Interactions of $[Mo(CO)_6]$ and $[Mo(CO)_3(C_6H_5CH_3)]$ with O_2N_2- and O_2N_3-Donor Macrocycles and the *X*-Ray Crystal Structure of Tetracarbonyl(6,7,16,17-tetrahydro-15*H*-dibenzo[*e,n*][1,4,8,12]dioxadiazacyclopentadecine)-molybdenum–Toluene (2/1)†

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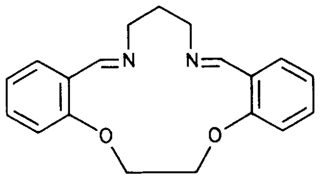
The reaction of $[Mo(CO)_6]$ with the macrocyclic ligand 6,7,16,17-tetrahydro-15*H*-dibenzo[*e,n*][1,4,8,12]dioxadiazacyclopentadecine (L^1) in n-octane, gives $[Mo(CO)_4L^1]$. The crystal and molecular structure of $[Mo(CO)_4L^1]\cdot0.5C_6H_5CH_3$ has been solved by *X*-ray diffraction methods. It is a monomer with Mo^0 co-ordinated to four carbon monoxide molecules and two imino-nitrogens in a pseudo-octahedral geometry; crystals are monoclinic, space group $P2_1/c$, with $a = 15.625(4)$, $b = 11.554(3)$, $c = 14.590(3)$ Å, $\beta = 109.01(2)°$, and $Z = 4$. Final $R = 0.065$ for 933 observed reflections. The reaction of $[Mo(CO)_3(C_6H_5CH_3)]$ with L^1 in methanol gives the orange-red crystalline complex $[\{Mo(CO)_3L^1\}_x]$ (**2**). By reacting the complex $[Mo(CO)_3(C_6H_5CH_3)]$ with *N,N*-bis(3-aminopropyl)methylamine and 2,2′-(ethylenedioxy)dibenzaldehyde (1 : 1 : 1 ratio), in toluene, the complex $[Mo(CO)_3L^2]$ (**5**) (L^2 = 6,7,16,17,20,21-hexahydro-15*H*, 19*H*-18-methyl-dibenzo[*e,r*][1,4,8,12,16]dioxatriazacyclononadecine) was obtained as an orange-red microcrystalline solid. Complexes (**2**) and (**5**) have been analytically and spectroscopically characterized.

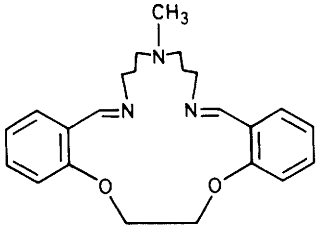
Complexes of Mo^0 with the metal bound to a quadridentate macrocycle (L) may provide useful methods for studying activation of co-ordinated carbon monoxide, as well as other small molecules. Besides that, complexes like $[Mo^0(CO)_xL]$ should undergo oxidative addition-like processes, so making accessible a new class of Mo^{II} complexes of general formula $[Mo^{II}(X)(Y)L]$.

Macrocyclic complexes of Mo^0 have been little studied; there are, to the best of our knowledge, only a few examples of tridentate macrocyclic tricarbonyl complexes.[1] A potentially quadridentate macrocycle (L) with an N_4 donor set was reacted with $[Mo(CO)_6]$;[2] no variation of the oxidation number of the metal occurred in the complex, $[Mo(CO)_4L]$, obtained. However, the metal is bound to only two of the four possible sites afforded by the macrocyclic ligand.

In this paper we report the results of the reactions of the N_2O_2 and N_3O_2 ligands L^1 and L^2 with $[Mo(CO)_6]$ and $[Mo(CO)_3(C_6H_5CH_3)]$. Reactions of $[Mo(CO)_6]$ with the analogous N_2O_2 linear Schiff-base ligands have been reported,[3] but in every case they were accompanied by oxidation of the metal centre, due to the presence of phenolic active protons in the ligands. The absence of active protons in L^1 and L^2 was a promising feature to eliminate the risk of undesired redox processes on the metal centre. $[Mo(CO)_3(C_6H_5CH_3)]$ was used in addition to $[Mo(CO)_6]$ to enable easier substitution by the macrocycle. Macrocycle L^2 was prepared *in situ* by reacting the appropriate triamine (**3**) and dialdehyde (**4**) in the presence of $[Mo(CO)_3(C_6H_5CH_3)]$; we obtained cyclization in the presence of the molybdenum complex under milder conditions and with better yields (despite using much more concentrated solutions) compared to the literature methods[4,5] which make no use of metal templates. This represents, as far as we know, a rare example[1a] of the use of Mo^0 as a template for cyclization reactions.



