11 J. Chatt, B. A. L. Crichton, J. R. Dilworth, P. Dahlstrom and J. Zubieta, *J. Chem. Soc. Dalton Trans.*, 1041 (1982).
12 J. R. Dilworth and J. Zubieta, *J. Am. Chem. Soc., 104*, 365 (1982).
13 G. Butler, J. Chatt, G. J. Leigh, A. R. P. Smith and G. A. Williams, *Inorg. Chim. Acta, 28*, 165 (1978).
14 F. C. March, R. Mason and K. M. Thomas, *J. Organomet. Chem., 96*, C43 (1975).
15 J. Chatt, J. R. Dilworth, P. Dahlstrom and J. Zubieta, *J. Chem. Soc., Chem. Comm.*, 786 (1980).
16 J. Chatt, J. R. Dilworth and J. Zubieta, unpublished results.
17 R. J. Burt, J. R. Dilworth, G. J. Leigh and J. A. Zubieta, *J. Chem. Soc. Dalton Trans.*, 2295 (1982).
18 J. Hutchinson, J. R. Hyde, L. Throop and J. Zubieta, unpublished results.
19 B. A. L. Crichton, J. R. Dilworth, P. Dahlstrom and J. Zubieta, *Trans. Metal Chem., 5*, 316 (1980).
20 J. R. Dilworth and J. A. Zubieta, *J. Chem. Soc. Chem. Comm.*, 132 (1981).

R16

Monomeric Mo(V) and Mo(VI) Complexes with Sterically Constrained Metal Centers

JOHN H. ENEMARK, KATSUMOTO YAMANOUCHI, KERRY BARNHART

Department of Chemistry, University of Arizona, Tucson, Ariz. 85721, U.S.A.

DAVID COLLISON and FRANK E. MABBS

The Chemistry Department, Manchester University, Manchester M13 9PL, U.K.

Bray has proposed a chemical mechanism for the reduction of xanthine oxidase by xanthine, which involves a monomeric molybdenum active center having *fac* stereochemistry [1]. This proposal has simulated our interest in preparation and characterization of monomeric Mo(V) and Mo(VI) complexes constrained to *fac* configuration by polydentate ligands such as hydrotris(3,5-dimethylpyrazolyl) borate, hereafter designated as $HB(Me_2pz)_3^-$.

The $HB(Me_2pz)_3^-$ ligand has been extensively used to stabilize a variety of low valent molybdenum compounds [2]. Moreover, the same ligand has been found to stabilize the Mo(V) center in $MoOCl_2\{HB(Me_2pz)_3\}$(*I*) [3]. The relative stability of these compounds is attributed partly to the steric bulk of 3-methyl group on the ligand.

Mo(V) complexes of the type $MoOXY\{HB(Me_2pz)_3\}$ (where X = Y = NCS; X = Cl, Y = OR or SPh; X = Y = SPh) have been prepared by the substitution reactions of *I* and spectroscopically characterized. Esr spectra of Mo(V) centers are sensitive to X and Y. Substitutions by thiolate ligands give smaller A_o(Mo) and larger g_o values. These substitutions also shift the Mo=O stretching vibration significantly to lower wave numbers. A preliminary kinetic study has revealed that the rates of ligand substitution are very slow in these complexes, compared to those of known $MoOCl_3L_2$ complexes (where L is a monodentate ligand) [4].

Mo(VI) complexes of the type $MoO_2X\{HB(Me_2pz)_3\}$ (X = Cl, Br, NCS) have been synthesized for the first time by the reaction of MoO_2X_2 (X = Cl, Br) or $MoO_2(NCS)_4^{2-}$ with the ligand, and characterized by spectroscopic methods including ^{95}Mo NMR.

Electrochemical studies and structural studies on these Mo(V) and Mo(VI) complexes will also be described.

1 R. C. Bray, in 'Biological Magnetic Resonance', Vol. 2, J. Reuben and L. J. Berliner (Eds.), Plenum Press, N.Y. 1980, p. 45.
2 S. Trofimenko, *Adv. Chem. Ser., 150*, 289 (1976). A. Shaver, *Organometal. Chem. Rev., 3*, 157 (1977).
3 S. Trofimenko, *Inorg. Chem., 10*, 504 (1971).
4 C. D. Garner, M. R. Hyde, F. E. Mabbs and V. I. Routledge, *J. Chem. Soc., Dalton Trans.*, 1198 (1977).

R17

Active Site Fe^{3+} Ligation by Substrates and Transition State Analogs of Protocatechuate 3,4 Dioxygenase

J. W. WHITTAKER and J. D. LIPSCOMB*

Department of Biochemistry, University of Minnesota, Minneapolis, Minn. 55455, U.S.A.

Current proposals for the mechanism [1] of Protocatechuate (PCA) 3,4 Dioxygenase (3,4 PCD) suggest monodentate (OH) binding of PCA to the active site Fe^{3+}. This would promote ketonization of PCA, thereby creating a carbanion at C-4 which could be directly attacked by O_2. We have tested this proposal using ketonized substrate analogs and various spectroscopic probes. Our results confirm that ketonization is an essential step in the mechanism, but suggest that it occurs later in the cycle than the initial substrate complex.

We have shown that water is a ligand for *Brevibacterium fuscum* 3,4 PCD by observing hyperfine broadening from $^{17}OH_2$ on all EPR resonances of the high spin Fe^{3+} [2]. The spectrum of the 3,4 PCD-PCA complex is too broad to detect direct displacement of H_2O by PCA. However, no broadening is observed in complexes with three slowly metabolized substrate analogs. In contrast, water remains bound in complexes with non-metabolized, monodentate analogs (*e.g.* 4-OH benzoate). Other small molecules also bind to Fe in 3,4 PCD. CN^- binds in two steps; first it forms a high spin and then a low spin complex. It is likely that 2 CN^- molecules bind sequen-