N-Monofunctionalized 1,4,7-Triazacyclononane Macrocycles as Building Blocks in Inorganic Crystal Engineering

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Received June 22, 2000

The syntheses of *N*-(3-prop-1-ene)-1,4,7-triazacyclononane molybdenum tricarbonyl (**2**), *N*-(4-but-1-ene)-1,4,7-triazacyclononane molybdenum tricarbonyl (**3**), *N*-(3-prop-1-ene)-1,4,7-triazacyclononane molybdenum trioxide (**5**), *N*-(4-but-1-ene)-1,4,7-triazacyclononane molybdenum trioxide (**6**), *N*-(hydroxyethyl)-1,4,7-triazacyclononane molybdenum trioxide (**7**), and *N*-(2-methylpyridyl)-1,4,7-triazacyclononane molybdenum trioxide (**8**) have been achieved. The objective of this work is to systematically vary the functionality of the pendant group in order to create different crystal packing in the solid state. This is evidenced in comparing the structures of 1,4,7-triazacyclononane molybdenum trioxide (**4**) and **5**−**8**, which were determined using X-ray crystallography. The synthesis and characterization of the new ligand *N*-(2-methylpyridyl)-1,4,7-triazacyclononane ($\mathbf{L^5}$) is reported.

Introduction

Inorganic crystal engineering, with a view to the directed design of new materials, is a rapidly growing field. As well as using covalent linkages to generate coordination polymers, there is also a great deal of interest in using hydrogen bonding and $\pi-\pi$ interactions in crystal engineering to generate multidimensional arrays.[1] Recent studies have highlighted the use of Mo═O units from molybdenum clusters to provide the building blocks in the production of such arrays.[2,3] The ability to control the construction of new three-dimensional arrays of inorganic molecules is a desirable target. We are interested in developing the role of simple mononuclear metal oxides, such as MoO_3, as templates for hydrogen-bonding interactions using monofunctionalized triazacyclononane ligands.

The chemistry of the ligand 1,4,7-triazacyclononane ($\mathbf{L^1}$) is wide and varied. The ability of this medium-ring macrocycle to form stable complexes with many metal centers forms the backbone to this chemistry.[4] Recently, this ligand and its trimethyl derivative have been used to stabilize and produce interesting organometallic chemistry of early (e.g., Ti[5] and Y[6]) and late (e.g., Rh[7]) transition metal centers. An example where triazacyclononane ligands have been used in crystal engineering has been reported recently, where the tris-functionalized nitrile derivatives have been used as building blocks to form multidimensional networks with Ag^I.[8]

Monofunctionalization of the nitrogen atoms of the macrocycle by conventional methods is synthetically more difficult than tris-functionalization because of the difficulty of separating the different products formed. (A review of pendant arm macrocyclic ligands has recently been written.[9]) A clean route to the monosubstitution of $\mathbf{L^1}$ was developed by Weisman et. al. through the reaction of orthoamide 1,4,7-triazacyclo[5.2.1.0$^{4.10}$]-decane (**1**) with the appropriate alkyl halide.[10−12] A range *N*-monofunctionalized ligands have been prepared, including alkene,[13] alkyne,[14] carboxylic acid/ester,[15] carboxylate, and phenolate derivatives.[16,17] These macrocycles have been subsequently used in the isolation of Cu, Pd, and Ni complexes.[8,11,18−20] The syntheses and reactivity of the bis-*N*-isopropyl derivatives of the functionalized triazacyclononane derivatives have been accessed by different routes.[21−23]

It is to this end that we report the synthesis, isolation, characterization, coordination properties, and crystal structures of a range of substituted Mo compounds. We also report an alternative method of preparation of *N*-(hydroxyethyl)-1,4,7-

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(1) Desiraju, G. R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2311.
(2) Zapf, P. J.; LaDuca, J. R. L.; Rarig, J. R. S.; Johnson, K. M.; Zubieta, J. *Inorg. Chem.* **1998**, *37*, 3411−3414.
(3) Bi, L.; Wang, E.; Xu, L.; Huang, R. *Inorg. Chim. Acta* **2000**, *305*, 163−171.
(4) Chaudhuri, P.; Wieghardt, K. *Prog. Inorg. Chem.* **1987**, *35*, 329−436.
(5) Wilson, P. J.; Blake, A. J.; Mountford, P.; Schröder, M. *J. Chem. Soc., Chem. Commun.* **1998**, 1007−1008.
(6) Hajela, S.; Schaefer, W. P.; Bercaw, J. E. *J. Organomet. Chem.* **1997**, *532*, 45−53.
(7) Zhen, H. S.; Wang, C. M.; Hu, Y. H.; Flood, T. C. *Organometallics* **1998**, *17*, 5397−5405.
(8) Tei, L.; Lippolis, V.; Blake, A. J.; Cooke, P. A.; Schroder, M. *J. Chem. Soc., Chem. Commun.* **1998**, 2633−2634.
(9) Wainwright, K. P. *Coord. Chem. Rev.* **1997**, *166*, 35−90.
(10) Weisman, G. R.; Vachon, D. J.; Johnson, V. B.; Gronbeck, D. A. *J. Chem. Soc., Chem. Commun.* **1987**, 886.
(11) Blake, A. J.; Fallis, I. A.; Parsons, S.; Ross, S. A.; Schroder, M. *J. Chem. Soc., Dalton Trans.* **1996**, 525−532.
(12) Blake, A. J.; Fallis, I. A.; Gould, S.; Parsons, S.; Ross, S. A.; Schroder, M. *J. Chem. Soc., Chem. Commun.* **1994**, 2467.
(13) Farrugia, L. J.; Lovatt, P. A.; Peacock, R. D. *Inorg. Chim. Acta* **1996**, *246*, 343−348.
(14) Ellis, D.; Farrugia, L. J.; Peacock, R. D. *Polyhedron* **1999**, *18*, 1229−1234.
(15) Kovacs, Z.; Sherry, A. D. *Tetrahedron Lett.* **1995**, *36*, 9269−9272.
(16) Stockheim, C.; Hoster, L.; Weyhermuller, T.; Wieghardt, K.; Nuber, B. *J. Chem. Soc., Dalton Trans.* **1996**, 4409−4416.
(17) Schulz, D.; Weyhermuller, T.; Wieghardt, K.; Nuber, B. *Inorg. Chim. Acta* **1995**, *240*, 217−229.
(18) Blake, A. J.; Champness, N. R.; Chung, S. S. M.; Li, W. S.; Schroder, M. *J. Chem. Soc., Chem. Commun.* **1997**, 1675−1676.
(19) Blake, A. J.; Fallis, I. A.; Heppeler, A.; Parsons, S.; Ross, S. A.; Schroder, M. *J. Chem. Soc., Dalton Trans.* **1996**, 31−43.
(20) Blake, A. J.; Fallis, I. A.; Gould, R. O.; Parsons, S.; Ross, S. A.; Schröder, M. *J. Chem. Soc., Dalton Trans.* **1996**, 4379−4387.
(21) Mountford, P. Personal communication.
(22) Halfen, J. A.; Young, V. G.; Tolman, W. B. *J. Am. Chem. Soc.* **1996**, *118*, 10920−10921.
(23) Halfen, J. A.; Jazdzewski, B. A.; Mahapatra, S.; Berreau, L. M.; Wilkinson, E. C.; Que, L.; Tolman, W. B. *J. Am. Chem. Soc.* **1997**, *119*, 8217−8227.

10.1021/ic0006854 CCC: $20.00

triazacyclononane, $\mathbf{L^4}$, using a simple protecting group that avoids the use of expensive materials for deprotection or ion exchange as part of the synthetic scheme. This compound had previously been reported[11,24] using two different synthetic routes, with comparable yields. Also of note is the synthesis of a new ligand, *N*-(2-methylpyridyl)-1,4,7-triazacyclononane, $\mathbf{L^5}$.

