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Octamolybdenum Oxo–Pyrazolate Clusters. Syntheses, Characterization, and Crystal and Molecular Structures of the Mo(V)/Mo(VI) and Mo(VI) Octamolybdenum Clusters $Mo_8(pz)_6O_{18}(pzH)_6$ and $Mo_8(pz)_6O_{21}(pzH)_6$

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Two octamolybdenum compounds, containing both bridging pyrazolate and terminal pyrazole ligands, have been prepared by the reaction of molten pyrazole with molybdenum oxides, and their structures have been determined by single-crystal X-ray diffraction. Crystals of $Mo_8(pz)_6O_{18}(pzH)_6\cdot 2pzH$ (**1**; pzH = pyrazole, $C_3H_4N_2$; pz = pyrazolate anion, $C_3H_3N_2$) are monoclinic, space group $C2/c$, with a = 23.026(3) Å, b = 13.345(3) Å, c = 23.314(2) Å, β = 114.827(8)°, and Z = 4; and those of $Mo_8(pz)_6O_{21}(pzH)_6\cdot 3pzH\cdot {}^1/_2H_2O$ (**2**) are trigonal, space group $R\bar{3}$ a = 20.005(2) Å, c = 30.567(5) Å, and Z = 6. The structures were solved by Patterson methods and were refined by full-matrix least-squares procedures to R = 0.026 and 0.030 for 9557 and 3683 reflections with $I \geq 3\sigma(I)$, respectively. The octamolybdenum species in **1** contains both Mo(VI) and Mo(V) ions, with the latter linked in pairs by metal–metal single bonds. Compound **2** involves a single-valent Mo(VI) octamolybdenum species and is photosensitive.

Introduction

Polyoxometalate chemistry is an active area of research with interest arising from the study of the varied physical properties of these compounds and from the application of polyoxometalates to areas such as catalysis and biological chemistry.[1–5] In the last 15 years, a particular aspect of the polyoxometalate field which has received growing attention is the preparation of organic derivatives of these compounds, and one avenue into this area has been the development of the coordination chemistry of isopolymolybdates. Initial efforts were directed toward the incorporation of oxygen donor species as in $[(HCO)_2Mo_8O_{28}]^{6-}$ [6] and $[Mo_8O_{24}(OCH_3)_4]^{4-}$,[7] and subsequently, nitrogen donor derivatives were reported.[8–12] During investigations of binary transition metal pyrazolates,[13–16] we discovered two compounds which contain octamolybdenum clusters incorporating coordinated pyrazole. Though structurally related to the octamolybdate species, they differ in that they are formally neutral and contain bridging pyrazolate anions in addition to oxo anions. We report here the structural characterization of a mixed-valence, Mo(V)/Mo(VI), compound with the formula $Mo_8(pz)_6O_{18}(pzH)_6\cdot 2pzH$ (**1**; pzH = pyrazole; pz = pyrazolate anion) and an analogous single-valent, Mo(VI), compound formulated as $Mo_8(pz)_6O_{21}(pzH)_6\cdot 3pzH\cdot {}^1/_2H_2O$ (**2**) (throughout this paper, **1** and **2** designate the solid materials; the molybdenum-containing clusters will be designated by their formulas).

Experimental Section

Materials. All materials used were of reagent grade. Molybdenum metal powder (BDH) and MoO_3 (MCB) were used as received. "Molybdenum blue", $Mo_4O_{10}(OH)_2$, was prepared according to the method of Brauer.[17] Pyrazole (Aldrich) was used without further purification. THF was dried by distillation, in a dinitrogen atmosphere, from sodium and benzophenone.

$Mo_8(pz)_6O_{18}(pzH)_6\cdot 2pzH$ (1). This compound was prepared via two different methods. In the first, molybdenum metal powder ($\sim$1 g) and pyrazole ($\sim$4 g) were combined and heated at 90 °C (melting point of pyrazole is 68 °C) in air for 18 h, without stirring. During that time all of the molten pyrazole had evaporated from the heated reaction mixture, leaving behind most of the molybdenum metal unreacted and small orange-red crystals (less than 2 mg), which were identified by single crystal, X-ray diffraction as **1**. A second preparative method afforded a bulk sample of this compound. "Molybdenum blue" (0.722 g, 5.00 mmol of Mo) was combined with pyrazole (2.72 g, 40.0 mmol), and the mixture was heated at 105 °C in a dinitrogen atmosphere for 24 h, with stirring. During this time, the color of the mixture changed from dark bluish black to orange-red. The reaction mixture was then cooled to room temperature, whereupon it solidified. The solid was extracted from the reaction vessel using 150 mL of dry THF in small portions, and the extracted slurry was suction-filtered, yielding a brown filtercake (63 mg) and a clear brown filtrate. The filtrate was left standing for 3 days, during which time a brown solid precipitated. The resulting mixture was suction-filtered, yielding a brown filtercake (380 mg) and a clear orange filtrate, which was concentrated from an initial volume of 150 mL to 25 mL by evaporation at room temperature over 4 days. The concentrate was heated at 105 °C in air, without stirring. Within the first 2 h of heating, a light orange solid had precipitated. After 3 days, the solution phase had concentrated to half of its initial volume and a considerable amount of blue solid had formed on the sides of the reaction vessel. Mixing of the blue solid back into the remaining solution phase caused the superheated solution to begin to boil, and after 24 h, the blue solid had dissolved, yielding a dark, viscous, orange-red solution. The solution was heated for a further 7 days, during which time pyrazole evaporated from the solution and dark orange-red crystals deposited. The remaining solution

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Table I. Crystallographic Data

compd	$Mo_8(pz)_6O_{18}(pzH)_6\cdot 2pzH$ (1)	$Mo_8(pz)_6O_{21}(pzH)_6\cdot 3pzH\cdot{}^1/_2H_2O$ (2)
formula	$C_{42}H_{50}Mo_8N_{28}O_{18}$	$C_{45}H_{55}Mo_8N_{30}O_{21.5}$
fw	2002.55	2127.64
crystal system	monoclinic	trigonal
space group	$C2/c$	$R\bar{3}$
a, Å	23.026(3)	20.005(2)
b, Å	13.345(3)	20.005(2)
c, Å	23.314(2)	30.567(5)
β, deg	114.827(8)	
V, Å^3	6502(2)	10594(3)
Z	4	6
ρ_{calc}, g/cm^3	2.046	2.001
T, °C	21	21
radiation	Mo	Mo
λ, Å	0.710 69	0.710 69
μ, cm^{-1}	15.75	14.28
transm factors	0.78–1.00	0.94–1.00
$R(F)^a$	0.026	0.030
$R_w(F)^b$	0.030	0.029

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $R_w = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2}$.

was decanted from the crystals, and they were washed with 30 mL of acetone, yielding 240 mg (29% yield based on Mo(V) available) of **1**. Anal. Calcd for $C_{42}H_{50}Mo_8N_{28}O_{18}$: C, 25.2; H, 2.5; N, 19.6. Found: C, 25.3; H, 2.6; N, 19.6. IR data (cm^{-1}): 3376 w,[18] 3175 s, 3142 s, 3134 s, 3121 s, 3115 s, 3031 m, 2985 m, 2859 w, 2787 vw, 2641 vw, 2608 vw, 2533 vw, 2463 vw, 1751 w, 1634 w, 1524 m, 1490 s, 1472 m, 1419 s, 1396 m, 1371 s, 1354 m, 1349 m, 1336 w, 1285 w, 1274 s, 1254 m, 1243 w, 1176 s, 1165 w, 1150 m, 1141 m, 1136 s, 1121 m, 1085 w, 1067 s, 1046 s, 1030 m, 967 s, 948 s, 911 s, 860 s, 833 s, 769 s, 751 s, 731 s, 722 m, 685 w, 669 w, 642 w, 624 m, 610 m, 535 w, 508 m, 486 m, 478 m, 430 m, 415 w, 375 w, 346 s, 339 s, 330 s, 313 w.

