$. Such effects are attributed to restricted motion, perhaps of axial ligand or solvent molecules, but no detailed analysis was attempted. Limits placed on the various parameters in Table 2 were arrived at by considering the degree of worsening of fit as the parameters were altered. Consideration of the stick spectra in Figure 4 will indicate the likely limits. The g and A values both here and later are consistent with other similar [Co^{II}(tspc)] cases.[11]

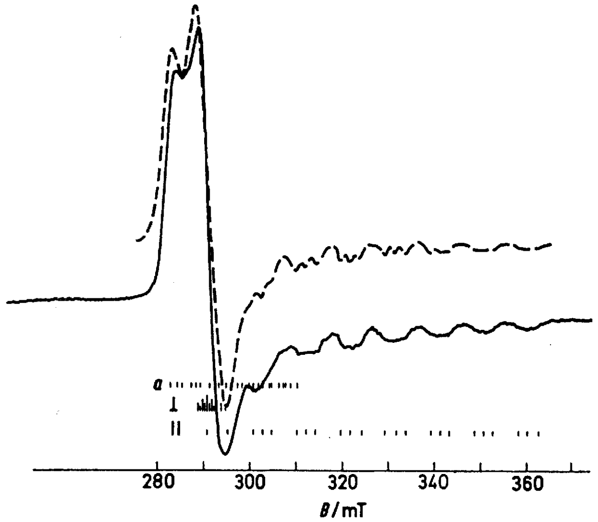

FIGURE 4 X-Band e.s.r. spectrum at −140 °C due to an aqueous solution of [Co^{II}(tspc)] (1.0 × 10^{-3} mol dm^{-3}) containing 10% v/v of hydrazine. The broken curve represents a computer simulation of the experimental spectrum using the parameters listed in Table 2. Variation in z or ' parallel ' linewidths with m_I has been allowed for

---

[14] M. J. Carter, D. P. Pillema, and F. Basolo, *J. Amer. Chem. Soc.*, 1974, **96**, 392.

[15] L. D. Rollman and S. I. Chan, *Inorg. Chem.*, 1971, **10**, 1978.

TABLE 2

Spin-Hamiltonian parameters for the monomeric [Co^{II}(tspc)]

Cobalt species	$g_{\parallel}$	$g_{\perp}$	Cobalt values (cm^{-1})		Nitrogen values (cm^{-1})		Linewidths (cm^{-1}) [see equation (3)]		
			$10^4A_{\parallel}$	$10^4A_{\perp}$	$10^4A_{\parallel}{}^N$	$10^4A_{\perp}{}^N$	10^4a	10^4b	$10^4\sigma_{\perp}$
	±0.005	±0.005	±1	±5	±1	±2	±1	±0.1	±4
[Co^{II}(tspc)(N_2H_4)] (in water)	1.996	2.238	90	6	20	13	8	0.6	15
(in 10% dmf–water)	2.004	2.243	90	6	20	10	15	0.6	20
[Co^{II}(tspc)(NH_2OH)] (in 10% dmf–water)	2.004	2.238	90	10	20	15	8	0.6	14

When oxygen was bubbled through the green solution the colour reverted to the original intense blue, and when this blue solution was allowed to stand in the absence of oxygen the green colour was regenerated. This cycle could be repeated until all the hydrazine was consumed. The blue colour was also regenerated by addition of acid to the green solution. However, additions of acid also caused a decrease in the e.s.r. signal intensity such that no signal was observed at pH <8.0, indicating that in this blue solution [Co^{II}(tspc)] is behaving as it would in an aqueous solution containing only [Co^{II}(tspc)] for which no signal was observed at this pH due to formation of polymeric [Co^{II}(tspc)] species. On addition of base to the green solution, the e.s.r. signal intensity increased, reaching a maximum at pH *ca.* 11.5. Further additions of base caused the solution to become yellow and the signal intensity decreased, such that at pH 13.0 no e.s.r. signal was observed. The colour change and the loss of signal intensity point to the formation of [Co^{I}(tspc)]$^-$ at pH >11.5.

