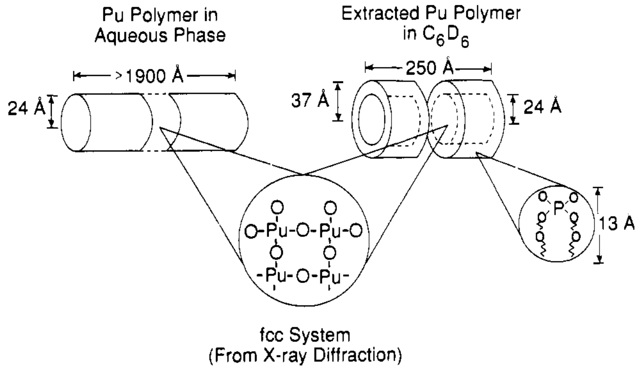

Figure 5. Schematic representation of a model for the observed Pu(IV) polymer.

particles in aqueous media. This differs from electron microscope findings[13,14] for other preparations of the polymer. The method of preparation may influence the morphology of polymers. All of the polymers studied share the same general shape, but those subjected to less heating were smaller in each dimension.

When uranium is present during polymerization of Pu(IV), shorter particles are formed than Pu(IV) polymer particles polymerized under the same conditions in the absence of uranium. The evidence supports earlier work[8] in which uranium was observed to inhibit the rate of Pu(IV) polymerization.

Although polymers have been extracted by HDHoEP, H_2MEHP, and other extractants previously,[12] the work was preliminary and involved only freshly prepared polymers. Here we report very large particles being extracted into deuteriobenzene solutions, preserving their highly ordered structure as shown by X-ray diffraction. In the process of extraction, the polymers are broken into shorter pieces, while the cross section of the polymeric core is preserved. Figure 5 provides a schematic representation of the structure of Pu(IV) polymers emerging from these studies.

An entirely different kind of polymer is formed upon extraction of the plutonium monomer by HDHoEP and H_2MEHP. Unlike those of the extracted species of hydrolytically formed Pu polymer, the sizes of these particles depend upon the extractant/Pu ratio and their optical spectra retain Pu(IV) monomer features.

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Registry No. Pu, 7440-07-5; U, 7440-61-1; bis(2-(hexyloxy)ethyl) phosphate, 3538-36-1; mono(2-ethylhexyl) phosphate, 1070-03-7.

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Chemistry and Electronic and Vibrational Spectroscopy of Mononuclear and Dinuclear (Tris(1-pyrazolyl)borato)- and Chloromolybdenum(V)-Oxo Complexes

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Hydrolysis of the Mo(V) complex $HB(pz)_3MoOCl_2$ leads to two geometric isomers of formula $[HB(pz)_3MoOCl]_2O$ (**2**). Crystal structures (Lincoln, S.; Koch, S. A. *Inorg. Chem.* **1986**, *25*, 1594–1602) show them to be linear μ-oxo-bridged Mo–O–Mo complexes. **2a** has a pseudo 2-fold axis of symmetry through the μ-oxo atom with respect to the chloro ligands, whereas **2b** is centrosymmetric with molecular and crystallographic C_i symmetry. Both dinuclear complexes exhibit an intense absorption at 462 nm ($\epsilon \geq 9000$ M^{-1} cm^{-1}). In the present study, infrared and (resonance) Raman experiments have been carried out to test the symmetry dependence of bands associated with the Mo–O–Mo bridge. Both of the dinuclear compounds possess very intense bands at ~380 cm^{-1}, identified for the first time as the symmetric stretch, ν_s(Mo–O–Mo), of $Mo_2O_3^{4+}$ complexes. The excitation profile of this mode tracks the 462-nm absorption, identifying it as a charge-transfer transition of the Mo–O–Mo group. The strong IR band at ~460 cm^{-1} is also intense in the Raman spectrum of **2a** but weak for **2b**. It has been identified as the bridge deformation mode of the $Mo_2O_3^{4+}$ unit. The resonance Raman spectra of both complexes show strong overtone and combination bands involving ν_s(Mo–O–Mo), δ(Mo–O–Mo), and ν_{as}(Mo–O–Mo). For the centrosymmetric species, these combination and overtone bands are strikingly intense because the fundamentals δ and ν_{as} are symmetry-forbidden vibrations. Vibrational spectroscopic assignments are supported by ^{18}O-isotope substitutions, symmetry, and intensity analyses. In addition, the dinuclear species $[Mo_2O_3Cl_8]^{4-}$ formed in 5–6 M HCl is characterized by Raman spectroscopy, supporting the linear, or nearly linear, Mo–O–Mo structure as originally proposed (Haight, G. P. *J. Inorg. Nucl. Chem.* **1962**, *24*, 663).

Introduction

The chemistry of Mo(V)-oxo complexes is of importance in industrial and biochemical catalysis.[1–7] In contrast to the intense investigation of mononuclear Mo═O compounds,[2,8–13] relatively little is known about the electronic spectroscopic properties of dinuclear $Mo_2O_3^{4+}$ complexes. The hydrotris(1-pyrazolyl)borate coordination compounds $HB(pz)_3MoOCl_2$, $[HB(pz)_3MoOCl]_2O$, and $[HB(pz)_3]_2Mo_2O_2(\mu\text{-}O)_2$ provide an opportune system for comparing chemical and spectral properties of mononuclear MoO^{3}+ and dinuclear $Mo_2O_3^{4+}$ complexes.

[†] University of Portland.

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(1) (a) Coughlan, M., Ed. *Molybdenum and Molybdenum-Containing Enzymes*; Pergamon: New York, 1980. (b) Newton, W. E.; Otsuka, S. *Molybdenum Chemistry of Biological Significance*; Plenum: New York, 1980. (c) Spiro, T. G., Ed. *Molybdenum Enzymes*; Wiley-Interscience: New York, 1986.
(2) Stiefel, E. I. *Prog. Inorg. Chem.* **1977**, *22*, 1–223 and references therein.
(3) Stiefel, E. I. In *Molybdenum and Molybdenum-Containing Enzymes*; Pergamon: New York, 1980; pp 41–98.
(4) Pope, M. T.; Still, E. R.; Williams, R. J. P. In *Molybdenum and Molybdenum-Containing Enzymes*; Pergamon: New York, 1980; pp 1–40.
(5) Spivack, B.; Dori, Z. *Coord. Chem. Rev.* **1975**, *17*, 99.

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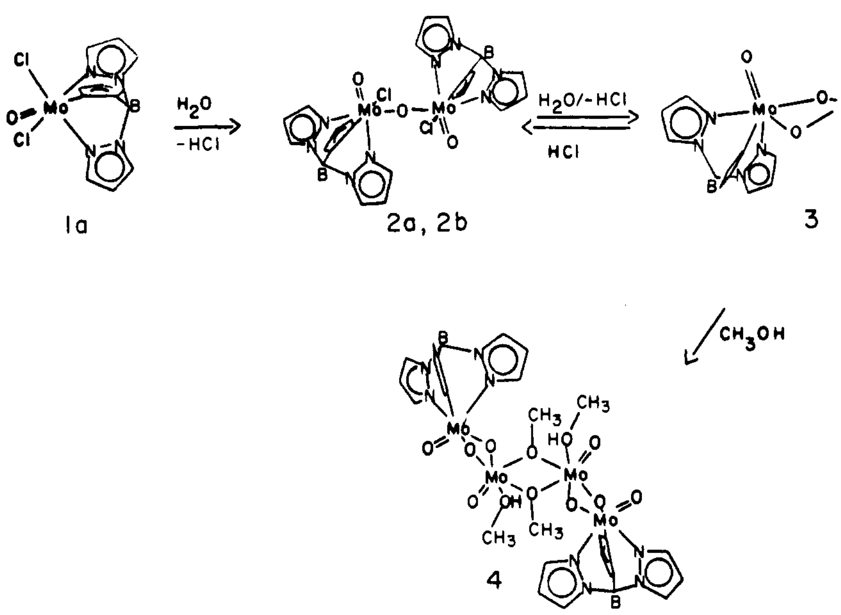
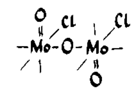
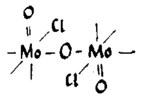
Scheme I



The structure of $HB(pz)_3MoOCl_2$ (**1a**) has been determined by X-ray crystallography,[14] and its electronic and infrared absorption properties are typical for an octahedral complex with a terminal oxo group.[2,13,14] Limited hydrolysis of **1a** produces two new complexes, **2a** and **2b**, with markedly altered spectral properties. Crystallography has shown these to be dinuclear species with a linear oxo bridge: $[HB(pz)_3MoOCl]_2O$ (Scheme I).[14] They form geometrical isomers that, depending upon the orientation of the chloro ligands, possess either a pseudo 2-fold axis ("C_2") or a rigorous center of symmetry ("C_i"); the terminal oxygens remain in a trans configuration. Both dinuclear complexes have a yellow-brown color in solution with an intense new absorption band at 462 nm ($\epsilon \simeq 9000$ M^{-1} cm^{-1}). These features of the poly(pyrazolyl)borato complexes **2a** and **2b** are unusual among structurally characterized $Mo_2O_3^{4+}$ complexes. The previous criterion for linear μ-oxo-bridged $Mo_2O_3^{4+}$ complexes was a purple color owing to an intense absorption at ~525 nm.[2] Clearly, the position of this band is somewhat ligand dependent. There has been a lack of consensus in the literature over the assignment of the visible absorption band of $Mo_2O_3^{4+}$ complexes as well as their ~460-cm^{-1} vibrational mode, which has been ascribed either to the symmetric stretch, ν_s(Mo–O–Mo), or to the deformation mode, δ(Mo–O–Mo).[2,15] In order to clarify these issues, we have undertaken electronic absorption, infrared, and Raman spectroscopic investigations of complexes **1** and **2**. These studies show that the 462-nm absorption band in **2a** and **2b** may be assigned to a charge-transfer (CT) transition of the Mo–O–Mo chromophore. The symmetric Mo–O–Mo stretch is identified for the first time at ~380 cm^{-1}, and the ~460-cm^{-1} band is shown to be the deformation mode of the linear bridge.