$Mo_8(pz)_6O_{21}(pzH)_6\cdot 3pzH\cdot{}^1/_2H_2O$ (2). Powdered MoO_3 (0.720 g, 5.00 mmol) and pyrazole (3.40 g, 50.0 mmol) were combined and heated in darkness at 100 °C for 6 days, with stirring. The reaction mixture was then cooled to room temperature, causing it to solidify. The solid was extracted from the reaction flask with dry THF, yielding a yellow filtrate and a pale yellow filtercake, which was washed further with THF and air-dried. This gave 1.203 g (90%) of **2**. Anal. Calcd for $C_{45}H_{55}Mo_8N_{30}O_{21.5}$: C, 25.4; H, 2.6; N, 19.8. Found: C, 25.1; H, 2.5; N, 19.5. IR data (cm^{-1}): 3338 s, 3213 s, 3135 s, 3104 m, 3066 m, 2987 m, 2931 w, 2896 w, 2867 w, 2809 vw, 2761 vw, 2739 vw, 2632 vw, 2602 vw, 2546 vw, 2515 vw, 2444 vw, 2421 vw, 1758 w, 1631 w, 1525 m, 1491 s, 1474 s, 1462 w, 1445 w, 1423 s, 1402 s, 1367 s, 1356 s, 1336 w, 1274 s, 1176 s, 1155 s, 1132 s, 1081 m, 1053 s, 964 m, 948 s, 936 s, 920 s, 890 s, 830 s, 790 s, 735 s, 683 s, 591 s, 570 s, 426 s, 372 s, 350 s, 336 s, 314 m, 302 s. Large single crystals of this compound were obtained by concentrating the filtrate to a solid residue and heating that residue for 3 days in darkness, without stirring. The resulting crystals were separated from the excess pyrazole by washing with acetone and drying in air.

X-ray Crystallographic Analyses of 1 and 2. Crystallographic data appear in Table I. The final unit-cell parameters were obtained by least-squares procedures on the setting angles for 25 reflections with 2θ = 47.9–54.5° for **1** and 32.8–35.9° for **2**. The intensities of three standard reflections, measured every 200 reflections throughout the data collections, remained constant for both complexes. The data were processed[19] and corrected for Lorentz and polarization effects and absorption (empirical, based on azimuthal scans for three reflections).

Both structures were solved by conventional heavy-atom methods, the coordinates of the Mo atoms being determined from the Patterson functions and those of the remaining non-hydrogen atoms from subsequent difference Fourier syntheses. For both structures, the systematic absences did not unambiguously determine the space groups: $C2/c$ or Cc is possible for **1**, and $R\bar{3}$ or $R3$ is possible for **2**. The structure analyses were both initiated in the centrosymmetric space groups ($C2/c$ and $R\bar{3}$, respectively, for **1** and **2**) on the basis of the Patterson functions. These choices were confirmed by the subsequent successful solutions and refinements of the structures. The $Mo_8(pz)_6O_{18}(pzH)_6$ molecule in **1** has exact (crystallographic) C_2 symmetry, and the $Mo_8(pz)_6O_{21}(pzH)_6$ molecule in **2** has exact C_3 symmetry.

The asymmetric unit of **1** contains half of the octamolybdenum molecule and one pyrazole solvate molecule. The N–H proton of the pyrazole solvate molecule was treated as 1:1 disordered with respect to the two nitrogen atoms. The identification of the solvate nitrogen atoms (as well as the disordering of the N–H proton) was based on hydrogen-bonding considerations. The asymmetric unit of **2** contains one-third of the octamolybdenum complex, one pyrazole solvate molecule, and one-sixth of a water molecule. The pyrazole solvate was found to be 1:1 orientationally disordered with one coincident atom. The remaining disordered atoms of the pyrazole solvate were refined as split atoms. The water molecule is situated at a point of S_6 symmetry, surrounded by six pyrazole molecules.

All non-hydrogen atoms of both structures except for the water oxygen atom in **2** were refined with anisotropic thermal parameters. The (necessarily) disordered water hydrogen atoms in **2** could not be located and were excluded from the model. All other hydrogen atoms in both structures were fixed in calculated positions (N–H/C–H = 0.98 Å, B(H) = 1.2 B(bonded atom)). Corrections for secondary extinction were not indicated and therefore were not applied. Neutral-atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from ref 20.

Physical Methods. Infrared spectra were recorded using a Bomem Model MB102 FTIR spectrometer. Nujol and hexachlorobutadiene mulls of samples were sandwiched between KRS-5 plates (Harshaw Chemical Co.). Magnetic measurements were made over the temperature range 2–300 K in an applied field strength of 10 kOe using a Quantum Design MPMS SQUID magnetometer as previously described.[13] The susceptibility measurements for **1** were corrected for the diamagnetism of the ligands and Mo atoms.[21] Differential scanning calorimetry (DSC) was performed in air using a Mettler DSC 20 standard cell and TC10 TA processor as described previously.[22] Powder X-ray diffractograms were recorded using an automated Rigaku Rotaflex RU-200BH rotating-anode powder X-ray diffractometer (graphite-monochromated, Cu Kα radiation). Elemental analyses were performed by P. Borda of this department.

Results

Structures of the Complexes. The overall geometries of $Mo_8(pz)_6O_{18}(pzH)_6$ and $Mo_8(pz)_6O_{21}(pzH)_6$ are similar; labeled diagrams of these molecules are shown in Figures 1 and 2; atomic positional parameters are listed in Tables II and III; selected bond lengths and angles are presented in Tables IV and V for $Mo_8(pz)_6O_{18}(pzH)_6$ and in Tables VI and VII for $Mo_8(pz)_6O_{21}(pzH)_6$. Because of the structural similarities of the two compounds, their features will be described concurrently. A schematic depiction illustrating the similarity of the two octamolybdates is shown in Figure 3. Both complexes consist of an octametallic framework which may be described as two basally connected flattened trigonal pyramids. Consequently, the molecules possess two types of molybdenum atoms: two axial and six equatorial. Compound **1** crystallizes in the monoclinic space group $C2/c$, and while $Mo_8(Hpz)_6O_{18}(pzH)_6$ possesses a crystallographic 2-fold rotation axis perpendicularly bisecting the Mo(1)–Mo(1)′ vector (Figure 1), the molecule has only an approximate 3-fold rotation axis passing through its apical molybdenum atoms. Compound **2** crystallizes in the trigonal space group $R\bar{3}$, and the complex has a crystallographic 3-fold rotation axis passing through the axial molybdenum atoms. Both molecules possess approximate D_3 point symmetry, and the axial molybdenum centers in both have octahedral *fac* MoN_3O_3 chromophores, the nitrogen donor atoms deriving from bridging pyrazolate ligands and the oxygen donor atoms being bridging oxo ligands. These bridging ligands connect the axial molybdenum centers to three equatorial molybdenum atoms, and it is the equatorial sites which are responsible for differences between the

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[18] Abbreviations: s, strong; m, medium; w, weak; vw, very weak.

