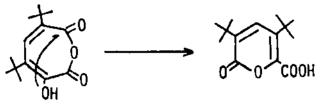
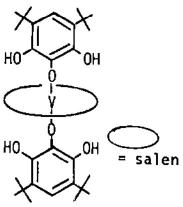


5 → *2* (2)

oxygenation of the pyrogallol *1* proceeds via the Hamilton intermediate similarly to oxygenation of 3,5-di-*tert*-butylcatechol [1].

Reaction of *1* with VO(salen) under nitrogen atmosphere gave a complex (*6*) as a black brown powder (mp 135–40 °C, dec.) which showed a similar catalytic activity for the oxygenation of *1* to that of VO(salen) [see eqn. (3)]. Based on the elemental analyses, IR, and ESR spectra, the structure of *6* was proposed as shown in Fig. 1. Thus,

$$\mathrm{VO(salen)} + 2\cdot\mathit{1} \rightarrow \mathit{6} \qquad (3)$$



6

Fig. 1. Structure of *6*.

the complex *6* can be regarded as a model complex for the enzyme-substrate complex. Coordination of the pyrogallol monoanion to the metal ion leading to the activation of the substrate is essential for the oxygenation of *1*.

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N9

$[Cu_4(SR)_6]^{2-}$, a Model approach for the Copper Binding Centre of Yeast Cu–Thionein

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Unlike aliphatic mercaptanes, thiophenol and $[Cu(CH_3CN)_4]ClO_4$ form crystalline complexes of the type $[Cu_4S_6]X_2$. Me_4N^+, Et_3NH^+ or Bu_4N^+ served as the respective suitable cation X. The copper to sulphur ratio was close to 1:1.5.

A comparison of the IR spectra of the free and the complexed ligand clearly demonstrates the disappearance of the characteristic ν(SH) vibration at 2570 cm^{-1} and supports the copper thiolate binding. From both the integration of the ^1H NMR spectra and the elemental analyses a metal to ligand ratio of 1:1.5 has been found.

The Cu_4S_6 cluster would nicely fit an adamantane-type structure as earlier described [1] (Fig. 1).

Cu-thionein from baker's yeast has a $[Cu(SR)_2]_4$ centre. According to EXAFS spectroscopy [2] each copper is tetrahedrally surrounded by four cysteine sulphurs. The best guess for arranging four $Cu(SR)_2$-units was a cubane type structure (Fig. 2).

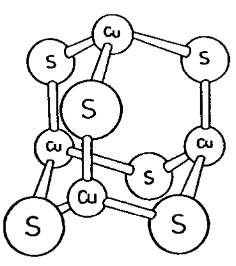

Fig. 1. Adamantane arrangement of $[Cu_4S_6]X_2$.

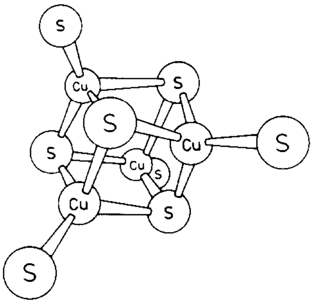

Fig. 2. The proposed Cu_4S_8 binding centre of yeast Cu–thionein.

At present the above mentioned low molecular weight $[Cu_4S_6]$ species are the closest models for the Cu–thionein metal binding centre. Of course a ratio of 1 Cu per 2 thiolate sulphurs would most successfully mimic the copper binding in this protein.

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N10

Active Centre Models for Non Heme Iron Dioxygenases

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In pyrocatechase, a non heme ferric dioxygenase, the substrate catechol is coordinated to the ferric centre, and subsequently cleaved by O_2 to give muconic acid (scheme) [1, 2]. Hitherto, this catalytic action could not be mimicked with model systems [2].

Resonance Raman data demonstrated the Fe(III) to the bound to phenolate groups of pyrocatechase