Synthesis and X-ray structure of a novel cavity-containing dinuclear nickel(II) complex

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Abstract. Compounds consisting of a substrate-binding site and a Ni II or Mn III salen moiety have been synthesized. These compounds are able to epoxidise a variety of alkenes in the presence of sodium hypochlorite or iodosylbenzene. The X-ray structure of the nickel(II) complex is reported.

The selective epoxidation of alkenes is an important goal in synthetic and industrial chemistry. As part of our work to develop catalytic systems capable of selectively epoxidising alkene substrates, we have synthesised complex 1 containing both a substrate-binding site and a catalytic centre. Earlier work in our group has demonstrated that molecular cleft 2 is capable of binding benzenediol derivatives through hydrogen bonding with the carbonyl urea units and π–π stacking interactions with the aromatic rings of the cleft walls. Binding constants as high as 6000 M⁻¹ have been measured in organic solvents. Salen ligands containing nickel(II) or manganese(III) centres and their derivatives have been reported as being able to efficiently epoxidise alkenes in the presence of an appropriate oxygen-atom donor, such as sodium hypochlorite or iodosylbenzene.

The catalyst reported here was constructed so that the catalytic centre is close to the binding site with the intention of favouring the selective epoxidation of substrates that are able to bind in the cleft. Compound 1 was prepared as shown in Scheme 1 starting from 2, which is synthesised in 3 steps from urea and diphenylglycoluril. Compound 2 was nitrated in the presence of excess 65% aqueous nitric acid in acetic anhydride to give the tetranitro derivative 3 in 89% yield. The tetranitrated compound was subsequently reduced to the corresponding nickel(II) complex 4 with triethylammonium thiosalicylic acid (TEAF) in the presence of Pd/C as catalyst in THF/methanol (2:1, v:v). The tetraamine was not worked up and was subsequently reacted with 6 equivalents of salicylaldehyde (2-hydroxybenzoic acid) to give the parent ligand 5 as a beige powder in 45% yield. The corresponding Ni II complex was prepared by reacting the parent ligand with Ni(OAc)₂·4H₂O in a MeOH/THF solution at room temperature to give a dark-red crystalline material in a yield of 95%.

Likewise, the Mn III complex was prepared either by direct reaction with Mn(OAc)₃ or by reaction with Mn(OAc)₂·4H₂O and subsequent oxidation in air to the Mn III oxidation state, yielding a brown microcrystalline solid in greater than 90% yield.

Single crystals of the Nickel(II) complex of 1 were grown in CHCl₃ by slow addition of methanol. The solid-state structure was determined by X-ray analysis. Crystals of 1a are triclinic, space group P₁, with a = 12.588(3), b = 16.855(4), c = 18.415(4) Å, α = 73.10(2), β = 76.96(2), γ = 75.89(2) Å. X-ray data were collected for a tiny crystal on an ENRAF-nomius CAD4 Rotating-anode diffractometer at 150 K. The current R value is 0.13 (all atoms isotropic). Further refinement, hampered by the weak data set, is in progress and full details will be published elsewhere.

Examination of the X-ray structure of 1 (shown in Figure 1) reveals that there is a twist in the cleft molecule so that two of the methoxy groups on the cleft walls are pointing into the cavity, while the other two face outward. This twist at the base of the compound gives the complex an intrinsic chirality. A space-filling representation of the X-ray structure (as drawn in Figure 2) shows that the carbonyl groups of the diphenylglycoluril moiety are blocked from hydrogen bonding and that part of the binding site in the cavity is thus obstructed. 1H-NMR binding studies in CDCl₃ with the nickel(II) complex of 1 and 1,3-benzenediol showed that no binding of 1,3-benzenediol occurs in the cleft. This result can be partly explained by the fact that the cavity is partially occluded and the carbonyl groups blocked, as shown in the X-ray structure.

We have successfully used the reported complexes as epoxidation catalysts with non-functionalised alkenes such as α-pinene, allylbenzene, styrene, and trans-stilbene in the presence of sodium hypochlorite or iodosylbenzene...
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Figure 1. X-ray structure of 1a.

Figure 2. Space-filling representation of X-ray structure of 1a showing occlusion of cleft by two of the methoxy groups of the cavity walls.

(epoxidation yields 4–40%)\(^6\). We did not, however, achieve selective epoxidation with benzenediol derivatives such as 5-allyl-1,3-benzenediol with these catalysts due to occlusion of the cleft. We are currently working on the synthesis of a modified cavity which avoids the problem of functional groups occupying the cleft and protecting the binding site from interaction with substrate molecules.

Acknowledgement

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References and notes

b H. Yoon and C. J. Burrows, J. Am. Chem. Soc. 110, 4087 (1988);
Compound 1a. IR: 1712 (C=O), 1608 (C=N), 1523, 1448. \(^1\)H NMR (CDCl\(_3\)) \(\delta\): 8.98, s, 4H, imine CH; 7.2, s, 10H, ArH; 7.14-6.98, m, 12H, saloph ArH; 6.53, t, 4H, saloph ArH; J 8 Hz; 5.60 and 3.89, 2d, 8H, NCH Ar; J 15.8 Hz; 3.67, s, 12H, OMe. FAB-MS (3-nitrobenzyl alcohol) \(m/z\): 1207 (M+H)+. Anal. calcd. for C\(_{64}\)H\(_{50}\)Ni\(_6\)O\(_{10}\): C 58.29, H 4.08, N 8.24; found: C 58.89, H 4.21, N 8.22%.

Compound 1b. IR: 1713 (C=O), 1603 (C=N), 1586, 1530. FAB-MS (3-nitrobenzyl alcohol) \(m/z\): 1198 (M-2CH\(_3\)COO)+. Anal. calcd. for C\(_{68}\)Ni\(_4\)O\(_8\): C 60.27, H 14.46, N 8.27; found: C 60.30, H 4.48, N 8.16%.

Compound 5. IR: 1711 (C=O), 1618 (C=N), 1460. \(^1\)H NMR (CDCl\(_3\)) \(\delta\): 8.45, s, 4H, imine CH; 7.09, s, 10H, ArH; 6.94-6.70, m, 12H, saloph ArH; J 8 Hz; 5.70 and 3.89, 2d, 8H, NCH Ar; J 15.8 Hz; 3.62, s, 12H, OMe.


6 Reaction conditions. In a typical reaction with compound 1b as catalyst, a Schlenk tube was charged with 0.3 mmole alkene, 0.15 mmole iodosylbenzene, 3.0 mole % catalyst, 30 mmole 4-methylpyridine (axial ligand), and 5 ml CH\(_2\)Cl\(_2\). The reaction mixture was then stirred at room temperature under an atmosphere of N\(_2\) for 3 h. Epoxide yields were determined by GLC analysis against an internal standard. Typical yields were as follows: \(\alpha\)-pinene (20%), \(\beta\)-pinene (16%), styrene (34%), allylbenzene (4%), and trans-stilbene (40%).