[19] TEXSAN/TEXRAY structure analysis package (Molecular Structure Corp., 1985).

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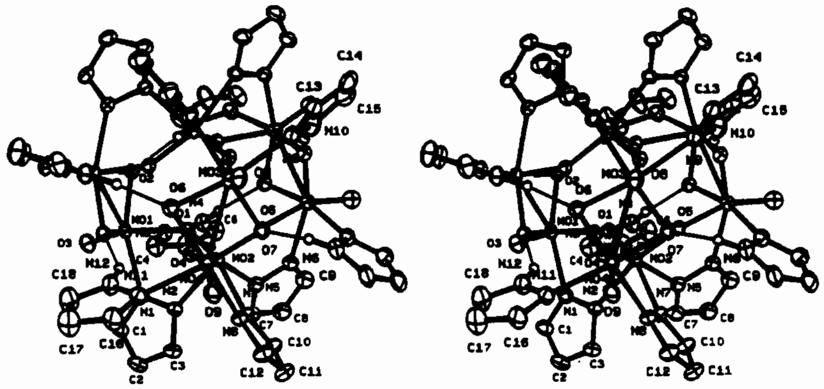

Figure 1. Stereoscopic ORTEP view of $Mo_8(pz)_6O_{18}(pzH)_6$. 33% probability thermal ellipsoids are shown for the non-hydrogen atoms.

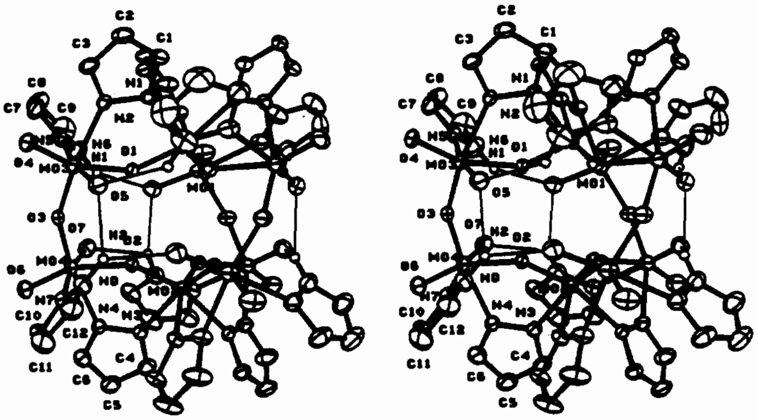

Figure 2. Stereoscopic ORTEP view of $Mo_8(pz)_6O_{21}(pzH)_6$. 33% probability thermal ellipsoids are shown for the non-hydrogen atoms.

two complexes. In both complexes, the equatorial molybdenum atoms are linked in pairs; in $Mo_8(pz)_6O_{18}(pzH)_6$, they are linked by two oxo bridges and a Mo–Mo bond, and in $Mo_8(pz)_6O_{21}(pzH)_6$, the metals are linked by a single oxo bridge. In $Mo_8(pz)_6O_{18}(pzH)_6$, coordination about the equatorial molybdenum atoms is completed by one terminal oxo ligand and a terminal neutral pyrazole ligand, yielding a $MoN_2O_4(Mo)$ seven-coordinate chromophore. The coordination polyhedron around the equatorial molybdenum atoms in $Mo_8(pz)_6O_{21}(pzH)_6$ is completed by two terminal oxo ligands arranged cis to one another and a terminal neutral pyrazole ligand, yielding an octahedral MoN_2O_4 chromophore. In both complexes, the terminal pyrazole ligands are intramolecularly hydrogen-bonded, although in different fashions. In $Mo_8(pz)_6O_{18}(pzH)_6$, each neutral pyrazole ligand forms one hydrogen bond to an adjacent terminal oxo ligand. In $Mo_8(pz)_6O_{21}(pzH)_6$, the pyrazoles exhibit two types of hydrogen bonding: three of the pyrazoles form single hydrogen bonds to adjacent terminal oxo species, and the other three pyrazoles form bifurcated hydrogen bonds to two different terminal oxo ligands. The crystal lattices of both clusters contain solvate molecules. There are two pyrazole molecules per complex molecule in **1**, and there are three pyrazole molecules and half of a water molecule associated with each complex molecule in **2**.

Syntheses and Physical Properties. The solid **1** can be prepared in low yield from the reaction of molten pyrazole and molybdenum metal in air while bulk quantities of this compound may be obtained from the reaction of molten pyrazole and $Mo_4O_{10}(OH)_2$. As reported in the Experimental Section, a total of 443 mg of byproduct precipitate was collected during the preparation of **1** from $Mo_4O_{10}(OH)_2$. That was precisely the mass of material that would be expected if the excess Mo(VI) present in the "molybdenum blue" starting material formed **2**. The solid **1** is slightly soluble in THF, sparingly soluble in acetone, and insoluble in acetonitrile and water. The presence of formally pentavalent molybdenum atoms in **1** prompted a variable-temperature magnetic susceptibility study of the compound, which revealed it to exhibit temperature-independent paramagnetism in the range 300–70 K ($\chi_M \approx 300 \times 10^{-6}$ cm^3 mol^{-1}). Below 70 K, the susceptibility of the compound increases as temperature decreases, a behavior which may be ascribed to the presence of a small amount of paramagnetic impurity in the sample.

The solid **2** was obtained from the reaction of molten pyrazole with MoO_3 in darkness. It is somewhat soluble in acetone, sparingly soluble in THF, and insoluble in acetonitrile and water. The compound is photosensitive, turning color from pale yellow to brown over a period of several hours of exposure to ambient light. This color change cannot be reversed by returning the compound to darkness. The powder X-ray diffractogram of the brown form of the compound does not differ from that of the yellow form. Compound **2** reacts with ethanol, in the presence of moisture, to produce an intensely blue soluble material which, preliminary characterization indicates, contains the pyrazolyl moiety and is paramagnetic.

A DSC study of **2**, in air, between room temperature and 350 °C showed the compound to undergo minor endothermic events at ~120 and ~240 °C, a major endothermic event at ~280 °C, and an exothermic event at 330 °C. The sample exhibited a mass loss of 45% over this temperature range, which is consistent with the loss of lattice water and all pyrazolyl fragments from the compound and the concomitant formation of MoO_3 (46% expected mass loss). A DSC study of **1** was not conducted; however, observation of a sample heated in air yielded the following results. The sample began to evolve a liquid at approximately 215 °C. At 265 °C, the sample began to darken visibly, and by 300 °C, the sample had decomposed, without melting, to a dark bluish black solid.

