Dioxygen binding to immobilized Co^{II} complexes in porous organic hosts: evidence for site isolation

John F. Krebs[b] **and A. S. Borovik***[a]

[a] *Department of Chemistry, University of Kansas, Lawrence, KS 66045, USA*
[b] *Department of Chemistry, Kansas State University, Manhattan, KS 66504, USA*

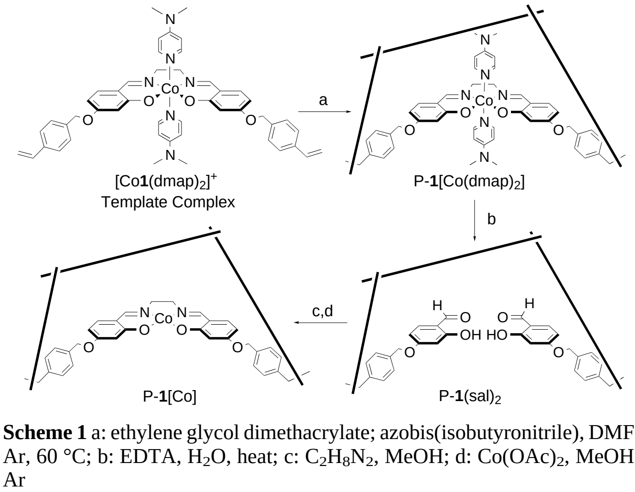
To model channel motifs and site isolation properties found in metalloproteins, a series of Co^{II} Schiff base complexes have been immobilized in porous organic hosts which stabilize Co–O$_2$ species at room temperature.

Immobilization of metal complexes in porous hosts is an effective way to regulate metal-based chemistry. In natural systems, this is exemplified by metalloproteins where the microenvironments around the metal-based active sites are controlled by protein structure.[1] In most cases, the active sites are located within the interior of the proteins, isolated from each other to prevent undesirable interactions. Access to external ligands (or substrates) is provided by channels that connect the active sites to the surface of the protein. To mimic these two structural properties in synthetic systems, *i.e.* site isolation and channel structure, we are using template polymerization techniques to immobilize metal complexes within porous organic hosts.[2,3] Results described herein show the feasibility of this approach in isolating metal sites in porous hosts *via* the stabilization of Co–O$_2$ adducts at room temperature.[4]

Incorporating metal sites with polymeric materials to model the dioxygen binding properties of metalloproteins has been reported.[5–7] While some promising results have been obtained, several of these systems use $<10\%$ crosslinked polymers that do not sufficiently isolate the metal sites or utilize only a small percentage of their immobilized metal sites in the binding of dioxygen.[8] Our approach for site isolating metal complexes is modeled after methods developed to make templated network polymers.[9] We have modified these published methods by using substitution-inert metal complexes as templates. Utilizing kinetically inert metallo-templates that are synthesized prior to polymerization is advantageous because they provide a way of controlling the architecture of the metal sites in the porous hosts. Copolymerization of the metallo-template with a large excess of an organic crosslinker in the presence of a porogenic agent results in materials with immobilized metal complexes that are dispersed throughout highly crosslinked hosts. In addition, the porous structure of the host permits the immobilized complexes to be chemically modified to bind dioxygen. To evaluate the extent of site isolation achieved by this approach, we have examined dioxygen binding to immobilized Co Schiff base complexes: these complexes are known to bind dioxygen to form superoxide adducts, yet at room temperature most complexes undergo rapid reactions to yield Co$^{III}_2$–peroxide species.[10] Thus monitoring the formation and stability of the cobalt–superoxide species in the porous hosts at room temperature will indicate whether the metal sites have the appropriate architecture to bind additional ligands, and provide a measure of the number of metal sites isolated within the host.

The kinetically inert six-coordinate [Co**1**(dmap)$_2$]$^+$ containing the styrene-modified salen ligand **1**[11] and two axially coordinated dimethylaminopyridine (dmap) ligands was immobilized into a methacrylate host by the procedure shown in Scheme 1. After grinding and sieving a dark red solid P-**1**[Co(dmap)$_2$]([Co] = 180 μmol g^{-1})[12] was obtained with a particle size of $\leqslant$125 μm and an average pore diameter of 80 Å. The nearly quantitative ($>90\%$) removal of Co^{III} ions and the dmap ligands was achieved by refluxing P-**1**[Co(dmap)$_2$] in an aqueous solution of 0.1 M Na$_2$H$_2$edta at a pH *ca.* 4. This metal ion removal process hydrolyzes the immobilized salen ligand to yield sites composed of two salicylaldehyde moieties covalently attached to the organic host [P-**1**(saI)$_2$]. This assignment is based on (i) the almost complete loss of nitrogen content in the polymer, (ii) the loss of the signature salen absorbance band at 380 nm, and (iii) the appearance of the characteristic carbonyl signal of salicylaldehyde at 1653 cm^{-1} in the DRIFT spectrum. The predisposition of the salicylaldehyde groups allows for regeneration of the salen ligands within the porous host by treating a suspension of P-**1**(sal)$_2$ in methanol with ethylenediamine under N$_2$ which affords P-**1**.