2a



2b

The speciation of Mo(V) in aqueous HCl solutions is also of interest in this connection. Crystal structures of both the monomeric $[MoOCl_5]^{2-}$ and dimeric $[Mo_2O_4Cl_4(H_2O)_2]^{2-}$ complex ions as found in ≥10 and ≤2 M HCl solutions, respectively, have been published.[16,17] However, the nature of the Mo(V) species in 5–6 M HCl remains ambiguous. Haight presented evidence that only one dinuclear species, $[Mo_2O_3Cl_8]^{4-}$, is in equilibrium with monomeric Mo(V) in 6 M HCl solution.[18] Subsequently, μ-oxo (linear and bent), μ-OH, and μ-Cl moieties were variously suggested for the dinuclear Mo(V) species.[2] In the present work, Raman studies of Mo(V) in HCl solutions have been conducted to determine the species responsible for the characteristic visible absorption band at ~450 nm; these support a linear (or nearly linear) Mo–O–Mo structure.

Experimental Section

Preparation of Compounds. All solutions were prepared under N_2 by using Schlenk techniques.

$HB(pz)_3MoOCl_2$ (1a) was prepared as described earlier.[14] IR (cm^{-1}; br = broad, m = medium, s = strong, sh = shoulder, v = very, w = weak): KBr, 2514 w (B—H), 964 s (Mo═O), 934 w, 928 w, 922 vw, 906 w, 815 w, 790 m, 770 s, 723 w, sh, 710 m, 668 w, 662 w, 655 w, 649 w, 615 m; Nujol mull, 376 w, 353 s, 342 s, 324 sh, w, 304 w, 279 w, 254 w, 245 w.

$HB(3,5\text{-}Me_2pz)_3MoOCl_2$ (1b). This compound was prepared in the same manner as $HB(pz)_3MoOCl_2$ and was recrystallized from chlorobenzene. IR (cm^{-1}): KBr, 2558 m (B—H), 961 s (Mo═O); Nujol mull, 374 m, 351 s, 333 s, 302 vw, 280 m, 254 m, 225 sh.

$[HB(pz)_3MoOCl]_2O$, "C_2 dimer" (2a), was prepared by a previous method and characterized by crystallography and by its ^1H NMR spectrum in $CDCl_3$.[14] IR (cm^{-1}): KBr, 2525 w (B—H), 964 s (Mo═O), 927 w, 921 w, 894 w, 860 w, 815 w, 804 w, 790 sh, 777 s, 768 s, 714 s, 665 m, 658 m, 652 m, 617 s; Nujol mull, 457 s, 368 m, 348 m, 333 s, br, 303 w, 282 mw, br, 245 w, sh, 225 w, sh.

$[HB(pz)_3MoOCl]_2O$, "C_i dimer" (2b), was prepared as previously described.[14] The crystalline product was characterized by X-ray crystal-

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(6) Grasseli, R. K. In *Surface Properties and Catalysis by Non-Metals: Oxides, Sulfides and Other Transition Metal Compounds*; D. Reidel: Dordrecht, The Netherlands 1983; pp 272–304.

(7) (a) Topsøe, H.; Clausen, B. S. *Catal. Rev.—Sci. Eng.* **1984**, *26*, 395. (b) Chianelli, R. R. *Catal. Rev.—Sci. Eng.* **1984**, *26*, 361.

(8) Winkler, J. R.; Gray, H. B. *Comments Inorg. Chem.* **1981**, *1*, 257.

(9) (a) Garner, C. D.; Lambert, P.; Mabbs, F. E.; King, T. J. *J. Chem. Soc., Dalton Trans.* **1977**, 1191 and references therein. (b) Garner, C. D.; Hill, L.; Howlader, N. C.; Hyde, M. R.; Mabbs, F. E.; Rutledge, V. I. *J. Less-Common Met.* **1977**, *54*, 27 and references therein.

(10) Marov, I. N.; Dubrov, Y. N.; Belyaeva, V. K.; Ermakov, A. N. *Dokl. Akad. Nauk SSSR* **1967**, *177*, 1106 (as referenced in ref 8).

(11) Rudolf, M. F.; Wolniak, A. *Z. Anorg. Allg. Chem.* **1974**, *408*, 214 and references therein.

(12) Young, C. G.; Roberts, S. A.; Ortega, R. B.; Enemark, J. H. *J. Am. Chem. Soc.* **1987**, *109*, 2938.

(13) Cleland, W. E.; Barnhart, K. M.; Yamanouchi, K.; Collison, D.; Mabbs, F. E.; Ortega, R. B.; Enemark, J. H. *Inorg. Chem.* **1987**, *26*, 1017.

(14) Lincoln, S. E.; Koch, S. A. *Inorg. Chem.* **1986**, *25*, 1594.

(15) Newton, W. E.; McDonald, J. W. *J. Less-Common Met.* **1977**, *54*, 51.

(16) Garner, C. D.; Hill, L. H.; Mabbs, F. E.; McFadden, D. L.; McPhail, A. T. *J. Chem. Soc.* **1977**, 1202.

(17) Glowiak, T.; Rudolf, M. F.; Sabat, M.; Jezowska-Trzebiatowska, B. *J. Less-Common Met.* **1977**, *54*, 35.

(18) (a) Haight, G. P. *J. Inorg. Nucl. Chem.* **1962**, *24*, 663 and references therein. (b) Haight, G. P. *J. Inorg. Nucl. Chem.* **1962**, *24*, 670.

Table I. Electronic Absorption Properties of $HB(pz)_3Mo^V$–Oxo Complexes in ~10^{-4} M CH_2Cl_2 Solutions[a]

$HB(pz)_3MoOCl_2$ (**1a**)		$HB(3,5-Me_2pz)_3MoOCl_2$ (**1b**)		$[HB(pz)_3MoOCl]_2O$ (**2a**)		$[HB(pz)_3MoOCl]_2O$ (**2b**)		$[HB(pz)_3]_2Mo_2O_4$ (**3**)	
λ_{max}	ϵ	λ_{max}	ϵ	λ_{max}	ϵ	λ_{max}	ϵ	λ_{max}	ϵ
670 br	44	690 br	58	698	485	676	496		
420 sh	45	450 sh		462	9000	462	9350		
350 sh	3100	340 sh	4260	350 sh	590	350 sh	690	310 sh	3320
272	7800	280 sh	7900	270 sh	9200	245 sh	9300	244 sh	7000

[a] λ_{max} in nm; ϵ in M^{-1} cm^{-1}.

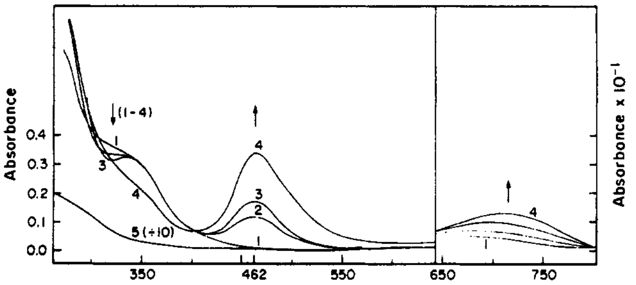


Figure 1. Changes in the absorption spectrum arising from the hydrolysis of $HB(pz)_3MoOCl_2$ (**1a**): (1) 1.02×10^{-3} M **1a** in dry CH_2Cl_2: (2) solution 1 after addition of a trace amount of H_2O; (3) a solution 3 days after addition of 2.6 mL of H_2O to 50 mL of solution 1; (4) solution 3 after 7 days; (5) solution 3 after 21 days (multiply left-hand A scale by 10). Path lengths of cells for spectra 1–4: <640 nm, 0.10 cm; >640 nm, 1.00 cm. Path length of cell for spectrum 5: 0.01 cm.

lography, by its ^1H NMR spectrum in $CDCl_3$, and by mass spectroscopy (found *m/e* 737, calcd *m/e* 737). IR (cm^{-1}): KBr, 2477 m (B—H), 958 s (Mo═O), 938 m, 921 w, 908 m, 891 m, 857 w, 809 w, 792 sh, 784 m, 767 s, 723 w, 713 s, 665 m, 657 m, 616 m; Nujol mull, 456 m, 387 vw, 367 m, 348 vw, 338 vw, sh, 326 s, 302 w, 284 w, 249 w.

^{18}O-Enriched $[HB(pz)_3MoOCl]_2O$, "C_i Dimer". This compound was synthesized in a manner analogous to that reported above for **2b**. A 0.225-g amount of $MoCl_5$ dissolved in 0.35 mL of 37% HCl diluted with 1.63 mL of $H_2{}^{18}O$ was added to 0.844 g of $KHB(pz)_3$ in 2.4 mL of $H_2{}^{18}O$ to produce highly enriched $[HB(pz)_3MoOCl]_2O$ for spectroscopic studies. The crystalline product was characterized by mass spectroscopy, which indicated that ^{18}O was incorporated into all three oxygen sites. Mass spectrum: found *m/e* 743, calcd *m/e* 743. The mode of preparation ensured ~85% ^{18}O enrichment. IR (cm^{-1}): KBr, 2478 m (B—H), 913 s (Mo═O), 891 m, 868 m, 816 w, 792 m, 767 s, 747 m, 725 w, 713 s, 665 m, 657 m, 616 m; Nujol mull, 437 m, 376 w, sh, 365 m, 348 w, 323 s, 300 w, 284 m, 247 w, 226 sh.