L^1



L^2

Results and Discussion

The reaction of $[Mo(CO)_6]$ with L^1 in refluxing n-octane gives a yellow microcrystalline air-stable product (**1**) in high yield; recrystallization of this solid from toluene gives single crystals suitable for *X*-ray analysis. Analytical data, n.m.r. spectrum, i.r. spectrum, which shows four absorptions in the terminal CO region (ν_{CO}: 1 810s, 1 860s, 1 890s, and 2 010m cm^{-1}; Nujol mull), and the diamagnetism of the compound are all con-

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† *Supplementary data available* (No. SUP 56299, 5 pp.): thermal parameters, calculated hydrogen positions. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Table 1. Bond distances (Å) and angles (°)

Mo–C(1)	1.954(17)	C(1)–O(1)	1.247(22)	C(11)–O(5)	1.359(18)	C(19)–C(20)	1.461(18)
Mo–C(2)	1.870(18)	C(2)–O(2)	1.201(24)	C(12)–C(13)	1.507(28)	C(20)–N(2)	1.255(25)
Mo–C(3)	1.915(20)	C(3)–O(3)	1.234(27)	C(12)–O(5)	1.469(27)	C(21)–C(22)	1.501(27)
Mo–C(4)	1.923(29)	C(4)–O(4)	1.194(36)	C(13)–O(6)	1.390(31)	C(21)–N(2)	1.464(20)
Mo–N(1)	2.312(13)	C(5)–C(6)	1.492(23)	C(14)–C(19)	1.396(19)	C(22)–C(23)	1.530(32)
Mo–N(2)	2.325(18)	C(5)–N(1)	1.199(26)	C(14)–O(6)	1.325(17)	C(23)–N(1)	1.482(23)

C(1)–Mo–C(2)	87.0(6)	C(4)–Mo–N(1)	98.5(5)	C(19)–C(20)–N(2)	124.2(12)
C(1)–Mo–C(3)	166.7(5)	C(4)–Mo–N(2)	175.8(5)	C(22)–C(21)–N(2)	114.0(11)
C(1)–Mo–C(4)	85.9(5)	N(1)–Mo–N(2)	77.6(4)	C(21)–C(22)–C(23)	117.4(12)
C(1)–Mo–N(1)	95.5(4)	Mo–C(1)–O(1)	170.6(10)	C(22)–C(23)–N(1)	109.6(11)
C(1)–Mo–N(2)	96.0(4)	Mo–C(2)–O(2)	175.5(12)	C(11)–O(5)–C(12)	117.8(10)
C(2)–Mo–C(3)	83.8(6)	Mo–C(3)–O(3)	168.8(11)	C(13)–O(6)–C(14)	118.3(11)
C(2)–Mo–C(4)	88.7(6)	Mo–C(4)–O(4)	176.3(12)	Mo–N(1)–C(5)	132.6(9)
C(2)–Mo–N(1)	172.5(5)	C(6)–C(5)–N(1)	124.7(12)	Mo–N(1)–C(23)	114.5(8)
C(2)–Mo–N(2)	95.1(5)	C(13)–C(12)–O(5)	110.7(12)	C(5)–N(1)–C(23)	111.8(11)
C(3)–Mo–C(4)	84.3(6)	C(12)–C(13)–O(6)	110.6(13)	Mo–N(2)–C(20)	128.3(9)
C(3)–Mo–N(1)	94.8(5)	C(19)–C(14)–O(6)	114.5(7)	Mo–N(2)–C(21)	114.0(8)
C(3)–Mo–N(2)	94.4(5)	C(14)–C(19)–C(20)	120.3(8)	C(20)–N(2)–C(21)	117.4(11)