The immobilized sites in P-**1** can rebind metal ions to form four-coordinate complexes: the EPR spectra of P-**1**[Co] and P-**1**[Cu] are consistent with the immobilized complexes having the expected square-planar arrangement of donors around the metal ions.[13] Note that these immobilized sites also have sufficient axial space for the coordination of external ligands, such as nitrogeneous bases and dioxygen. This space is a consequence of the [Co**1**(dmap)$_2$]$^+$ complex used in the copolymerization. Hence, $>80\%$ of the immobilized Co^{II} sites are converted to five-coordinate complexes when P-**1**[Co] is treated with *ca.* 15 equiv. of either pyridine or dmap under an Ar atmosphere. Fig. 1(*a*) shows the rhombic EPR spectrum of P-**1**[Co(dmap)] measured at 77 K which is indicative of a low-spin Co^{II} complex where the dmap ligand binds axially to afford a square-pyramidal coordination geometry around the Co^{II} ions.[11,14,15] These five-coordinate Co sites in P-**1**[Co(dmap)] and P-**1**[Co(py)] form 1 : 1 Co–O$_2$ adducts at room temperature under 1 atm of O$_2$: the EPR spectra of both systems contain the characteristic EPR signals of Co–superoxide complexes (Fig. 1).[10] Double integration of the 77 K EPR signal for P-**1**[Co(dmap)(O$_2$)], shows that 70% of the immobilized five-coordinate Co^{II} sites in P-**1**[Co(dmap)] form Co–O$_2$ adducts.[16] For P-**1**[Co(py)(O$_2$)], the percentage of stable Co–O$_2$ sites is



Scheme 1 a: ethylene glycol dimethacrylate; azobis(isobutyronitrile), DMF, Ar, 60 °C; b: EDTA, H$_2$O, heat; c: C$_2$H$_8$N$_2$, MeOH; d: Co(OAc)$_2$, MeOH, Ar

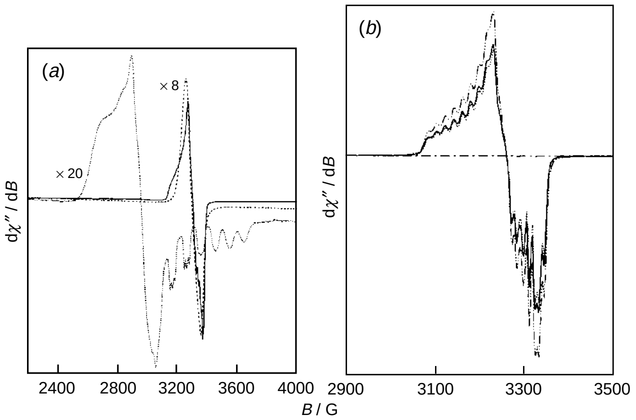
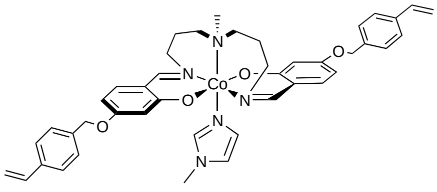


Fig. 1 (*a*) X-Band EPR spectra of P-**1**[Co(dmap)] collected at 77 K (···); P-**1**[Co(dmap)(O_2)] 1 hour after exposure to O_2 and collected at 77 K (—) and collected at 298 K (- - - -). EPR parameters for P-**1**[Co(dmap)]: g_1 = 2.45; g_2 = 2.25; g_3 = 2.20; A_3 = 96 G, d_3^N = 16 G; P-**1**[Co(dmap)$_2$(O_2)]: 77 K $g_\parallel$ = 2.10; $g_\perp$ = 2.02; $A_\parallel$ = 17 G; $A_\perp$ = 13 G; (298 K) g_{iso} = 2.02. (*b*) X-Band EPR spectra collected at 77 K of P-**2**[Co(O_2)] 1 hour after exposure to O_2 (-···-); P-**2**[Co(O_2)] after 40 h (———); P-**2**[Co] generated by flushing the sample after 40 h with N_2 (-——-); and rebinding of O_2 by P-**2**[Co] (···). EPR parameters for P-**2**[Co(O_2)]: $g_\parallel$ = 2.09; $g_\perp$ = 2.02; $A_\perp$ = 18 G; $A_\perp$ = 12 G.