$[HB(pz)_3]_2Mo_2(O)_2(\mu\text{-}O)_2$ (3) was prepared as described earlier.[14] Mass spectrum: found *m/e* 682, calcd *m/e* 682. IR (cm^{-1}), Nujol mull: 2500 (B—H), 960 (Mo═O), 750 (Mo—O—Mo), 733 (Mo—O—Mo), 460 (Mo—O—Mo).

Spectroscopy. Raman spectra were recorded on a computerized Jarrell-Ash 25-300 spectrophotometer equipped with Spectra-Physics Model 164 Ar and Kr ion lasers, a cooled RCA C31034 photomultiplier, and an ORTEC Model 9302 amplifier/discriminator. Solid and solution samples were placed in glass melting-point capillaries and then inserted into a copper cold finger immersed in liquid N_2, cooling the specimen to ~90 K. Typical experiments used a backscattering geometry. Without cooling, samples blackened and decomposed where exposed to the laser, producing no Raman signals. However, the 90 K samples gave high quality and reproducible results, with similar Raman and IR spectra where allowed by symmetry considerations. The solvent CH_2Cl_2 (ν_1 = 702 cm^{-1}) was used as the internal standard in determining the excitation profiles of **2a** and **2b** by comparison of the intensity (peak heights) of sample modes to that of the internal standard. Polarization experiments were carried out by using 90° scattering on liquid samples at ~180 K with a Varian variable-temperature accessory. Infrared spectra were recorded on a Perkin-Elmer 1800 FTIR spectrophotometer. Electronic spectra were recorded on a Cary 17 spectrophotometer with matched quartz cells. Mass spectra were measured on a Hewlett-Packard 5980A mass spectrometer.

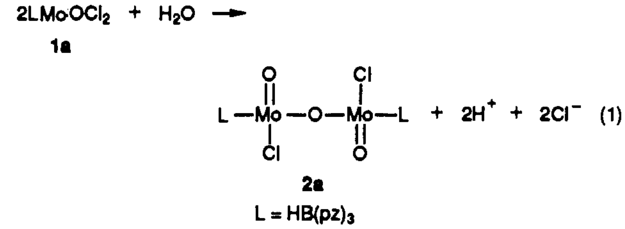
Results

Hydrolysis of Monomeric Mo(V). The room-temperature hydrolysis of $HB(pz)_3MoOCl_2$ (**1a**) (Scheme I) was followed by absorption spectroscopy, resulting in a series of spectra (Figure 1) reminiscent of those obtained by Haight[18] for Mo(V) in HCl and H_2SO_4 systems. When water was added to a CH_2Cl_2 solution of **1a** under an N_2 atmosphere and stirred, the reaction mixture turned from pale green to an intense yellow-brown during the first 7 days and then slowly lightened to a pale yellow color. The hydrolysis product responsible for the intense yellow-brown color had an electronic absorption spectrum similar to those of the $[HB(pz)_3MoOCl]_2O$ dinuclear complexes, **2a** and **2b** (Table I). The 462-nm band exhibited the usual intensity enhancement with time (Figure 1) observed in dinuclear complex formation of Mo(V)–oxo complexes.[11,18,19] In addition, the ~670-nm band of **1a** shifted to ~700 nm with a significant increase in intensity; both changes are consistent with formation of $[HB(pz)_3MoOCl]_2O$ (**2a**) (eq 1). When the hydrolysis of **1a** had proceeded for 11

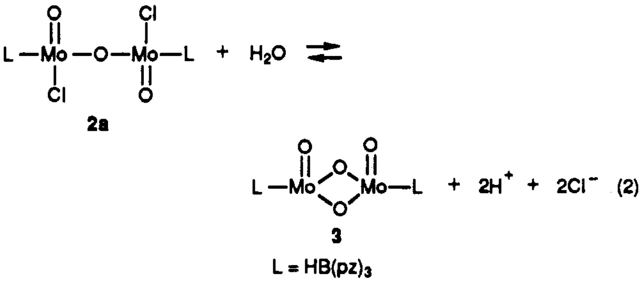
Table II. Changes in the Absorptivities (M^{-1} cm^{-1}) at Selected λ_{max} (nm) in the Electronic Absorption Spectrum of the $HB(pz)_3MoOCl_2/H_2O$ System with Addition of HCl

	λ_{max}				
sample[a]	698	462	456	444	350 (sh)
1	200	3300			~2300
2	260	4270			1920
3	260	4000			2200
4	135		2980		2000
5	135		2900		2000
6				525	sh

[a] Sample 1: 2.0 mL of H_2O added to 50 mL of 1×10^{-3} M $HB(pz)_3MoOCl_2$ (**1a**) in CH_2Cl_2; spectrum recorded after 4 days. Sample 2: 0.2 mL of 6 M HCl added to sample 1. Samples 3–5: 0.5 mL of 12 M HCl added to each preceding solution. Sample 6: same as sample 5, after 15 h.



$$2LMoOCl_2 + H_2O \longrightarrow L(O)(Cl)Mo{-}O{-}Mo(Cl)(O)L + 2H^+ + 2Cl^- \quad (1)$$



$$L(O)(Cl)Mo{-}O{-}Mo(Cl)(O)L + H_2O \rightleftharpoons LMo(O)(\mu\text{-}O)_2Mo(O)L + 2H^+ + 2Cl^- \quad (2)$$

days, the intense 462-nm band characteristic of the mono(μ-oxo) dinuclear complex began to diminish in intensity, and the solution began to turn pale yellow. All absorption maxima >350 nm disappeared with time, being replaced by new peaks at 310 and 244 nm, as found in the yellow complex, 3, indicating further hydrolysis to a final bis(μ-oxo) $Mo_2O_4^{2+}$ species (eq 2). We suggest that this $Mo_2O_4^{2+}$ species is identical with 3. The elec-

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(19) Jezowska-Trzebiatowska, B.; Rudolf, M. F.; *Trans. R. Inst. Technol., Stockholm* **1972**, *258*, 142.

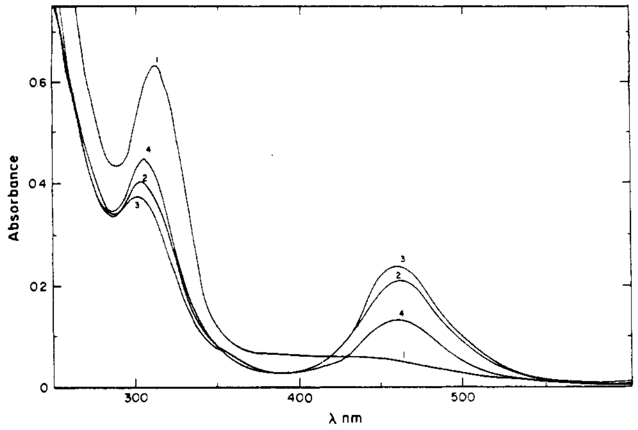

Figure 2. Changes in the absorption spectrum resulting from the addition of HCl to $[HB(pz)_3]_2Mo_2(O)_2(\mu\text{-}O)_2$ (**3**): (1) 1.01×10^{-3} M **3** in 1:1 (v/v) CH_2Cl_2/CH_3OH; (2) solution 1 after addition of 1 mL of 6 M HCl to 25 mL of sample; (3) solution 2 after 1 h; (4) solution 2 after addition of 0.15 mL of 1 M NaOH to 2.3 mL of solution.

tronic spectrum of **1a** in dry CH_2Cl_2 was unchanged over this period of time, indicating stability of the mononuclear complex in the absence of water and oxygen.

Reversibility of Hydrolysis. HCl was added to the equilibrium solution formed by the addition of H_2O to $HB(pz)_3MoOCl_2$ to test the reversibility of the hydrolysis reactions (Table II, Scheme I). When the reaction of **1a** with water had proceeded for 4 days, addition of a few drops of 6 M HCl resulted in an increased brightness of color. There was an intensification of the 462-nm band and a corresponding diminution at 350 nm, as expected for an increased concentration of the Mo–O–Mo dinuclear complex and a decreased concentration of the $Mo_2O_4^{2+}$ species (eq 2). Further addition of HCl results in diminution of the intense 462-nm band characteristic of the linear μ-oxo species. A concomitant increase in intensity at 350 nm suggests some monomer formation (eq 1). However, further HCl addition eventually yields a new band at 444 nm ($\epsilon \simeq 525$ M^{-1} cm^{-1}), suggesting that the blue shift and intensity decrease were due to formation of the dinuclear oxo chloro complex, $[Mo_2O_3Cl_8]^{4-}$. Apparently, at this level of $[H^+]$, the $HB(pz)_3^-$ ligand is released from the mono(oxo)-bridged complex **2** and is substituted by chloride ions. The hydrolysis of **1a** to **2** does not seem to be completely reversible under the conditions of this study, whereas the $Mo_2O_3^{4+} \rightleftarrows Mo_2O_4^{2+}$ reaction apparently is reversible (Scheme I).

Reaction of 3 with HCl. An effect similar to that observed above for the $Mo_2O_3^{4+} \rightleftarrows Mo_2O_4^{2+}$ equilibrium resulted when HCl was added to a 1:1 $CH_2Cl_2/MeOH$ solution of complex **3** (Figure 2). The most noticeable effect was a heightened brightness caused by growth of an intense band at 462 nm. The resulting spectrum also displayed a new weaker peak at 680–720 nm (not shown) and diminution of the original 310-nm peak, as expected for the formation of the linear oxo-bridged complex **2** (Scheme I). NaOH addition reverses the equilibrium, as seen by intensity diminution at 462 and 680–720 nm and intensification of the 310-nm band (Figure 2). These reactions suggest that complex **3** formed from direct synthesis is the same as that formed by the extended hydrolysis of $[HB(pz)_3MoOCl]_2O$ as described above.