The infrared spectra of the compounds exhibit bands characteristic of the pyrazolyl moiety and the pyrazole molecule with strong broad N–H stretching absorptions in the 3100–3400 cm^{-1} region. The pyrazolyl ring vibrations and Mo–O modes overlap, making definite assignment of the bands difficult; however, on

Table II. Fractional Atomic Coordinates and B_{eq} Values (Å^2) for **1** (Esd's in Parentheses)

atom	x	y	z	B_{eq}[a]
Mo(1)	0.54078(1)	0.10476(1)	0.22559(1)	2.255(6)
Mo(2)	0.592813(8)	0.36352(1)	0.255665(8)	1.868(5)
Mo(3)	0.50461(1)	0.53200(2)	0.126081(9)	2.293(6)
Mo(4)	0.391549(9)	0.45945(2)	0.093517(8)	2.214(6)
O(1)	0.54330(7)	0.2644(1)	0.21372(7)	2.20(5)
O(2)	0.44859(7)	0.1263(1)	0.18831(7)	2.48(5)
O(3)	0.5558(1)	–0.0170(1)	0.21905(9)	3.51(7)
O(4)	0.58780(7)	0.3581(1)	0.32874(6)	2.13(5)
O(5)	0.54696(7)	0.4691(1)	0.21974(7)	2.19(5)
O(6)	0.46858(7)	0.4033(1)	0.09185(7)	2.52(6)
O(7)	0.43706(7)	0.5656(1)	0.15244(7)	2.52(5)
O(8)	0.49763(9)	0.6043(1)	0.06410(8)	3.44(7)
O(9)	0.34707(8)	0.5161(1)	0.02418(8)	3.23(7)
N(1)	0.64266(9)	0.1446(2)	0.2650(1)	2.66(7)
N(2)	0.66452(8)	0.2401(1)	0.28011(9)	2.44(6)
N(3)	0.5375(1)	0.1247(2)	0.1282(1)	2.87(7)
N(4)	0.5220(1)	0.2090(2)	0.0937(1)	3.09(8)
N(5)	0.62724(9)	0.3918(2)	0.18085(9)	2.54(7)
N(6)	0.5940(1)	0.4612(2)	0.13483(9)	2.51(7)
N(7)	0.67771(9)	0.4551(2)	0.31434(9)	2.54(7)
N(8)	0.68401(9)	0.4844(2)	0.37331(9)	2.48(6)
N(9)	0.5645(1)	0.6563(2)	0.1867(1)	2.98(7)
N(10)	0.5854(1)	0.6655(2)	0.2498(1)	3.48(8)
N(11)	0.3487(1)	0.3145(2)	0.0462(1)	2.94(7)
N(12)	0.3668(1)	0.2239(2)	0.0731(1)	3.47(8)
N(13)	0.3049(3)	0.1866(5)	0.5482(3)	12.0(3)
N(14)	0.3524(6)	0.2335(5)	0.5553(4)	15.4(6)
C(1)	0.6929(1)	0.0829(2)	0.2879(1)	3.4(1)
C(2)	0.7485(1)	0.1378(2)	0.3174(1)	3.8(1)
C(3)	0.7286(1)	0.2357(2)	0.3114(1)	3.17(9)
C(4)	0.5551(2)	0.0598(2)	0.0946(1)	4.2(1)
C(5)	0.5515(2)	0.1041(3)	0.0400(2)	5.1(1)
C(6)	0.5301(2)	0.1984(2)	0.0408(1)	4.2(1)
C(7)	0.6711(1)	0.3500(2)	0.1650(1)	3.2(1)
C(8)	0.6674(1)	0.3912(2)	0.1089(1)	3.8(1)
C(9)	0.6181(1)	0.4590(2)	0.0915(1)	3.3(1)
C(10)	0.7252(1)	0.4983(2)	0.3045(1)	3.3(1)
C(11)	0.7633(1)	0.5547(2)	0.3566(1)	3.9(1)
C(12)	0.7353(1)	0.5440(2)	0.3981(1)	3.4(1)
C(13)	0.5938(1)	0.7294(2)	0.1697(1)	3.7(1)
C(14)	0.6328(2)	0.7844(2)	0.2220(2)	4.5(1)
C(15)	0.6263(2)	0.7415(2)	0.2717(2)	4.4(1)
C(16)	0.3160(2)	0.2958(3)	–0.0149(1)	4.4(1)
C(17)	0.3126(2)	0.1950(3)	–0.0268(1)	5.7(2)
C(18)	0.3456(2)	0.1506(2)	0.0300(1)	5.0(1)
C(19)	0.3230(3)	0.1076(4)	0.5792(2)	6.6(2)
C(20)	0.3860(3)	0.1052(4)	0.6082(2)	7.5(2)
C(21)	0.4049(3)	0.1903(7)	0.5919(4)	12.2(5)

[a] $B_{eq} = (8/3)\pi^2\sum\sum U_{ij}a_i^*a_j^*(\mathbf{a}_i\cdot\mathbf{a}_j)$.

Table III. Fractional Atomic Coordinates and B_{eq} Values (Å^2) for **2** (Esd's in Parentheses)

