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# Synthesis of Dioxomolybdenum(VI) Complexes of Heterocyclic-N,O and -N,S Ligands

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## Abstract

Benzimidazolylalcohols, benzimidazolylthiols, and pyrazolylphenols react with $MoO_2(acac)_2$ to give octahedral $MoO_2L_2$ complexes in the case of the N,O ligands but dimeric $Mo_2O_4L_2$ complexes with the N,S ligands. Heterocycles apparently do not provide enough steric bulk to allow generation of skew-trapezoidal complexes.

## Introduction

The study of dioxomolybdenum(VI) complexes has thrived for several years because of the interest in modelling the molybdenum oxidases, enzymes that catalyze a number of biologically important oxo-transfer reactions such as the conversion of nitrate to nitrite, sulfite to sulfate, and xanthine to uric acid [1]. Stiefel [2] and Holm [3] have demonstrated that the coordination geometries in Mo(VI) species can be manipulated by the steric constraints of the ligand set, and it is within that context that we have pursued the work reported here.

We have focussed on two different aspects of Mo(VI) coordination chemistry. First, we were interested in whether skew-trapezoidal $MoO_2(N{-}O)_2$ complexes could be formed (N–O denotes a chelating ligand having an N and an O donor). While bis(hydroxylamine)dioxomolybdenum(VI) complexes show such a structure [4], there are no analogous species having the N and O donors separated by other atoms, as would be the case in a metalloprotein. Stiefel has suggested that a S···S interaction may be important for stabilizing the skew-trapezoidal geometry in $MoO_2(N{-}S)_2$ complexes [2]; however, that type of interaction would be relatively unimportant for the oxygen analogs. Our other interest in molybdenum coordination chemistry that prompted this study is the nature of Mo(VI) complexes with nitrogen heterocycles as ligands. Few of these species have been prepared [3, 5], despite the ubiquity of metal–histidine(imidazole) interactions in metalloproteins.

We report here several new Mo(VI) complexes having pyrazolylphenolate, benzimidazolylalcoholate, and benzimidazolylthiolate ligands. The N–O ligands bind to Mo(VI) to give distorted-octahedral complexes while use of the N–S ligands results in reduction of Mo(VI) to produce dimeric oxo-bridged Mo(V) complexes.

## Experimental

All reagents and solvents were purchased from commercial sources unless noted otherwise. The following compounds have been prepared previously: bis(acetylacetonyl)dioxomolybdenum [6], hydroxybenzimidazoles **1**–**3** [7], thiomethylbenzimidazoles **4**–**5** [8], and *o*-methoxyphenylhydrazine [9]. NMR spectra were recorded using a Bruker WM 250 instrument at 250.13 MHz and infrared spectra were taken on a Beckman IR 4250. Melting points were obtained with use of a Fisher-Johns apparatus and are uncorrected. Microanalyses were performed by MicAnal Laboratories, Inc., Tucson, Ariz.

*1-(o-Methoxyphenyl)pyrazole (**11**)*

A mechanically stirred solution of 21.3 g (0.154 mol) of *o*-methoxyphenylhydrazine and 30.4 g (0.185 mol) of malonaldehydebis(dimethylacetal) in 250 ml of 80% aqueous ethanol at 0 °C was treated with 15.1 g (0.154 mol) of concentrated $H_2SO_4$. The original orange color of the hydrazine solution turned yellow–green after complete addition of the acid. Upon warming to room temperature all of the solid dissolved, and the clear brown solution was heated under reflux for 10 h. After cooling, the reaction mixture was made basic by the addition of sodium carbonate. The dark organic layer was separated from the aqueous layer and the solvent removed under vacuum. The aqueous phase was extracted with three 100 ml portions of methylene chloride and the combined organic layers were washed with water, dried over $MgSO_4$, filtered and concentrated. Distillation in a Kugelrohr apparatus at 75 °C (5 torr) yielded

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16.4 g (61%) of product. $^1$H NMR ($CDCl_3$): δ 4.80 (s, 3H, $-OCH_3$), 6.38 (t, 1H, PzH), 6.92–7.04 (m, 2H, ArH), 7.24 (t of d, 1H, ArH), 7.68 (m, 1H, ArH), 7.71 (d, 1H, PzH), 8.10 (d, 1H, PzH).