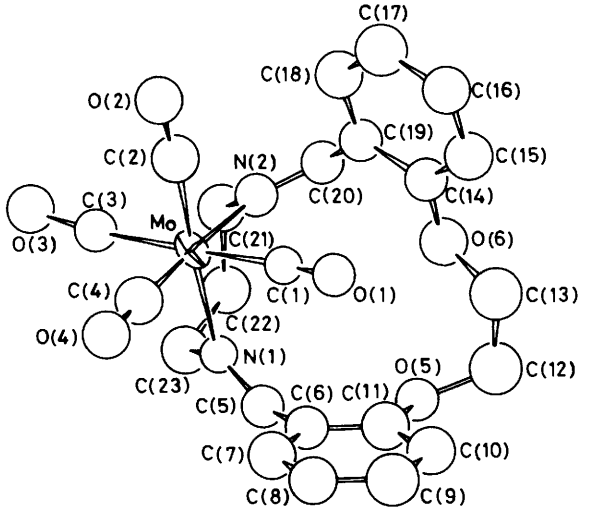
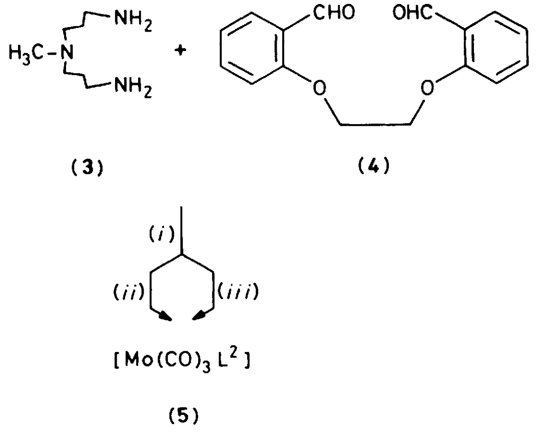


Figure. The structure of $[Mo(CO)_4L^1]\cdot 0.5C_6H_5CH_3$ showing the atomic numbering. Hydrogen atoms and the crystallization solvent (toluene) are omitted for clarity

sistent[6] with the formulation of this product as the complex *cis*-$[Mo(CO)_4L^1]$ (**1**). The *X*-ray crystal structure confirmed this hypothesis. A view of the complex $[Mo(CO)_4L^1]\cdot 0.5C_6H_5CH_3$ is shown in the Figure and the main bond distances and angles are listed in Table 1.

The metal lies at the centre of a slightly distorted octahedron and is bonded only to two of the four possible sites afforded by the macrocyclic ligand, *viz.* to the imino-nitrogens; the co-ordination sphere around the metal is completed by four carbon monoxide molecules. Metal–nitrogen, metal–carbon, and carbon–oxygen bond lengths fall in the range of values found in similar structures.[7,8] The two mutually *trans* carbonyl groups have a longer mean value of the Mo–C distances than the two *trans* to the imino-nitrogens, as might be expected since CO is a better π acceptor than the imino-nitrogens and since the carbonyl groups have a larger *trans* effect.

If $[Mo(CO)_3(C_6H_5CH_3)]$ instead of $[Mo(CO)_6]$ is reacted with L^1 in methanol, a red solution immediately forms and an orange microcrystalline air-stable product (**2**) precipitates in nearly quantitative yield. No gas development occurs in the reaction; (**2**) is diamagnetic and analytical data as well as the i.r. spectrum of the solid agree with the formulation of (**2**) as $[\{Mo(CO)_3L^1\}_x]$ (ν_{CO}: 1 750s, 1 780s, and 1 900s cm^{-1}; Nujol mull).



Scheme. (*i*) + $[Mo(CO)_3(C_6H_5CH_3)]$, toluene; (*ii*) CH_3OH, room temperature, 12 h; (*iii*) toluene, reflux, 6 h

Compound (**2**) is insoluble in common organic solvents except dimethylformamide and Me_2SO. The n.m.r. spectrum of (**2**), which does not show a different chemical environment for the methylene protons of the OCH_2CH_2O moiety compared to the free macrocycle L^1 and complex (**1**), suggests that the oxygens of the ligand are not involved in the co-ordination to molybdenum. However, the molecular nuclearity of (**2**) was not readily discernible because: (*i*) although (**2**) is obtainable in a fine crystalline form under the appropriate dilution conditions, gemination always prevented meaningful *X*-ray analysis, (*ii*) mass spectra could not be performed owing to its extremely low volatility, (*iii*) cryoscopy in Me_2SO gave poor results, probably because of the action of the solvent which sets up equilibria between different species; moreover cryoscopy data in any other solvent were not accessible because of its low solubility. These elements, together with the observation [gained from the *X*-ray crystal structure of complex (**1**)] that the hole of the macrocyclic ligand is probably too small to accommodate the metal inside, lead us to suggest, for complex (**2**), the same 'external' co-ordination mode, through the two imino-nitrogens, as in (**1**). We consider unlikely the hypothesis of a mononuclear, 16-electron five-co-ordinate complex for (**2**) because of its extremely low solubility and volatility and its air-stability.