atom	x	y	z	B_{eq}[a]	occ[b]
Mo(1)	0	0	0.14224(2)	1.80(1)	0.333
Mo(2)	0	0	0.28847(2)	1.80(1)	0.333
Mo(3)	0.19953(2)	0.05282(2)	0.16328(1)	2.91(1)	
Mo(4)	0.20296(2)	0.14168(2)	0.26843(1)	2.92(1)	
O(1)	0.0917(1)	0.0516(1)	0.16667(8)	2.3(1)	
O(2)	0.0912(1)	0.0392(1)	0.26390(8)	2.3(1)	
O(3)	0.2279(1)	0.1097(2)	0.21586(9)	3.1(1)	
O(4)	0.2837(2)	0.0705(2)	0.1407(1)	4.7(1)	
O(5)	0.1591(2)	–0.0391(2)	0.1836(1)	3.7(1)	
O(6)	0.2897(2)	0.2019(2)	0.2921(1)	4.4(1)	
O(7)	0.1706(2)	0.2005(2)	0.2490(1)	4.0(1)	
N(1)	0.0677(2)	–0.0245(2)	0.0940(1)	2.4(1)	
N(2)	0.1462(2)	0.0094(2)	0.1000(1)	2.8(1)	
N(3)	0.0708(2)	0.0907(2)	0.3370(1)	2.5(1)	
N(4)	0.1496(2)	0.1306(2)	0.3313(1)	3.1(1)	
N(5)	0.2231(2)	0.1679(2)	0.1319(1)	3.5(1)	
N(6)	0.1902(3)	0.2095(2)	0.1435(1)	5.1(2)	
N(7)	0.2196(2)	0.0414(2)	0.2979(1)	3.6(2)	
N(8)	0.1852(2)	–0.0306(2)	0.2811(1)	3.9(2)	
C(1)	0.0511(3)	–0.0631(3)	0.0599(1)	3.3(2)	
C(2)	0.1172(3)	–0.0555(3)	0.0372(1)	3.9(2)	
C(3)	0.1749(3)	–0.0104(3)	0.0659(1)	4.1(2)	
C(4)	0.0566(3)	0.1114(3)	0.3762(1)	3.6(2)	
C(5)	0.1246(3)	0.1637(3)	0.3964(2)	5.2(2)	
C(6)	0.1805(3)	0.1738(3)	0.3668(2)	5.2(2)	
C(7)	0.2710(3)	0.2061(3)	0.0998(2)	4.8(2)	
C(8)	0.2679(4)	0.2722(4)	0.0904(2)	7.0(3)	
C(9)	0.2171(4)	0.2726(3)	0.1182(2)	7.1(3)	
C(10)	0.2617(3)	0.0403(4)	0.3311(2)	5.0(2)	
C(11)	0.2546(4)	–0.0320(4)	0.3348(2)	6.1(3)	
C(12)	0.2053(3)	–0.0762(3)	0.3024(2)	5.0(2)	
N(9)	–0.0740(8)	0.1806(8)	0.4896(5)	7.4(7)	0.52
N(9*b*)	–0.019(1)	0.142(1)	0.4759(6)	6.5(7)	0.48
N(10)	–0.0542(7)	0.2538(7)	0.4833(4)	6.1(5)	0.52
N(10*b*)	0.028(1)	0.217(1)	0.4804(5)	7.8(8)	0.48
C(13)	–0.0006(6)	0.2763(7)	0.4610(4)	11.6(6)	
C(14)	0.025(1)	0.241(1)	0.4434(5)	8.3(9)	0.52
C(14*b*)	–0.077(1)	0.206(1)	0.4560(7)	8(1)	0.48
C(15)	–0.027(2)	0.172(1)	0.4634(8)	8(1)	0.52
C(15*b*)	–0.084(1)	0.134(1)	0.4627(9)	8(1)	0.48
O(8)	0	0	$^1/_2$	19.4(8)	0.167

[a] $B_{eq} = (8/3)\pi^2\sum\sum U_{ij}a_i^*a_j^*(\mathbf{a}_i\cdot\mathbf{a}_j)$. [b] Site occupancy.

Table IV. Selected Bond Lengths (Å) for $Mo_8(pz)_6O_{18}(pzH)_6$ (Esd's in Parentheses)

Mo(1)–Mo(1)′	2.5722(5)	Mo(3)–O(8)	1.688(2)
Mo(1)–O(1)	2.152(2)	Mo(3)–N(6)	2.196(2)
Mo(1)–O(2)	1.948(2)	Mo(3)–N(9)	2.240(2)
Mo(1)–O(2)′	1.939(2)	Mo(4)–O(4)′	2.149(2)
Mo(1)–O(3)	1.681(2)	Mo(4)–O(6)	1.941(2)
Mo(1)–N(1)	2.195(2)	Mo(4)–O(7)	1.945(2)
Mo(1)–N(3)	2.256(2)	Mo(4)–O(9)	1.686(2)
Mo(2)–O(1)	1.753(2)	Mo(4)–N(8)′	2.206(2)
Mo(2)–O(4)	1.757(1)	Mo(4)–N(11)	2.240(2)
Mo(2)–O(5)	1.749(2)	N(1)–N(2)	1.361(3)
Mo(2)–N(2)	2.231(2)	N(3)–N(4)	1.341(3)
Mo(2)–N(5)	2.230(2)	N(5)–N(6)	1.380(3)
Mo(2)–N(7)	2.223(2)	N(7)–N(8)	1.377(3)
Mo(3)–Mo(4)	2.5752(4)	N(9)–N(10)	1.348(3)
Mo(3)–O(5)	2.153(2)	N(11)–N(12)	1.345(3)
Mo(3)–O(6)	1.928(2)	N(13)–N(14)	1.21(1)
Mo(3)–O(7)	1.950(2)		

the basis of the infrared spectra of related polymolybdates,[12,23–26] we have tentatively assigned the strong bands at 967, 948, and 911 cm^{-1} in the spectrum of **1** and at 964, 948, 936, and 920 cm^{-1} in the spectrum of **2** as terminal Mo–O stretching modes.

Discussion

Structures of the Complexes. Comparison of the structure of $Mo_8(pz)_6O_{21}(pzH)_6$ with those of the classical isopolymolybdates and more recent coordination derivatives reveals some similarities but also several features unique to the octamolybdenum complexes reported here. Like known isopolymolybdates, $Mo_8(pz)_6O_{21}(pzH)_6$ obeys Lipscomb's restriction,[27] and according to Pope's classification scheme,[28] it is a "type II" compound, which means it contains terminal *cis*-dioxo fragments. Examination of the bond lengths and angles in the MoN_2O_4 octahedra of $Mo_8(pz)_6O_{21}(pzH)_6$ (Tables VI and VII) reveals that the molybdenum atoms exhibit the expected displacement toward the terminal *cis*-dioxo ligands. Polyoxometalates are customarily depicted using polyhedral representations,[5] and such a representation is shown for $Mo_8(pz)_6O_{21}(pzH)_6$ in Figure 4 (top). This figure shows clearly that $Mo_8(pz)_6O_{21}(pzH)_6$ possesses a skeleton of corner-linked MoL_6 octahedra (where L = O or N), which makes for a rather open octamolybdenum structure. With the exception of the $[Mo_2O_7]^{2-}$ anion,[5] this entirely corner-linked structure is unique

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Table V. Selected Bond Angles (deg) for $Mo_8(pz)_6O_{18}(pz)_6$ (Esd's in Parentheses)

