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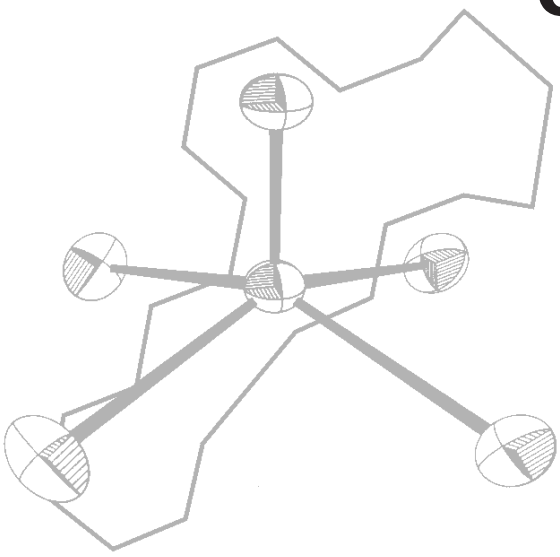

Volume 53, 2000


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*Aust. J. Chem.*, 2000, **53**, 687–691

# Synthesis and Characterization of Hydrophilic Hydroxypyridinones and Their Complexes with Molybdenum(VI)

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We have prepared four *N*-substituted hydroxypyridinones containing alcohol and morpholine groups. Complexes of the type *cis*-$MoO_2L_2$, where L represents the hydroxypyridinonato ligands have also been synthesized. The ethanolamine derivative, *cis*-$MoO_2(hep)_2$ (5), has been characterized by an X-ray diffraction study whereby the pyridinone ligands are bound to molybdenum in a *cis* bidentate fashion via the deprotonated hydroxy groups and the ketone moieties. Crystals of (5) are triclinic, with *a* 9.1930(7), *b* 14.2718(8), *c* 14.6219(9) Å, α 106.816(5), β 95.902(5), γ 96.350(5)°, *Z* 4, space group $P\bar{1}$.

*Keywords*. Molybdenum; pyridinones; hydrophilicity; heart dysfunction.

## Introduction

2-Alkyl-3-hydroxypyridin-4-ones are a family of bidentate chelating ligands that are of interest in medicinal chemistry for a number of different applications.[1–17] For instance, L-mimosine (Fig. 1), a naturally occurring amino acid containing the hydroxypyridinone unit, is the principal component in *Leucaena leucocephala* believed to be responsible for chemical defleecing in sheep.[1] In the search for improved chemical defleecing agents, several analogues of mimosine have been generated and tested for their inhibitory activities on wool growth.[2–4]

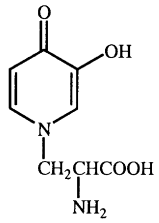



**Fig. 1.** L-Mimosine.

α-Hydroxypyridinones have also been used to form complexes with aluminium(III), gallium(III), and indium(III) for the radioisotopic imaging of tumours.[5–8] Their chemical stability and high affinity for iron[9] also make these compounds powerful therapeutic agents for the treatment of physiological iron overload in humans.[10–13] However, the overall efficacy of these drugs is usually limited by poor gastrointestinal absorption. As a result, a number of *N*-substituted pyridinones with various physical properties have been prepared in order to improve the pharmacological activities of these chelating agents.[13] Vanadium compounds containing pyridinone,[14,15] and related pyrone, ligands have found recent utility as insulin mimics. For example, $VO(ma)_2$ (ma = deprotonated 3-hydroxy-2-methyl-4-pyrone) displays potent insulinomimetic properties and has been the subject of numerous chemical and physiological studies.[16,17]

Our interest in this area lies in developing molybdenum complexes for the treatment of cardiac dysfunction associated with diabetes.[18] We have recently found that sodium molybdate prevents depression in cardiac function from occurring in diabetic hearts. In order to ascertain the effects molybdenum complexes have on heart function we have begun to synthesize numerous complexes containing pyridinone ligands with different physical and chemical properties. In this paper we report our initial efforts in generating novel hydrophilic hydroxypyridinones along with the corresponding molybdenum(VI) complexes.

## Experimental

Chemicals used were of reagent grade. Maltol and amines were obtained from Aldrich Chemicals and molybdic acid was purchased from Strem. Tetrahydrofuran, hexane, and diethyl ether were distilled from sodium benzophenone ketyl. Methylene chloride and chloroform were distilled from $CaH_2$. N.m.r. spectra were recorded on a JEOL

Manuscript received 17 July 2000  10.1071/CH00093 0004-9425/00/080687

JNM-GSX270 Fourier-transform n.m.r. spectrometer. $^1$H n.m.r. chemical shifts are reported in ppm and referenced to residual protons in $CDCl_3$, $D_2O$ and $(CD_3)_2SO$ at 270 MHz. $^{13}C\{^1H\}$ n.m.r. chemical shifts are referenced to internal solvent peaks at 68 MHz. Infrared spectra were obtained with Nujol on KBr/NaCl plates by using a Perkin–Elmer 710B and a Mattson Polaris spectrophotometer and are reported in $cm^{-1}$. Melting points were measured uncorrected with a Mel-Temp apparatus. Microanalyses for C, N, and H were carried out at Desert Analytics (Tucson, Arizona).