*1-(o-Methoxyphenyl)-3,5-dimethylpyrazole (12)*

A mixture of 6.6 g (47 mmol) of *o*-methoxyphenylhydrazine and 9.8 g (97 mmol) of 2,4-pentanedione in 125 ml of anhydrous ethanol was heated under reflux for 14 h. The ethanol was removed under vacuum and the remaining oil dissolved in diethyl ether. The ethyl layer was extracted with three 50 ml-portions of 10% NaOH, dried over $MgSO_4$, filtered and concentrated to give a light orange oil. Distillation at 65 °C (6 torr) yielded 7.0 g (79%) of a pale yellow oil. $^1$H NMR ($CDCl_3$): δ 2.1 (s, 3H, Pz–$CH_3$), 2.3 (s, 3H, Pz–$CH_3$), 3.7 (s, 3H, $-OCH_3$), 5.9 (s, 1H, PzH), 6.7–7.5 (m, 4H, ArH).

*1-(o-Hydroxyphenyl)pyrazole (13)*

The same procedure was followed as reported for the preparation of **14** to give an oil (60%) which was purified by distillation at 74 °C (6 torr) in a Kugelrohr apparatus. $^1$H NMR ($CDCl_3$): δ 6.44 (s, 1H, –OH), 6.86 (t of d, 1H, PzH), 7.10 (m, 2H, ArH), 7.30 (d of d, 2H, ArH), 7.68 (d, 1H, PzH), 7.95 (d, 1H, Pz–H).

*1-(o-Hydroxyphenyl)-3,5-dimethylpyrazole (14)*

A solution of 2.0 g (9.9 mmol) of **12** in 25 ml of 48% hydrobromic acid was heated under reflux for 24 h. The cooled solution was treated with concentrated NaOH until the solution reached pH 10. The aqueous layer was extracted with methylene chloride to remove *o*-cresol, and the pH was readjusted to neutral. The aqueous layer was then extracted with three 35 ml portions of methylene chloride which were combined, washed with water, dried over $MgSO_4$, filtered and concentrated. The resulting solid was recrystallized from ethanol–water to give 1.1 g (59%) of **14**, melting point 133–135 °C. $^1$H NMR ($CDCl_3$): δ 2.31 (s, 3H, Pz–$CH_3$), 2.40 (s, 3H, Pz–$CH_3$), 6.04 (s, 1H, PzH), 6.85–7.10 (m, 4H, ArH). *Anal.* Calc. for $C_{11}H_{12}N_2O$: C, 70.78; H, 6.43; N, 14.88. Found: C, 69.92; H, 6.42; N, 14.80%.

*o-Toluene methanesulfonate (15)*

A solution of 20 ml of methylene chloride, 12 g (0.06 mol) of *o*-cresol and 41.5 g (0.12 mol) of triethylamine was cooled to 0 °C. Over 45 min, 14.3 g (0.065 mol) of methanesulfonyl chloride was added dropwise. The reaction was stirred an additional 10 min at room temperature. Water was added and the reaction stirred 24 h to remove excess methanesulfonyl chloride. The methylene chloride layer was separated from the aqueous layer which was subsequently extracted with two 75 ml portions of methylene chloride. The combined methylene chloride portions were extracted with 5% NaOH, washed with 5% HCl, dried over $MgSO_4$, filtered and concentrated to give 17.6 g (85%) of **15** after distillation at 70 °C (2 torr) in a Kugelrohr apparatus. $^1$H NMR ($CDCl_3$): δ 2.3 (s, 3H, Ar–$CH_3$), 3.1 (s, 3H, $-SO_2-CH_3$), 7.2 (m, 4H, ArH).