Provided that the pH was kept below 11.5, the formation of the hydrazine adduct, as monitored by the e.s.r. signal intensity, could be controlled reversibly by adjusting the pH. However, addition of acid to solutions at pH >11.5, such that the final pH was, for example, 11.5, did not result in the complete recovery of the signal intensity when compared with the signal intensity of a solution at pH 11.5 which had not been taken above this value. As the pH was increased above 11.5 the extent of recovery of the signal intensity decreased until eventually no e.s.r. spectrum was obtained at pH 11.5 from a solution originally at pH 13.0 to which acid had been added in the presence of air. In effect, the formation of the hydrazine adduct is not completely reversible if the solution pH is raised above 11.5. However, in such a situation, lowering the pH to *ca.* 7.0 produced the original blue solution of [Co^{II}(tspc)] and the catalytic process could be once more recommenced by increasing the pH.

Similar changes in e.s.r. signal intensity and colour were observed in solutions containing 1.0×10^{-4} mol dm^{-3} [Co^{II}(tspc)], and on addition of hydrazine to a 10% dmf–water solution of [Co^{II}(tspc)]. The spectrum (Figure 5) was analysed and interpreted as that in Figure 4, using equations (2) and (3). Again there was no evidence for a quadrupole term, so that $P = 0$. It is apparent from these observations that once [Co^{I}(tspc)] is formed it persists over a wide pH range and only when the pH is adjusted such that the reducing and co-ordinating ability of hydrazine is diminished, as a result of protonation, is the cobalt(I) chelate reoxidized to [Co^{II}(tspc)].

The oxidation of hydrazine has been shown to involve the initial formation of a binary adduct with [Co^{II}(tspc)]. In addition the catalytic process occurs at pH values as low as 9.0, but most effectively at pH 11.5 where the concentration of the binary adduct reaches a maximum. The pH dependence of the initial formation of the binary adduct most probably involves deprotonation of the species $NH_2NH_3^+$ (p*K* *ca.* 8.14).[16] The subsequent pH dependence of the reaction is similar to that relating to the formation of an oxygenated species. However, no evidence for the formation of a ternary adduct involving [Co^{II}(tspc)], hydrazine, and oxygen was found. At high pH the reduction to a cobalt(I) species indicates that hydrazine is oxidized by a simple electron-transfer reaction.

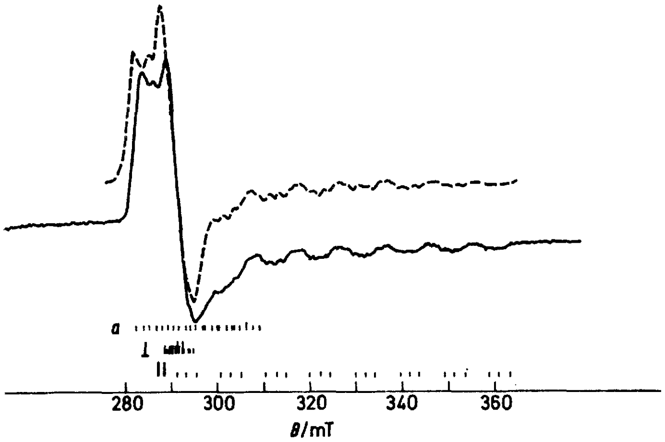

FIGURE 5 *X*-Band e.s.r. spectrum at −140 °C due to a 10% dmf–water solution of [Co^{II}(tspc)] containing 10% v/v of hydrazine. The broken curve was simulated as in Figure 4

Catalytic Autoxidation of Hydroxylamine.—No e.s.r. spectra were observed from frozen aqueous solutions at −140 °C of [Co^{II}(tspc)] (1.0×10^{-3} mol dm^{-3}) to which hydroxylamine (1.0×10^{-2} mol dm^{-3}) had been added prior to freezing. Signals were observed from aqueous solutions containing 10% v/v of dmf and consequently all the measurements were carried out using this solution composition.

---

[16] K. Sallavo and P. Lumme, *Suomen Kem.*, 1967, **B40**, 155.