Experimental Section

General. Standard inert atmosphere techniques were used throughout. Acetonitrile and methylene chloride were distilled from CaH_2. Diethyl ether and THF were distilled from Na/Ph_2CO. NMR solvents were degassed by three freeze−pump−thaw cycles and stored over 4 Å molecular sieves in a drybox, except D_2O. All reagents were purchased in reagent grade and used without further purification. ^1H and ^{13}C NMR spectra were recorded on a Bruker 250 MHz NMR spectrometer. IR spectra were recorded on a Perkin-Elmer 1600 spectrometer. Mass spectrometry was performed by the University of Leeds Mass Spectrometry Service. Elemental analyses were performed by the University of Leeds Microanalytical Services. 1,4,7-Triazacyclononane, its orthoamide derivative, 1,4,7-triazacyclo[5.2.1.0$^{4.10}$]decane and the ligands $\mathbf{L^2}$, $\mathbf{L^3}$,[13] and 2-(2-bromoethoxy)-tetrahydropyran[25] were prepared according to published procedures.

***N*-(Hydroxyethyl)-1,4,7-triazacyclononane, $\mathbf{L^4}$.** A solution of 1,4,7-triazacyclo[5.2.1.0$^{4.10}$]decane, **1** (4.25 g, 0.031 mol), in THF (30 mL) was prepared and cooled to 0 °C. To this was added, dropwise with stirring, a solution of 2-(2-bromoethoxy)-tetrahydropyran (6.51 g, 0.031 mol). The solution was stirred at room temperature for 4 days until precipitation was complete. After this time the THF was removed under reduced pressure. The remaining white solid was taken up in water (50 mL) and heated to reflux for 5 h. The water was then removed under reduced pressure. To the remaining yellow oil was added ethanol (50 mL) and excess potassium hydroxide pellets. The mixture was heated to reflux overnight. After this time the ethanol was removed under reduced pressure. The residue was taken up in the minimum amount of water and extracted into chloroform (10 × 80 mL). The extracts were combined, dried over magnesium sulfate, and filtered. The chloroform was removed under reduced pressure to leave the tetrahydropyranal-protected 1-hydroxyethyl triazacyclononane as a viscous yellow oil. A solution of this oil (3.01 g, 0.012 mol) in ethanol (100 mL) was prepared and cooled to 0 °C. Concentrated hydrochloric acid solution was added dropwise with stirring, producing an off-white precipitate. The acid was added until precipitation was complete. The suspension was stirred at room temperature overnight. After this time the precipitate was filtered off and washed with ethanol. The NMR data for this precipitate are similar to that reported for the dihydrobromide salt of the same compound.[24] ^1H NMR δ ($CDCl_3$): 2.83 (t, $J = 5.6$ Hz, 2H, NCH_2CH_2OH), 3.00 (m, 4H), 3.29 (m, 4H), 3.56 (m, 4H), (NCH_2 ring), and 3.72 (t, $J = 5.\ 6$ Hz, 2H, NCH_2CH_2OH). ^{13}C NMR δ ($CDCl_3$): 43.0, 44.2, 48.4, (NCH_2 ring), 56.5 (NCH_2CH_2OH), and 58.5 (NCH_2CH_2OH)].

The solid was dissolved in the minimum amount of water (10 mL), and the pH was raised to 14 by the addition of potassium hydroxide pellets. The water layer was extracted into chloroform (10 × 50 mL). The extracts were combined, dried over magnesium sulfate, and filtered. The chloroform was removed under reduced pressure to leave the title compound as a viscous oil (1.44 g, 69%). Analytical data were consistent with reported data.[11]

***N*-(2-Methylpyridyl)-1,4,7-triazacyclononane, $\mathbf{L^5}$.** To a solution of **1** (3.93 g, 0.0280 mol) in THF (20 mL), cooled to 0 °C, was added dropwise, with stirring, a solution of 2-chloromethylpyridine (3.70 g, 0.0266 mol) in THF (10 mL). The resultant solution was stirred at room temperature for 7 days. After this time the THF was removed under reduced pressure, leaving a red-brown solid. This solid was dissolved in water (20 mL), and the solution was refluxed for 5 h. The water was removed under reduced pressure, and the resultant red-brown oil was taken up in ethanol. Excess potassium hydroxide pellets were added, and the resultant suspension was heated to reflux overnight. The ethanol was removed under reduced pressure, and the remaining oily solid was dissolved in the minimum amount of water. The water solution was extracted with chloroform (6 × 50 mL). The chloroform extracts were combined, dried over magnesium sulfate, and filtered. The chloroform was removed under reduced pressure to give the title compound as a yellow oil (5.23 g, 0.0241 mol, 91%). MS (EI) *m*/*z* M + 2: 220. ^1H NMR δ ($CDCl_3$): 2.55 (m, 8H, NCH_2 ring), 2.64 (m, 4H, NCH_2 ring), 2.71 (s, br, 2H, NH), 3.74 (s, 2H, NCH_2-py), 7.00 (m, 1H, py), 7.31 (m, 1H, py), 7.47 (m, 1H, py). and 8.37 (m, 1H, py). ^{13}C NMR δ ($CDCl_3$): 46.8, 46.9, 52.6 (NCH_2 ring), 62.6 (NCH_2-py), 121.9 (py), 123.0 (py), 136.2 (py), 148.8 (py), 159.9 (py). Found: C, 64.9; H, 9.3; N, 25.6. Anal. Calcd for $C_{12}N_3O_3H_{19}Mo$: C, 65.4; H, 9.2; N, 25.4.

***N*-(3-Prop-1-ene)-1,4,7-triazacyclononane Molybdenum Tricarbonyl, 2.** To a suspension of molybdenum hexacarbonyl (0.700 g, 0.0027 mol) in diglyme (25 mL) was added a solution of $\mathbf{L^2}$ (0.467 g, 0.0027 mol) in diglyme (25 mL). The suspension was heated to reflux for 4 h. After this time a yellow precipitate was observed to have developed in the flask. The suspension was allowed to cool and the diglyme filtered off. The precipitate was washed with diethyl ether and dried to afford the product as an orange powder (0.60 g, 62%). KBr disk, ν cm^{-1}: 1893(s) 1766(s, broad). MS (EI) *m*/*z* M + 2: 351. ^1H NMR δ (DMSO-d_6): 2.5−2.8 (m, 10H, NCH_2 ring), 2.85−3.05 (m, 2H, NCH_2 ring), 3.61 (d, 2H, $J = 7.5$ Hz, NCH_2CHCH_2), 5.2−5.3 (m, 2H), 5.4−5.6 (s, br, 2H, NH), and 6.1−6.4 (m, 1H, NCH_2CHCH_2). ^{13}C NMR δ (DMSO-d_6): 47.2, 48.3, 53.2 (NCH_2 ring), 67.0 (NCH_2CHCH_2), 121.5 (NCH_2CHCH_2), and 133.9 (NCH_2CHCH_2), 229.1, 231.0, CO. Found: C, 40.8; H, 5.6; N, 12.4. Anal. Calcd for $C_{12}N_3O_3H_{19}Mo$: C, 41.3; H, 5.5; N, 12.0.

***N*-(4-But-1-ene)-1,4,7-triazacyclononane Molybdenum Tricarbonyl, 3.** To a suspension of molybdenum hexacarbonyl (1.92 g, 0.0073 mol) in diglyme (60 mL) was added a solution of $\mathbf{L^3}$ (1.48 g, 0.0080 mol) in diglyme (40 mL). The suspension was heated to reflux for 4 h. After this time the reaction was allowed to cool and the diglyme removed under reduced pressure. The resulting brown powder was washed with diethyl ether and dried to leave the product as an orange-brown powder (1.55 g, 59%). IR KBr disk ν cm^{-1}: 1892 (s), 1767 (s, br). MS EI, M + 2: 365. ^1H NMR δ (DMSO-d_6): 2.5−2.6 (m, 12H, NCH_2 ring), 2.73 (m, 2H, NCH_2 arm), 2.9 (m, 2H, NCH_2CH_2 arm), 5.0 (m, 2H, NCH_2CHCH_2 arm), 5.4 (s, br, 2H, NH), and 5.7 (m, 1H, NCH_2CHCH_2 arm). ^{13}C NMR δ (DMSO-d_6): 30.3 ($NCH_2CH_2CHCH_2$), 47.2, 48.5, 53.3 (NCH_2 ring), 63.3 ($NCH_2CH_2CHCH_2$), 116.8 ($NCH_2CH_2CHCH_2$), 136.4 ($NCH_2CH_2CHCH_2$), 229.1, 231.0 CO.