*Synthesis of 3-Hydroxy-1-(2-hydroxyethyl)-2-methylpyridin-4(1*H*)-one (Hhep) (1)*

Maltol (3.14 g, 24.93 mmol) and ethanolamine (4.67 g, 76.40 mmol) were combined in water (15 $cm^3$) and heated to reflux for 67 h. Solvent was removed under vacuum to give a dark brown oil which was triturated with propan-1-ol (10 $cm^3$) and suction-filtered. The resultant solid was recrystallized from water (5 $cm^3$) to afford light brown crystals. Yield: 2.21 g (53%); m.p. 199°C. $^1$H n.m.r. (in $D_2O$): δ 7.49, d, *J* 5 Hz, CH; 6.36, d, *J* 5 Hz, CH; 4.06, t, *J* 5 Hz, $CH_2$; 3.74, t, *J* 5 Hz, $CH_2$; 2.26, s, $CH_3$. $^{13}C\{^1H\}$ n.m.r. (in $D_2O$): δ 171.5, 147.2, 141.6, 137.4, 114.7, 62.8, 58.4, 14.3. I.r. (Nujol): 3298, 2936, 2864, 1622, 1562, 1500, 1462, 1377, 1339, 1230, 1083, 1064.

*Synthesis of 3-Hydroxy-1-(3-hydroxypropyl)-2-methylpyridin-4(1*H*)-one (Hhmp) (2)*

Maltol (0.99 g, 7.82 mmol) and 3-aminopropan-1-ol (0.59 g, 7.87 mmol) were combined in water (5 $cm^3$) and heated to reflux for 66 h. An organic extraction was performed with chloroform (3×10 $cm^3$) to remove impurities and the aqueous layer was collected. Removal of water under vacuum afforded a dark brown oil which was dissolved in propan-2-ol (2 $cm^3$) to which acetone (1 $cm^3$) was added. After 18 h at 5°C, a light beige powder precipitated and was collected by suction filtration and was washed with ice-cold acetone (20 $cm^3$). Yield: 0.25 g (18%); m.p. 122–124°C. $^1$H n.m.r. (in $D_2O$): δ 7.58, d, *J* 8 Hz, CH; 6.44, d, *J* 5 Hz, CH; 4.12, t, *J* 8 Hz, $CH_2$; 3.57, t, *J* 5 Hz, $CH_2$; 2.36, s, $CH_3$; 1.93, m, *J* 5 Hz, $CH_2$. $^{13}C\{^1H\}$ n.m.r. (in $D_2O$): δ 171.4, 147.8, 140.7, 137.1, 114.9, 60.6, 54.0, 34.7, 14.0. I.r. (Nujol): 3361, 3157, 2893, 1626, 1566, 1504, 1350, 1237, 1078, 1034, 919, 824.

*Synthesis of 3-Hydroxy-2-methyl-1-morpholinopyridin-4(1*H*)-one (Hmmp) (3)*

Maltol (1.00 g, 7.87 mmol) and 4-aminomorpholine (1.05 g, 10.30 mmol) were combined in water (10 $cm^3$). The reaction mixture was heated to reflux for 42 h and cooled to 5°C, upon which light brown crystals precipitated. After 24 h, the solid was collected by suction filtration and washed with cold propan-2-ol (3×5 $cm^3$). The filtrate volume was reduced to 5 $cm^3$ under vacuum and the solution cooled again to 5°C. More of the light brown solid precipitated and was collected by suction filtration and washed with propan-2-ol (3×5 $cm^3$). Combined yield: 0.68 g (41%); m.p. 277–278°C. $^1$H n.m.r. (in $CDCl_3$): δ 7.53, d, *J* 5 Hz, CH; 6.47, d, *J* 8 Hz, CH; 4.02, d, *J* 11 Hz, $CH_2$; 3.81, t, *J* 11 Hz, $CH_2$; 3.19, t, *J* 8 Hz, $CH_2$; 2.94, ov m; 2.42, s, $CH_3$. $^{13}C\{^1H\}$ n.m.r. (in $(CD_3)_2SO$): δ 168.9, 144.3, 132.8, 130.7, 110.8, 66.2, 53.6, 11.0. I.r. (Nujol): 3174, 3085, 2891, 1619, 1581, 1524, 1499, 1455, 1376, 1217, 1111, 919, 820.