Taking account of all these considerations the complex (**2**) has to be considered, in our opinion, as at least dimeric, with metal–metal bonds. The metal–metal bond order has to be formally considered as two if (**2**) is considered to be a dimer, $[\{Mo(CO)_3L^1\}_2]$, while single metal–metal bonds would have to be claimed to explain higher molecular complexities.

Quantitative conversion of (**2**) into $[Mo(CO)_6]$ at $P_{CO} = 1$ atm (*ca.* 10^5 Pa) and $T = 20$ °C [3 mol equiv. CO per mol equiv. (**2**) absorbed] does however suggest a certain degree of kinetic lability toward cleavage reactions of metal–metal bonds in this complex.

The N_3O_2 macrocycle L^2 differs from L^1 in that it has a larger cavity and one more donor atom (an amino-nitrogen). Complexation of Mo^0 by the ligand L^2 was performed by reacting $[Mo(CO)_3(C_6H_5CH_3)]$ in refluxing toluene with the triamine (**3**) and the dialdehyde (**4**) (1:1:1 molar ratio) using a Dean–Stark apparatus to remove the water formed in the condensation reaction; on cooling an orange-red microcrystalline solid (**5**) was obtained in good yield (80%). Analogous results were obtained when the reaction was performed in methanol at room temperature; no CO evolution occurs in the reaction as shown by carrying it out in a gas-volumetric apparatus.

Analytical and n.m.r. data for (**5**) suggest the formation of the N_3O_2 macrocycle L^2 and of the complex $[Mo(CO)_3L^2]$ (Scheme). The i.r. spectrum of (**5**) shows three intense absorptions in the region of terminal CO (ν_{CO}: 1 750s, 1 790s, and 1 900s cm^{-1}; Nujol mull), suggesting a *fac*-tridentate ligation of L^2 in the octahedral, 18-electron complex, provided the dissimilar bonding properties of the central aliphatic nitrogen and of the imino-nitrogens are considered.

The co-ordination of Mo^0 to L^2 is probably external, through the three nitrogens which traditionally are better co-ordinating agents for Mo^0 than ethereal oxygens. The failure of Mo^0 to be accommodated inside L^2, although the L^2 cavity is surely large enough, may be attributed to the lower affinity of the macrocyclic ethereal oxygens compared to that of carbon monoxide for Mo^0. Substitution of CO by ethereal oxygens in the co-ordination sphere of Mo^0 is in fact quite a difficult process as shown by the severe thermal conditions used in the synthesis of tricarbonyl(2,5,8-trioxanonane)molybdenum from $[Mo(CO)_6]$.[9]

Experimental

All manipulations and reactions involving metal complexes were carried out under strictly anhydrous nitrogen. Solvents were carefully dried by conventional methods prior to use. I.r. spectra were recorded with a Perkin-Elmer model 283 instrument equipped with a grating monochromator. Proton n.m.r. spectra were recorded on a Varian T60 instrument; chemical shifts (p.p.m.) are relative to $SiMe_4$. Commercial $[Mo(CO)_6]$ (Merck) was used while L^1 (ref. 10) and $[Mo(CO)_3(C_6H_5CH_3)]$[11] were prepared according to literature methods.

Preparation of $[Mo(CO)_4L^1]$ (**1**).—$[Mo(CO)_6]$ (1.584 g, 6.0 mmol) and L^1 (1.848 g, 6.0 mmol) were mixed in n-octane (50 cm^3) and refluxed for 2 h. After cooling, the yellow microcrystalline solid was filtered off and washed with n-pentane, dried *in vacuo* and analysed without further purification (yield 85%) (Found: C, 53.7; H, 3.80; N, 5.40. Calc. for $C_{23}H_{20}MoN_2O_6$: C, 53.5; H, 3.85; N, 5.40%). I.r. bands (Nujol): 2 010m, 1 890s, 1 860s, and 1 810s (ν_{CO}); 1 645m cm^{-1} (ν_{CN}). N.m.r. $\delta_H[(CD_3)_2SO]$: 8.55 (2 H, s, CH=N), 8.00—6.85 (8 H, m, C_6H_4), 4.35 (4 H, s, OCH_2), 3.35 (4 H, br t, NCH_2), 2.05 (2 H, br m, $NCH_2CH_2CH_2N$).