The conversion of **3** to the mono(μ-oxo) dinuclear complex, **2a**, also takes place readily when 2 M HCl is added to solid **3** in air. Dark crystals are formed which have a unit cell identical to that of the "C_2" dinuclear complex **2a**.[14] When several drops of 3 M HCl are added to a saturated methanolic solution of **3** under an atmosphere of N_2, however, orange platelike crystals of the tetranuclear complex **4**, $Mo_4[HB(pz)_3]_2(O)_4(\mu\text{-}O)_4(\mu\text{-}OMe)_2(MeOH)_2$, are formed. Compound **4**, whose crystal structure has been reported earlier,[14] can also be prepared by allowing **3** to slowly react with methanol in air (Scheme I).

Raman and FTIR Spectra of 2a and 2b. The Raman spectra of the "C_2" and "C_i" dinuclear complexes each display a very intense band at ~380 cm^{-1} (Figure 3) that has been identified as the symmetric Mo–O–Mo stretching vibration (see below). This dominant band is absent from the IR spectra of the mononuclear complexes **1a** and **1b**, the dinuclear complexes **2a** and **2b**, and from the Raman spectrum of **1b** (Figure 3). The IR spectrum of **2b** is shown in Figure 4. The peak at 958 cm^{-1} is an Mo=O stretch of the terminal oxo groups, whereas those at 784 and 456 cm^{-1} are the asymmetric stretch and the deformation mode of the linear oxo-bridged unit, respectively (see below). Excitation profiles of **2a** and **2b** in CH_2Cl_2 show that the ~380-cm^{-1} band is the most strongly enhanced feature in each spectrum with excitation wavelengths near the 462-nm electronic transition (Figure 5). Qualitatively, a number of other vibrations follow a similar excitation profile but these have much lower intensities and smaller enhancements. Although the vibrational spectra of the two dinuclear complexes are quite similar, one striking difference in their Raman spectra is that the ~460-cm^{-1} band is significantly more intense in the C_2 complex at excitation wavelengths between 454.5 and 568.2 nm, whereas a weak band at 457 cm^{-1} is only visible in C_i at excitation wavelengths close to the 460-nm maximal absorption (Figure 3). No new Raman bands are observed when the samples are irradiated with near-UV laser wavelengths of 363.8 and 406.7 nm. Depolarization studies of **2a** and **2b** in liquid CH_2Cl_2 solutions at ~180 K with the nearly off-resonance excitation line at 514.5 nm yield ρ values of 0.38–0.57 for all bands. The consistent, low depolarization ratio values indicate a loss of overall molecular symmetry in solution such that all bands behave as symmetric modes of vibration (C_1 symmetry).

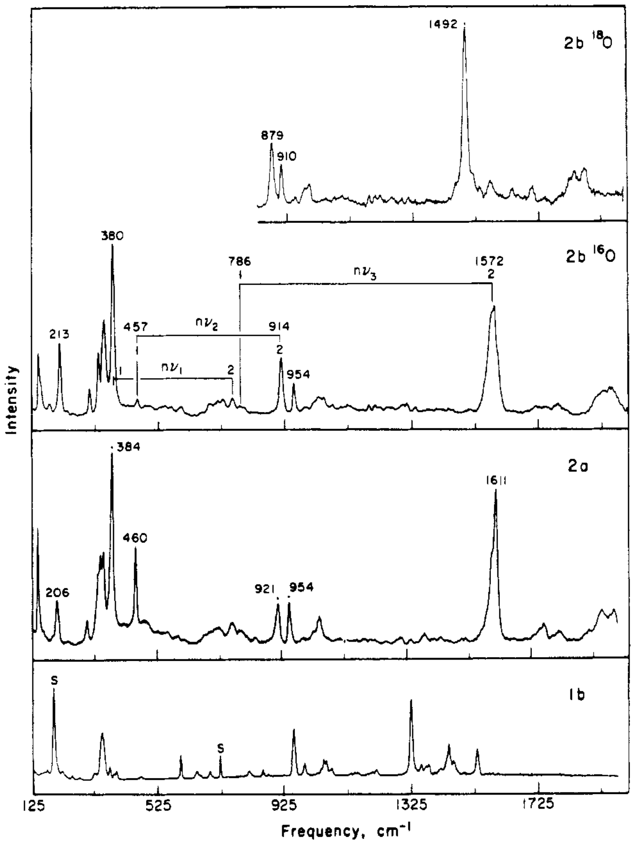

Figure 3. Raman spectra of mononuclear $HB(3,5\text{-}diMe_2pz)_3MoOCl_2$ (**1b**) and the dinuclear $[HB(pz)_3MoOCl]_2O$ complexes **2a** and **2b**. The high-frequency region of complex **2b** prepared from $H_2{}^{18}O$ is also shown. All spectra were obtained from microcrystalline solids at ~90 K with 457.9-nm excitation in a backscattering geometry. The bands marked S in the spectrum of **1b** are from $NaNO_3$ added to the solid (125–1025-cm^{-1} spectral region). The spectrum of **1b** above 1025 cm^{-1} is from the pure material.

Vibrational Spectra of Mononuclear L′MoOCl₂ (1b). Since complex **1a** was found to either "dimerize" or decompose under the various laser wavelengths, Raman spectra of the more stable $HB(3,5\text{-}Me_2pz)_3MoOCl_2$ complex, **1b**, were recorded for comparison with the spectra of the dinuclear complexes (Figure 3, Table III). As anticipated, an excitation profile of **1b** reveals

Table III. Vibrational Frequencies of $LMoOCl_2$, $L'MoOCl_2$, and $L_2Mo_2O_3$ Complexes[a]

1a	**1b**	**2a**	**2b** ^{16}O	**2b** ^{18}O	**2b** Δ	assignment	band label
(964) s	958 s	954	954	910	−44	$\nu(Mo{=}O)$	
		921	914	879	−35	$2\delta(Mo–O–Mo)$	$2\nu_2$
		(777)	786	748	−38	$\nu_{as}(Mo–O–Mo)$	ν_3
		460	457	440	−17	$\delta(Mo–O–Mo)$	ν_2
		384	380	~379	−1	$\nu_s(Mo–O–Mo)$	ν_1
(353) s	350 s	357	352	352	0	$\nu_s(Mo–Cl)$	A
(342) s		347	346	345	−1	ν_{ligand}	
(324) w, sh	334 s	338 sh	333	333	0	$\nu_{as}(Mo–Cl)$	
(304) w	304 w	304	304	304	0	$\nu(Mo–N)$	B
			287	287	0	$\nu(Mo–N')$	C
			252	252	0	$\delta(O{=}Mo–Y)$	D
			233	230	−3	$\delta(O{=}Mo–X)$	E
		206	213	210	−3	$\delta(O{=}Mo–O_{br})$	F
(279) w	280 w		287	287	0		

[a] All frequencies, cm^{-1}, from Raman spectra of crystalline solids at ~90 K; frequencies given in parentheses are from IR spectra (>400 cm^{-1}, KBr pellets; <400 cm^{-1}, Nujol mulls with CsI windows).

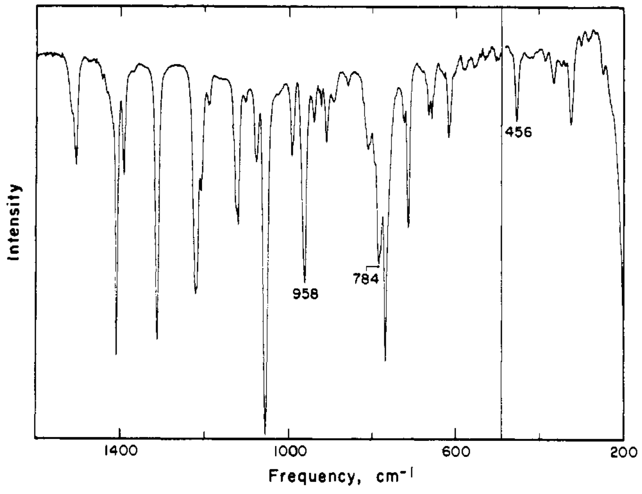

Figure 4. FTIR spectrum of the "C_i" complex $[HB(pz)_3MoOCl]_2O$ (**2b**): >500 cm^{-1}, KBr pellet; <500 cm^{-1}, Nujol mull/CsI.

no intensity enhancement of bands by 460-nm excitation. Moreover, the intense 380-cm^{-1} vibrational mode of the dinuclear complexes is noticeably absent from the Raman spectra of **1b**. The ~457-cm^{-1} band is also absent from the Raman and FTIR spectra of **1b** as well as from the FTIR spectrum of **1a**. Vibrational spectra of **1b** display virtually identical frequencies <600 cm^{-1}, although the 334-cm^{-1} band is relatively much stronger in the IR spectrum. The 350- and 334-cm^{-1} bands are the only strong IR absorptions below 600 cm^{-1}. These frequencies are in the correct region for Mo–Cl stretching modes.[20] The FTIR spectrum of **1a** is similar to that of **1b** below ~600 cm^{-1} with frequencies at 353, 342, 324, 304, and 279 cm^{-1}. Raman peaks common to both **1b** and the dinuclear **2a** and **2b** lie at ~350 and ~330 cm^{-1}. The latter band is the strongest for both **2a** and **2b** in the FTIR spectrum <450 cm^{-1}. On the basis of their intensities and frequencies, these two bands in the spectra of the dinuclear complexes are assigned as $\nu_s(Mo–Cl)$ and $\nu_{as}(Mo–Cl)$, respectively. The Raman frequency at 304 cm^{-1} is in the region expected for the Mo–N vibrations, and we tentatively assign the band accordingly.[21]