slightly less at 52%. In contrast to these results, monomeric Co**1**(dmap) and Co**1**(py) complexes dissolved in a 1 : 1 CH_2Cl_2–toluene mixture yield < 10% of the Co–O_2 adducts 1 h after exposure to dioxygen at room temperature.

The above results demonstrate that the porous organic host can influence the chemistry of the immobilized metal complexes compared to that observed in solution. The design of P-**1** requires the binding of an external base to efficiently bind dioxygen. To circumvent the need for an external base, immobilized sites containing the pentadentate Schiff base ligand bis(2-hydroxybenzyliminopropyl)methylamine (smdpt) were synthesized using [Co**2**(1-MeIm)]$^+$ as the template complex. [Co**2**(1-MeIm)]$^+$, modeled after a similar complex reported by Marzilli *et al.*,[17] was copolymerized into a methacrylate host following the procedure used for P-**1**[Co(dmap)$_2$]. P-**2**[Co],[18] having a cobalt concentration of 150 μmol g^{-1} readily forms Co–O_2 adducts: double integration of the EPR signal obtained for P-**2**[Co–O_2] shows that 88% of the immobilized cobalt sites bind O_2 at room temperature and 1 atm of O_2 [Fig. 1(*b*)]. After 40 h at room temperature, the Co–O_2 EPR signal corresponds to 62% of the immobilized sites Co–O_2 adducts.[19] Reversion of P-**2**[Co–O_2] to P-**2**[Co] (40 h after the initial O_2 exposure) is accomplished by flushing the system with N_2 for 30 min. Rebinding of O_2 to P-**2**[Co] produces an identical EPR spectrum to that obtained after 40 h [Fig. 1(*b*)].[20]



[Co**2**(1-MeIm)]$^+$

The room temperature dioxygen binding properties of P-**1**[Co] and P-**2**[Co] illustrates that this approach for immobilization of metal complexes in porous organic hosts is a useful method for designing functional metal complexes. For comparison, the large number of cobalt sites that stabilize Co–O_2 adducts in these materials are a significant improvement over results reported for similar complexes immobilized in zeolite cages: only 1% of the immobilized [Co(salen)(py)] in zeolite NaY form Co–O_2 adducts and 25% of the immobilized Co(smdpt) in zeolite NaEMT bind O_2.[7] The highly crosslinked porous hosts in P-**1**[Co] and P-**2**[Co] provide robust matrices that are sufficiently rigid to retain the metal site architecture and isolate the metal sites. This type of porous host thus prevents unwanted metal–metal interactions that are observed in solution. Extension of this technique toward the design of new reactive metal complexes is underway.

We thank the donors of Petroleum Research Fund administered by the American Chemical Society (26743-G3), NSF (OSR-9255223) and ONR (N00014-96-1-1216) for financial support of this work.

Notes and References

1 W. H. Armstrong, in *Metal Clusters in Proteins, ACS Symposium Series 372,* ed. L. Que, Jr., Am. Chem. Soc., Washington, DC, 1988, p. 1; Y. Lu and J. S. Valentine, *Curr. Opin. Struct. Biol.,* 1997, **7**, 495; L. Regan, *Trends Biochem. Sci.,* 1995, **20**, 280.

2 J. F. Krebs and A. S. Borovik, *J. Am. Chem. Soc.,* 1995, **117**, 10 593.

3 Recent examples of immobilized metal complexes in organic hosts: P. K. Dhal and F. H. Arnold, *Macromolecules*, 1992, **25**, 7051; B. B. De, B. B. Lohray, S. Sivaram and P. K. Dhal, *Macromolecules*, 1994, **27**, 1291; J. H. Golden, H. Deng, F. J. DiSalvo, J. M. J. Fréchet and P. M. Thompson, *Science*, 1995, **268**, 1463.

4 Evidence for site isolation has been reported in a titanocene/divinylbenzene-styrene copolymer: R. Grubbs, C. P. Lau, R. Cukier and C. Brubaker Jr., *J. Am. Chem. Soc.*, 1977, **99**, 4517.