Preparation of $[\{Mo(CO)_3L^1\}_x]$ (**2**).—A solution of $[Mo(CO)_3(C_6H_5CH_3)]$ (1.348 g, 4.95 mmol) in CH_3OH (30 cm^3) was dropped in a solution of L^1 (1.53 g, 4.95 mmol) in CH_3OH (70 cm^3). The microcrystalline red-orange solid which immediately formed was filtered off, washed with methanol and dried *in vacuo* (yield 80%) (Found: C, 54.0; H, 4.0; N, 5.5. Calc. for $C_{22}H_{20}MoN_2O_5$: C, 54.1; H, 4.1; N, 5.15%). I.r. bands (Nujol): 1 900s, 1 780s, and 1 750s (ν_{CO}); 1 630m cm^{-1} (ν_{CN}). N.m.r. $\delta_H[(CD_3)_2SO]$: 8.55 (2 H, s, CH=N), 7.95—6.85 (8 H, m, C_6H_4), 4.35 (4 H, s, OCH_2), 3.40 (4 H, br t, NCH_2), 2.10 (2 H, br m, $NCH_2CH_2CH_2N$).

Preparation of $[Mo(CO)_3L^2]$ (**5**).—*Method* (*a*). $[Mo(CO)_3(C_6H_5CH_3)]$ (1.204 g, 4.43 mmol), the triamine (**3**) (0.642 g, 4.43 mmol), and the dialdehyde (**4**) (1.196 g, 4.43 mmol) were mixed in toluene (100 cm^3). The solution was refluxed and the water–toluene azeotrope was removed with a Dean–Stark apparatus. When no more water formed (6 h) the reaction was stopped. After cooling the red-orange microcrystalline solid was filtered off, washed with toluene, dried *in vacuo*, and analysed without further purification (yield 80%) (Found: C, 55.75; H, 5.30; N, 7.45. Calc. for $C_{26}H_{29}MoN_3O_5$: C, 55.8; H, 5.20; N, 7.50%). I.r. bands (Nujol): 1 900s, 1 790s, and 1 750s (ν_{CO}); 1 630w cm^{-1} (ν_{CN}). N.m.r. $\delta_H[(CD_3)_2SO]$: 9.00 (2 H, s, CH=N), 8.20—7.10 (8 H, m, C_6H_4), 4.50 (4 H, s, OCH_2), 3.50 (4 H, t, $C=NCH_2$), 2.30 (4

Table 2. Fractional atomic co-ordinates in $[Mo(CO)_4L^1]\cdot0.5C_6H_5CH_3$. Estimated standard deviations in parentheses refer to the last digit

Atom	*X/a*	*Y/b*	*Z/c*
Mo	0.816 6(1)	−0.097 5(2)	0.826 9(1)
O(1)	0.684 8(9)	0.110 0(15)	0.835 8(11)
O(2)	0.678 9(11)	−0.264 5(15)	0.864 3(12)
O(3)	0.928 6(10)	−0.327 3(16)	0.880 4(12)
O(4)	0.887 0(12)	−0.051 1(15)	1.049 4(16)
O(5)	0.808 6(9)	0.261 2(13)	0.655 0(10)
O(6)	0.652 2(10)	0.127 2(14)	0.585 7(11)
N(1)	0.919 2(10)	0.013 7(14)	0.781 7(12)
N(2)	0.771 1(11)	−0.126 2(14)	0.660 2(13)
C(1)	0.732 8(12)	0.029 3(17)	0.823 3(14)
C(2)	0.729 8(14)	−0.196 3(20)	0.847 4(16)
C(3)	0.892 1(13)	−0.232 2(19)	0.856 7(16)
C(4)	0.862 9(15)	−0.070 6(20)	0.964 4(21)
C(5)	0.927 5(13)	0.116 2(18)	0.774 7(15)
C(6)	0.880 8(10)	0.205 6(14)	0.815 1(8)
C(7)	0.899 8(10)	0.220 0(14)	0.914 7(8)
C(8)	0.860 9(10)	0.311 5(14)	0.949 6(8)
C(9)	0.803 1(10)	0.388 6(14)	0.884 9(8)
C(10)	0.784 1(10)	0.374 2(14)	0.785 3(8)
C(11)	0.8229 (10)	0.282 7(14)	0.750 4(8)
C(12)	0.725 7(16)	0.307 5(26)	0.584 3(20)
C(13)	0.643 4(17)	0.246 3(23)	0.592 6(20)
C(14)	0.593 8(8)	0.059 5(12)	0.608 7(11)
C(15)	0.513 8(8)	0.096 1(12)	0.622 5(11)
C(16)	0.458 3(8)	0.016 2(12)	0.647 6(11)
C(17)	0.482 8(8)	−0.100 3(12)	0.659 0(11)
C(18)	0.562 8(8)	−0.137 0(12)	0.645 3(11)
C(19)	0.618 3(8)	−0.057 1(12)	0.620 1(11)
C(20)	0.697 7(14)	−0.097 9(22)	0.597 6(18)
C(21)	0.842 1(13)	−0.172 8(19)	0.625 5(16)
C(22)	0.918 2(14)	−0.089 8(23)	0.633 9(16)
C(23)	0.975 9(14)	−0.052 2(20)	0.735 9(17)
C(24)	0.467 1(27)	0.034 7(34)	0.070 1(30)
C(25)	0.539 5(22)	−0.024 9(29)	0.093 9(24)
C(26)	0.582 6(24)	−0.062 3(29)	0.021 4(28)
C(27)	0.643 7(35)	−0.114 6(49)	0.034 5(38)