*Synthesis of 3-Hydroxy-2-methyl-1-(3-morpholinopropyl)pyridin-4(1*H*)-one (Hmpp) (4)*

Maltol (1.00 g, 7.87 mmol) and 4-(3-aminopropyl)morpholine (1.15 g, 7.97 mmol) were combined in water (12 $cm^3$) and heated to reflux for 6 h. Solvent was removed under vacuum to afford a brown oil which was dissolved in tetrahydrofuran (6 $cm^3$) and stored at 5°C. After several weeks a light brown solid precipitated and was collected by suction filtration. Yield: 0.13 g (7%); m.p. 178°C. $^1$H (in $CDCl_3$): δ 7.33, d, *J* 8 Hz, CH; 6.39, d, *J* 8Hz, CH; 4.48, br s; 4.02, t, *J* 8 Hz, $CH_2$; 3.72, ov m; 2.41, ov m; 2.34, t, *J* 5 Hz, $CH_2$; 1.91, t, *J* 5 Hz, $CH_2$. $^{13}C\{^1H\}$ n.m.r. (in $CDCl_3$): δ 169.7, 146.5, 137.4, 128.0, 111.1, 67.1, 54.4, 53.7, 51.3, 27.3, 12.0. I.r. (Nujol): 3159, 2971, 2882, 1627, 1566, 1535, 1507, 1460, 1376, 1232, 1111, 1021, 958, 837.

*Synthesis of* cis*-Bis(3-hydroxy-1-(2-hydroxyethyl)-2-methylpyridin-4(1*H*)-onato)dioxomolybdenum*(VI) *($MoO_2$(hep)$_2$) (5)*

Molybdic acid (0.16 g, 0.46 mmol) was dissolved in water (10 $cm^3$) and then cooled in an ice-water bath for 5 min before solid pyridinone Hhep (1) (0.35 g, 2.05 mmol) was added slowly. The reaction mixture was stirred at 0°C and was filtered cold after 2 h to afford a bright yellow solid. This precipitate was recrystallized from hot water (5 $cm^3$) to give orange-yellow *crystals*. Yield: 0.23 g (56%); m.p. 278°C (dec.) (Found: C, 41.2; H, 4.5; N, 6.0. $C_{16}H_{20}MoN_2O_8$ requires C, 41.4; H, 4.4; N 6.0%). $^1$H n.m.r. (in $(CD_3)_2SO$): δ 7.85, d, *J* 5 Hz, CH; 6.55, d, *J* 5 Hz, CH; 5.20, br s; 4.27, br m, $CH_2$; 3.78, br m, $CH_2$; 2.49, s, $CH_3$. $^{13}C\{^1H\}$ n.m.r. (in $(CD_3)_2SO$): δ 169.9, 154.4, 138.7, 133.7, 108.3, 60.1, 56.2, 12.2. I.r. (Nujol): 2934, 2869, 1612, 1552, 1461, 1377, 1269, 1075, 931, 887, 823, 703, 637.

*Synthesis of* cis*-Bis(3-hydroxy-1-(3-hydroxypropyl)-2-methylpyridin-4(1*H*)-onato)dioxomolybdenum*(VI) *($MoO_2$(hmp)$_2$) (6)*

Molybdic acid (0.04 g, 0.12 mmol) was stirred in water (1 $cm^3$) for 0.5 h, until completely dissolved. This solution was stirred in an ice-water bath for 5 min upon which solid pyridinone Hhmp (2) (0.09 g, 0.49 mmol) was added slowly. After 24 h, a yellow precipitate was collected by suction filtration and washed with acetone (5 $cm^3$). The solid was recrystallized from hot water (2 $cm^3$) to afford orange-yellow *crystals*. Yield: 0.09 g (78%); m.p. 228°C (dec.) (Found: C, 41.4; H, 4.4; N 5.3. $C_{18}H_{24}MoN_2O_8{\cdot}1.5H_2O$ requires C, 41.6; H, 5.3; N, 5.4%). $^1$H (in $(CD_3)_2SO$): δ 7.90, d, *J* 5 Hz, CH; 6.54, d, *J* 5 Hz, CH; 4.83, br s; 4.28, t, *J* 8 Hz, $CH_2$; 3.55, ov m, $CH_2$; 2.57, s, $CH_3$; 1.95, m, $CH_2$. $^{13}C\{^1H\}$ n.m.r. (in $(CD_3)_2SO$): δ 169.7, 154.6, 137.9, 133.2, 108.6, 57.2, 51.5, 33.0, 11.7. I.r. (Nujol): 3434, 2944, 1612, 1550, 1494, 1467, 1357, 1265, 1054, 917, 883, 716, 642.