1,4,7-Triazacyclononane Trioxide, 4. To a suspension of molybdenum trioxide (0.995 g, 0.0069 mol) in water (15 mL) was added a solution of 1,4,7-triazacyclononane (0.893 g, 0.0069 mol) in water (10 mL). The suspension was heated to reflux for 4 h. After this time the suspension was allowed to cool to room temperature and was filtered. The water was removed from the filtrate under reduced pressure to leave the title compound as a white powder (0.630 g, 33%). MS (FAB) M + 2: 276. ^1H NMR δ (D_2O): 2.9 (m, 6H, NCH_2 ring), 3.2 (m, 6H, NCH_2 ring). ^{13}C NMR δ (D_2O): 47.0 (NCH_2 ring). Found: C, 26.4; H, 5.5; N, 15.4. Anal. Calcd for $C_6H_{15}N_3O_3Mo$: C, 26.4; H, 5.8; N, 15.4.

***N*-(3-Prop-1-ene)-1,4,7-triazacyclononane Molybdenum Trioxide, 5.** To a suspension of molybdenum trioxide (0.148 g, 0.0010 mol) in water (10 mL) was added a solution of $\mathbf{L^2}$ (0.189 g, 0.0011 mol) in water (5 mL). The suspension was refluxed for 24 h. After this time the suspension was allowed to cool to room temperature and was filtered. The water was removed from the filtrate under reduced pressure to leave the title compound as a white powder (0.209 g, 65%). ^1H NMR δ (D_2O): 2.9 (m, 8H, NCH_2 ring), 3.0 (m, 4H, NCH_2 ring), 3.9 (d, $J = 7.1$ Hz, 2H, NCH_2CHCH_2), 5.4 (m, 2H, NCH_2CHCH_2), and 6.1 (m, 1H, NCH_2CHCH_2). ^{13}C NMR δ (D_2O): 46.5, 47.0, 52.3 (NCH_2 ring), 63.0, (NCH_2CHCH_2), 123.4 (NCH_2CHCH_2), and 130.7(NCH_2CHCH_2). Found: C, 32.6; H, 6.4; N, 12.8. Anal. Calcd for $C_9H_{19}N_3O_3Mo{\cdot}H_2O$: C, 32.6; H, 6.4; N, 12.7.

***N*-(4-But-1-ene)-1,4,7-triazacyclononane Molybdenum Trioxide, 6.** To a suspension of molybdenum trioxide (0.504 g, 0.0035 mol) in water (15 mL) was added a solution of $\mathbf{L^3}$ (0.585 g, 0.0032 mol) in

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(24) Creaser, S. P.; Lincoln, S. F.; Pyke, S. M. *J. Chem. Soc., Perkin Trans. 1* **1999**, 1211−1213.

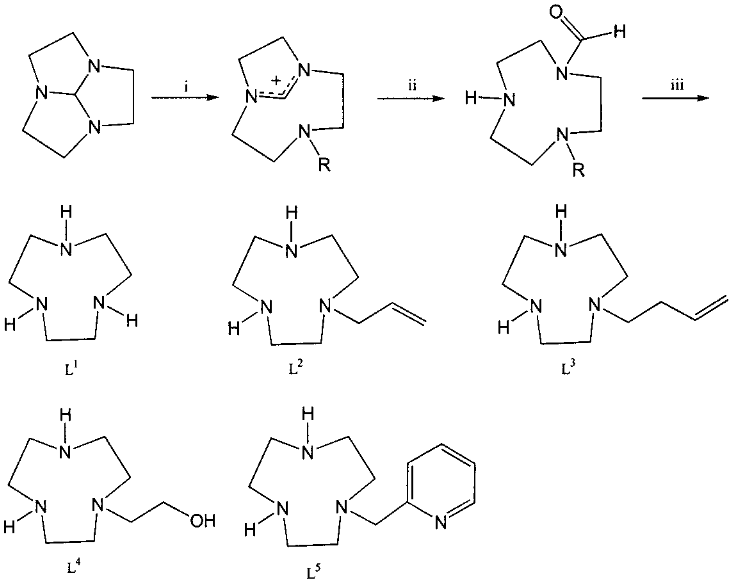
(25) Parham, W. E.; Anderson, E. L. *J. Am. Chem. Soc.* **1948**, *70*, 4187.

Table 1. Crystallographic Details for **4**−**8**

	4	**5**	**6**	**7**	**8**
chemical formula	$C_6H_{15}MoN_3O_3{\cdot}3H_2O$	$C_9H_{19}MoN_3O_3.H_2O$	$C_{10}H_{21}MoN_3O_5$	$C_8H_{19}MoN_3O_4{\cdot}H_2O$	$C_{12}H_{26}MoN_4O_6$
fw	327.20	331.23	359.24	335.22	418.31
a, Å	7.7224(2)	7.52140(10)	7.5207(2)	7.4714(2)	7.0029(2)
b, Å	14.7860(3)	12.0922(3)	11.2913(2)	12.5388(3)	14.9415(6)
c, Å	10.7979(2)	14.3460(4)	17.2166(5)	13.0858(3)	17.2168(4)
α, deg	90	90	90	90	72.3960(18)
β, deg	91.2790(12)	90	90	90	82.723(2)
γ, deg	90	90	90	90	89.190(2)
vol, Å^3	1232.63(5)	1304.77(5)	1462.01(6)	1225.91(5)	1702.71(9)
Z	4	4	4	4	4
space group	$P2_1/c$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P\bar{1}$
temp, °C	−123(2)	−93(2)	−123(2)	−123(2)	−123(2)
λ, Å	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
$\rho_{(calcd)}$, g/cm^3	1.763	1.686	1.632	1.816	1.632
abs coeff, mm^{-1}	1.083	1.013	0.916	1.085	0.805
R1 (all data)[a]	0.0590	0.0207	0.0323	0.0258	0.0438
wR2[b]	0.1573	0.0557	0.0849	0.0700	0.1119

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

Scheme 1. Reagents and Conditions[a]



[a] i, RX/THF; ii, H_2O; iii, KOH/EtOH.

water (25 mL). The suspension was heated to reflux for 2 h. After this time the suspension was allowed to cool to room temperature and was filtered. The water was removed from the filtrate under reduced pressure to leave the title compound as a white powder (0.649 g, 62%). ^{1}H NMR *δ* (D_2O): 2.5 (m, 2H, (NC*H*$_2$CH$_2$CHCH$_2$), 2.86 (m, 4H), 3.0 (m, 4H), 3.2 (m, 4H), (NC*H*$_2$ ring), 3.4 (m, 2H, (NCH$_2$C*H*$_2$CHCH$_2$), 5.1 (m, 2H, (NCH$_2$CH$_2$CHC*H*$_2$), 5.9 (m, 1H, (NCH$_2$CH$_2$C*H*CH$_2$). ^{13}C NMR *δ* (D_2O): 28.0 (N*C*H$_2$CH$_2$CHCH$_2$), 46.6, 46.9, 52.2 (N*C*H$_2$ ring), 59.4 (NCH$_2$*C*H$_2$CHCH$_2$), 117.1 (NCH$_2$CH$_2$CH*C*H$_2$), and 136.1 (NCH$_2$-CH$_2$*C*HCH$_2$). Found: C, 36.4; H, 6.6; N, 13.0. Anal. Calcd for $C_{10}H_{21}N_3O_3Mo$: C, 36.7; H, 6.5; N, 12.8.

***N*-(Hydroxyethyl)-1,4,7-triazacyclononane Molybdenum Trioxide, 7.** To a suspension of molybdenum trioxide (0.08 g, 0.00056 mol) in water (15 mL) was added a solution of **L**^{4} (0.107 g, 0.0006 mol) in water (5 mL). The suspension was heated to reflux for 4 h. After this time the suspension was allowed to cool to room temperature and was filtered. The water was removed from the filtrate under reduced pressure to leave the title compound as a white powder (0.056 g, 33%). ^{1}H NMR (D_2O): 2.9 (m, 4H), 3.1 (m, 4H), 3.3 (m, 4H), (NC*H*$_2$ ring), 3.3 (t, *J* = 7.5 Hz, 2H, NC*H*$_2$CH$_2$OH), and 4.0 (t, *J* = 7.5 Hz, 2H, NCH$_2$C*H*$_2$-OH). ^{13}C NMR (D_2O): 46.6, 46.9, 52.7, (N*C*H$_2$ ring), 57.7 (N*C*H$_2$-CH$_2$OH), and 61.0 (NCH$_2$*C*H$_2$OH). Found: C, 28.3; H, 6.3; N, 12.0. Anal. Calcd for $C_8H_{19}N_3O_4Mo{\cdot}H_2O$: C, 28.7; H, 6.3; N, 12.5.