*o-(α-Bromomethyl)phenyl methanesulfonate (16)*

Under a nitrogen atmosphere, 6.0 g (34 mmol) of *N*-bromosuccinimide, 6.0 g (32 mmol) of mesylate **15** and 0.21 g (0.9 mmol) of benzoyl peroxide were added to 200 ml of carbon tetrachloride. The reaction was heated under gentle reflux until all the *N*-bromosuccimide was converted into succimide which floated to the top of the solution. The mixture was cooled in an ice bath and the succinimide removed by gravity filtration. The solvent was evaporated on a rotary evaporator with little warming. $^1$H NMR ($CDCl_3$): δ 2.3 (s, Ar–$CH_3$), 3.1 (s, $-SO_2-CH_3$), 3.2 (s, $-SO_2-CH_3$), 4.5 (s, $-CH_2-$Br), 7.1–7.6 (m, ArH).

*1-(o-Hydroxyphenylmethylpyrazole (17)*

Under a nitrogen atmosphere, 1.43 g (21 mmol) of pyrazole in 5 ml of DMF was added to a slurry of 0.6 g (25 mmol) of NaH in 60 ml of DMF and the mixture stirred for one hour. Approximately 5.6 g (21 mmol) of bromide **16** in 10 ml of DMF was added dropwise; and after stirring at room temperature for 12 h, the solution was treated with 300 ml of water. The solution was extracted with three 75 ml portions of toluene which were washed with water to remove residual DMF, dried over $MgSO_4$, filtered and concentrated to give a dark oil. After several days, a white crystalline solid separated from the oil which was isolated by filtration and recrystallized from ethanol–water to give 0.85 g (25%) of product; melting poing 122–123 °C. $^1$H NMR ($CDCl_3$): δ 5.22 (s, 2H, $-CH_2-$), 6.23 (t, 1H, PzH), 6.85–7.30 (m, 4H, ArH), 7.47 (d, 1H, PzH), 7.53 (d, 1H, PzH), 10.29 (s, 1H, OH). *Anal.* Calc. for $C_{10}H_{10}N_2O$: C, 68.95; H, 5.79; N, 16.08. Found: C, 68.88; H, 5.85; N, 16.07%.

*Synthesis of Complexes*

The molybdenum complexes were prepared by the following general procedure. A filtered solution containing 1.1 g (3.38 mmol) of $MoO_2(acac)_2$ in 20 ml of methanol was treated with 6.8 mmol of the ligand in 25 ml of methanol at 0 °C. The resulting precipitate was collected and recrystallized if necessary. Analytical and infrared spectral data are given in Table I.

TABLE I. Analytical and Infrared Spectral Data for Molybdenum Complexes

| Complex | Formula | Crystal solvent | Analysis (%) | | | | | | IR ($cm^{-1}$)[b] | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | Calc. | | | Found | | | $\nu$(Mo=O) | $\nu$(Mo–O–Mo) |
| | | | C | H | N | C | H | N | | |
| **6** | $C_{17}H_{18}MoN_4O_5$[a] | methanol | 48.37 | 4.30 | 13.27 | 48.65 | 4.52 | 13.27 | 918, 880 | – |
| 7 | $C_{19}H_{22}MoN_4O_5$[a] | methanol | 47.31 | 4.56 | 11.61 | 47.27 | 4.69 | 11.61 | 894, 869 | – |
| **8** | $C_{23}H_{28}MoN_4O_5$[a] | acetone-ether | 51.50 | 5.26 | 10.45 | 51.94 | 5.64 | 10.29 | 894, 873 | – |
| **9** | $C_{16}H_{14}Mo_2N_4O_4S_2$ | methanol | 33.00 | 2.42 | 9.62 | 33.50 | 2.71 | 9.71 | 980 | 744, 485 |
| **10** | $C_{18}H_{18}Mo_2N_4O_4S_2$ | methanol | 35.40 | 2.97 | 9.18 | 35.67 | 2.94 | 9.08 | 978 | 750, 485 |
| **18**[c] | $C_{18}H_{14}MoN_4O_4$ | methanol | 48.45 | 3.16 | 12.55 | 48.33 | 3.33 | 12.41 | 940, 895 | – |
| **18**[d] | $C_{18}H_{14}MoN_4O_4$ | methanol | 48.45 | 3.16 | 12.55 | 48.37 | 3.20 | 12.46 | 931, 905 | – |

[a]Presence of solvate molecule verified by NMR. [b]KBr pellet. [c]Kinetic isomer. [d]Thermodynamic isomer.