Figure 6 shows the e.s.r. spectrum at −140 °C due to aqueous solutions of [Co^{II}(tspc)] and hydroxylamine at various pH. At pH <3.0 [curve (*a*)] the e.s.r. spectrum at −140 °C is very similar to that observed for solutions of similar composition prior to the addition of hydroxylamine. Increasing the pH resulted in a decrease in intensity of the signal due to [Co^{II}(tspc)] and the appearance of a signal attributed to a [Co^{III}(tspc)(O$_2$)] adduct. At pH *ca.* 4 the signal due to [Co^{II}(tspc)] had changed in appearance and, as the pH was further increased to *ca.* 5.0, the signal of the oxygen adduct disappeared and a single narrow line of the type attributed to a free-radical species was observed. Further increases in pH resulted in an increase in the free-radical signal, although the signal due to the [Co^{II}(tspc)] species did not change in shape between pH 5.1 and 10.0. This latter signal, at high instrumental gain, showed splitting of the hyperfine lines in the $g_{\parallel}$ region of the spectrum, attributed to the formation of a hydroxylamine adduct in the range pH 5.0—10.0. Above pH 6.5 the free-radical signal decreased in intensity and was quite weak at pH 8.5. Above pH 10.5 the solution changed colour from blue to green, and there was a corresponding change in the e.s.r. spectrum of the [Co^{II}(tspc)] species, as well as a decrease in intensity at the highest pH. The colour change, and the decrease in signal intensity, may be accounted for by the formation of a cobalt(I) species, even though a cobalt(II) species is still present at pH 12.9. Representative magnetic parameters for the spectra of low-spin [Co^{II}(tspc)] are given in Table 2, based on a fit to Figure 6(*d*). These results were obtained as for Figures 4 and 5.

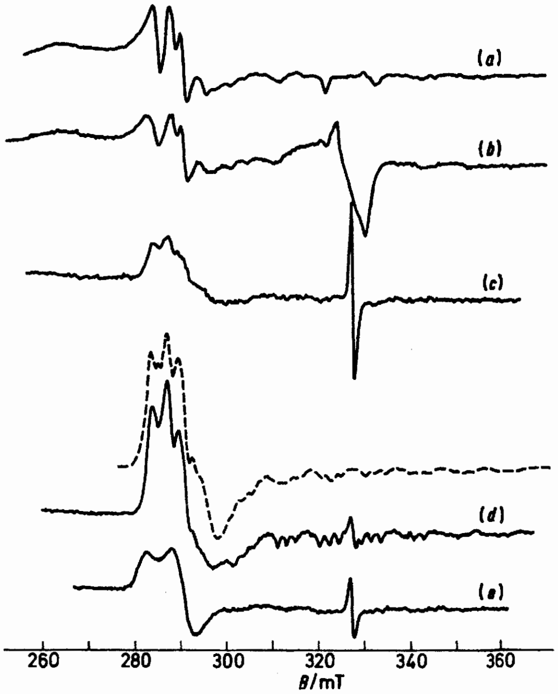

FIGURE 6 *X*-Band e.s.r. spectra at −140 °C due to a 10% dmf–water solution of [Co^{II}(tspc)] (1.0 × 10^{-3} mol dm^{-3}) containing 1.0 × 10^{-2} mol dm^{-3} hydroxylamine at pH 1.8—3.0 (*a*), 3.5—4.5 (*b*), 5.5—7.0 (*c*), 7.5—10.1 (*d*), and 10.9—13.1 (*e*). The broken curve was simulated as in Figure 4

Many of the effects observed on manipulation of the solution conditions when hydrazine is involved can be paralleled in solutions containing hydroxylamine. A most surprising aspect of the hydroxylamine system is the observation of a signal due to an oxygen adduct and the narrow range of pH in which it occurs, *i.e.* pH 3.5—4.5. No such signal was observed in the absence of hydroxylamine and the substrate must be playing a part in its formation. The intensity of this signal increased on exposure to pure oxygen, and its generation and subsequent disappearance could be controlled by adjusting the pH of the solution. Increasing the pH above 4.5 resulted in the formation of the hydroxylamine adduct and the replacement of the oxygen signal by one due to a free-radical species. However, the oxygen signal could be regenerated by reducing the pH to 3.5—4.5, or by bubbling oxygen through the solution at the higher pH.