***N*-(2-Methylpyridyl)-1,4,7-triazacyclononane Molybdenum Trioxide, 8.** To a suspension of molybdenum trioxide (0.257 g, 0.0018 mol) in water (15 mL) was added a solution of **L**^{5} (0.481 g, 0.0022 mol) in water (10 mL). The suspension was heated to reflux for 3 h. After this time the suspension was allowed to cool to room temperature and was filtered. The water was removed from the filtrate under reduced pressure to leave the title compound as a white powder (0.546 g, 84%). ^{1}H NMR *δ* (D_2O): 2.85 (m, 6H, NCH$_2$ ring), 3.3 (m, 6H, NC*H*$_2$ ring), 4.57 (s, 2H, NC*H*$_2$C$_5$H$_4$N), 7.42 (t of d, 1H, NCH$_2$C$_5$*H*$_4$N), 7.55 (d, *J* = 7.5 Hz, 1H, NCH$_2$C$_5$*H*$_4$N), 7.89 (t of d, *J* = 7.7 Hz, 1H, NCH$_2$C$_5$*H*$_4$N), and 8.52 (d, 1H, py, NCH$_2$C$_5$H$_4$N). ^{13}C NMR *δ* (D_2O): 46.4, 46.9, 51.6 (N*C*H$_2$ ring), 63.3 (N*C*H$_2$C$_5$H$_4$N), 124.6, 127.7, 138.5, 149.0 (*C*H of NCH$_2$C$_5$H$_4$N), 153.1 (*C* of NCH$_2$C$_5$H$_4$N).

Crystallographic Data Collection and Structure Analysis. Data for compounds **4**−**8** were collected on a Nonius KappaCCD area-detector diffractometer using graphite monochromated Mo Kα radiation (*λ* = 0.710 73 Å) using 1.0° *ϕ*-rotation frames. Pertinent crystallographic details are given in Table 1.

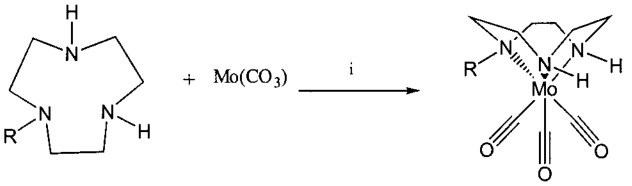
The structures of all four compounds were solved by direct methods using SHELXS 86. Refinement, by full-matrix least squares on F^2 using SHELXL 97, was similar for all five compounds except for compound **8**, which was found to be disordered. The disorder was modeled over two sites using appropriate thermal and positional restraints. Non-hydrogen atoms were constrained to idealized positions using a riding model (with free rotation for methyl groups) with the exception of the hydrogen atoms of water molecules in **4**, **5**, **7**, and **8**, which were all located on Fourier difference syntheses and freely refined with isotropic

Table 2. Bond Lengths and Angles for **4**−**8**[a]

	4	**5**	**6**	**7**	**8** molecule 1	**8** molecule 2
Mo(1)−N(1)	2.334(5)	2.396(2)	2.386(2)	2.397(2)	2.412(2)	2.430(2)
Mo(1)−N(2)	2.305(4)	2.320(2)	2.317(3)	2.320(2)	2.303(3)	2.274(3)
Mo(1)−N(3)	2.306(5)	2.301(2)	2.301(3)	2.292(2)	2.306(3)	2.290(3)
N(2)−Mo(1)−N(1)	71.7(2)	72.71(6)	73.02(10)	72.85(8)	72.27(9)	72.48(10)
N(3)−Mo(1)−N(2)	72.2(2)	72.17(7)	72.19(11)	71.88(9)	72.12(9)	72.25(10)
N(3)−Mo(1)−N(1)	71.9(2)	72.61(6)	72.82(9)	73.00(8)	72.42(8)	72.76(9)

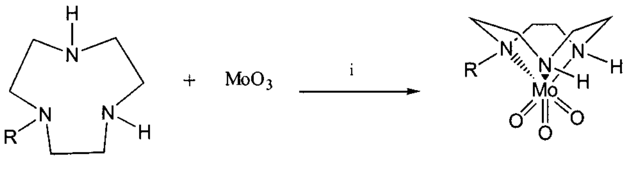
[a] There are two molecules of **8** per asymmetric unit, and the values are included.

Scheme 2. Formation of **2** (R = $CH_2CH{=}CH_2$) and **3** (R = $CH_2CH_2CH{=}CH_2$) from $Mo(CO)_6$ and $\mathbf{L^2}$ and $\mathbf{L^3}$, Respectively[a]



[a] Reagents and conditions: i, diglyme/reflux

Scheme 3. Formation of **4** (R = H), **5** (R = $CH_2CH{=}CH_2$), **6** (R = $CH_2CH_2CH{=}CH_2$), **7** (R = CH_2CH_2OH), and **8** (R = $CH_2C_5H_5N$) from MoO_3 and $\mathbf{L^1}$, $\mathbf{L^2}$, $\mathbf{L^3}$, $\mathbf{L^4}$, and $\mathbf{L^5}$, Respectively[a]



[a] Reagents and conditions: i, H_2O/reflux.

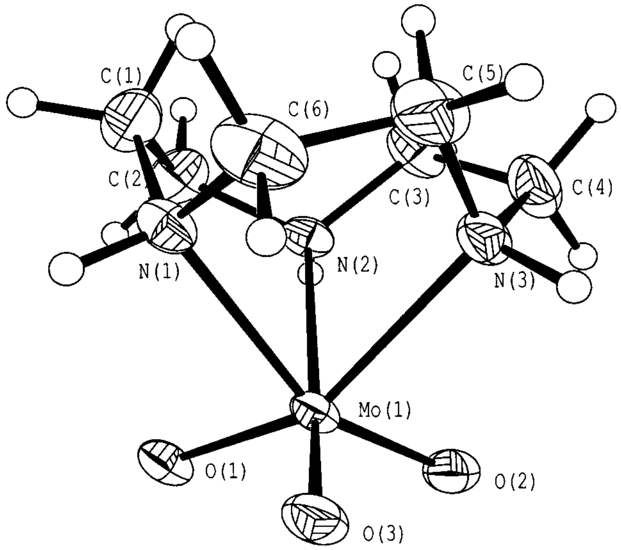


Figure 1. View of **4** without hydrogen-bonding interactions with 40% probability ellipsoids.

displacement parameters. The hydrogen atoms of the water molecule in compound **6** were not located.

Results and Discussion

Entry into functionalization of the triazacyclononane moiety was provided by the reaction of orthoamide **1** with an alkyl halide.[20] The general synthetic route is outlined in Scheme 1.

