of carbon dioxide from **28** to give pyridine **12**. Loss of CO_2 from the initial ring opened intermediate **27** also occurs to produce nitrile ylide **21** which ultimately affords pyridines **12–14**. A strong argument can be made that the cyclization of **27** to **28** is faster than loss of carbon dioxide. This is predicated on the fact that Δ^2-oxazolinones lose CO_2 at a much faster rate than the isomeric Δ^3-oxazolinone system.[16]

We are continuing to investigate the more intriguing mechanistic aspects of these interesting extrusion reactions and will report additional findings at a later date.

Acknowledgment. We gratefully acknowledge support of this work by the National Institutes of Health.

Stable Monomeric Complexes of Molybdenum(III) and Tungsten(III)

Michelle Millar*

Department of Chemistry
New York University, New York, New York 10003

Sr. Sandra Lincoln S.H.C.J. and Stephen A. Koch*

Department of Chemistry
State University of New York at Stony Brook
Stony Brook, New York 11794

Received August 3, 1981

In recent years various facets of the inorganic chemistry of molybdenum have been closely scrutinized in order to provide models for the molybdenum-containing enzymes.[1,2] Enzyme intermediates containing molybdenum in the +3 oxidation state have been proposed many times, although no definitive evidence for molybdenum(III) biological systems has ever been produced.[3] The inorganic chemistry of molybdenum(III) is also sparse in comparison to that of the more fully developed chemistry of the +4, +5, and +6 oxidation states.[2] Complexes of molybdenum (III) which have been characterized are readily oxidized by air and a variety of mild oxidizing reagents.[2] We report that the coordination of tridentate polypyrazolylborate ligands[4] can stabilize molybdenum(III) complexes with respect to oxidation to such an extent that the +3 oxidation state becomes predominate.

The reaction of $KHB(3,5\text{-}Me_2pz)_3$ with $MoCl_3(THF)_3$ gives the yellow crystalline compounds $K(THF)_3HB(3,5\text{-}Me_2pz)_3MoCl_3$ (**1**). Its magnetic susceptibility (3.69 μ_B), electronic spectrum, and ESR spectrum are consistent with a d^3, $S = {}^3/_2$ ground state. An X-ray diffraction study (Figure 1) of $[Et_4N][HB(3,5\text{-}Me_2pz)_3MoCl_3]CH_3CN$ (**2**) reveals a monomeric anion with near octahedral coordination about the metal. The facial C_{3v} geometry imposed by the ligand is in contrast to the meridional structure established for $MoCl_3(pyridine)_3$ and believed to exist in other MoX_3L_3 compounds.[2] Compound **2** undergoes two one-electron oxidations at +0.49 V [Mo(III)/Mo(IV)] and +1.55 V [Mo(IV)/Mo(V)] vs. SCE. Oxidation of **2** by ceric ammonium nitrate or by controlled potential electrolysis gives the red monomeric Mo(IV) compound $HB(3,5\text{-}Me_2px)_3\ MoCl_3$[6] in excellent yield. Interestingly, this product can be directly obtained by the reaction of $(Et_4N)[HB(3,5\text{-}Me_2pz)_3Mo(CO)_3$ thionyl chloride.[7a] As anticipated from the quite positive Mo(III)/Mo(IV) couple, the Mo(IV) compound is readily reduced to the Mo(III) anion by such mild reductants as sulfide and alcohols. Solutions containing $[HB(3,5\text{-}Me_2pz)_3Mo^{III}Cl_3]^-$ react with air only very slowly (over a period of several months) to give the green oxomolybdenum(V) complex $HB(3,5\text{-}Me_2pz)_3MoCl_2O$.[7b] The stabilizing effect of polypyrazolylborate coordination on the +3 oxidation state results from the interaction of the Mo dπ orbitals with the ligand π^* orbitals.