The colour changes and decrease in signal intensity at pH >11.0 may be accounted for in terms of a reduction to a cobalt(I) species. As in the case of hydrazine, the e.s.r. spectral behaviour associated with the reaction between [Co^{II}(tspc)] and the hydroxylamine substrate could be regenerated from solutions containing cobalt(I) species provided that the pH was first decreased sufficiently to produce the [Co^{II}(tspc)] complex (in this case to pH <3.5). The pH could then be increased again to form the 1 : 1 adduct. The formation of a hydroxylamine adduct at a lower pH than that required for the formation of a hydrazine complex is related to the lower p*K* value for the ionization of hydroxylamine, *i.e.* p*K* *ca.* 6.06.[17]

Two possibilities exist when considering the nature of possible intermediates involved in the catalytic process. These are first a cobalt(II) complex of the type [Co^{II}(tspc)(NH$_2$OH)(O$_2$)], and secondly [Co^{III}(tspc)(NH$_2$OH)(O$_2$)] in which the electron density is localized mainly on the oxygen molecule. The oxygen signal is similar to that observed in the case of an alkaline solution of [Co^{II}(tspc)] containing no hydroxylamine, although the presence of cobalt(II) species is also evident. It is likely therefore that an equilibrium exists between the cobalt(II)- and cobalt(III)-oxygen complexes in this pH range, although the role of hydroxylamine in producing such an equilibrium mixture is not obvious. There is no evidence for the formation of a hydroxylamine adduct in this pH range, which would provide unequivocal evidence for the presence of a ternary adduct involving [Co^{II}(tspc)], hydroxylamine, and oxygen.

The origin of the free-radical species is unclear. The intensity of the free-radical signal is unaltered under controlled oxygen-free conditions and may therefore possibly arise from the formation of a reduced form of [Co^{II}(tspc)] in which the unpaired electron is delocalized throughout the phthalocyanine ring. However, no

---

[17] P. Lumme, P. Lahermo, and J. Tummavouri, *Acta Chem. Scand.*, 1965, **19**, 2175.

hyperfine structure was observed on the free-radical signal.

Catalytic Autoxidation of Cysteine.—The e.s.r. spectral changes associated with the reaction of cysteine and [Co(tspc)] are shown in Figure 7. As with hydroxylamine, the reaction was studied in an aqueous solution containing 10% v/v of dmf. The catalytic process can be followed quite readily, since the product, cystine, is only sparingly soluble in water.

The e.s.r. spectrum at −140 °C of [Co^{II}(tspc)] (1.0 × 10^{-3} mol dm^{-3}) in an aqueous solution at pH 2.1 to which 10% dmf v/v and 1.0 × 10^{-1} mol dm^{-3} cysteine had been added prior to freezing was typical of that obtained due to monomeric [Co^{II}(tspc)] in solution.

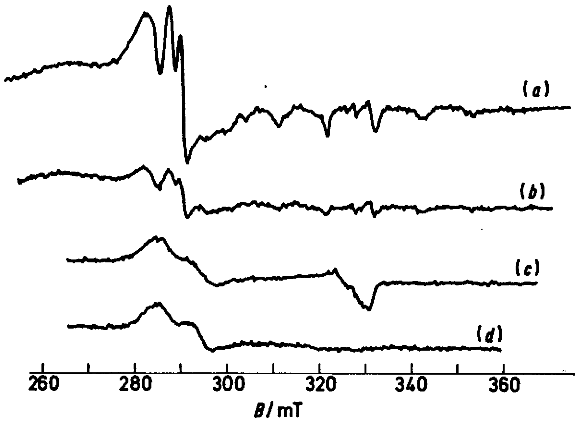

FIGURE 7 *X*-Band e.s.r. spectra at −140 °C due to a 10% dmf–water solution of [Co^{II}(tspc)] (1.0 % 10^{-3} mol dm^{-3}) containing 1.0 × 10^{-2} mol dm^{-3} cysteine at pH 2.1 (*a*), 3.1—9.1 (*b*), 9.7—12.6 (*c*), and 13.1 (*d*)

Increasing the pH caused the signal intensity to decrease. At pH >4.0, cystine precipitated, the amount increasing up to pH 9.0. At pH 5.1 the signal intensity was only about one quarter of its value at pH 2.1, although the solution still retained its blue colour. When the pH was increased above 5 the e.s.r. signal changed form and the solution became green in colour, until pH *ca.* 9.5 at which stage the original blue colour was restored. At this pH a signal which could be attributed to the [Co^{III}(tspc)(O$_2$)] adduct was observed and the cystine redissolved. At the very highest pH the oxygen signal again disappeared.