*Bis(o-pyrazolylphenolato)dioxomolybdenum(VI), $MoO_2(pzp)_2$, (18)*

*Thermodynamic isomer.* A filtered solution of 0.30 g (0.94 mmol) of $MoO_2(acac)_2$ in 20 ml of methanol was heated to reflux and 0.3 g (1.9 mmol) of Hpzp (**13**) in 5 ml of methanol was added. The reaction mixture was heated under reflux for 45 min and then slowly cooled to room temperature. As the solution cooled, yellow crystals formed which were isolated by filtration to yield 0.16 g (40%) of **18**, melting point 200 °C (dec.).

*Kinetic isomer.* A filtered solution of 0.1 g (0.31 mmol) of $Mo_2(acac)_2$ in 20 ml of methanol was cooled to −15 °C in an ice-salt bath. To the cooled solution was added 0.1 g (0.62 mmol) of Hpzp (**13**) in 5 ml of methanol. The mixture was stirred for 45 minutes at −15 °C and then allowed to warm to room temperature. The yellow crystals were collected by filtration to give 0.052 g of **18** (76%), melting point 200 °C (dec.).

*X-ray Data Collection and Structure Determination*

The X-ray data collection and the solution of the crystal structure for both **8** and **18** were carried out in the same manner. The crystal was mounted in a capillary and a preliminary diffractometer search revealed the appropriate symmetry. Diffraction data were collected at 293 K on an Enraf-Nonius CAD-4 computer controlled diffractometer using Mo Kα radiation (0.7107 Å) from a graphite crystal monochromator. The unit cell constants were derived from a least squares refinement of the setting angles of 24 reflections. The $\omega - 2\theta$ scan technique was used to record the intensities for a unique set of reflections. Peak counts were corrected for background counts which were obtained by extending the final scan by 25% at each end to yield net intensities, $I$, which were assigned standard deviations calculated with a conventional $\rho$ factor selected as 0.01. Intensities were corrected for Lorentz and polarization effects, and showed no decay during the data collection. The data were further corrected for absorption effects using an empirical correlation based on psi scans. A three-dimensional Patterson synthesis was used to locate the molybdenum atom position, and a series of difference Fourier maps revealed the remaining non-hydrogen atoms. The refinement was effected by full-matrix least squares techniques. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ where $|F_o|$ and $|F_c|$ are observed and calculated structure amplitudes and the weight, $w$, is $4F_o/\sigma^2(F_o^2)$. Hydrogen atom positions were calculated and included during the later stages of refinement in the structure factor calculations, although they were not refined. Programs used for the structure solution and refinement were supplied as a package by Enraf-Nonius. Atomic scattering factors for the nonhydrogen atoms were taken from ref. 10 and those for hydrogen atoms from Stewart *et al.* [11]. Additional information concerning the data collection and refinement is collected in Table II. Final positional parameters for **8** are given in Table III, and bond distances and angles are included in Table IV. Final positional parameters for **18** are shown in Table V, and bond distances and angles are given in Table VI. Other distances and angles, final thermal parameters and the structure factors are deposited with the Editor-in-Chief.