Table 3. Hydrogen-Bonded Distances (Å) and Angles (deg)[a]

D−H···A	D−H	H···A	D···A	bond angle
4				
N1−H1···O3W	0.93	2.47	3.395(7)	171.6
N2−H2···O1	0.93	2.03	2.903(6)	156.3
N3−H3···O3	0.93	1.99	2.889(6)	162.3
O1W−H1AW···O3W	0.89(11)	1.84(11)	2.727(8)	179(10)
O1W−H1BW···O3	0.71(11)	2.19(11)	2.748(7)	137(11)
O2W−H2AW···O1W	0.976(5)	1.733(5)	2.667(7)	158.8(4)
O2W−H2BW···O1	0.940(5)	1.794(4)	2.718(6)	167.1(3)
5				
N2−H2···O3	0.93	1.98	2.893(2)	166.2
N3−H3···O3	0.93	1.93	2.836(2)	163.5
O1W−H2W···O2	0.79(3)	2.02(3)	2.785(3)	163(3)
O1W−H1W···O1	0.73(3)	2.09(3)	2.818(3)	169(3)
7				
N2−H2···O3	0.93	1.96	2.876(3)	169.3
N3−H3···O3	0.93	1.95	2.859(3)	165.8
O8−H8···O1W	0.84	1.95	2.732(4)	153.7
O1W−H1AW···O1	0.89(4)	1.86(4)	2.735(4)	168(3)
O1W−H1BW···O2	0.52(4)	2.25(4)	2.763(4)	167(7)
8				
N2−H2···O4	0.93	2.00	2.889(3)	159.0
N3−H3···O2	0.93	2.20	3.006(3)	144.6
N3−H3···O1	0.93	2.43	3.219(4)	142.4
O1W−H1WA···O4W	0.90(5)	1.94(5)	2.827(4)	170(4)
O2W−H2WB···O5	0.78(5)	1.96(5)	2.727(4)	166(5)
O2W−H2WB···O3	0.72(5)	2.07(5)	2.769(4)	164(5)
O3W−H3WA···O2W	0.86(5)	1.94(5)	2.736(5)	152(4)
O3W−H3WB···O1W	0.70(5)	2.06(5)	2.763(5)	174(6)
O4W−H4WA···N13	0.75(4)	2.05(5)	2.792(4)	177(5)
O4W−H4WB···O3W	0.76(5)	1.96(5)	2.721(5)	175(5)
O5W−H5WA···O6W	0.98(5)	1.91(5)	2.810(4)	152(4)
O5W−H5WB···N26	0.74(4)	2.35(4)	3.076(4)	167(4)
O6W−H6WA···O6	0.82(5)	1.94(5)	2.758(4)	171(5)
O6W−H6WB···O2	0.70(5)	2.14(5)	2.811(4)	164(5)

[a] Standard uncertainties are included in parentheses for values that do not involve fixed and riding hydrogen atoms. OW and HW refer to the hydrogen and oxygen atoms of water molecules. D and A refer to donor and acceptor, respectively.

The preparation of the ligands $\mathbf{L^2}$ and $\mathbf{L^3}$ was achieved through published methods.[13] Compound $\mathbf{L^4}$ was synthesized by using the tetrahydropyranyl-protected version of 2-bromoethanol. Deprotection was achieved by reaction of the protected form with ethanolic hydrochloric acid in 69% yield.

The compound $\mathbf{L^5}$ was synthesized in 91% yield through the reaction of 2-chloromethylpyridine and **1**. The compound was isolated as a yellow oil and was characterized by ^1H and ^{13}C NMR spectroscopy, mass spectrometry, and microanalysis. Synthesis of a substituted pyridyl analogue has been reported,[26] as have the bis[27] and tris *N*-functionalized pyridyl derivatives.[28] Synthesis of *N*-(2-methylpyridyl)-*N′*,*N″*-(diisopropyl)-1,4,7-tri-

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(26) Koikawa, M.; Jensen, K. B.; Matsushima, H.; Tokii, T.; Toftlund, H. *J. Chem. Soc., Dalton Trans.* **1998**, 1085−1086.

(27) McLachlan, G. A.; Fallon, G. D.; Martin, R. L.; Spiccia, L. *Inorg. Chem.* **1995**, *34*, 254−261.

(28) Wieghardt, K.; Schoffman, E.; Nuber, B.; Weiss, J. *Inorg. Chem.* **1986**, *25*, 4877−4883.

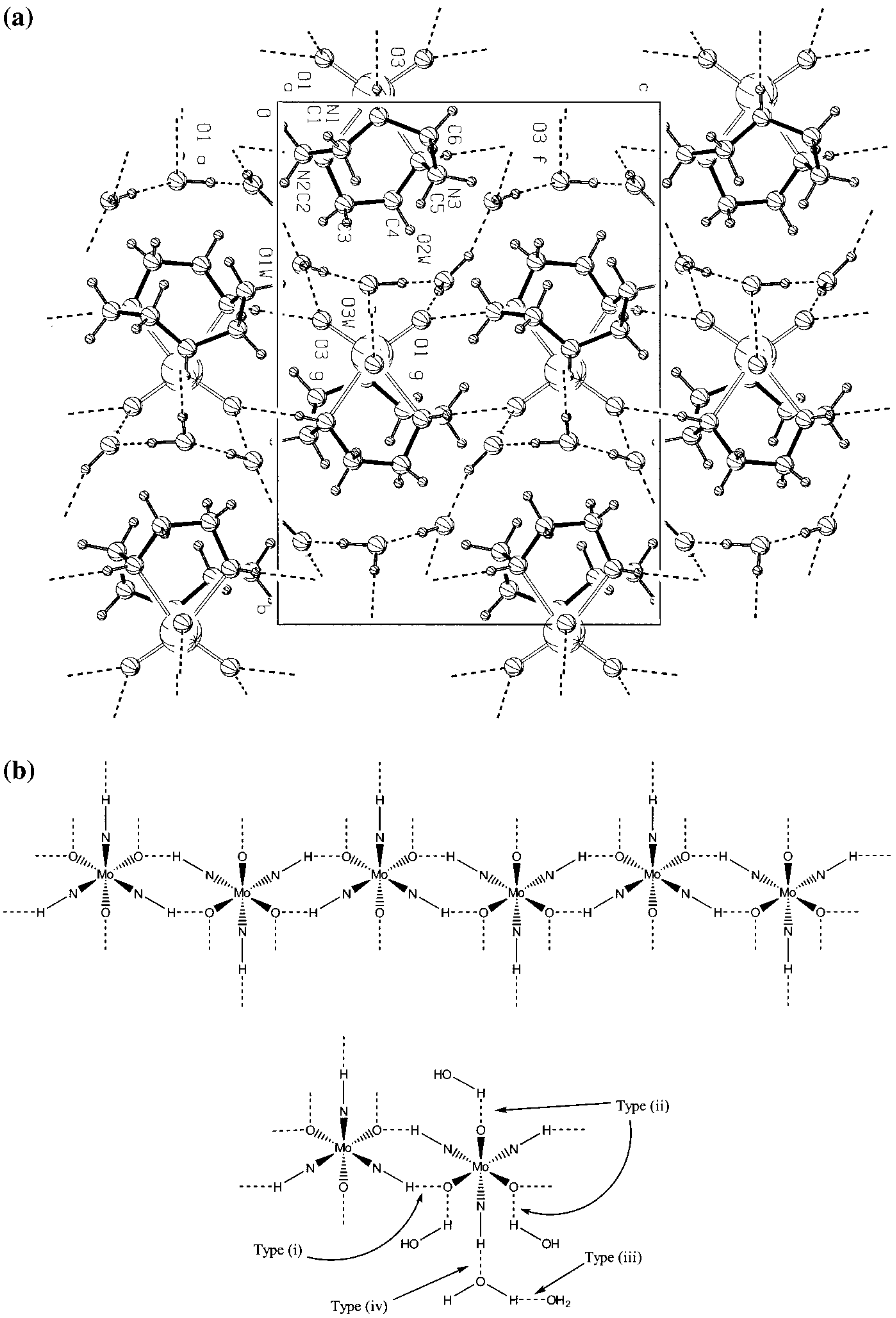

Figure 2. (a) Crystal packing pattern in **4** viewed along the crystallographic *a* axis showing the network of $LMoO_3$ molecules linked together by H_2O molecules in a 3-D network. (b) Schematic representation of **4**, which illustrates the crystal packing and the different types of H bonds. The $-CH_2CH_2-$ units of the macrocyclic ring are omitted for clarity.

azacyclononane and Cu derivatives has been reported by Tolman et al.[22,23]

Anchoring the functionalized triazacyclononane molecules to a transition metal center in both high oxidation state and low oxidation states was achieved by using the starting materials of MoO_3 and $Mo(CO)_6$, respectively. Following the method of Wieghardt et. al.,[29] refluxing $Mo(CO)_6$ with 1 equiv of the appropriate ligand yields **2** and **3** in 62% and 58% yield, respectively, as shown in Scheme 2.

