for states C, D′ and D (an investigation of a state A model has already been published [7]). Using the nomenclature propsed in [8], the main RR frequencies are given in Table I.

TABLE I. RR Frequencies (cm^{-1}) of [$Fe^{II}(T_{piv}PP)(X^-)$-(L)]Na^+18C6 Complexes.

Complex		Porphyrin vibrations					Fe–L vibr.
X^-	L	A	B	C	D		
$C_6HF_4S^-$		1341	a	a	a	369	
Cl^-		1343	1355	1494	1545	369	
OH^-		1344	1355	a	a	371	
$C_6HF_4O^-$		1343	1354	a	1545	369	
$C_6HF_4S^-$	CO	1364		a	1567	380	479
$C_6HF_4S^-$	O_2	1366		a	a	379	

[a]Not observed.

All the pentacoordinated ferrous species exhibit very similar porphyrinic frequencies. They compare well with the frequencies of the typical high spin ferrous complex Fe(TPP)(2-Me Im) (A = 1345, B = 1361, C = 1500 and D = 1538 [8]). Moreover the A frequency of the carboxy adduct is very close to that of Fe(TPP)(py)(CO) [12], whereas that of the oxy adduct is the same as that of Fe(T_{piv}PP)(1-Me Im)-(O_2) [9]. Therefore our RR data do not stress any special π donor properties of the RS^- ligand that would induce an extra lowering of the oxidation state marker band frequencies.

Soret excitation of the low frequency RR spectrum is readily accessible for the carboxy adduct λ_{max} Soret 448 nm, λ_{exc} 454,5 nm: it reveals a new strong polarized band at 479 cm^{-1}. The intensity of this band decreases with partial photodissociation of the CO ligand. An isotopic substitution experiment, using ^{13}CO, induces a 5 cm^{-1} lowering of its frequency. This is in good agreement with a calculated shift of -5 cm^{-1} for the stretching vibration of the Fe–CO moiety, using the harmonic oscillator approximation. This leads to the assignment of this band to the Fe–CO stretching vibration. This value is to be compared to those observed for MbCO, HbCO [10] and P_{450}–CO (work in progress).

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N8

Vanadium Catalyzed Oxygenation of 4,6-Di-*tert*-butylpyrogallol. A Model Reaction for Intradiol Dioxygenase

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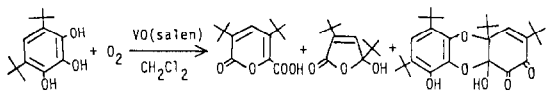
Recently, we have reported the intradiol cleavage of 3,5-di-*tert*-butylcatechol with molecular oxygen catalyzed by several vanadium complexes as a model reaction for intradiol dioxygenase [1]. Although the enzymatic [2] or the base catalyzed [3] cleavage of pyrogallol are known, metal catalyzed oxygenations of pyrogallol have not been reported yet. Here we wish to report vanadium catalyzed oxygenation of 4,6-di-*tert*-butylpyrogallol (*1*) and discuss the reaction mechanism based on the isotopic labelling experiment and the structure of the isolated reaction intermediate complex.

Oxidation of *1* (0.1 *M* in CH_2Cl_2) in the presence of a catalytic amount of VO(salen) (1 mol%) with molecular oxygen at room temperature for 20 h produced 3,5-di-*tert*-butyl-2-pyrone-6-carboxylic acid (*2*) (41%), 3,5-di-*tert*-butyl-5-hydroxy-2-furanone (*3*) (8%) besides a quinone dimer (*4*) (24%) [see eqn. (1)]. These products were characterized from elemental analyses, IR, ^1H NMR and mass spectra.



1 *2* *3* *4* (1)

^{18}O isotopic labelling experiments indicated that ^{18}O atoms were incorporated into *2* (one atom) and *3* (two atoms) and that an ^{18}O atom in *2* was located in the carboxylic acid moiety, but not in the lactone moiety. These facts suggest that the main product *2* is formed by rearrangement of an intermediate (*5*) arising from the intradiol ring cleavage of *1* just as in the enzymatic reaction [see eqn. (2)]. As the compound *5* corresponds to the seven membered lactone intermediate proposed by Hamilton [4] in the enzyme reaction, the vanadium catalyzed

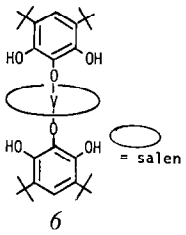
(2)

5 *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,

$$VO(salen) + 2 \cdot 1 \rightarrow 6 \qquad (3)$$



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).

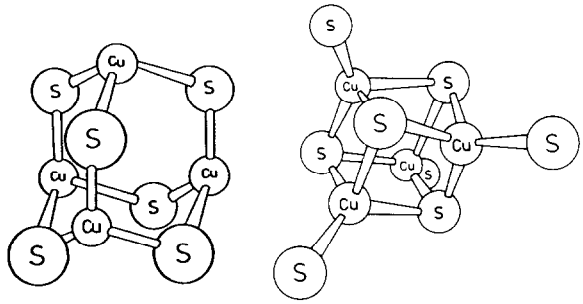

Fig. 1. Adamantane arrangement of $[Cu_4S_6]X_2$.

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