*Synthesis of* cis*-Bis(3-hydroxy-2-methyl-1-morpholinopyridin-4(1*H*)-onato)dioxomolybdenum*(VI) *($MoO_2$(mmp)$_2$) (7)*

The pyridinone Hmmp (3) (0.10 g, 0.48 mmol) was mixed with molybdic acid (0.04 g, 0.10 mmol) in water (5 $cm^3$) and the reaction was allowed to proceed for 20 h. The bright yellow *precipitate* that formed was collected by suction filtration and washed with water (2×7 $cm^3$) and diethyl ether (2×10 $cm^3$). Yield: 0.09 g (82%); m.p. 266–269°C (dec.) (Found: C, 42.5; H, 5.0; N, 9.9. $C_{20}H_{26}MoN_4O_8{\cdot}H_2O$ requires C, 42.6; H, 5.0; N, 9.9%). $^1$H n.m.r. (in $(CD_3)_2SO$): δ 8.44, d, *J* 5 Hz, CH; 6.66, d, *J* 8 Hz, CH; 4.01, d, *J* 11 Hz, $CH_2$; 3.76, t, *J* 11Hz, $CH_2$; 3.29, d, *J* 11 Hz, $CH_2$; 3.13, t, *J* 8 Hz, $CH_2$; 2.49, s, $CH_3$. $^{13}C\{^1H\}$ n.m.r. (in $(CD_3)_2SO$): δ 169.8, 153.5, 135.2, 133.6, 108.5, 66.1, 53.9, 11.4. I.r. (Nujol): 3542, 2976, 2976, 2881, 2838, 1608, 1553, 1516, 1453, 1376, 1296, 1111, 920, 894, 819, 734.

*Synthesis of* cis*-Bis(3-hydroxy-2-methyl-1-(3-morpholinopropyl)pyridin-4(1*H*)-onato)dioxomolybdenum*(VI) *($MoO_2$(mpp)$_2$) (8)*

*cis*-$MoO_2(ma)_2$ (ma = maltolato)[18] (1.00 g, 2.65 mmol) was combined with 4-(3-aminopropyl)morpholine (0.77 g, 5.30 mmol) in water (8 $cm^3$) and ethanol (4 $cm^3$). The mixture was heated to reflux for 8.5 h and, after cooling to room temperature, solvent was removed under vacuum to afford a dark brown oil. Trituration with tetrahydrofuran (10×10 $cm^3$) afforded an orange-yellow *solid*. Yield: 0.59 g (39%); m.p. 166°C (dec.) (Found: C, 48.9; H, 5.9; N, 8.6. $C_{26}H_{38}MoN_4O_8{\cdot}H_2O$ requires C, 48.1; H, 6.2; N, 8.6%). $^1$H n.m.r. (in $CDCl_3$): δ 7.41, d, *J* 5 Hz, CH; 6.51, d, *J* 5 Hz, CH; 4.13, t, *J* 8 Hz, $CH_2$; 3.72, br m; 2.51, s, $CH_3$; 2.42, br m; 2.35, t, *J* 5 Hz, $CH_2$; 1.92, br t, *J* 5 Hz, $CH_2$. $^{13}C\{^1H\}$ n.m.r. (in $CDCl_3$): δ 170.7, 155.7, 136.8, 133.4, 109.7, 66.6, 54.2, 53.3, 52.3, 26.7, 12.4. I.r. (Nujol): 3535, 3416, 2891, 1608, 1553, 1516, 1485, 1464, 1365, 1295, 1263, 1229, 1062, 920, 895.

## Crystallography

*Crystal Data*

Complex (5). $C_{16}H_{20}MoN_2O_8$, mol. wt 464.3, triclinic, space group $P\bar{1}$, *a* 9.1930(7), *b* 14.2718(8), *c* 14.6219(9) Å, α 106.816(5), β 95.902(5)°, γ 96.350(5)°, *V* 1806.7(3) Å$^3$, *F*(000) 944, *Z* 4, $D_c$ 1.707 g $cm^{-3}$, μ (Mo Kα) 7.74 $cm^{-1}$, temperature 180 K.

Yellow tabular prism, 0.52{101} by 0.42{02$\bar{1}$} by 0.36{$\bar{1}$11}, 2θ range 4.0–56.0°, 9111 collected reflections, 8584 independent ($R_{int}$ 0.0147), 7712 observed ($F \geq 6\sigma(F)$), final $R$ factor 0.0228, $wR$ 0.0360, goodness of fit 2.64, min./max. transmission 0.7180/0.8005.