## Results and Discussion

We began this study by preparing ligands in which an alcoholate is tethered to a benzimidazole moiety (**1**–**3**) since we thought that heterocyclic rings might have the steric bulk to force non-octahedral coordination. For comparison, we also examined the mercapto analogs **4** and **5**. All ligands were prepared by the standard reaction between the appropriate carboxylic acid and *o*-phenylenediamine (Scheme 1) [12], and the N–O ligands reacted with $MoO_2(acac)_2$ to give colorless, crystalline Mo(VI) complexes (**6**–**8**). On

TABLE II. Crystallographic Details

| Complex | 8 | 18 |
|---|---|---|
| Formula | $C_{23}H_{28}MoN_4O_5$ | $C_{18}H_{14}MoN_4O_4$ |
| Space group | $P2_1/n$ | $C2/C$ |
| $a$ (A) | 12.330(7) | 14.854(2) |
| $b$ (A) | 13.704(4) | 10.817(2) |
| $c$ (A) | 14.860(5) | 11.855(4) |
| $\beta$ (deg) | 96.39(4) | 115.63(2) |
| $V$ (A$^3$) | 2495(3) | 1717(4) |
| $Z$ | 4 | 4 |
| $\rho$ (g/cm$^3$) (calc.) | 1.43 | 1.73 |
| (found) | 1.41 | 1.71 |
| Crystal dimensions (mm) | 0.25 × 0.30 × 0.40 | 0.20 × 0.22 × 0.30 |
| Collection range | $+h, +k, \pm l$ $2.0° \leq 2\theta \leq 55.0°$ | $+h, +k, \pm l$ $2.0° \leq 2\theta \leq 55.0°$ |
| Transmission factors | | |
| min | 0.955 | 0.930 |
| max | 0.999 | 0.999 |
| Absorbance coefficient (cm$^{-1}$) | 5.60 | 7.89 |
| Number of data | 4817 | 1660 |
| Number of data with $[I \geq 3\sigma(I)]$ | 2476 | 1059 |
| $R$ | 0.053 | 0.059 |
| $R_w$ | 0.044 | 0.055 |

TABLE III. Final Positional Parameters for $MoO_2(hmb)_2$

| Atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| Mo | 0.14494(6) | 0.13265(5) | −0.16722(4) |
| O1 | 0.2077(4) | 0.1066(3) | −0.2613(3) |
| O2 | 0.0325(4) | 0.0609(3) | −0.1763(3) |
| O1A | 0.0650(3) | 0.2518(3) | −0.1999(3) |
| O1B | 0.2505(3) | 0.0579(3) | −0.0868(3) |
| OS1 | 0.2688(5) | 0.4922(5) | 0.2278(4) |
| N1A | 0.2687(4) | 0.2629(4) | −0.1394(3) |
| N1B | 0.1118(4) | 0.1658(4) | −0.0197(3) |
| N2A | 0.2955(5) | 0.4187(4) | −0.1656(3) |
| N2B | 0.1372(4) | 0.1121(4) | 0.1214(3) |
| C1A | 0.1108(6) | 0.3409(5) | −0.2232(4) |
| C2A | 0.0429(6) | 0.4265(5) | −0.1936(5) |
| C3A | 0.1183(6) | 0.3438(6) | −0.3243(4) |
| C4A | 0.2251(5) | 0.3438(4) | −0.1741(4) |
| C5A | 0.3748(6) | 0.2838(5) | −0.1078(4) |
| C6A | 0.3922(6) | 0.3840(5) | −0.1234(4) |
| C7A | 0.4928(6) | 0.4279(6) | −0.1020(5) |
| C8A | 0.5743(6) | 0.3705(6) | −0.0639(5) |
| C9A | 0.5589(6) | 0.2711(6) | −0.0489(5) |
| C10A | 0.4607(6) | 0.2262(5) | −0.0716(5) |
| C1B | 0.2358(5) | 0.0292(5) | 0.0015(4) |
| C2B | 0.3448(6) | 0.0236(6) | 0.0580(5) |
| C3B | 0.1771(6) | −0.0685(5) | −0.0013(5) |
| C4B | 0.1637(5) | 0.1045(4) | 0.0366(4) |
| C5B | 0.0416(5) | 0.2178(5) | 0.0304(4) |
| C6B | 0.0587(5) | 0.1855(5) | 0.1199(4) |
| C7B | 0.0012(6) | 0.2232(5) | 0.1867(5) |
| C8B | −0.0757(6) | 0.2922(6) | 0.1608(5) |
| C9B | −0.0942(6) | 0.3232(5) | 0.0716(5) |
| C10B | −0.0358(6) | 0.2868(5) | 0.0051(5) |
| CS1 | 0.3018(9) | 0.3291(8) | 0.2332(10) |
| CS2 | 0.2699(7) | 0.4185(7) | 0.1895(6) |
| CS3 | 0.2385(12) | 0.4095(9) | 0.0967(7) |