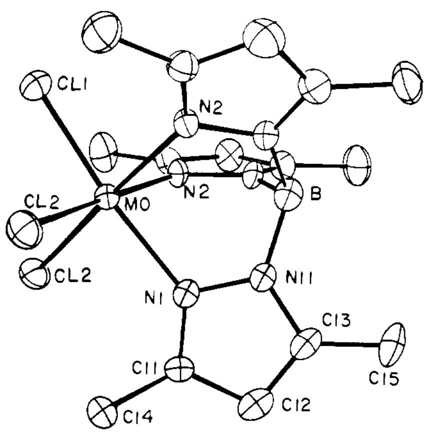

Figure 1. ORTEP view of the structure of the anion of **2**. Selected bond lengths (Å) and bond angles (deg) are as follows: Mo–Cl(1), 2.433 (1); Mo–N(1), 2.198 (5); N(1)–Mo–N(2), 85.67 (13); N(1)–Mo–Cl(2), 91.27 (9); Cl(1)–Mo–Cl(2), 93.10 (4).

Further evidence for this effect comes from our observation that a Mo(III) complex, $HBpz_3MoCl_2(pyrazole)$ (**4**) is obtained from the reaction of molybdenum(V) chloride with $KHBpz_3$ in aqueous HCl solution without the addition of a reducing agent. The structure of **4**[8] is similar to that of **2** with a pyrazole replacing one of the chlorides. Presumably this product is formed by the disproportionation reaction of Mo(V)[9]; a driving force for this reaction may well be the stability of the Mo(III) compound.

Analogous polypyrazolylborate chemistry of tungsten provides synthetic access to monomeric W(III) complexes. The first definitive example of this class of compounds has only recently been obtained.[10,11] The chemistry of W(III) monomers has been precluded by their oxidative instability and/or their strong tendency to form metal–metal bonded dimers.[11] The reaction of $(Et_4N)[LW(CO)_3]$ [where L = $HBpz_3^-$ and $HB(3,5\text{-}Me_2pz)_3^-$] with thionyl chloride gives $LW^{IV}Cl_3$[6] in 80–90% yield. $HB(3,5\text{-}Me_2pz)_3WCl_3$ exhibits a reversible one-electron reduction at −0.33 V and a one-electron oxidation at +1.02 V. The 0.8-V difference in the M(III)/M(IV) couples for M = Mo and W is a quantitative measure of a known periodic trend, the instability of the lower

---

[1] Coughlan, M. "Molybdenum and Molybdenum-Containing Enzymes,"; Pergamon Press: New York, 1980. Newton, W. E.; Otsuka, S. "Molybdenum Chemistry of Biological Significance"; Plenum Press: New York, 1980.

[2] Stiefel, E. I. *Prog. Inorg. Chem.* **1977**, *22*, 1–223.

[3] Ketchum, P. A.; Johnson, D.; Taylor, R. C.; Young, D. C.; Atkinson, A. W. *Adv. Chem. Ser.* **1977**, *No. 162*, 408–420. Jacob, G. S.; Orme-Johnson, W. H. In "Molybdenum and Molybdenum-Containing Enzymes"; Coughlan, M., Ed.; Pergamon Press: New York, 1980; pp 327–344 and references therein. Averill, B. A.; Orme-Johnson, W. H. *Inorg. Chem.* **1980**, *19*, 1702–1705.

[4] Hydrotris(1-pyrazolyl)borate ≡ $HBpz_3^-$; hydrotris(3,5-dimethyl-1-pyrazolyl)borate ≡ $HB(3,5\text{-}Me_2pz)_3^-$.

[5] Compound **2** is orthorhombic (*Pnma*) with a = 16.242 (2) Å, b = 10.931 (4) Å, c = 18.219 (2) Å and V = 3235 Å^3. This and the subsequent structures were solved by Patterson and difference Fourier methods. Final refinement using 2002 reflections with $I > 3.0\sigma(I)$ gave R = 0.0458 and R_w = 0.0748. Full details for the structures described in this paper will be published at a latter date.

[6] Mass spectroscopy indicates a momomeric formulation.

[7] (a) This reaction was reported by Trofimenko[6b] to give an unidentified red compound which in fact is **3**. (b) Trofimenko, S. *Inorg. Chem.* **1971**, *10*, 504–507.

[8] Compound **4** crystallized in the monoclinic space group $P2_1/n$ with a = 8.705 (1) Å, b = 12.889 (2) Å, c = 15.684 (3) Å, β = 104.01, and V = 1707.3 (10) Å^3. All hydrogens including the pyrazole N–H were located in a difference Fourier map and were included in final structure factor calculations. Final refinement using 2063 reflections with $I > 3.0\sigma(I)$ gave R = 0.026 and R_w = 0.037.