*Data Collection, Structure Resolution and Refinement*

Data for (5) were collected on a Nicolet LT2 equipped Siemens P4 diffractometer using the ω method ($4 \leq 2\theta \leq 56°$). The data were corrected for absorption by a faced-indexed analytical method. Three standard reflections every 100 showed no significant decay. The structures were solved by Patterson and Fourier methods, and refined by full matrix least squares (SHELXTL IRIS).[19] A weighting scheme of $w^{-1} = \sigma^2(F) + 0.00005F^2$ was used in the last cycles of refinement. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located by a difference Fourier but included by the riding model method with refined isotropic thermal parameters. Hydroxy (OH) protons were fixed in found positions. $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; $Rw = [\Sigma(w(|F_o|-|F_c|)^2/\Sigma(w|F_o|)^2]^{1/2}$.

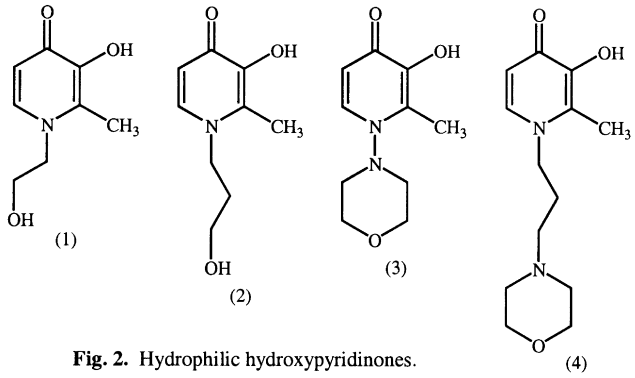
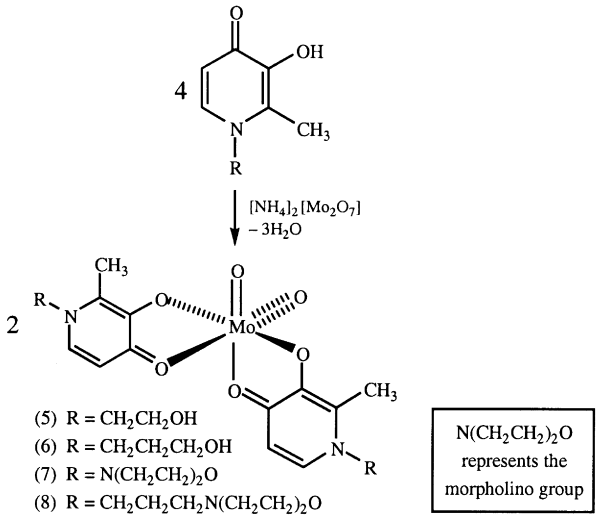



**Fig. 2.** Hydrophilic hydroxypyridinones.

## Results and Discussion

Four hydroxypyridinones have been prepared (Fig. 2) by the addition of the corresponding primary amine to aqueous solutions of maltol (3-hydroxy-2-methyl-4-pyrone, Hma) at elevated temperatures. Functionalization of the ring nitrogen in the hydroxypyridinones allows for fine tuning of physical properties such as water solubility and hydrolytic stability.[20] Biological studies of maltol-based pyridinones (1) and (2), respectively, derived from 2-aminoethan-1-ol and 3-aminopropan-1-ol, have been conducted.[21] Compounds (1) and (2) were isolated in low to moderate yields (18–53%) with both being water-soluble. The morpholine-derived pyridinones (3) and (4) could also be prepared by a similar methodology where the propylmorpholine derivative (4) has increased solubility in common organic solvents compared to (3). Similar diarylpyridinones have been prepared recently.[22]

The molybdenum compounds (5)–(8) prepared in this study (Scheme 1), could be generated by either direct addition of the hydroxypyridinone to molybdic acid or by addition of the precursor amine to aqueous solutions of preformed maltolato complex *cis*-$MoO_2(ma)_2$.[18,23] The second methodology provides an easy route to making a wide variety of *N*-substituted pyridinone molybdenum complexes owing to the ease of isolation, increased yields, milder conditions, and shorter reaction times. The molybdenum centre not only acts as a protecting group for the hydroxy group, thereby reducing the amount of hydrogen bonding involved in these systems, but its electron-deficient nature




**Scheme 1.** Molybdenum pyridinone complexes.

also makes the coordinated pyrone more susceptible to nucleophilic attack by the amine.[5,6]

Although metal complexes containing *N*-substituted 3-hydroxypyridin-4-ones are well known,[11,14,15,20,24-28] the only molybdenum complexes reported have simple alkyl or aryl groups attached to the ring nitrogen.[18,27] This work represents examples of molybdenum complexes containing pyridinone ligands with alcohol and morpholine appendages. The four-band infrared spectral pattern between 1400 and 1610 $cm^{-1}$, characteristic of pyridinone ligands,[29,30] is observed upon complexation with molybdenum. These four bands are assigned collectively as ν(C=C) and ν(C=O). N.m.r. data are also consistent with complexes of the type *cis*-$MoO_2L_2$ where L represents the hydroxypyridinonato ligands. A single-crystal X-ray diffraction study was carried out on $MoO_2(hep)_2$ (5) to confirm this assignment.