TABLE IV. Bond Distances and Angles for $MoO_2(hmb)_2$

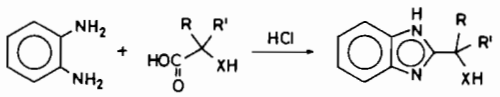
| | |
|---|---|
| Distances (A) | |
| Mo–O2 | 1.693(3) |
| Mo–N1A | 2.355(4) |
| Mo–O1A | 1.941(4) |
| Mo–O1B | 1.956(3) |
| Mo–N1B | 2.319(4) |
| Mo–O1 | 1.710(3) |
| Angles (deg) | |
| O1–Mo–O2 | 104.73(17) |
| O1–Mo–O1B | 93.40(15) |
| O1–Mo–N1B | 163.25(16) |
| O2–Mo–O1B | 103.21(15) |
| O2–Mo–N1B | 87.74(16) |
| O1A–Mo–N1A | 72.99(15) |
| O1B–Mo–N1A | 85.14(14) |
| N1A–Mo–N1B | 82.22(14) |
| O1–Mo–O1A | 103.60(15) |
| O1–Mo–N1A | 87.62(15) |
| O2–Mo–O1A | 94.57(16) |
| O2–Mo–N1A | 164.43(16) |
| O1A–Mo–O1B | 151.43(14) |
| O1A–Mo–N1B | 86.17(15) |
| O1B–Mo–N1B | 72.56(14) |

TABLE V. Final Positional Parameters for $MoO_2(pzp)_2$ (18)

| Atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| Mo | 0.0000(0) | 0.0766(1) | 0.2500(0) |
| O1 | 0.0727(4) | 0.1700(5) | 0.2108(5) |
| O2 | 0.0965(3) | 0.0312(5) | 0.4191(4) |
| N1 | 0.0841(4) | −0.0968(5) | 0.2160(5) |
| N2 | 0.1701(4) | −0.1451(6) | 0.3034(5) |
| C1 | 0.1943(5) | 0.0130(7) | 0.4624(6) |
| C2 | 0.2344(5) | −0.0753(7) | 0.4109(6) |
| C3 | 0.3369(5) | −0.0959(7) | 0.4634(6) |
| C4 | 0.3988(5) | −0.0309(7) | 0.5686(7) |
| C5 | 0.3608(5) | 0.0562(7) | 0.6179(7) |
| C6 | 0.2604(5) | 0.0781(8) | 0.5660(6) |
| CP1 | 0.0502(5) | −0.1789(8) | 0.1228(7) |
| CP2 | 0.1138(6) | −0.2799(7) | 0.1502(7) |
| CP3 | 0.1887(6) | −0.2570(7) | 0.2651(7) |

TABLE VI. Bond Distances and Angles for $MoO_2(pzp)_2$

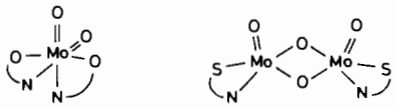
| | |
|---|---|
| Distances (A) | |
| Mo–O1 | 1.684(4) |
| Mo–O2 | 1.957(3) |
| Mo–N1 | 2.382(5) |
| Angles (deg) | |
| O1–Mo–O1′ | 106.22(28) |
| O1–Mo–O2 | 99.23(16) |
| O1–Mo–O2′ | 98.09(16) |
| O1–Mo–N1 | 88.27(17) |
| O1–Mo–N1′ | 164.74(17) |
| O2–Mo–O2′ | 150.95(21) |
| O2–Mo–N1 | 76.75(15) |
| O2–Mo–N1′ | 80.47(15) |
| N1–Mo–N1′ | 76.16(20) |



1 X = O, R = R′ = H
2 X = O, R = H, R′ = $CH_3$
3 X = O, R = R′ = $CH_3$
4 X = S, R = R′ = H
5 X = S, R = H, R′ = $CH_3$

Scheme 1.

the other hand, the benzimidazolylthiols gave only orange, dimeric Mo(V) complexes (**9** and **10**). The infrared spectra for all five complexes unambiguously support their assigned structures represented by the schematic figures below.