Identification of Mo–O Vibrational Modes. To assist with the identification of vibrations of the Mo–O–Mo bridge unit, the ^{18}O analogue of **2b** was synthesized in which all three oxygens were ~85% enriched. The Raman frequencies and isotope shifts are given in Tables III and IV. In the FTIR spectrum of **2b**, isotope shifts were observed for bands at 958 cm^{-1} [$\nu(Mo{=}O)$], which shifted to 913 cm^{-1}; at 784 cm^{-1}, which moved to 747 cm^{-1} [$\nu_{as}(Mo–O–Mo)$] (Figure 6); and at 456 cm^{-1}, which shifted to 437 cm^{-1} [$\delta(Mo–O–Mo)$]. Raman studies of ^{18}O-enriched **2b** also revealed a shift in a 914-cm^{-1} band to 879 cm^{-1}, which we assign as $2\delta(Mo–O–Mo)$ and a shift in an unexpectedly intense vibration at 1572 to 1492 cm^{-1} (Figure 3) assigned as $2\nu_{as}(Mo–O–Mo)$. In both cases, these are first overtones of infrared-active, Raman-forbidden fundamentals ($A_u \times A_u = A_g$). Of the resonance enhanced peaks <400 cm^{-1}, only the vibrations at 380, 233, and 213 cm^{-1} displayed ^{18}O-sensitive shifts. The band at 380 cm^{-1} [$\nu_s(Mo–O–Mo)$] experienced a shift of −1 cm^{-1}, which although

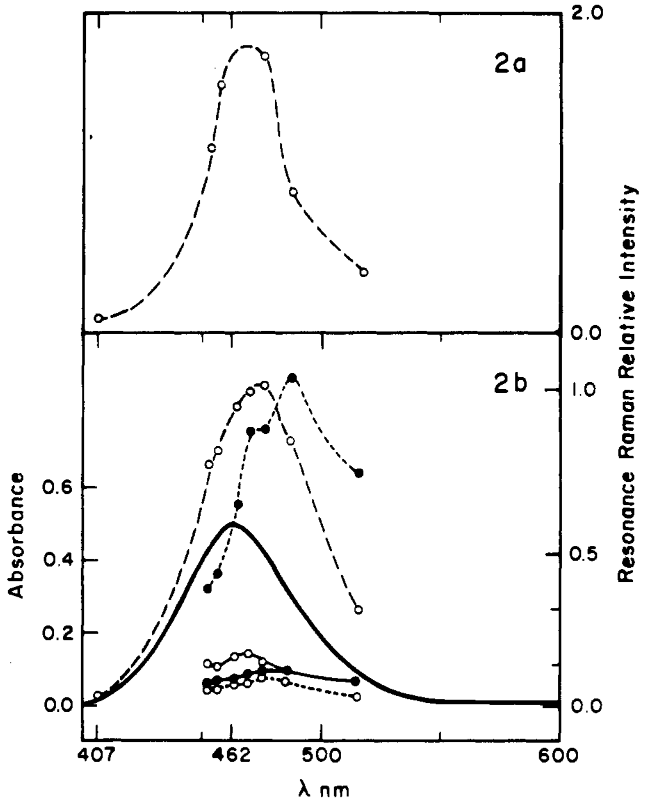

Figure 5. Resonance Raman enhancement of selected Mo–O–Mo and Mo═O vibrational frequencies of complexes **2a** and **2b** in CH_2Cl_2. The absorption spectrum of **2b** is shown in the lower panel; that of **2a** is similar. **2a**: $\nu_s(Mo–O–Mo)$ at 384 cm^{-1}. **2b**: (○– –○) ν_1, $\nu_s(Mo–O–Mo)$ at 380 cm^{-1}; (○- - -○) ν_2, $\delta(Mo–O–Mo)$ at 457 cm^{-1}; (●—●) ν_3, $\nu_{as}(Mo–O–Mo)$ at 786 cm^{-1}; (●- - -●) $2\nu_3$ at 1572 cm^{-1}; (○—○) ν(Mo═O) at 954 cm^{-1}.

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(20) Collin, R. J.; Griffith, W. P.; Pawson, D. *J. Mol. Struct.* **1973**, *19*, 531.

(21) Mo–N stretching frequencies involving heterocyclic aromatic amines have not been widely discussed. For the Mo(VI) complex of 8-mercaptoquinoline, Willis et al.[22] reported a value of 276 cm^{-1}. For the triply bridged $[HB(pz)_3Fe(CH_3COO)]_2O$ complex, a dominant Fe–N-(pz) stretching frequency is at 275 cm^{-1}, assigned on the basis of an extensive spectral study and normal coordinate analysis.[23]

(22) Willis, L. J.; Loehr, T. M.; Miller, K. F.; Bruce, A. E.; Stiefel, E. I. *Inorg. Chem.* **1986**, *25*, 4289 and references therein.

(23) Czernuszewicz, R. S.; Sheats, J. E.; Spiro, T. G. *Inorg. Chem.* **1987**, *26*, 2063.

Table IV. Overtone and Combination Bands in Raman Spectra of the Crystalline "C_i" Dinuclear Complex **2b**, $[HB(pz)_3MoOCl]_2O$[a]

assignment	obs freq, cm^{-1} ^{16}O	^{18}O	Δ
ν_1 [ν_s(Mo–O–Mo)]	380	379	−1
ν_1 + F[b]	593	589	−4
ν_1 + B	682	681	−1
$2\nu_1$	760	758	−2
ν_2 [δ(Mo–O–Mo)]	457	440	−17
ν_2 + E	687	667	−20
$\nu_2 + \nu_{ligand}$[c]	(809)	(791)	(−18)
$2\nu_2$	914	879	−35
$2\nu_2 + \nu_1$	1293	1259	−34
ν_3 [ν_{as}(Mo–O–Mo)]	786	748	−38
ν_3 + F	993	956	−37
ν_3 + E	1018	978	−40
ν_3 + D	1035	999	−36
$\nu_3 + \nu_L$[d]	1581	1543	−38
ν_3 − E	549	517	−32
ν_3 − D[e]	532	495	−7
$2\nu_3$	1572	1492	−80
$2\nu_3$ + F[b]	1785	1703	−82
$2\nu_3$ + A	1923	1844	−79
$2\nu_3 + \nu_1$	1952	1873	−79
ν_L[d]	797	794	−3
$2\nu_L$[d]	1594		

[a] Sample dispersed in solid $NaNO_3$; 457.9- and 514.5-nm excitation lines; frequencies in parentheses are from IR spectra. [b] Although these assignments are combinations of symmetric + antisymmetric modes, the ^{18}O data as well as the low intensities of the features support such an identification. [c] This combination is not observed in the Raman spectrum; an alternative possibility is ν_2 + A. [d] ν_L is ascribed to a ligand mode at 797 cm^{-1}. [e] Alternative possibility: $2\nu_2 - \nu_1$.

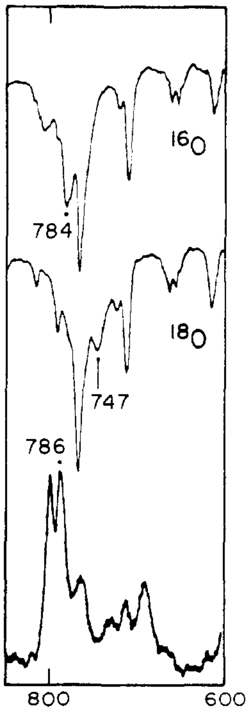

Figure 6. FTIR and Raman spectra of the ν_{as}(Mo–O–Mo) region of C_i "dimer" $[HB(pz)_3MoOCl]_2O$ (**2b**): (top spectrum) IR, complex prepared in $H_2{}^{16}O$; (middle spectrum) IR, complex prepared in $H_2{}^{18}O$; (bottom spectrum) Raman, 514.5-nm excitation, frozen solution of complex in $H_2{}^{16}O$.

small, was consistently observed. The strong band at 213 cm^{-1} moves to 210 cm^{-1} upon ^{18}O substitution. The 213-cm^{-1} mode is tentatively assigned as $\delta(O{=}Mo{-}O_{br})$ on the basis of its frequency position, its relatively high intensity, its isotope sensitivity, and excitation behavior that parallels that of other Mo–O–Mo bridge modes (lattermost data not shown). The weak band at 233 cm^{-1} shifts about 3 cm^{-1} in the ^{18}O complex and appears to increase in intensity. This intensity increase may arise from molecules containing unsymmetrical ^{18}O substitution, which would remove the inversion center and make the band more allowed. This 233-cm^{-1} frequency is in the appropriate region for a $\delta(O{=}Mo{-}X_{eq})$ mode.

Raman Spectra of $KHB(pz)_3$. The free polypyrazole ligand reveals many vibrations in the region <400 cm^{-1}; however, most of these are shifted significantly or are missing from the IR spectrum of the complex **1a**. In $KHB(pz)_3$, the strongest Raman bands in this region occur at 317, 311, and 153 cm^{-1}; moderate bands occur at 345 and 233 cm^{-1}. Weak bands at 150 and 345 cm^{-1} found in the off-resonance Raman spectrum of **2b** (^{18}O and ^{16}O) and **2a** may correspond to ligand absorptions. However, these ligand vibrations, in general, pose little or no problem in the Raman spectra of the dinuclear complexes.