The molecular structure of one of the two independent molecules of (5), found in the unit cell, is shown in Fig. 3, atomic coordinates are given in Table 1, and bond distances and angles are provided in Tables 2 and 3, respectively. The conformationally different molecules both have a *cis* arrangement of the oxo ligands, and the Mo=O bond lengths (average 1.709 (2) Å) are comparable to those found in other oxomolybdenum(VI) complexes.[18] The two ketonic oxygen atoms of the pyridinone moieties are *trans* to the oxo ligands and the stronger-field hydroxy oxygens are *trans* to one another. A slight lengthening of the ketone C=O bond is observed upon complexation, with a mean distance of 1.298(3) Å, which results in the molybdenum–oxygen (ketone) bond being somewhat longer (average 2.211(3) Å) than the molybdenum–deprotonated oxygen distance, the average being only 1.995(2) Å. This observation illustrates the distinction between Lewis acid–base versus covalent bonding for these two types of oxygen atoms.

The bond distances within the pyridinone ring also display similar trends to that described earlier for other metal–pyridinone complexes.[18] A pronounced localization of the formal double bonds in the ring is clearly indicated by the short C(2)–C(3), C(5)–C(6), and ketone C(1)–O(3) bonds.

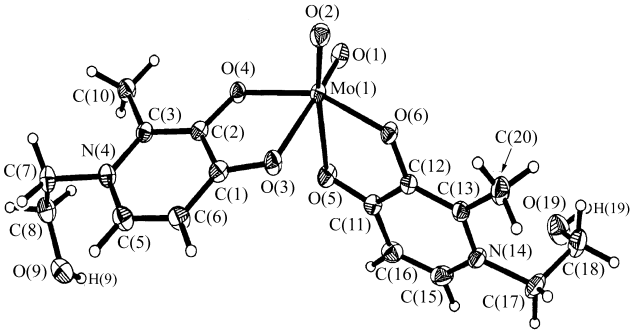



**Fig. 3.** The molecular structure of $MoO_2(hep)_2$ (5).

**Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å$^2$) for (5)**

| Molecule | Atom | $10^4x$ | $10^4y$ | $10^4z$ | $10^4U_{eq}$[A] |
|---|---|---|---|---|---|
| 1 | Mo(1) | 1019.5(2) | 4373.8(1) | 2846.3(1) | 160.3(6) |
| | O(1) | 2671(2) | 4571(1) | 3568(1) | 252(5) |
| | O(2) | 391(2) | 5498(1) | 3183(1) | 245(5) |
| | O(3) | –781(2) | 3778(1) | 1616(1) | 223(5) |
| | O(4) | 1975(1) | 4397(1) | 1683.4(9) | 187(4) |
| | O(5) | 1170(2) | 2795(1) | 2447(1) | 235(5) |
| | O(6) | –456(2) | 3843(1) | 3546(1) | 192(4) |
| | C(1) | –341(2) | 3672(1) | 782(1) | 195(6) |
| | C(2) | 1170(2) | 4037(1) | 803(1) | 170(6) |
| | C(3) | 1761(2) | 4028(1) | –28(1) | 179(6) |
| | N(4) | 856(2) | 3610(1) | –894(1) | 194(5) |
| | C(5) | –570(2) | 3217(2) | –932(2) | 239(7) |
| | C(6) | –1199(2) | 3233(2) | –119(2) | 244(7) |
| | C(7) | 1417(2) | 3580(2) | –1813(1) | 239(7) |
| | C(8) | 2323(2) | 2763(2) | –2155(2) | 263(7) |
| | O(9) | 1438(2) | 1825(1) | –2373(1) | 305(5) |
| | C(10) | 3322(2) | 4464(2) | 7(2) | 259(7) |
| | C(11) | 393(2) | 2332(1) | 2917(1) | 197(6) |
| | C(12) | –528(2) | 2887(1) | 3519(1) | 170(6) |
| | C(13) | –1409(2) | 2491(2) | 4057(1) | 193(6) |
| | N(14) | –1321(2) | 1533(1) | 4044(1) | 232(6) |
| | C(15) | –434(3) | 994(2) | 3483(2) | 281(7) |