A crystal structure of the most hindered of the N–O complexes, $MoO_2(hmb)_2$ (**8**), was undertaken to determine if there are any unusual distortions within the Mo coordination sphere and its structure is presented in Fig. 1. This compound has the distorted-octahedral structure that is common among dioxomolybdenum(VI) species with the alkoxide donors adopting the usual *trans* orientation [5]. The Mo=O distances of 1.710 and 1.693 Å, the O=Mo=O angle of 104.7°, and the Mo–OR bond lengths of 1.940 and 1.956 Å are all within the normal ranges [13]. The principal distortion results from repulsion of the lone pair in the $sp^2$ orbital on the alkoxide donor with the $\pi$-orbital of the neighboring oxo group (O1a–O1 and O1b–O2). This results in an increase in the O1a–Mo–O1 angle (103.6°) compared with the O1b–Mo–O1 angle

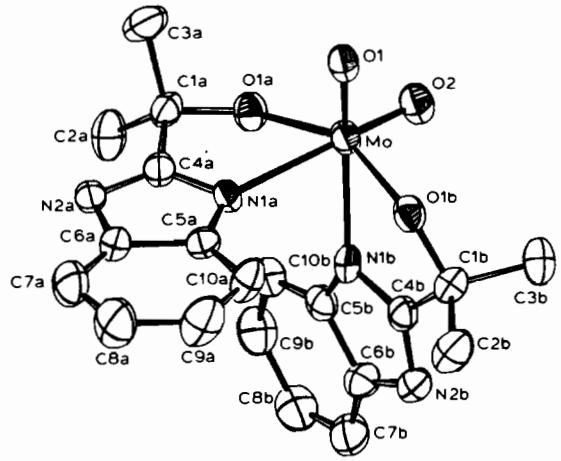
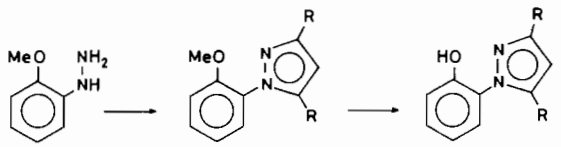



Fig. 1. Structure of $MoO_2(hmb)_2$ showing 40% probability thermal elipsoids.

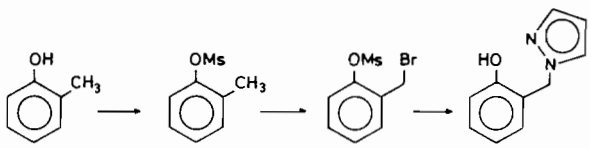
(93.4°), a phenomenon that has been discussed previously [14].

Since phenolate coordination from tyrosine residues provides an alternate to alkoxide as an oxygen ligand in metalloproteins, we also attempted preparation of a skew-trapezoidal complex with *o*-pyrazolylphenol ligands **13**, **14** and **17** prepared by the routes shown in Schemes 2 and 3. The unsubstituted pyra-



**11** R = H
**12** R = $CH_3$
**13** R = H
**14** R = $CH_3$

Scheme 2.

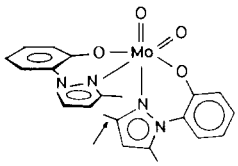


**15** **16** **17**

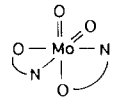
Scheme 3.

zole ligand **13** readily forms a dioxomolybdenum(VI) complex (**18**), but its 3,5-dimethyl analog fails to bind. The methyl groups in 3,5-dimethylpyrazolyl ligands generally do not hinder binding to other transition metals [15, 16]; therefore, we postulate that inclusion of the methyl groups in **14** might lead to the situation pictured in **19**. The interligand steric repulsions between the methyl groups on adjacent pyrazole nuclei may prevent formation of the normal octahedral complex; and the failure to isolate isomer **20** follows the normal pattern for Mo(VI)$O_2$ com-

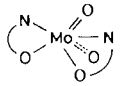
plexes that anionic donors do not bind *trans* to the oxo groups. Furthermore, ligand **14** also does not bind to molybdenum to give the skew-trapezoidal complex **21**, consistent with the notion that the S···S interaction is necessary for stabilization in the previously reported compounds [2].