Mo(1)′–Mo(1)–O(1)	96.96(4)	O(6)–Mo(3)–O(7)	94.23(7)
Mo(1)′–Mo(1)–O(2)	48.41(5)	O(6)–Mo(3)–O(8)	106.54(8)
Mo(1)′–Mo(1)–O(2)′	48.72(5)	O(6)–Mo(3)–N(6)	83.03(7)
Mo(1)′–Mo(1)–O(3)	104.89(7)	O(6)–Mo(3)–N(9)	164.78(8)
Mo(1)′–Mo(1)–N(1)	131.70(5)	O(7)–Mo(3)–O(8)	109.67(8)
Mo(1)′–Mo(1)–N(3)	136.32(5)	O(7)–Mo(3)–N(6)	155.61(7)
O(1)–Mo(1)–O(2)	83.11(6)	O(7)–Mo(3)–N(9)	89.56(7)
O(1)–Mo(1)–O(2)′	89.33(6)	O(8)–Mo(3)–N(6)	94.25(8)
O(1)–Mo(1)–O(3)	157.96(8)	O(8)–Mo(3)–N(9)	85.92(9)
O(1)–Mo(1)–N(1)	74.48(6)	N(6)–Mo(3)–N(9)	87.43(8)
O(1)–Mo(1)–N(3)	75.24(7)	Mo(3)–Mo(4)–O(4)′	98.61(4)
O(2)–Mo(1)–O(2)′	94.61(6)	Mo(3)–Mo(4)–O(6)	48.06(5)
O(2)–Mo(1)–O(3)	109.24(8)	Mo(3)–Mo(4)–O(7)	48.68(5)
O(2)–Mo(1)–N(1)	157.49(7)	Mo(3)–Mo(4)–O(9)	104.24(6)
O(2)–Mo(1)–N(3)	87.92(7)	Mo(3)–Mo(4)–N(8)′	133.50(5)
O(2)′–Mo(1)–O(3)	107.20(8)	Mo(3)–Mo(4)–N(11)	130.63(6)
O(2)′–Mo(1)–N(1)	83.26(7)	O(4)′–Mo(4)–O(6)	83.89(6)
O(2)′–Mo(1)–N(3)	163.96(7)	O(4)′–Mo(4)–O(7)	89.99(6)
O(3)–Mo(1)–N(1)	92.69(8)	O(4)′–Mo(4)–O(9)	157.09(7)
O(3)–Mo(1)–N(3)	86.76(8)	O(4)′–Mo(4)–N(8)′	74.17(6)
N(1)–Mo(1)–N(3)	88.35(8)	O(4)′–Mo(4)–N(11)	76.56(7)
O(1)–Mo(2)–O(4)	102.59(7)	O(6)–Mo(4)–O(7)	93.98(7)
O(1)–Mo(2)–O(5)	102.74(7)	O(6)–Mo(4)–O(9)	110.26(8)
O(1)–Mo(2)–N(2)	79.82(7)	O(6)–Mo(4)–N(8)′	158.03(7)
O(1)–Mo(2)–N(5)	93.04(7)	O(6)–Mo(4)–N(11)	82.74(7)
O(1)–Mo(2)–N(7)	163.06(7)	O(7)–Mo(4)–O(9)	106.30(8)
O(4)–Mo(2)–O(5)	103.02(7)	O(7)–Mo(4)–O(8)′	84.99(7)
O(4)–Mo(2)–N(2)	93.72(7)	O(7)–Mo(4)–N(11)	166.40(7)
O(4)–Mo(2)–N(5)	162.75(7)	O(9)–Mo(4)–N(8)′	90.99(8)
O(4)–Mo(2)–N(7)	79.90(7)	O(9)–Mo(4)–N(11)	87.18(8)
O(5)–Mo(2)–N(2)	161.93(7)	N(8)′–Mo(4)–N(11)	93.12(8)
O(5)–Mo(2)–N(5)	80.23(7)	Mo(1)–O(1)–Mo(2)	136.22(8)
O(5)–Mo(2)–N(7)	92.85(7)	Mo(1)–O(2)–Mo(1)′	82.88(6)
N(2)–Mo(2)–N(5)	81.77(7)	Mo(2)–O(4)–Mo(4)′	135.31(8)
N(2)–Mo(2)–N(7)	83.32(7)	Mo(2)–O(5)–Mo(3)	136.48(8)
N(5)–Mo(2)–N(7)	83.03(7)	Mo(3)–O(6)–Mo(4)	83.46(7)
Mo(4)–Mo(3)–O(5)	97.11(4)	Mo(3)–O(7)–Mo(4)	82.78(6)
Mo(4)–Mo(3)–O(6)	48.48(5)	Mo(1)–N(1)–N(2)	123.3(1)
Mo(4)–Mo(3)–O(7)	48.54(5)	Mo(2)–N(2)–N(1)	118.1(1)
Mo(4)–Mo(3)–O(8)	103.96(6)	Mo(1)–N(3)–N(4)	126.2(2)
Mo(4)–Mo(3)–N(6)	131.14(5)	Mo(2)–N(5)–N(6)	117.3(1)
Mo(4)–Mo(3)–N(9)	138.01(6)	Mo(3)–N(6)–N(5)	123.6(1)
O(5)–Mo(3)–O(6)	90.32(6)	Mo(2)–N(7)–N(8)	117.9(1)
O(5)–Mo(3)–O(7)	81.46(6)	Mo(4)′–N(8)–N(7)	122.6(1)
O(5)–Mo(3)–O(8)	158.57(8)	Mo(3)–N(9)–N(10)	126.7(2)
O(5)–Mo(3)–N(6)	74.35(6)	Mo(4)–N(11)–N(12)	124.1(1)
O(5)–Mo(3)–N(9)	75.66(7)		

Table VI. Selected Bond Lengths (Å) for $Mo_8(pz)_6O_{21}(pzH)_6$ (Esd's in Parentheses)

Mo(1)–O(1)	1.760(2)	Mo(4)–O(2)	2.154(3)
Mo(1)–N(1)	2.215(3)	Mo(4)–O(3)	1.887(3)
Mo(2)–O(2)	1.754(2)	Mo(4)–O(6)	1.701(3)
Mo(2)–N(3)	2.219(3)	Mo(4)–O(7)	1.707(3)
Mo(3)–O(1)	2.146(3)	Mo(4)–N(4)	2.156(3)
Mo(3)–O(3)	1.885(3)	Mo(4)–N(7)	2.370(4)
Mo(3)–O(4)	1.687(3)	N(1)–N(2)	1.376(4)
Mo(3)–O(5)	1.714(3)	N(3)–N(4)	1.376(4)
Mo(3)–N(2)	2.169(3)	N(5)–N(6)	1.341(6)
Mo(3)–N(5)	2.315(4)	N(7)–N(8)	1.351(5)

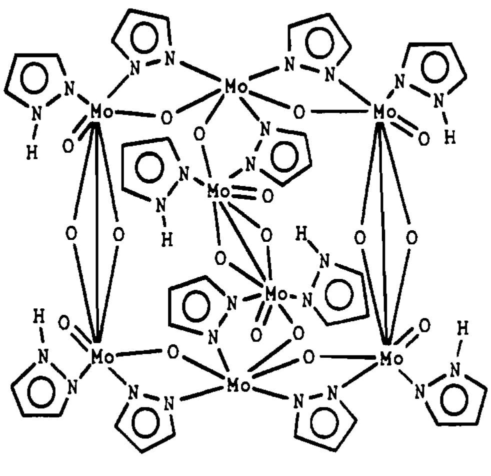
Table VII. Selected Bond Angles (deg) for $Mo_8(pz)_6O_{21}(pzH)_6$ (Esd's in Parentheses)