| | C(16) | 401(2) | 1344(2) | 2910(2) | 257(7) |
| | C(17) | –2100(3) | 1084(2) | 4688(2) | 321(8) |
| | C(18) | –1332(3) | 1459(2) | 5719(2) | 331(8) |
| | O(19) | 136(2) | 1255(1) | 5746(1) | 410(7) |
| | C(20) | –2443(2) | 3075(2) | 4625(2) | 285(7) |
| 2 | Mo(2) | 5596.5(2) | 372.3(1) | 7586.8(1) | 184.3(6) |
| | O(21) | 4650(2) | –802(1) | 7125(1) | 274(5) |
| | O(22) | 7352(2) | 231(1) | 7361(1) | 292(5) |
| | O(23) | 6178(2) | 1986(1) | 8002(1) | 223(5) |
| | O(24) | 4729(2) | 733.0(9) | 6441.6(9) | 203(4) |
| | O(25) | 3563(2) | 859(1) | 8219.1(9) | 226(5) |
| | O(26) | 6092(2) | 614(1) | 8996.2(9) | 228(5) |
| | C(21) | 5729(2) | 2363(1) | 7337(1) | 189(6) |
| | C(22) | 4913(2) | 1691(1) | 6472(1) | 172(6) |
| | C(23) | 4318(2) | 2006(1) | 5729(1) | 174(6) |
| | N(24) | 4534(2) | 3012(1) | 5848(1) | 197(5) |
| | C(25) | 5338(2) | 3657(2) | 6655(2) | 251(7) |
| | C(26) | 5974(2) | 3366(2) | 7386(2) | 242(6) |
| | C(27) | 3766(2) | 3434(2) | 5156(2) | 255(7) |
| | C(28) | 2263(2) | 3647(2) | 5417(2) | 259(7) |
| | O(29) | 2480(2) | 4335(1) | 6342(1) | 371(6) |
| | C(30) | 3459(2) | 1290(2) | 4825(1) | 242(6) |
| | C(31) | 3821(2) | 1182(1) | 9159(1) | 204(6) |
| | C(32) | 5215(2) | 1086(1) | 9596(1) | 194(6) |
| | C(33) | 5657(2) | 1477(1) | 10575(1) | 194(6) |
| | N(34) | 4683(2) | 1953(1) | 11129(1) | 214(5) |
| | C(35) | 3295(2) | 1992(2) | 10739(2) | 254(7) |
| | C(36) | 2823(2) | 1611(2) | 9768(2) | 244(7) |
| | C(37) | 5174(3) | 2594(2) | 12137(1) | 253(7) |
| | C(38) | 5377(2) | 3677(2) | 12182(2) | 240(7) |
| | O(39) | 6232(2) | 3880(1) | 11489(1) | 289(5) |
| | C(40) | 7148(2) | 1382(2) | 11034(2) | 256(7) |

[A] Equivalent isotropic $U$ defined as one-third of the trace of the orthogonalized $U_{ij}$ tensor.

* L′ = 3-hydroxy-1-*p*-methoxyphenyl-2-methylpyridin-4(1*H*)-one.
† L′′ = 3-hydroxy-1,2-dimethylpyridin-4(1*H*)-one.

An N(4)–C(7) bond distance of 1.479(3) Å is similar to that reported for the free ligands L′* (cf. 1.474(1) Å)[29] and L′′† (cf. 1.482(4) Å).[31] Of the four hydrogen bonds formed, three (from H(9), H(29), and H(39)) are bonded to molybdenum oxygens in neighbouring molecules. The fourth hydrogen bond links molecule 1 to 2 in a head-to-tail fashion via O(19)–H(19)···O(9B) (B = $x$, $y$, 1+$z$) and essentially results in a three-dimensional polymeric sheet structure [O(9)–H(9)···O(25A), 2.721(2) Å; O–H···O, 167°; O(19)–H(19)···O(9B), 2.734(2) Å; O–H···O, 175°; O(29)–H(29)···O(2C), 2.815(2) Å; O–H···O, 164°; O(39)–H(39)···O(3D), 2.756(2) Å; O–H···O, 164°]. Atomic coordinates, thermal parameters, bond lengths and angles, and alternative views of complex (5) have been deposited as