Combinations and Overtones of Mo–O–Mo Resonant Modes. The complexes **2a** and **2b** exhibit Raman spectra rich in combination and overtone bands involving the Mo–O–Mo bridge moiety. Clark and co-workers[24,25] have shown that, for a series of D_{4h} linear μ-oxo dinuclear complexes, excitation by wavelengths close to the CT band typical of such compounds results in prominent resonance Raman peaks assigned as ν_s(Mo–O–Mo), 2δ(Mo–O–Mo), $2\nu_{as}$(Mo–O–Mo), and weaker combinations of these modes. In the Raman spectra of **2b**, ^{18}O shifts reveal that most of the remaining peaks can be accounted for as overtones and combination bands of the bridge vibrations ν_s(Mo–O–Mo), ν_{as}(Mo–O–Mo), and δ(Mo–O–Mo) (Figure 3 and Table IV). For excitation wavelengths between 488.0 and 514.5 nm, the most intense Raman band of **2b** in CH_2Cl_2 at 90 K is at 1572 cm^{-1}; it shifts to 1492 cm^{-1} with ^{18}O substitution. Since this feature does not shift with deuterated solvent (1:1 CD_2Cl_2/CD_3OD), it rules out its origin as an OH bending mode. Moreover, there is no band at this energy in the IR spectra of **2a**, **2b**, or **1a** or in the Raman spectrum of **1b**. Apparently, it is the overtone $2\nu_3$ of a Raman-forbidden fundamental ν_3 at 786 cm^{-1} assignable as the asymmetric Mo–O–Mo stretch. In C_i symmetry, $2\nu_3$ is Raman allowed. As in the solids, C_i symmetry of **2b** is retained in frozen solutions at ~90 K. The dinuclear iron complex $[HB(pz)_3Fe(CH_3COO)]_2O$ also exhibits a resonance Raman spectrum rich in overtones and combination bands involving its Fe–O–Fe modes. Here, too, $2\nu_{as}$(Fe–O–Fe) was observed to be more intense than the fundamental.[23]

Excitation profiles for ν_3 and $2\nu_3$ of **2b** display a second maximum at ~490 nm (Figure 5), suggesting the existence of a weaker CT (or, possibly, a ligand field) band, also associated with the Mo–O–Mo bridge, lying under the envelope of the intense 462-nm CT transition. Combination bands of the fundamental ν_{as}(Mo–O–Mo) (786 cm^{-1} in **2b**) coupled with various deformation modes of the terminal oxo group ($O{=}Mo{-}X$) become more prominent with 514.5-nm excitation, where enhancement by the 462-nm band is greatly diminished. The combination bands shift, as expected, with ^{18}O substitution (Table IV). The intensity of several of these combination bands (e.g., 1035, 1018, and 993 cm^{-1}) may be enhanced by coupling with ligand vibrations. In the IR, bands at 1053 (vs) and 991 cm^{-1} occur in **2a** and **2b** that are invariant to ^{18}O substitution and are also found in the monomer **1a**. Weak ligand bands also occur in the Raman spectrum of **1b** at 990, 1032, 1046, and 1053 cm^{-1}.

In solid **2b**, the intense overtone band is more complex in that a combination band appears at 1579 cm^{-1} with shoulders at ~1572 and 1594 cm^{-1}. With 514.5-nm excitation, a weak peak is clearly seen at ~797 cm^{-1} of both **2a** and **2b** (Figure 6). Apparently, the 797-cm^{-1} mode combines with the adjacent ν_3 (786 cm^{-1}) to give the band observed at 1579 cm^{-1} in solid **2b**. With ^{18}O substitution, where ν_3 is lower in energy, both the 797-cm^{-1} band and the combination band, now observed at 1543 cm^{-1}, appear only

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(24) Campbell, J. R.; Clark, R. J. H. *J. Chem. Soc., Faraday Trans. 2* **1980**, *76*, 1103.

(25) Clark, R. J. H.; Franks, M. L.; Turtle, P. C. *J. Am. Chem. Soc.* **1977**, *99*, 2473.

Table V. Raman Frequencies of Mo(V) Species in 2, 6, and 10 M HCl Solutions[a]

$[MoOCl_5]^{2-}$ [b]		$[Mo_2O_4Cl_4(H_2O)_2]^{2-}$ [c]	$[Mo_2O_3Cl_8]^{4-}$ [d]			assignment for
90 K	300 K	300 K	300 K	90 K	$\Delta(H_2{}^{18}O)$	$[Mo_2O_3Cl_8]^{4-}$
			1595	1608	−82	$2\nu_{as}$(Mo–O–Mo)
991	995	981	991, 984[e]	981	−48	ν(Mo═O)
			866	887	−34	2δ(Mo–O–Mo)
			802	805	−40	ν_{as}(Mo–O–Mo)
		741				
			434	444	−18	δ(Mo–O–Mo)
			384	380	−6 to −10	ν_s(Mo–O–Mo)
	333 br	312	327	315	0	ν(Mo–Cl)
	236			223	0	

[a] Data obtained with 457.9-nm excitation; frequencies in cm^{-1}. [b] 0.05 to 0.54 M in 10 M HCl. [c] 0.05 M in 2 M HCl. [d] 0.163 M $[Mo_2O_3Cl_8]^{4-}$ in 6 M HCl. [e] The 991-cm^{-1} peak is strongly polarized, revealing a small component at 984 cm^{-1}; most likely, this is the asymmetric Mo═O vibration, but a contribution from Mo═O of $[Mo_2O_4Cl_4(H_2O)_2]^{2-}$ cannot be entirely ruled out.

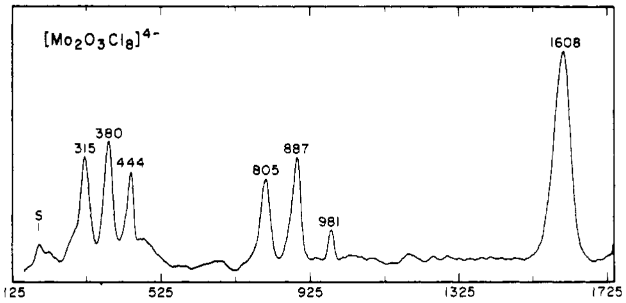

Figure 7. Resonance Raman spectrum of $[Mo_2O_3Cl_8]^{4-}$ obtained from 0.326 M Mo(V) in 6 M HCl at ~90 K with 457.9-nm excitation (S denotes solvent band).

as very weak features. The 797-cm^{-1} band may be a ligand mode since a similar band is also present in the IR spectrum of **1a**, as well as in the IR spectra of **2a** and **2b**. The shoulder at ~1594 cm^{-1} apparently is the first overtone of the 797-cm^{-1} mode; it disappears with ^{18}O substitution.

The high-frequency Raman spectrum of **2a** is not completely understood, although its general appearance resembles that of **2b**. The vibrational energies in the spectrum of **2a** in solution differ from those of crystalline **2a** and also from those of **2b**. In the solution spectrum of **2a**, the intense Raman band is at 1581 cm^{-1}, with a shoulder at ~1545 cm^{-1} that is proposed as $2\nu_3$. However, in crystalline **2a**, the maximum appears at 1611 cm^{-1} with a partially resolved band at 1598 cm^{-1}. The 1611-cm^{-1} maximum may be the first overtone of a weak 806-cm^{-1} mode. The 806-cm^{-1} vibrational itself appears to be a combination band of ν_2 and the mode at 347 cm^{-1} (Tables III and IV).

Raman Spectra of Chloromolybdenum(V) Species. Raman studies of Mo(V) in 2–10 M HCl at 90 K were conducted to further test the assignment of the 380-cm^{-1} ν_s(Mo–O–Mo) band and to test Haight's hypothesis that the binuclear species present in 5–6 M HCl, which is responsible for the intense visible band at ~450 nm, is the μ-oxo $[Mo_2O_3Cl_8]^{4-}$ complex.[18] Spectroscopic results and assignments are given in Figure 7 and Table V.[26,27]

The Raman bands of Mo(V) in 5 M versus 6 M HCl were identical in energy, but the species in 6 M HCl solution gives more intense peaks. Studies of $H_2{}^{18}O$ solutions at 90 K show oxygen-isotope-dependent vibrations at 981, 887, 805, 444, and 380 cm^{-1} (Table V). The 981-cm^{-1} Mo═O peak is of surprisingly low intensity (Figure 7). The 380-cm^{-1} band shifts by 6 to 8 cm^{-1} upon ^{18}O substitution. Preliminary results show that the intensity of the 380-cm^{-1} frequency follows the strong 450-nm electronic transition characteristic of the dinuclear complex. The 380-cm^{-1} band, absent from the Raman spectra of both $[MoOCl_5]^{2-}$ (≥10 M HCl) and $[Mo_2O_4Cl_4(H_2O)_2]^{2-}$ (≤2 M HCl), and by analogy with the data of complexes **2a** and **2b**, is assigned as ν_s(Mo–O–Mo). However, the greater-than-expected ^{18}O-isotope shift for a linearly bridged system could suggest that the predicted C_{2h} or C_{2v} symmetry of the $Mo_2O_3^{2+}$ species in 6 M HCl may not hold perfectly in solution.

A slightly weaker 444-cm^{-1} band shifts to 426 cm^{-1} upon ^{18}O substitution; its first overtone, a more intense band at 887 cm^{-1}, shifts to 853 cm^{-1}. The intensities of the latter two bands decrease quickly with increasing excitation wavelengths and are quite weak with 514.5-nm excitation. These results support the assignment of δ(Mo–O–Mo) for the 444-cm^{-1} mode by analogy to the poly(pyrazolyl)borate complexes. A third low-frequency peak at 315 cm^{-1} in the 6 M HCl species is invariant to ^{18}O substitution and is assigned as an Mo–Cl mode.

The first overtone of the 805-cm^{-1} band at 1608 cm^{-1} is very intense, suggesting that the resonance-enhanced fundamental at 805 cm^{-1} is a forbidden mode. D_2O studies of the 6 M HCl Mo(V) species at 90 K reveal no observable deuterium shifts, making OH^- and H_2O ligation unlikely. Decrease of the Mo(V) concentration to a value as low as 0.01 M in 6 M HCl reveals no significant change in the Raman spectral frequencies. Neither the 805- nor 1608-cm^{-1} intensities appear to follow the 450-nm electronic transition but rather increase in intensity with 488.0–514.5-nm excitation. We tentatively assign the 805-cm^{-1} mode (799 cm^{-1} at 25 °C) as ν_{as}(Mo–O–Mo). Polarization studies of Mo(V) in 6 M HCl were inconclusive, with none of the peaks being unambiguously *de*polarized, indicating that there may be a mixture of $[Mo_2O_3Cl_8]^{4-}$ species present. The terminal oxo groups may be syn or anti, yielding different symmetries with different depolarization ratios.