The compounds are moisture-sensitive orange powders and have been characterized by ^1H and ^{13}C NMR spectroscopy;

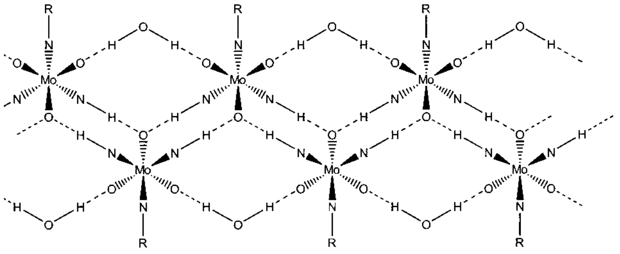

Figure 3. Schematic representation of the regular motif that is common to all the cases of monosubstitution of the macrocyclic ring. The $-CH_2$-CH_2- units of the macrocyclic ring are omitted for clarity.

while **2** is analytically pure, successive attempts at microanalysis of **3** proved unsuccessful. The infrared spectra of both complexes

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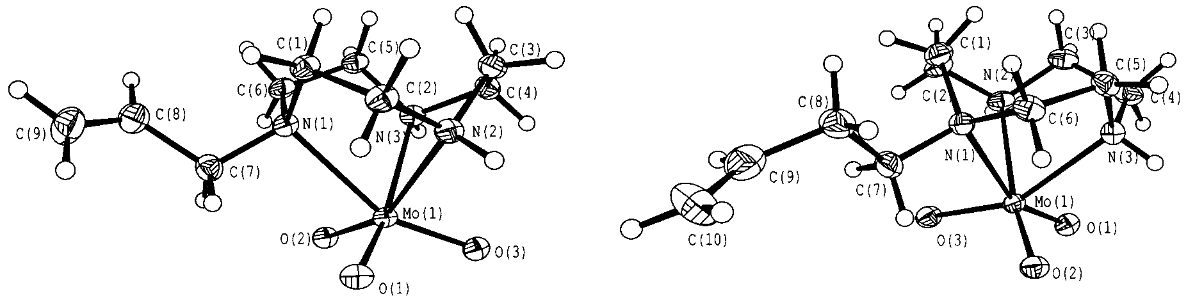
(29) Chauduri, P.; Wieghardt, K.; Tsai, Y.-H.; Krüger, C. *Inorg. Chem.* **1984**, *23*, 427−432.



5 **6**

Figure 4. Views of **5** and **6** without hydrogen bonding with 40% probability ellipsoids.

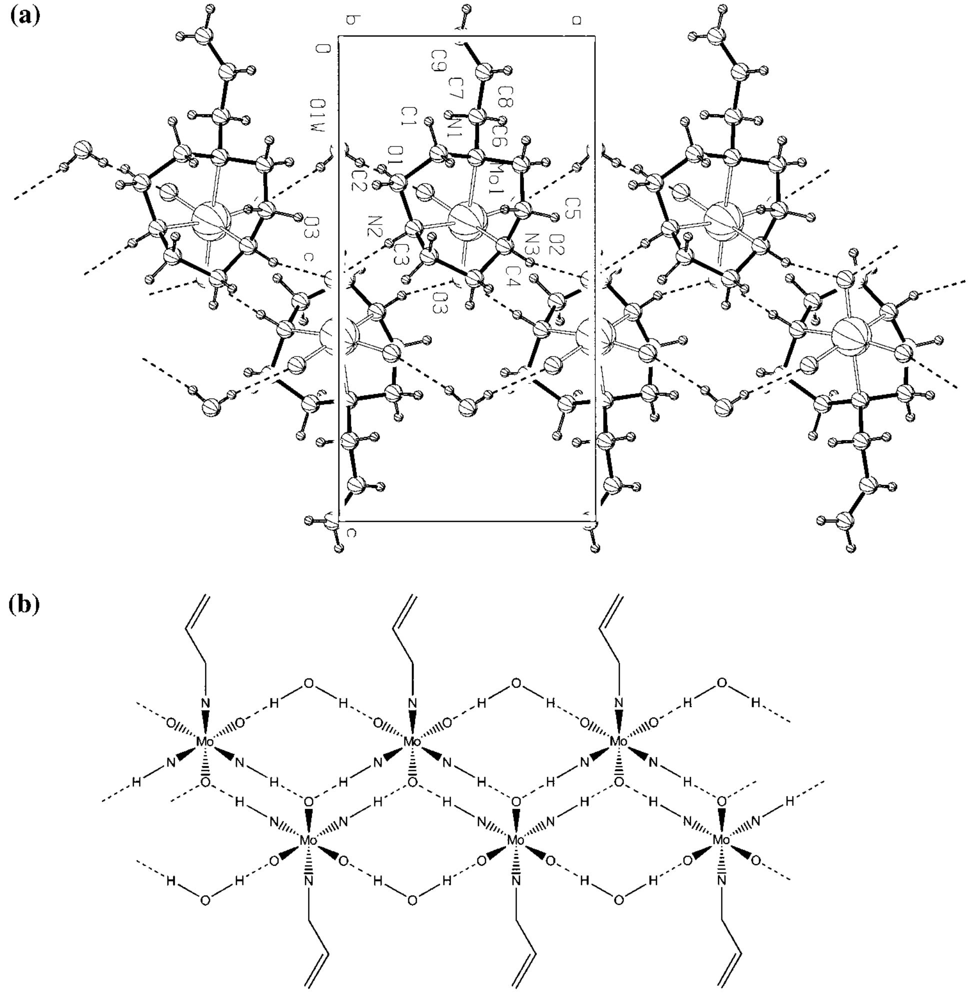


Figure 5. (a) Crystal packing pattern in **5** viewed along the crystallographic *b* axis showing the network of $\mathbf{L}^2MoO_3$ molecules in a chain linked together by H_2O molecules. There are no hydrogen-bonding interactions between the chains. (b) Schematic representation of **5**. The $-CH_2CH_2-$ units of the macrocyclic ring are omitted for clarity.

have been recorded. The carbonyl signals (**2**, $\nu_{(CO)} = 1893$ and $1766\ cm^{-1}$; **3**, $\nu_{(CO)} = 1892$ and $1767\ cm^{-1}$) confirm that both complexes are of "piano stool" type structures. They are comparable with $L^1Mo(CO)_3$, $\nu_{(CO)} = 1850$ and $1730\ cm^{-1}$.[29]

Refluxing the ligands with MoO_3 in water produces complexes of the general formula $LMoO_3$ in high yield, as shown in Scheme 3. Also synthesized was the unsubstituted triazacyclononane derivative **4**, which, although previously reported, was characterized only by microanalysis.[30] These air- and water-stable complexes are recrystallized from water to produce crystallographic quality crystals. Characterization of the analytically pure materials **4**−**8** was provided by ^1H and ^{13}C NMR spectroscopy, and the X-ray structures of each compound have been determined.

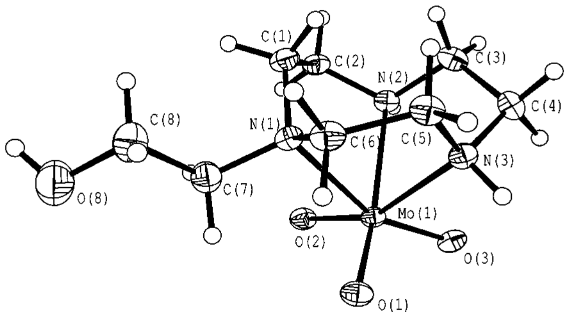


Figure 6. View of **7** without hydrogen bonding with 40% probability ellipsoids.