H, t, $CH_2N(Me)CH_2$), 2.15 (3 H, s, NCH_3), 1.70 (4 H, q, $NCH_2CH_2CH_2N$).

Method (*b*). [$Mo(CO)_3(C_6H_5CH_3)$] (0.430 g, 1.58 mmol), the *triamine* (**3**) (0.225 g, 1.58 mmol) and the dialdehyde (**4**) (0.4266 g, 1.58 mmol) were stirred in methanol (50 cm^3) overnight. The orange solid was filtered off, washed with methanol, and dried *in vacuo* (yield 70%). Analytical and spectroscopic data were identical to those of a sample of [$Mo(CO)_3L^2$] prepared according to method (*a*).

X-*Ray Data Collection and Structure Refinement for* [$Mo(CO)_3L^1$]·$0.5C_6H_5CH_3$.—Recrystallization from toluene of complex (**1**) gave yellow prisms suitable for *X*-ray analysis. A crystal with dimensions 0.20 × 0.15 × 0.10 mm was mounted on a computer-controlled Philips PW1100 single-crystal diffractometer, equipped with graphite-monochromatized Mo-K_α radiation. The crystals are monoclinic. The cell dimensions were determined by a least-squares calculation based on the setting angles of 25 reflections.

Crystal data. $C_{26.5}H_{24}MoN_2O_6$, $M = 562.4$, $a = 15.625(4)$, $b = 11.554(3)$, $c = 14.590(3)$ Å, $\beta = 109.01(2)°$, $U = 2\,490.29$ Å^3, space group $P2_1/c$ (from systematic extinctions), $Z = 4$, $D_c = 1.5042$ g cm^{-3}, $F(000) = 1\,148$, $\lambda = 0.710\,69$ Å, $\mu = 5.17$ cm^{-1}.

The intensities were collected up to to $2\theta = 40°$; the ω—2θ scan technique was employed, the scan range being 1.7° and the speed 0.05° s^{-1}. A total of 4 898 reflections were measured, giving 2 838 independent reflections. Due to the poor quality of the crystal under examination, only 933 reflections, with $I \geqslant 3\sigma(I)$, have been retained for the refinement. Three standard reflections which were measured periodically showed no apparent variation in intensity during data collection. The data were corrected for Lorentz and polarization factors. A semi-empirical absorption correction was applied on the basis of the variation in intensity during the azimuthal scans of some reflections according to the method of North *et al.*;[12] the transmission factors were in the range 0.95—0.59.

The structure was solved by Patterson methods and refined by the full-matrix least-squares method with the SHELX-76[13] package of programs. The phenyl groups were constrained to perfect hexagons (C–C = 1.395 Å) and refined as rigid groups. The hydrogen atoms were included at the calculated positions (C–H = 1.08 Å) with overall isotropic parameters of 0.14 Å^2. Anisotropic thermal parameters were refined for the Mo atom only, because of the unfavourable reflections/parameters ratio. The refinement converged at $R = 0.065$ and $R' = 0.067$ for 128 parameters and 933 observed reflections; $R' = [\Sigma w(|F_o| - |F_c|)^2]^{\frac{1}{2}}/(\Sigma w F_o^2)$, $w = [\sigma^2(F_o) + 0.000\,237F_o^2]^{-1}$. Atomic scattering factors were taken from ref. 13 for O, N, C, and H and from ref. 14 for Mo; the correction for anomalous dispersion was included. The atomic positions are listed in Table 2.

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