The present results support the assignments of the Mo–O–Mo vibrational modes in $Mo_2O_3^{4+}$ complexes and suggest that the molybdenum species responsible for the strong 450-nm electronic transition in 6 M HCl is the linear or nearly linear μ-oxo complex, $[Mo_2O_3Cl_8]^{4-}$.

Discussion

Vibrational spectra of Mo(V) dinuclear complexes containing the $Mo_2O_3^{4+}$ moiety show characteristic IR bands at ~950 cm^{-1} for ν(Mo═O), ~750 cm^{-1} for ν_{as}(Mo–O–Mo), and ~430 ± 25 cm^{-1}, which has been attributed variously to ν_s(Mo–O–Mo) or to a deformation of the bridge unit.[2,15] Two Mo═O stretching modes are predicted for the dinuclear compounds **2a** and **2b**; for

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(26) An earlier paper by Colton and Rose (*Aust. J. Chem.* **1968**, *21*, 883) reports vibrational data different from ours for "$[Mo_2O_3Cl_8]^{4-}$". However, these authors state that their compound has an electronic absorption spectrum "identical with that given by Haight for solutions of molybdenum(V) in 1 M acid". More recently, the structure of this dinuclear complex in 1–2 M HCl has been determined crystallographically to be the bis(μ-oxo) species, $[Mo_2O_4Cl_4(H_2O)_2]^{2-}$.[17]

(27) Himeno and Hasegawa[28] have reported limited Raman data on Mo(V) in HCl solutions at 1, 5, 6, and >8 M. Although there is superficial agreement between spectra, we strongly disagree in spectroscopic assignments. Their study benefited from neither isotopic labeling nor multiple excitation wavelengths, and hence, these authors failed to observe the strong resonance enhancements. We cannot duplicate their 1 M HCl data and are especially perplexed about their strong 372-cm^{-1} band that is absent in our spectra. On the other hand, our data for 6 and ~10 M HCl solutions agree well in frequencies. As stated above, our spectral data in 5 and 6 M solutions were more nearly identical than indicated in the referenced study. Finally, these authors make no mention of the electronic spectral properties of these Mo(V) species.

(28) Himeno, S.; Hasegawa, M. *Inorg. Chim. Acta* **1984**, *83*, L17.

the centrosymmetric complex **2b**, only the symmetric mode (ν_s) is Raman active and only the antisymmetric mode (ν_{as}) is infrared active. The IR peaks at 964 and 958 cm^{-1} in **2a** and **2b**, respectively, are the most intense bands in that region and are assigned as ν(Mo=O) modes. In Raman spectra, a 954-cm^{-1} peak is intense in both **2a** and **2b**.[29] Although the intensities of these 954-cm^{-1} bands follow the 462-cm electronic transition, their intensities are second only to those of the 380-cm^{-1} ν_s(Mo–O–Mo) bands when the off-resonance excitation lines at 568.2 and 363.8 nm are used; thus, the 954-cm^{-1} bands display the characteristics of totally symmetric modes. For complex **2a**, only one Mo=O band is observed in the infrared and Raman spectra even though both the symmetric and antisymmetric Mo=O modes are allowed in each. If the in-phase and out-of-phase Mo=O modes of **2a** are only weakly coupled, these stretching vibrations may be close in energy and, hence, not resolved.

Assignment of Mo–O–Mo Deformation Mode. On the basis of the very different intensities of the ~460-cm^{-1} mode in the two dinuclear complexes, our results indicate that this vibration cannot be ν_s(Mo–O–Mo). This view is supported by the large shift of −17 cm^{-1} upon ^{18}O substitution. For the "C_i" complex **2b**, only the antisymmetric Mo–O–Mo mode should be IR active, whereas only the symmetric mode will be seen in the Raman spectrum. The 457-cm^{-1} band is very species dependent. The band is absent in the IR spectrum of mononuclear **1a** but is the most intense band in the IR spectra of "C_2" and "C_i" in the region <600 cm^{-1}. The ~457-cm^{-1} band is present as a rather intense band in the resonance Raman spectra of C_2 at laser wavelengths between 454.5 and 568.2 nm but appears only as a very weak feature in C_i Raman spectra at excitation wavelengths close to the 462-nm absorption maximum. Hence, the ~457-cm^{-1} vibration has the correct symmetry behavior for a δ(Mo—O—Mo) mode in a linear M–O–M system, as was suggested by Newton and McDonald.[15] If the ~457-cm^{-1} band is indeed a bending mode, then the Mo–O–Mo symmetric stretch had never been identified in previous studies of $Mo_2O_3^{4+}$ complexes.

Although the δ(Mo–O–Mo) band itself is Raman forbidden for the centrosymmetric complex, the 2 × δ(Mo–O–Mo) mode at 914 cm^{-1} is allowed and is very prominent in Raman spectra of **2b**. The intensity of 2δ(Mo–O–Mo) falls off rapidly with excitation on either side of the 462-nm absorption, becoming very weak with, for example, 568.2-nm excitation. In the Raman spectrum of the ^{18}O analogue of **2b**, the 2δ(Mo–O–Mo) mode shifts from 914 to 879 cm^{-1}, commensurate with the observed isotope shift of the fundamental δ mode. In the FTIR spectrum, the overtone 2δ(Mo–O–Mo) is a weak band in both **2a** and **2b**, as may be expected. Campbell and Clark[24] have previously noted the prominence of the 2δ(M–O–M) mode in the Raman spectra of linear oxo-bridged D_{4h} systems when these are excited within the electronic transitions associated with the M–O–M bridge; in such D_{4h} systems, the fundamental δ(M–O–M) mode is also Raman inactive.

A similar band is observed at 887 cm^{-1} in the frozen solution spectrum of $[Mo_2O_3Cl_8]^{4-}$ that moves to 853 cm^{-1} with ^{18}O. In the 6 M HCl Mo(V) complex, both δ(Mo–O–Mo) and 2δ(Mo–O–Mo) are prominent in the Raman spectrum using excitation wavelengths near its electronic absorption maximum of 450 nm. Although it is possible to consider a ν_{as}(Mo–O$_t$) assignment for the 914-cm^{-1} band in the pyrazolylborate complexes, the fact that this frequency is always exactly double the fundamental δ(Mo–O–Mo) band with various solvents and different ligands strongly supports our assignment.

Assignment of Mo–O–Mo Symmetric Stretch. The resonance Raman spectra of the polypyrazolyl complexes **2a** and **2b** exhibit their ν_s(Mo–O–Mo) modes at ~380 cm^{-1}; these are the most striking features of their spectra <1500 cm^{-1}. This band is absent from the Raman spectra of the monomeric complex **1b**. Placement of the ν_s(Mo–O–Mo) 380-cm^{-1} band at a lower frequency than the δ(Mo–O–Mo) mode is rather unusual and deserves further comment. In the symmetric Mo–O–Mo stretching motion of the linear bridge, most of the movement involves the heavy molybdenum atoms, resulting in a very low energy for this vibration. The very small ^{18}O shift of ~1 cm^{-1} for the 380-cm^{-1} band is consistent with the bridging oxygen being fairly stationary in such a linear complex. A recent Raman study of μ-oxo-bridged dinuclear iron complexes from the OGI laboratory reveals that, as the Fe–O–Fe bridge angle increases from 124 to 175°, the ν_s(Fe–O–Fe) modes decrease in energy from 528 to 363 cm^{-1}.[33] Accordingly, the linearity of the Mo–O–Mo angles, 177.3 and 180° for **2a** and **2b**, respectively, would support a low energy for the ν_s(Mo–O–Mo) mode in these complexes. The fact that earlier investigations either were IR studies usually done >400 cm^{-1} or involved sulfur ligands that absorb at ~370 cm^{-1} [ν(Mo–S)][22] could explain why the prominent low-energy ν_s(Mo–O–Mo) vibration in $Mo_2O_3^{4+}$ complexes was not detected previously. Resonance Raman studies by San Filippo and co-workers[34] of linear μ-oxo-bridged complexes $[M_2OCl_{10}]^{4-}$ (M(IV) = Ru, Os, W) found the ν_s(M–O–M) mode at 254 cm^{-1} for Ru and at 225 cm^{-1} for both W and Os. In more recent studies on $[M_2OX_{10}]^{4-}$ complexes, Clark and co-workers[24,25] confirmed the low-energy assignment of ν_s(M–O–M) for these D_{4h} complexes and assigned the higher energy 469-cm^{-1} IR-active, Raman-forbidden band as δ(M–O–M). Although the electronic structure of the dinuclear Mo(V)–oxo complexes is quite different from that of the $[M_2OX_{10}]^{4-}$ complexes of D_{4h} symmetry, the common linear M–O–M bridge geometry apparently gives a ν(M–O–M) vibration at lower energy than the δ(M–O–M) for **2a** and **2b**. The weak vibrational mode observed at 250 cm^{-1} cannot be assigned as ν_s(M–O–M) in **2a** and **2b**, since this band is present in the IR spectra of **2a**, **2b**, **1a**, and **1b**, as well as in the Raman spectrum of the mononuclear complex **1b**.

The intensity of the 462-nm electronic transition (ϵ = 9000 M^{-1} cm^{-1}) of **2a** and **2b** suggests a CT assignment for this band. Our Raman studies indicate that the atoms involved in the CT transition are also involved in the 380-cm^{-1} vibration. Although an assignment of ν(Mo–Cl) or ν(Mo–N) could be considered for the 380-cm^{-1} frequency, the absence of a 380-cm^{-1} band in the mononuclear complexes **1a** and **1b** led us to reject such an assignment in favor of ν_s(Mo–O–Mo). Moreover, the Raman and IR spectra of the mononuclear complexes clearly display the Mo–Cl stretches at frequencies ~350 and ~331 cm^{-1}. The presence of an intense resonance-enhanced band at 380 cm^{-1} in the $[Mo_2O_3Cl_8]^{4-}$ species in 6 M HCl argues against the 380-cm^{-1} band in **2a** and **2b** being linked to the poly(pyrazolyl)borate ligand. Assignment of the 380-cm^{-1} Raman vibration as ν_s(Mo–O–Mo) leads us to conclude that the intense 462-nm electronic band, which is responsible for the resonance enhancement of this vibration, is most likely a CT band arising from a transition among the molecular orbitals of the Mo–O–Mo linear bridge.