O(1)–Mo(1)–O(1)′ [a]	103.3(1)	O(2)–Mo(4)–O(3)	87.0(1)
O(1)–Mo(1)–N(1)	80.7(1)	Mo(4)–N(4)–N(3)	122.4(2)
O(1)–Mo(1)–N(1)′	93.6(1)	Mo(3)–N(5)–N(6)	126.0(3)
O(1)–Mo(1)–N(1)″	161.1(1)	Mo(4)–N(7)–N(8)	123.0(3)
N(1)–Mo(1)–N(1)′	80.6(1)	O(2)–Mo(4)–O(6)	155.2(1)
O(2)–Mo(2)–O(2)′	103.0(1)	O(2)–Mo(4)–O(7)	93.6(1)
O(2)–Mo(2)–N(3)	79.9(1)	O(2)–Mo(4)–N(4)	74.6(1)
O(2)–Mo(2)–N(3)′	160.1(1)	O(2)–Mo(4)–N(7)	74.8(1)
O(2)–Mo(2)–N(3)″	95.3(1)	O(3)–Mo(4)–O(6)	104.6(1)
N(3)–Mo(2)–N(3)′	80.3(1)	O(3)–Mo(4)–O(7)	101.2(1)
O(1)–Mo(3)–O(3)	87.9(1)	O(3)–Mo(4)–N(4)	157.8(1)
O(1)–Mo(3)–O(4)	156.1(1)	O(3)–Mo(4)–N(7)	82.2(1)
O(1)–Mo(3)–O(5)	92.2(1)	O(6)–Mo(4)–O(7)	105.3(2)
O(1)–Mo(3)–N(2)	75.4(1)	O(6)–Mo(4)–N(4)	88.4(1)
O(1)–Mo(3)–N(5)	74.7(1)	O(6)–Mo(4)–N(7)	85.0(2)
O(3)–Mo(3)–O(4)	104.7(1)	O(7)–Mo(4)–N(4)	92.4(1)
O(3)–Mo(3)–O(5)	100.2(1)	O(7)–Mo(4)–N(7)	167.8(1)
O(3)–Mo(3)–N(2)	160.3(1)	N(4)–Mo(4)–N(7)	81.1(1)
O(3)–Mo(3)–N(5)	84.5(1)	Mo(1)–O(1)–Mo(3)	137.2(1)
O(4)–Mo(3)–O(5)	105.0(2)	Mo(2)–O(2)–Mo(4)	138.6(1)
O(4)–Mo(3)–N(2)	87.6(1)	Mo(3)–O(3)–Mo(4)	151.6(2)
O(4)–Mo(3)–N(5)	86.3(2)	Mo(1)–N(1)–N(2)	118.4(2)
O(5)–Mo(3)–N(2)	91.1(1)	Mo(3)–N(2)–N(1)	121.8(2)
O(5)–Mo(3)–N(5)	166.0(1)	Mo(2)–N(3)–N(4)	118.0(2)
N(2)–Mo(3)–N(5)	81.0(1)		

[a] Primes and double primes refer to the symmetry operations $-y, x-y, z$ and $y-x, -x, z$, respectively.

in an isopolymolybdenum cluster. It is a consequence of two factors: a high ligand to metal atom ratio and the presence of two-atom bridging pyrazolate ligands.

In discussing isopolymolybdate structures, several authors have made use of an empirical bond length–bond strength correlation, based on the valence-bond formalism, of the form $s = (d/R)^{-N}$ where s is Pauling's bond strength (bond order), d is the metal–ligand bond length, and R (1.882 Å for Mo) and N (6.0 for Mo) are empirical parameters.[29] In spite of the fact that the expression was developed to describe bond strengths for molybdenum–oxygen bonds, it has been applied to molybdenum–nitrogen bonds in substituted octamolybdates,[8,10,12] all of which possess the γ-Mo_8O_{26} structure,[30] and Table VIII compares the values of the bonding parameters from these literature reports to those of $Mo_8(pz)_6O_{21}$-


(*a*)

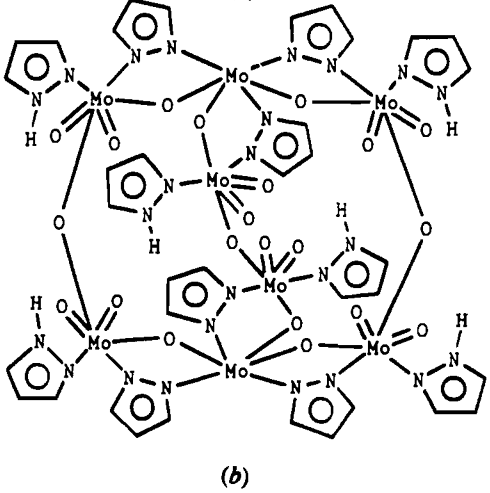

(*b*)

Figure 3. Schematic representations of (a) $Mo_8(pz)_6O_{18}(pzH)_6$ and (b) $Mo_8(pz)_6O_{21}(pzH)_6$.

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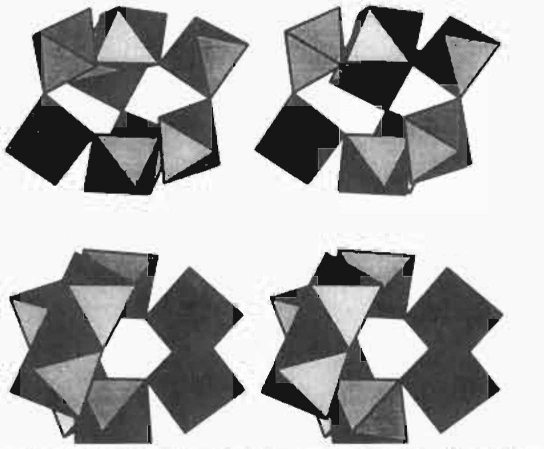


Figure 4. Polyhedral depictions of $Mo_8(pz)_6O_{21}(pzH)_6$ (top) and $Mo_8(pz)_6O_{18}(pzH)_6$ (bottom). Vertices of the polyhedra represent coordinating O or N atoms.

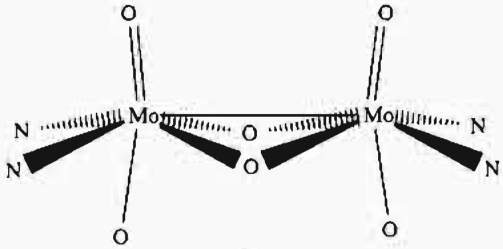
Table VIII. Bond Lengths (*d*, Å) and Bond Strengths (*s*) for the MoN_xO_{6-x} Octahedra in Nitrogen Ligand Containing Mo(VI) Octamolybdenum Complexes

		Mo–N		Mo–O[a]		
N donor	chromophore	*d*	*s*	*d*	*s*	ref
pyridine[b]	$MoNO_5$	2.279	0.32	1.881	1.00	8
pzH[b]	$MoNO_5$	2.243	0.35	1.868	1.04	12
pzH[c]	MoN_2O_4	2.315	0.29	1.714	1.75	*d*
	MoN_2O_4	2.370	0.25	1.707	1.80	
pz[b]	MoN_3O_3	2.215	0.38	1.760	1.50	*d*
	MoN_3O_3	2.219	0.37	1.754	1.52	
pz[b]	MoN_2O_4	2.169	0.43	1.885	0.99	*d*
	MoN_2O_4	2.156	0.44	1.887	0.98	
NCS^- [b]	$MoNO_5$	2.143	0.46	1.893	0.96	10

[a] Mo–O *trans* to the Mo–N bond. [b] *Trans* oxo ligand is bridging. [c] *Trans* oxo ligand is terminal. [d] This work.