**19**



**20**



**21**

Ligand **17** provides a different type of structural change. The steric effects result not from crowding between groups on different ligands, but rather from conformational factors within the seven-membered ring that would form upon chelation of a metal ion. As in the case of **14**, no Mo(VI) complex could be isolated using **17** and only the ligand crystallized from solution. The ease in forming Mo(VI) species decreases in proportion to the size of the chelate in the order $5 > 6 \gg 7$-membered rings [5].

The synthesis of $MoO_2(pzp)_2$, **18**, while straightforward, gives two isomers depending on the experimental conditions. The differences, which are apparent only in the solid state, are manifested by slightly different frequencies for the Mo=O stretches in the infrared region and by different crystal habitats. In solution, the NMR, IR and electronic spectra for the two isomers are identical. We determined the structure for the kinetic isomer (Fig. 2) but could not obtain suitable crystals of the thermodynamic one for comparison. As was the case for compound **8**, the geometry is distorted-octahedral; however, for **18**, the molecule lies on a two-fold axis. The distances and angles within the coordination sphere are within the normal ranges and compare well with those values found for $MoO_2$(8-hydroxyquinoline), the only other bis(phenolate-heterocycle)-dioxomolybdenum complex that has been structurally characterized [17].

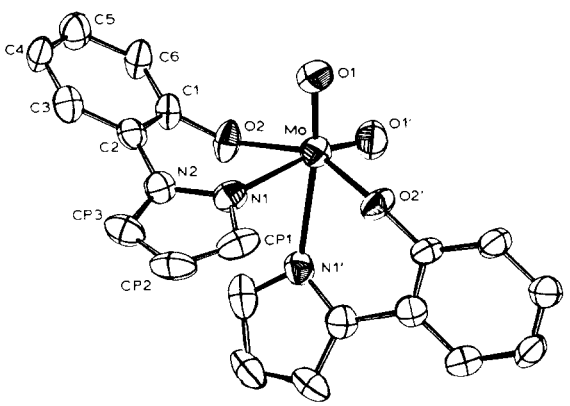



Fig. 2. Structure of $MoO_2(pzp)_2$ showing 40% probability thermal elipsoids.

The principal structural difference between **8** and **18** is that for the latter complex, the O1–Mo–O2 and O1–Mo–O2′ angles are very similar (99 and 98°, respectively) and lie about midway between the values for the corresponding angles in **8** of 93 and 104° (*vide supra*). We postulate that the thermodynamic isomer of **18** may have a more distorted coordination sphere like that of **8** resulting from repulsions between the orbitals on the oxo groups with those of the phenolate oxygen atoms.

## Conclusions

Using several bidentate ligands that can provide an N–O donor set, we obtained only 'normal' distorted-octahedral dioxomolybdenum(VI) complexes with the anionic donors mutually *trans*. Ligands containing heterocyclic-nitrogen donors apparently do not provide the steric bulk necessary to cause substantial geometrical changes in the molybdenum coordination sphere when they bind. However, if the steric requirements of the ligand are enhanced, for example by the addition of a methyl group alpha to the ligating nitrogen (*cf.* **14**), then no discrete complex was isolated.

We further note that the benzimidazolylthiolates, which sterically and electronically might have forced skew-trapezoidal coordination, instead caused reduction of the Mo(VI) starting material to yield Mo(V) dimers having one ligand per molybdenum atom. The reducing ability of such ligands is evidently greater than for simple aliphatic amine–thiolate chelating agents.

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