[9] Lamache-Duhameaux, M. "Proceeding of the Climax Third International Conference on the Chemistry and Uses of Molybdenum"; Barry, H. F., Mitchel, P. C. H., Eds.; Climax Molybdenum Co.: Ann Arbor, MI, 1979; p 253–258.

[10] Brenčič, J. V.; Čeh, B.; Leban, I. *Acta Crystallogr., Sect. B* **1979**, *B35*, 3028–3030. Brenčič, J. V.; Čeh, B.; Segedin, P. *J. Inorg. Nucl. Chem.* **1980**, *42*, 1409–1412.

[11] Dori, Z. *Prog. Inorg. Chem.* **1981**, *28*, 239–307.

0002-7863/82/1504-0288$01.25/0

oxidation states of tungsten relative to those of molybdenum. Monomeric $LW^{III}Cl_3^-$ complexes, which are obtained by chemical (hydrazine) or electrochemical reduction of $LW^{IV}Cl_3$, react with air in solution but not in the solid state. Structural characterization of the mixed cation salt $(NH_4)_{0.5}(Et_4N)_{0.5}HBpz_3WCl_3$[12] (**5**) demonstrates that the anion is monomeric and nearly isostructural with **2**. The ammonium cations are "coordinated" by the six chlorides from two anions in a trigonal antiprismatic geometry with N–Cl distances of 3.24 Å.

With respect to the bioinorganic chemistry of molybdenum this work suggests that (1) the +3 oxidation state should not be ruled out a priori due to incompatibility with biological redox potentials and (2) if Mo(III) is found in biological systems, it very well might be coordinated to histidine residues.[13]

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for grants to M.M. and S.K.

Supplementary Material Available: Tables of fractional atomic coordinates and thermal parameters (5 pages). Ordering information is given on any current masthead page.

---

(12) Crystals of compound **5** which display pyritohedral morphology are cubic (*Pa*3, No. 205) with $a = 16.085$ (2) Å and $V = 4161$ Å^3. The anion possesses a threefold axis. The ammonium cation lies at special position 4b, while the nitrogen of the NEt_4 cation is at special position 4a. The ethyl groups of this cation are, therefore, substantially disordered. Least-squares refinement using 600 reflections with $I > 3.0\sigma(I)$ of all nonhydrogen atoms excluding the ethyl groups gave $R = 0.061$ and $R_w = 0.094$.

(13) The use of polypyrazolylborate ligands to model the coordination by histidines has been previously recognized: Thompson, J. S.; Marks, T. J.; Ibers, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 4180–4192.

Nuclear Shielding of Trapped Xenon Obtained by Proton-Enhanced, Magic-Angle Spinning ^{129}Xe NMR Spectroscopy

John A. Ripmeester

Division of Chemistry
National Research Council of Canada
Ottawa, Ontario, Canada K1A 0R9

Received August 21, 1981

The nuclear shielding of the spin $^1/_2$ ^{129}Xe nucleus (natural abundance 26.24%) is extremely sensitive to its physical environment as shown by its strong dependence on density in the pure phases.[1,2] Using such solid-state NMR techniques as ^{1}H dipolar decoupling,[3] ^{129}Xe–^{1}H cross-polarization,[3] and magic-angle spinning,[4,5] several examples of the ^{129}Xe NMR "physical shift" are illustrated. For trapped xenon atoms it is shown that the nuclear shielding and shielding anisotropy depend on the nature of the trapping site.

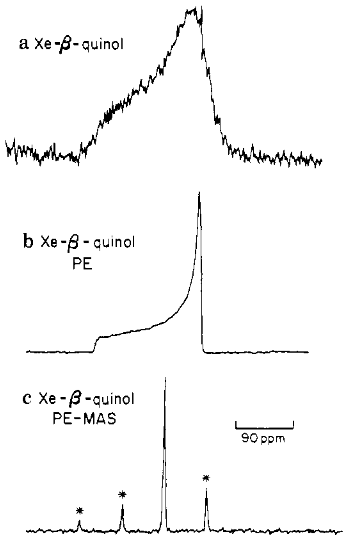

Figure 1. ^{129}Xe NMR spectrum of xenon trapped in β-quinol. (a) Obtained using 120 (N_s) single pulses at 12-min repetition rate (τ_r); (b) obtained using proton enhancement (PE) cross-polarization time (τ_{cp}) of 30 ms, $\tau_r = 60$ s, $N_s = 80$; (c) obtained using proton enhancement (PE) and magic angle spinning (MAS), $N_s = 24$, $\tau_{cp} = 30$ ms, $\tau_r = 60$ s.