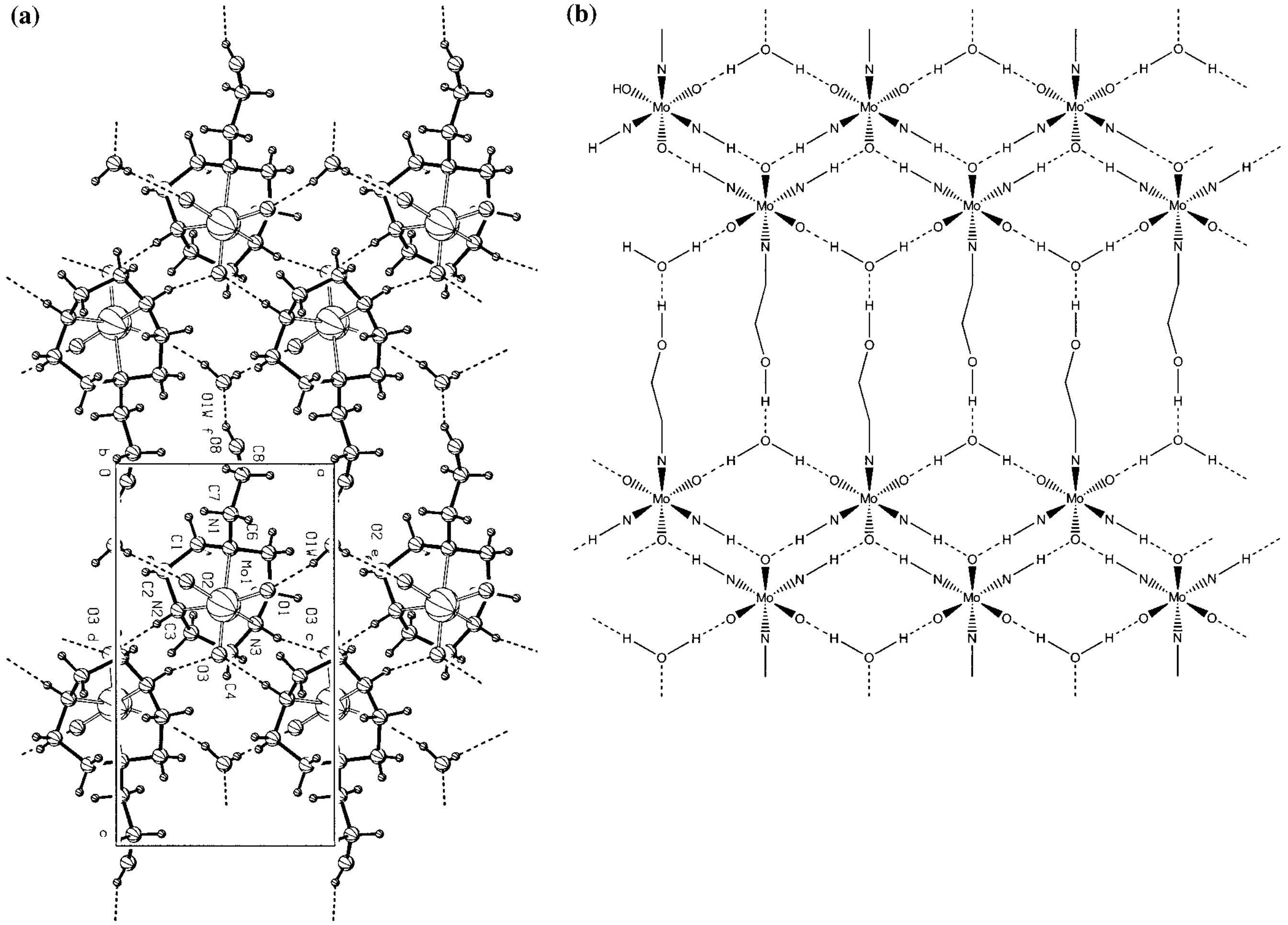


Figure 7. (a) Crystal packing pattern in **7** viewed along the crystallographic *x* axis showing the network of L^4MoO_3 molecules linked together by H_2O molecules to form discrete layers that have no interlayer hydrogen bonding. (b) Schematic representation of **7**. The $-CH_2CH_2-$ units of the macrocyclic ring are omitted for clarity.

Bond lengths and angles for complexes **4**−**8** are given in Table 2. By comparison of the crystal structure data for the substituted complexes with the unsubstituted complex, it can be seen that the distance between the secondary amine nitrogen atoms and the metal center remains unchanged. However, upon substitution, there is an increase in the distance between the substituted nitrogen atom and the Mo center. In all of the crystal lattices, the individual molecular units are held together by a complex and intricate pattern of hydrogen bonds to water molecules. The relevant hydrogen-bonding distances and angles are given in Table 3.

The crystal structure of **4** is shown in Figure 1, which shows a “piano-stool-like” Mo trioxide structure containing a triazacyclononane ring. From the packing diagram of **4** (Figure 2a), it can be seen that there are chains of L^1MoO_3 molecules linked to each other through hydrogen bonds. Each molecule links to the next using one M═O unit and one N−H unit. This pattern involves two of the M═O units and two of the N−H units of each molecule, leaving one of each unit that is not involved in the direct metal complex−metal complex hydrogen bond linkages. These remaining sites are used to secure a complex pattern of water molecules that bind the single chains into a complex 3-D lattice. The $LMoO_3$ fragments are linked together by several different types of hydrogen bonds using three water molecules per $LMoO_3$ unit (illustrated in Figure 2b, with bond lengths and angles contained in Table 2): type i N−H···O═Mo, which occurs between one of the amino hydrogens from the triazacyclononane moiety and one of the oxides attached to a different Mo center [N2−H2···O1Mo = 2.903(6) Å and N3−H3···O3Mo = 2.889(6) Å]; type ii HO−H···O═Mo [O1W−H1BW···O3═Mo = 2.748(7) Å, O2W−H2BW···O1═Mo = 2.718(6) Å and angles of 137(11)° and 167.1(3)° respectively]; type iii HO−H···OH_2 [bond lengths of O2W−H2AW···O1W = 2.667(7) Å, O1W−H1AW···O3W = 2.727(8) Å and angles of 158.8(4)° and 179(10)°, respectively]; type iv N−H···OH_2, which has a N1−H1···OW3 bond length of 3.395(3) Å]. Types ii and iii hydrogen bonds exhibit similar bond lengths but quite different bond angles; this can be explained by the O atom in one water molecule H_2O(W3) being hydrogen-bonded to an N−H and an M═O unit, whereas the other two water molecules are bound to each other and M═O. This means that the water molecule, H_2O(W3), is using both lone pairs of electrons of the oxygen atom and both hydrogens for hydrogen bonding,

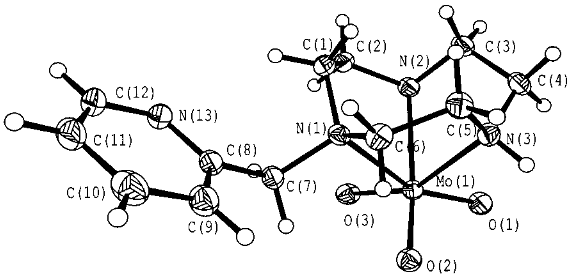


Figure 8. View of one of the molecules from the asymmetric unit of **8** without hydrogen bonding with 40% probability ellipsoids.