$(pzH)_6$. It is apparent that the Mo–N bonds are generally weak with bond orders, *s*, less than 0.5. Kamenar *et al.* have previously claimed that the larger value of *s* for NCS^- versus neutral nitrogen donors is due to the presence of an electrostatic component in the bonding of the anionic ligand.[10] The results for $Mo_8(pz)_6O_{21}(pzH)_6$ support this conclusion, as the values of *s* for the pyrazolate ligand are larger than those of the neutral ligands. Previous studies have revealed that octamolybdates containing nitrogen donor ligands have these ligands coordinated *trans* to a bridging oxygen. $Mo_8(pz)_6O_{21}(pzH)_6$ provides a case where the neutral pyrazole ligand is located *trans* to a terminal oxo ligand and the *trans* influence of the strongly bound terminal oxygen[23,31] appears in the rather long Mo–N bond length (average 2.342 Å) and low value of *s* (average 0.27). The summation of the *s* values for a given molybdenum atom corresponds, roughly, to the oxidation state of the molybdenum. In $Mo_8(pz)_6O_{21}(pzH)_6$, the values of Σs for the axial and equatorial molybdenum atoms are 5.65 (average of two values) and 5.80 (average of two values), respectively. $Mo_8(pz)_6O_{18}(pzH)_6$ is a mixed-valence octamolybdenum species in which the axial molybdenum atoms are hexavalent and the equatorial molybdenum centers are pentavalent. Application of the bond strength formula described above lends further support to this assignment of oxidation states; the values of Σs for the axial and equatorial molybdenum atoms in this complex are 5.68 and 4.79 (average of three values), respectively.

The polyhedral depiction of $Mo_8(pz)_6O_{18}(pzH)_6$ (Figure 4 (bottom)) shows its close relationship to $Mo_8(pz)_6O_{21}(pzH)_6$. $Mo_8(pz)_6O_{18}(pzH)_6$ may be considered a condensation/reduction product of $Mo_8(pz)_6O_{21}(pzH)_6$ with the mixed-valence compound generated formally by shearing the equivalent upper and lower halves of the single-valent species along edges between pairs of equatorial octahedra. $Mo_8(pz)_6O_{18}(pzH)_6$ has a more compact structure than $Mo_8(pz)_6O_{21}(pzH)_6$ as a result of the three pairs of edge sharing octahedra. Furthermore, these pairs are dimeric units (structure **a**) in which the Mo(V) centers participate in a metal–metal bond with an average Mo–Mo bond length of 2.574 Å. This bond length corresponds to a metal–metal single bond. The Mo_2O_4 core of the dimeric Mo(V) unit is well-known,[32] and the subtleties of its geometry have been described.[33] The presence of a metal–metal bond ensures that the Mo_2O_4 dimeric unit is essentially diamagnetic. Our study shows $Mo_8(pz)_6O_{18}(pzH)_6$ to exhibit weak temperature-independent paramagnetism with a susceptibility magnitude of approximately 100 × 10^{-6} cm^3/mol of dimeric Mo(V) unit in the complex. This is in excellent agreement with the value of magnetic susceptibility of the Mo(V) dimer $BaMo_2O_4(C_2O_4)\cdot5H_2O$, reported by French and Garside (92 × 10^{-6} cm^3 mol^{-1}).[34] Unlike polyoxomolybdenum(VI) complexes, there are relatively few high-nuclearity Mo(V) compounds, and $Mo_8(pz)_6O_{18}(pzH)_6$ is only the second structurally characterized octametallic Mo(V)-containing cluster reported.[26]



a

Syntheses and Reactivities. The preparation of **1** by the reaction of molten pyrazole with molybdenum metal in the presence of air yields only a small quantity of the product relative to the amount of molybdenum available in the reaction mixture, whereas the compound is formed in much greater yield by the reaction of pyrazole with $Mo_4O_{10}(OH)_2$. The low yield of **1** when derived from molybdenum metal may arise from the possibility that the pyrazole does not react with the bulk metal *per se* but rather with a thin layer of molybdenum oxide species covering the surface of the metal particles. Despite the fact that $Mo_8(pz)_6O_{18}(pzH)_6$, while in solution, was exposed to the atmosphere for 11 days at more than 100 °C, no oxidation of the Mo(V) appeared to have taken place. $Mo_8(pz)_6O_{21}(pzH)_6$ is the formal oxidation product of the mixed-valence compound, and the reluctance of the latter to oxidize indicates the presence of a substantial kinetic barrier, at least to oxidation by molecular oxygen.

Compound **2** is readily synthesized in high yield by the reaction of MoO_3 with molten pyrazole, and mass balance observations suggest that it also forms as a byproduct in the preparation of **1** from $Mo_4O_{10}(OH)_2$. The photosensitivity of **2** has precedent in related octamolybdates,[6,35–37] and by analogy with earlier reports, the photoinduced darkening of **2** from pale yellow to brown may actually involve reduction of some of the Mo(VI) atoms to Mo(V). The chemical reduction of heteropolymolydates to form mixed-valence "heteropoly blues" is well-known.[5] Preliminary investigations of **2** revealed that, in the presence of moisture, it dissolves in alcohols to form an intensely blue soluble species that is paramagnetic, behavior which is analogous to that

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of the "heteropoly blues". The ability of polyoxometalates to act as electron sinks and/or oxygen relays is a key factor in their catalytic behavior, and because the Mo(VI) pyrazolyl complex reported here appears to exhibit similar redox activity, further exploration of its chemistry is warranted.

An attempt was made to prepare a tungsten analog of $Mo_8(pz)_6O_{21}(pzH)_6$ by the reaction of molten pyrazole with WO_3. Even after 2 weeks of heating, no product formation was observed. This is likely due to the differing solid-state structures of MoO_3 and WO_3; the molybdenum oxide has a layered structure, while the tungsten oxide has a 3-dimensional, cubic structure.[38] One might envisage the MoO_3 structure permitting pyrazole molecules easier access to molybdenum sites than the closed structure of WO_3. We are currently investigating other tungsten starting materials for routes to pyrazolyl–polyoxotungsten compounds.

Conclusion

Two octamolybdenum oxo–pyrazolate clusters, $Mo_8(pz)_6O_{18}(pzH)_6$ and $Mo_8(pz)_6O_{21}(pzH)_6$, have been synthesized and their structures determined by single-crystal X-ray diffraction. The former species contains both Mo(VI) and Mo(V) centers with the Mo(V) atoms linked in pairs via a metal–metal single bond, while the latter contains only hexavalent molybdenum. These are the first polyoxomolybdenum compounds reported which contain bridging pyrazolate ligands. Although the two complexes are formally related as a redox pair, conversion of one to the other has not been observed. $Mo_8(pz)_6O_{21}(pzH)_6 \cdot 3pzH \cdot {}^1/_2H_2O$ is photosensitive and can be reduced by alcohols, in the presence of moisture, to form a paramagnetic blue species.

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Supplementary Material Available: Tables of complete crystallographic data, final atomic coordinates and equivalent isotropic thermal parameters, hydrogen atom parameters, anisotropic thermal parameters, torsion angles, intermolecular contacts, and least-squares planes along with packing diagrams for 1 and 2 (50 pages). Ordering information is given on any current masthead page.

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