Structure of 6 M HCl Mo(V) Species. The resonance Raman data on the Mo(V)/6 M HCl system support Haight's original formulation of $[Mo_2O_3Cl_8]^{4-}$ for the dinuclear species that is responsible for the intense electronic absorption at ~450 nm. Our Raman data for this species parallel those observed for the tris(pyrazolyl)borato complexes **2a** and **2b**, including the observation of the δ(Mo–O–Mo) mode being at higher frequency than ν_s(Mo–O–Mo) and the strong overtone activity of δ(Mo–O–Mo)

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[29] The long Mo=O bond distance of 1.779 (6) Å in the crystal structure of **2b** versus the "normal" distance of 1.671 (4) Å in **2a** suggested that these compounds are an example of distortional or "bond stretch" isomerism.[30,31] However, the identity of the Raman-active Mo=O stretching frequencies of **2a** and **2b** is surprising when compared to the clear differences in the IR frequencies in these types of isomers.[32]

[30] Nugent, W. A.; Mayer, J. M. In *Metal-Ligand Multiple Bonds*; John Wiley & Sons: New York, 1988; p 152 and references therein.

[31] (a) Jean, Y. Private communication. (b) Jean, Y.; Lledos, A.; Burdett, J. K.; Hoffmann, R. *J. Am. Chem. Soc.* **1988**, *110*, 4506.

[32] Wieghardt, K.; Backes-Dahmann, G.; Nuber, B.; Weiss, J. *Angew. Chem.* **1985**, *24*, 777.

[33] Sanders-Loehr, J.; Wheeler, W. D.; Shiemke, A. K.; Averill, B. A.; Loehr, T. M. *J. Am. Chem. Soc.* **1989**, *111*, 8084.

[34] San Filippo, J., Jr.; Grayson, R. L.; Sniadoch, H. J. *Inorg. Chem.* **1976**, *15*, 269. San Filippo, J., Jr.; Fagan, P. J.; Di Salvo, F. J. *Inorg. Chem.* **1977**, *16*, 1016.

and ν_{as}(Mo–O–Mo); together, they suggest that this species has a linear or nearly linear μ-oxo bridge. However, the large ^{18}O-isotope effect seen for ν_s(Mo–O–Mo) and the high intensity of the otherwise forbidden ν_{as}(Mo–O–Mo) seen at 805 cm^{-1} are unexpected for a linearly bridged M–O–M ion. Calculations on the distortional isomers **2a** and **2b** show that moving the bridging oxygen away from the symmetrical position is slightly *stabilizing* in both isomers.[31] Perhaps such a distortion is also operative in $[Mo_2O_3Cl_8]^{4-}$ to account for these effects.

A linearly bridged $Mo_2O_3^{4+}$ unit is expected to be diamagnetic, and in fact, all known examples of $Mo_2O_3^{4+}$ complexes, including **2a** and **2b**, are diamagnetic.[14,17] While paramagnetic Mo(V) species are very likely present in 6 M HCl solution, an earlier suggestion[2,35] that a "paramagnetic dimer" is responsible for the strong electronic absorption band at ~450 nm appears to warrant reinterpretation. A recent X-ray absorption study indicated the coexistence of significant fractions of the dinuclear $Mo_2O_4^{2+}$ and $Mo_2O_3^{4+}$ and the mononuclear MoO^{3+} species in 5 to 6 M HCl solutions.[36] This fact alone makes XAFS an ambiguous technique for the extraction of structural information. No information on the determination of phase shifts or multiple scattering was presented. Since second-shell distances are difficult to determine accurately and no authentic $Mo_2O_3^{4+}$ complexes were used as models for the XAFS analysis, the evaluation of a Mo–O–Mo angle of ~107° is open to question. Furthermore, this study does not independently establish the existence of a "paramagnetic μ-oxo dimer" of Mo(V).

Conclusions

Resonance Raman studies have clarified both the electronic and vibrational spectroscopic assignments associated with the linear μ-oxo bridge of the poly(pyrazolyl)borate $Mo_2O_3^{4+}$ dinuclear complexes **2a** and **2b**. The ~457-cm^{-1} band characteristic of $Mo_2O_3^{4+}$ has been definitively assigned as δ(Mo–O–Mo), and ν_s(Mo–O–Mo) has been found at ~380 cm^{-1} for **2a** and **2b**, as well as the 6 M HCl chloro complex $[Mo_2O_3Cl_8]^{4-}$. The intense 462-nm electronic transition, which is responsible for the resonance enhancement of the strong 380-cm^{-1} Raman-active vibration, is assigned as a CT band associated with the unique chromophore arising from the linear μ-oxo-bridged system.[34] Spectral studies reveal that limited hydrolysis of $HB(pz)_3MoOCl_2$ produces the linear μ-oxo species $[HB(pz)_3MoOCl]_2O$ (**2a**) and further hydrolysis converts **2a** to $Mo_2O_4[HB(pz)_3]_2$ (**3**) in a reversible pH-dependent reaction. For the Mo(V)/6 M HCl system, resonance Raman studies indicate that the intense ~450-nm electronic band is associated with a linear or nearly linear μ-oxo $[Mo_2O_3Cl_8]^{4-}$ species that is expected to be diamagnetic.

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(35) Hare, C. R.; Bernal, I.; Gray, H. B. *Inorg. Chem.* **1962**, *1*, 831.

(36) Yokoi, K.; Matsubayashi, N.; Miyanaga, T.; Watanabe, I.; Ikeda, S.; Murata, K. *Polyhedron* **1988**, *8*, 45.

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Comparison of Laser-Desorption and Fast-Atom-Bombardment Mass Spectra of a Series of $Rh(PPh_3)_2(CO)Y$ Complexes

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The mass spectra of a series of involatile $Rh(PPh_3)_2(CO)Y$ complexes (anion Y^- is F^-, Cl^-, I^-, $-NCO^-$, $-NCS^-$, $O_2CCH_3^-$, ONO_2^-, $O_2PF_2^-$, or $OSO_2CF_3^-$; $Rh(PPh_3)_2(CO)$ is shortened to $RhL_2(CO)$ hereafter) were obtained by using both laser-desorption Fourier-transform ion cyclotron resonance (LDFTICR) and fast-atom-bombardment (FAB) techniques. The FAB positive-ion spectra (sulfolane matrix) showed molecular ions for all complexes except $RhL_2(CO)OSO_2CF_3$, the species containing the most weakly coordinating anion. These FAB spectra also exhibited fragment ions resulting from loss of CO and PPh_3. The sulfolane adduct of $RhL_2(CO)^+$ and a derivative were also observed for the series, especially prominent in spectra of complexes of the less tightly bound anions. The LDFTICR positive-ion spectra were less consistent in fragmentation/rearrangement patterns over the range of anions Y^- than were their FAB counterparts; peak intensities of the former spectra were also highly variable due to difficulties in preparing consistent probe samples. Although the $[M + K]^+$ pseudomolecular ion was detected for every complex except $RhL_2(CO)OSO_2CF_3$, only several molecular ions were observed in the series; otherwise, fragmentation patterns similar to those of the FAB experiments were seen. No molecular ions were seen for any $RhL_2(CO)Y$ in the LDFTICR negative-ion spectra; however, $Rh(CO)Y^-$, $Rh(PPh_3)(CO)Y^-$, and $Rh_2(CO)_2Y_2^-$ were characteristically observed, with peak intensities again quite variable. Several tetrarhodium species, $Rh_4(CO)_xY_2^-$ (x = 2–4), were detected as well.

Introduction

New techniques in mass spectrometry are being applied with increasing frequency in inorganic chemistry for characterizing involatile compounds and studying their chemical properties. Newer techniques used to produce gaseous ions from transition-metal complexes include fast-atom-bombardment (FAB),[1,2] laser-desorption Fourier-transform ion cyclotron resonance (LDFTICR),[3-5] field desorption (FD),[2f,6] thermospray,[2f] fast-heating chemical ionization,[2f] and liquid secondary-ion (SI) mass spectrometry.[7]

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(1) Bruce, M. I.; Liddell, M. J. *Appl. Organomet. Chem.* **1987**, *1*, 191.

(2) (a) Thomas, B. J.; Mitchell, J. F.; Theopold, K.-H.; Leary, J. A. *J. Organomet. Chem.* **1988**, *348*, 333. (b) Divisia-Blohorn, B.; Kyriakakou, G.; Ulrich, J. *Org. Mass Spectrom.* **1985**, *20*, 463. (c) Miller, J. M.; Balasanmugam, K.; Nye, J.; Deacon, G. B.; Thomas, N. C. *Inorg. Chem.* **1987**, *26*, 560. (d) Cohen, A. I.; Glavan, K. A.; Kronauge, J. F. *Biomed. Mass Spectrom.* **1983**, *10*, 287. (e) Unger, S. E. *Anal. Chem.* **1984**, *56*, 393. (f) Unger, S. E.; McCormick, T. J.; Treher, E. N.; Nunn, A. D. *Anal. Chem.* **1987**, *59*, 1145. (g) Barber, M.; Bordoll, R. S.; Sedgwick, R. D.; Tyler, A. N. *Nature (London)* **1981**, *293*, 270.

(3) Forest, E.; Marchon, J.-C.; Wilkins, C. L.; Yang, L.-C. *Org. Mass Spectrom.* **1989**, *24*, 197.

0020-1669/90/1329-1915$02.50/0