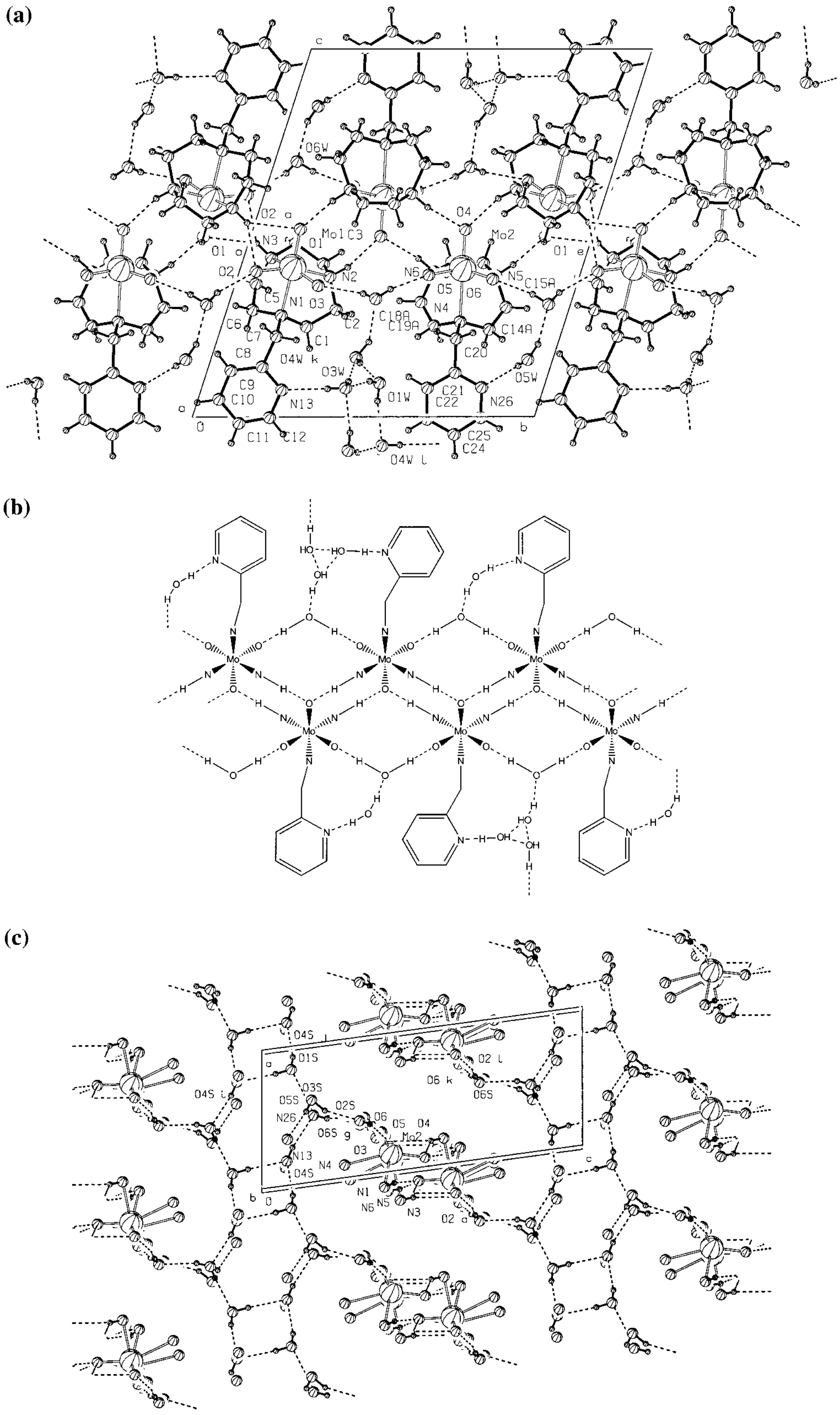


Figure 9. (a) Crystal packing pattern in **8** viewed along the crystallographic *b* axis where the carbon/hydrogen skeleton of the ligand is removed. (b) Crystal packing pattern in **8** viewed along the *a* axis. The two different types of water chains linking the pyridine arm with the O=Mo can be seen. (c) Schematic representation of **7**. The $-CH_2CH_2-$ units of the macrocyclic ring are omitted for clarity.

whereas the other two water molecules are using one lone pair from the oxygen and both hydrogens.

Upon monosubstitution of the triazacyclononane ring, the packing produced is simplified dramatically. A regular motif develops that is common to all the cases of monosubstitution studied and is represented schematically in Figure 3. This is a different chain motif from that of the unsubstituted case. The ring was substituted with three different types of pendant arm, and in each case there was no interaction between the arm and the metal center.

Monosubstitution of one of the nitrogen atoms with 3-propenyl or 4-butenyl groups gives $\mathbf{L^2}MoO_3$, **5**, and $\mathbf{L^3}MoO_3$, **6**, respectively, the crystal structures of which are shown in Figure 4. This creates a system where one of the N−H groups is replaced with a hydrophobic group, which is unable to take part in any hydrogen bonding. The packing diagram for **5** (Figure 5a) shows that in the solid state, chains of $\mathbf{L^2}MoO_3$ units are linked together by the hydrogen bonds between the Mo═O unit of one molecule and the N−H bonds of two adjacent molecules; this is illustrated schematically in Figure 5b. The remaining Mo═O units are linked to the adjacent $\mathbf{L^2}MoO_3$ units by hydrogen bonding through the H atoms of different water molecules. Only one water molecule per molecule of $LMoO_3$ is required for crystallization. The oxygen atom of the water molecule is prevented from taking part in hydrogen-bonding interactions in the crystal lattice of this compound by the hydrophobic pendant arm.

Thus, there are only two types of hydrogen bonding associated with **5**: type i N−H···O═Mo, which has values of N2−H2···O3Mo = 2.893(2) Å and N3−H3···O3Mo = 2.836(2) Å and type ii HO−H···O═Mo, which has similar bond lengths of O1W−H2W···O2 = 2.785(3) Å, O1W−H1W···O1═Mo = 2.818(3) Å. It is not possible to fully evaluate the hydrogen bonding in **6** because the H atoms of the water molecules were not located in the difference map from the crystallographic data; however, the position of the water molecules indicates that the same type of hydrogen bonding occurs.

Another variable can be introduced that can have an effect on crystal packing. This is achieved when one of the N−H units is substituted with a pendant ethanol unit to produce compound **7**, shown in Figure 6. This provides an arm that has a group capable of taking part in H-bond interactions, although no interaction is seen between the arm and an M═O unit. The crystal packing situation is shown in Figure 7a and represented schematically in Figure 7b. It is similar to that exhibited by compound **5**/**6**, in that the same regular chain motif is present; however, in this case, the ethanol group links the chains together into a sheet. The chains are linked through the O−H group of the ethanol subunit, forming an H bond to the previously unused oxygen atom already present in the chain [$-CH_2CH_2OH\cdots OH_2$, O8−H8···O1W, 2.735(4) Å]. Thus, an oxygen lone pair from a water molecule is being used in hydrogen bonding for **7**, whereas this was not the case for **5**. From the packing diagrams it is clear that there is no hydrogen-bonding interaction between the sheets.

The final case studied used a methylpyridyl arm to produce $\mathbf{L^5}MoO_3$, **8**; the X-ray structure is shown in Figure 8. This type of arm combines the ability to take part in hydrogen bonding through the nitrogen atom of the pyridine and a hydrophobic side chain. Again, the same chain motif is present, but even though the pendant pyridine function takes part in hydrogen bonding, the arm does not link the chains together in the same way as with an alcohol functionality. Instead, the chains are linked together by a ladder type structure of water molecules as shown in Figure 9a. There are two molecules of **8** per asymmetric unit, and they differ in that the pyridine arm occupies a different orientation in one molecule of **8** compared to the other. This can be explained by the ladder of water molecules, which are forcing the pyridine arms away from each other; this can be seen in Figure 9b. There is also disorder for one of the molecules of **8** in the asymmetric unit, which has been modeled to fit the occupancy of two sites of the linking $-CH_2CH_2-$ of the macrocyclic ring.

Thus, in addition to types i and ii hydrogen bonding, illustrated for **5**/**6**, there is also a different type of hydrogen-bonding pattern associated with each pyridyl arm. The different pyridyl units of the $\mathbf{L^5}MoO_3$ molecules are linked to water molecules through $C_5H_5N\cdots H_2O$ interactions [O4W−H4WA···N13, 2.792(4) Å, 177(5)° and O5W−H5WA···N26, 3.076(4) Å, 167(4)°, respectively. In the first case there are three water molecules between the H_2O molecule hydrogen bound directly to the N of the pyridyl group and the Mo═O group (i.e., a total of four water molecules between the N and O═Mo). The $C_5H_5N\cdots H-OH$ distance is longer, and the $C_5H_5N\cdots H-OH$ angle is more acute in the second case because of the fact that the H_2O molecule hydrogen bound to the N of the pyridyl group is linked to another H_2O, which in turn is linked to the metal oxide (i.e., a total of two water molecules between the N and O═Mo). This can be seen in Figure 9b, which also shows the different numbers of H_2O molecules between the arms and represented schematically in Figure 9c.

Conclusion

An investigation into the effect on the crystal packing of simple molybdenum oxide complexes by altering the macrocylic ligand attached has been carried out. It has been found that the addition of a pendant group to the macrocycle and variation in the functionality attached to the arm produce a variety of crystal architectures, including (a) chains (**5**/**6**), (b) layers (**7**), and (c) complex 3-D lattices (**4** and **8**). This represents a novel and systematic study into controlling the syntheses of hydrogen-bonded crystal architectures using a simple metal complex template.

Acknowledgment. We acknowledge the EPSRC for an award to T.J.P. and K. K. (Mimi) Hii for helpful discussions.

Supporting Information Available: Five X-ray crystallographic files, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(30) Wieghardt, K.; Hahn, M.; Smirdioff, W.; Weiss, J. *Inorg. Chem.* **1984**, *23*, 94.