**Table 2. Bond distances (Å) for (5), together with hydrogen bonds**

| Bond distances | | Hydrogen bonds[A] | |
|---|---|---|---|
| Molecule 1 | | O(9)–H(9) | 0.97 |
| | | H(9)···O(25A) | 1.77 |
| Mo(1)–O(1) | 1.703(1) | O(9)···O(25A) | 2.721(2) |
| Mo(1)–O(2) | 1.719(2) | O(19)–H(19) | 0.94 |
| Mo(1)–O(3) | 2.211(1) | H(19)···O(9B) | 1.80 |
| Mo(1)–O(4) | 1.999(1) | O(19)···O(9B) | 2.734(2) |
| Mo(1)–O(5) | 2.182(1) | O(29)–H(29) | 0.91 |
| Mo(1)–O(6) | 1.992(2) | H(29)···O(2C) | 1.93 |
| | | O(29)···O(2C) | 2.815(2) |
| Molecule 2 | | O(39)–H(39) | 0.91 |
| | | H(39)···O(3D) | 1.87 |
| Mo(2)–O(21) | 1.711(1) | O(39)···O(3D) | 2.756(2) |
| Mo(2)–O(22) | 1.702(2) | | |
| Mo(2)–O(23) | 2.193(1) | | |
| Mo(2)–O(24) | 2.005(2) | | |
| Mo(2)–O(25) | 2.259(2) | | |
| Mo(2)–O(26) | 1.984(1) | | |

[A] Symmetry codes: A = $x$, $y$, –1+$z$; B = $x$, $y$, 1+$z$; C = –$x$, 1–$y$, 1–$z$; D = 1+$x$, $y$, 1+$z$.

**Table 3. Selected bond angles (degrees) for (5)**

| Molecule 1 | | Molecule 2 | |
|---|---|---|---|
| O(1)–Mo(1)–O(2) | 103.9(1) | O(21)–Mo(2)–O(22) | 103.5(1) |
| O(1)–Mo(1)–O(3) | 162.4(1) | O(21)–Mo(2)–O(23) | 162.6(1) |
| O(2)–Mo(1)–O(3) | 91.8(1) | O(22)–Mo(2)–O(23) | 90.4(1) |
| O(1)–Mo(1)–O(4) | 93.1(1) | O(21)–Mo(2)–O(24) | 90.9(1) |
| O(2)–Mo(1)–O(4) | 103.6(1) | O(22)–Mo(2)–O(24) | 102.6(1) |
| O(3)–Mo(1)–O(4) | 75.1(1) | O(23)–Mo(2)–O(24) | 75.7(1) |
| O(1)–Mo(1)–O(5) | 87.8(1) | O(21)–Mo(2)–O(25) | 88.6(1) |
| O(2)–Mo(1)–O(5) | 163.7(1) | O(22)–Mo(2)–O(25) | 165.6(1) |
| O(3)–Mo(1)–O(5) | 78.7(1) | O(23)–Mo(2)–O(25) | 79.3(1) |
| O(4)–Mo(1)–O(5) | 86.9(1) | O(24)–Mo(2)–O(25) | 84.7(1) |
| O(1)–Mo(1)–O(6) | 105.2(1) | O(21)–Mo(2)–O(26) | 106.5(1) |
| O(2)–Mo(1)–O(6) | 89.6(1) | O(22)–Mo(2)–O(26) | 94.0(1) |
| O(3)–Mo(1)–O(6) | 82.7(1) | O(23)–Mo(2)–O(26) | 82.4(1) |
| O(4)–Mo(1)–O(6) | 154.3(1) | O(24)–Mo(2)–O(26) | 152.4(1) |
| O(5)–Mo(1)–O(6) | 76.2(1) | O(25)–Mo(2)–O(26) | 74.8(1) |
| Mo(1)–O(3)–C(1) | 113.7(1) | Mo(2)–O(23)–C(21) | 113.6(1) |
| Mo(1)–O(4)–C(2) | 119.4(1) | Mo(2)–O(24)–C(22) | 118.7(1) |
| Mo(1)–O(5)–C(11) | 113.0(1) | Mo(2)–O(25)–C(31) | 111.2(1) |
| Mo(1)–O(6)–C(12) | 118.3(1) | Mo(2)–O(26)–C(32) | 119.5(1) |

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## Conclusions

A series of hydrophilic hydroxypyridinones, and their corresponding dioxomolybdenum(VI) complexes, have been prepared and characterized by a number of physical methods, including X-ray diffraction studies for the case of *cis*-$MoO_2(hep)_2$ (5). The resulting metal complexes, like the hydroxypyridinone ligands, have appreciable solubility in aqueous solvents. We are currently investigating the biological activities of these molybdenum complexes for their ability to control heart dysfunction in diabetics and will report our results in due course.

## Acknowledgments

Thanks are gratefully extended to the Heart and Stroke Foundation of New Brunswick, the University of Waterloo, and Mount Allison University for financial support. We also thank Dan Durant, Roger Smith and Jacqueline Jacob (Mount Allison University) for their expert technical assistance. Anonymous reviewers are thanked for helpful comments.

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