5 J. H. Wang, *Acc. Chem. Res.*, 1970, **3**, 90; J. P. Collman and C. A. Reed, *J. Am. Chem. Soc.*, 1973, **95**, 2048; O. Leal, D. L. Anderson, R. G. Bowman, F. Basolo and R. L. Burwell, Jr., *J. Am. Chem. Soc.*, 1975, **97**, 5125; R. S. Drago, J. Gaul, A. Zombeck and D. K. Straub, *J. Am. Chem. Soc.*, 1980, **102**, 1033; D. Wöhrle and H. Bohlen, *Makromol. Chem.*, 1986, **187**, 2081.

6 T. Aida and D.-L. Jiang, *Chem. Commun.*, 1996, 1523; J. P. Collman, L. Fu, A. Zingg and F. Diederich, *Chem. Commun.*, 1997, 193.

7 R. F. Howe and J. H. Lunsford, *J. Am. Chem. Soc.*, 1975, **97**, 5156; N. Herron, *Inorg. Chem.*, 1986, 4714; P. K. Dutta and C. Bowers, *Langmuir*, 1991, **7**, 937; R. J. Taylor, R. S. Drago and J. P. Hage, *Inorg. Chem.*, 1992, **31**, 253; D. E. De Vos, E. J. P. Feijen, R. A. Schoonheydt and P. A. Jacobs, *J. Am. Chem. Soc.*, 1994, **116**, 4746.

8 Selected examples of metal complexes with cavity motifs that in solution reversibly bind dioxygen at room temperature: J. P. Collman, *Acc. Chem. Res.*, 1977, **10**, 265; M. Momenteau and C. A. Reed, *Chem. Rev.*, 1994, **94**, 659; D. H. Busch and N. W. Alcock, *Chem. Rev.*, 1994, **94**, 585.

9 Selected reports: G. Wülff, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1812 and references therein: K. Mosbach, *Trends Biochem. Sci.*, 1994, **19**, 92; K. J. Shea, *Trends Polym. Sci. A*, 1994, **32**, 166; B. B. De, B. B. Lohray, S. Sivaram and P. K. Dhal, *Tetrahedron Asymmetry*, 1995, **9**, 2105.

10 R. D. Jones, D. A. Summerville and F. Basolo, *Chem. Rev.*, 1979, **79**, 139.

11 Y. Fujii, K. Matsutani and K. Kikuchi, *J. Chem. Soc., Chem. Commun.*, 1985, 415.

12 The concentration of cobalt in P-**1**[Co(dmap)$_2$] ranges from 180 to 200 μmol g^{-1} in samples prepared independently.

13 P-1[Co]: [Co] = 170 μmol g^{-1}; EPR parameters: g = 1.98 and a broad feature centered at g = 3.28. P-**1**[Cu]: EPR parameters: $g_\parallel$ = 2.21; $g_\perp$ = 2.04; $A_\parallel$ = 202 G at 77 K.

14 EPR spectra recorded on samples of polymer suspended in toluene for 1 h after exposure to O_2.

15 X-Band EPR parameters for: P-**1**[Co(py)] at 77 K: g_1 = 2.48; g_2 = 2.26; g_3 = 2.01; A_3 = 99 G; a_3^N = 16 G; P-**1**[Co(py)(O_2)] at 77 K: $g_\parallel$ = 2.08; $g_\perp$ = 2.02; $A_\perp$ = 16 G; P-**1**[Co(py)(O_2)] at 298 K: g_{iso} = 2.02.

16 Exposure of O_2 to P-**1**[Co(dmap)] results in an immediate color change (orange–brown to purple) and formation of P-**1**[Co(dmap)(O_2)] is completed in < 4 min (the concentration of dioxygen is saturating at *ca.* 0.009 M in toluene). Similar results were observed for P-**1**[Co(py)] and P-**2**[Co].

17 T. J. Kristenmacher, L. G. Marzilli and P. A. Marzilli, *Inorg. Chem.*, 1974, **13**, 2089.

18 P-**2**[Co] was synthesized by same procedure used for P-**1**[Co] (Scheme 1) substituting 3,3′-diamino-*N*-methyldipropylamine for ethylenediamine.

19 The EPR spectrum of P-**2**[Co-O_2] obtained 125 h after initial O_2 exposure was identical to that measured after 40 h.

20 P-**1**[Co(py)] also reversibly binds O_2 at room temperature.

Received in Bloomington, IN, USA, 3rd November 1997; 7/07909E