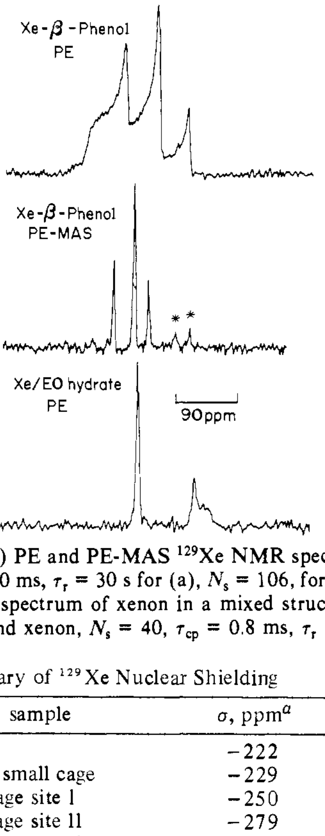

Figure 2. (a), (b) PE and PE-MAS ^{129}Xe NMR spectrum of xenon in β-phenol, $\tau_{cp} = 10$ ms, $\tau_r = 30$ s for (a), $N_s = 106$, for (b) $N_s = 40$; (c) PE ^{129}Xe NMR spectrum of xenon in a mixed structure I hydrate of ethylene oxide and xenon, $N_s = 40$, $\tau_{cp} = 0.8$ ms, $\tau_r = 30$ s.

Table I. Summary of ^{129}Xe Nuclear Shielding

sample	σ, ppm[a]	Δσ, ppm
β-quinol	−222	−160
β-phenol small cage	−229	−171
large cage site I	−250	−105
large cage site II	−279	−53
Xe/EO structure I hydrate		
small cage	−240	
large cage	−150	30

[a] Referred to Xe gas at zero density.

Figure 1a–c shows the ^{129}Xe NMR spectrum[6] of xenon atoms trapped in the cages of the β-quinol clathrate.[7] The line shape shown in Figure 1a, obtained by using single pulses and without ^{1}H decoupling, required an accumulation time of 24 h, whereas the line shape in Figure 1b, obtained by using ^{129}Xe–^{1}H cross-polarization and ^{1}H dipolar decoupling, required only 1.5 h[8] and thus nicely illustrates some of the advantages of the second techniques. The cages in the β-quinol clathrate of ~4.2-Å free diameter have $\bar{3}$ symmetry and are elongated slightly along the

---

(1) D. Brinkman and H. Y. Carr, *Phys. Rev.*, **150**, 174 (1966).

(2) C. J. Jameson, A. K. Jameson, and S. M. Cohen, *J. Chem. Phys.*, **62**, 4224 (1975).

(3) A. Pines, M. C. Gibby, and J. S. Waugh, *J. Chem. Phys.*, **59**, 569 (1973).

(4) J. Schaefer, S. H. Chin, and S. I. Weissman, *Macromolecules*, **5**, 798 (1972).

(5) J. Schaefer, E. O. Stejskal, and R. Buchdahl, *Macromolecules*, **10**, 384 (1977).

(6) ^{129}Xe NMR spectra were obtained at 49.8 MHz using a Bruker CXP-180 NMR spectrometer. 500 or 1k datum points (sweep width 50 kHz) were collected after a single pulse or a single matched cross-polarization sequence before zero filling and Fourier transformation. Radio-frequency field amplitudes were ~30 kHz. For the magic-angle spinning experiments, a Kel-F rotor of the Andrew type was used at spinning frequencies of 2.5–3 kHz.

(7) H. M. Powell in "Non-Stoichiometric Compounds", L. Mandelcorn, Ed., Academic Press, New York, 1964. The β-quinol sample used had ~60% of the cages occupied with Xe.

(8) The protons are probably relaxed quite efficiently by spin diffusion to paramagnetic centers. The ^{129}Xe atoms, being quite dilute, do not have such a mechanism so that extremely long T_1s result.

0002-7863/82/1504-0289$01.25/0