The nature of the intermediate formed by the interaction of [Co^{II}(tspc)] with cysteine is of particular interest in view of the proposal by Kundo and Keier[8] that a reduced state of [Co^{II}(tspc)] is involved. Cysteine is an active complexing agent with reducing properties and consequently a cysteine adduct or a reduced species may be formed. In an attempt to establish the nature of the intermediate, the absorption spectra of [Co^{II}(tspc)] in the presence of reducing agents were compared to that in the presence of cysteine. The changes in the absorption spectra were of the same general form and it is concluded that the reaction with cysteine produces a mixture of cobalt(I) and cobalt(II) species. The e.s.r. data are in agreement with this conclusion. The 75% decrease in the signal intensity as the pH is increased favours the formation of a reduced cobalt species. In addition, the green colour so produced would be expected if reduction of the phthalocyanine was incomplete, although this may also be accounted for by the reoxidation of [Co^{I}(tspc)]$^-$ in the presence of oxygen. The regeneration of the blue solution at high pH, as well as the presence of an oxygen signal, indicates that [Co^{II}(tspc)] is reacting independently of cysteine, forming the [Co^{III}(tspc)(O$_2$)] adduct as described previously. Loss of the oxygen signal at higher pH probably results from irreversible oxidation to a cobalt(III) species.

The redissolution of cystine at pH 9.5, as well as the reformation of the cobalt(II) species, indicates that the catalytic cycle is reversed at this pH. The complex [Co^{I}(tspc)]$^-$ is a reducing agent and consequently cystine is reduced to cysteine which is soluble in water. The catalytic process may therefore be summarized by equations (4) and (5). These equations show that the

$$[\mathrm{Co^{II}(tspc)}] + \text{cysteine} \longrightarrow [\mathrm{Co^{I}(tspc)}]^- + \text{cystine} \xrightarrow{\mathrm{O_2}} [\mathrm{Co^{II}(tspc)}] + \text{cystine} \quad (\text{pH } 4.0\text{—}9.0) \quad (4)$$

$$[\mathrm{Co^{I}(tspc)}]^- + \text{cystine} \longrightarrow [\mathrm{Co^{II}(tspc)}] + \text{cysteine} \xrightarrow{\mathrm{O_2}} [\mathrm{Co^{III}(tspc)(O_2)}] + \text{cysteine} \quad (\text{pH } 9.5\text{—}12.0) \quad (5)$$

effective catalytic autoxidation of cysteine proceeds only in the range pH 4.0—9.0, with the rate increasing with increasing pH. Above pH *ca.* 9.5, however, oxygenation of [Co^{II}(tspc)] is the dominating reaction. The overall picture is therefore in basic agreement with the mechanism proposed by Kundo and Keier[8] although their studies were confined to the pH 8.5—10.0 region. As was found in the case of hydrazine and hydroxylamine, the e.s.r. data indicate that the catalytic process proceeds over a wider pH range than at first reported.

EXPERIMENTAL

The cobalt(II) chelate of 3,10,17,24-tetrasulphophthalocyanine was prepared by the method of Weber and Busch.[18] Hydrazine hydrate, hydroxylamine hydrochloride, and cysteine hydrochloride were obtained from commercial sources and used without further purification. Measurements and adjustments of pH were made using a Radiometer model 23 pH meter fitted with a glass electrode and a saturated calomel electrode. Visible absorption spectra were recorded at room temperature using a Varian 635 u.v.–visible spectrophotometer. E.s.r. measurements were made on a Varian E12 spectrometer operating at 9 142 MHz.

We thank the Australian Research Grants Committee for awards of grants for equipment and a Research Assistantship (to P. R. H.). D. J. C. acknowledges receipt of a Commonwealth postgraduate award.

[6/1319 *Received, 6th July,* 1976]

---

[18] J. H. Weber and D. H. Busch, *Inorg. Chem.*, 1965, **4**, 469.