Characterisation of Tridentate Macrocyclic Complexes of Molybdenum(0) with Tetra-aza Macrocycles. Crystal Structure of $[Mo(CO)_3L^1](L^1 = C\text{-}meso\text{-}5,5,7,12,12,14\text{-Hexamethyl-}1,4,8,11\text{-tetra-azacyclotetradecane})$ †

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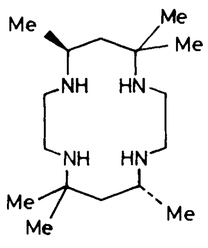
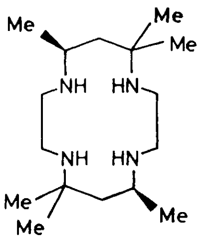
The tetra-aza macrocyclic ligands L^1 (C-*meso*) and L^2 (C-*racemic*) (5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane) react with $[Mo(CO)_6]$ in dry dimethylformamide to give the diamagnetic $[Mo(CO)_3L^1]$ and $[Mo(CO)_3L^2]$ respectively in which the potentially quadridentate ligand is tridentate. The $[Mo(CO)_3L^1]$ complex has been characterised by *X*-ray crystallography. It crystallises as yellow needles [monoclinic, a = 8.699(2), b = 19.839(4), c = 12.518(2) Å, β = 90.79(1)°; R converged to 0.022 for 2 243 independent reflections for which $I/\sigma(I) > 6.0$]. The crystal structure establishes that the ligand L^1 co-ordinates *via* N(1), N(4), and N(8). Hydrogen bonding N(11) ··· H–N(1) occurs within the complex. Cyclic voltammograms of both complexes determined using $MeNO_2$ solvent display a quasi-reversible one-electron oxidation process corresponding to the $Mo^{(0)}/Mo^{(I)}$ oxidation, with $E_{\frac{1}{2}}$ = −0.28 (L^1) and = −0.27 V (L^2) *versus* ferrocene—ferrocenium.

In recent years there has been growing interest in macrocyclic complexes of second- and third-row transition elements. A variety of metal complexes of first-row transition-metal ions (Cu^{II}, Ni^{II}, Co^{III}, Cr^{III}) with the macrocyclic tetra-aza ligands L^1 and L^2 have been well studied.[1] The ligand L^1 is known to fold with difficulty, while L^2 folds readily to give *cis* complexes.[1,2] Our interest in the reactions of tetra-aza macrocycles with second-row transition elements led us to investigate the reactions between molybdenum hexacarbonyl and L^1 and L^2. We report the preparation and characterisation of unique complexes in which the tetra-aza macrocycle is found to be tridentate. A preliminary report of this work has appeared.[3] Two platinum complexes containing potentially tridentate nitrogen macrocycles have been reported.[4]



(C - *meso*)
L^1



(C - *racemic*)
L^2

Experimental

The ligands $L^1\cdot 2H_2O$ and $L^2\cdot H_2O$ were prepared as previously described.[5]

$[Mo(CO)_3L^1]$.—Molybdenum hexacarbonyl (0.50 g, 1.89 mmol) and $L^1\cdot 2H_2O$ (0.60 g, 1.88 mmol) were added to deoxygenated, dry dimethylformamide (dmf) (15 cm^3) and the reactants gently refluxed under a nitrogen atmosphere for 5 h. On standing overnight at room temperature, yellow crystals deposited from the brown solution. The crystals were filtered off, washed with dmf and diethyl ether, and dried *in vacuo*. Yield 0.63 g (72%) (Found: C, 49.2; H, 8.0; N, 11.8. $C_{19}H_{36}MoN_4O_3$ requires C, 49.1; H, 7.8; N, 12.1%). The i.r. spectrum (KBr disc) has ν(CO) at 1 886 and 1 743 cm^{-1}. The complex is a non-electrolyte in $MeNO_2$ (Λ_M = 4 S cm^2 mol^{-1} for a 1.1×10^{-3} mol dm^{-3} solution). Magnetic susceptibility measurements confirmed that the compound was diamagnetic.

$[Mo(CO)_3L^2]$.—This compound was prepared in a similar manner. On standing overnight at room temperature, yellow crystals deposited from the brown solution. The crystals were filtered off, washed with dmf and diethyl ether, and dried *in vacuo*. Yield 0.60 g (68%) (Found: C, 49.2; H, 8.2; N, 11.8. $C_{19}H_{36}MoN_4O_3$ requires C, 49.1; H, 7.8; N, 12.1%). The i.r. spectrum (KBr disc) has ν(CO) at 1 884 and 1 741 cm^{-1}. The complex is a non-electrolyte in $MeNO_2$ and is diamagnetic in the solid state.

Physical Measurements.—Infrared spectra were recorded between 4 000 and 400 cm^{-1} on powdered samples dispersed in KBr discs (*ca.* 5% by weight) using a Shimadzu IR-435 spectrophotometer. Conductivity measurements were made using 10^{-3} mol dm^{-3} solutions in nitromethane at 20 °C on a PTI-18 digital conductivity meter. Magnetic susceptibilities of powdered samples were measured on a Johnson Matthey magnetic susceptibility balance.

Electrochemical experiments were carried out using a Princeton Applied Research electrochemistry system, model 170 on *ca.* 10^{-3} mol dm^{-3} solutions in nitromethane containing 0.1 mol dm^{-3} tetra-*n*-butylammonium hexafluorophosphate as supporting electrolyte. Dry nitrogen gas was flushed through the electrolytic solutions before each measurement. The electrochemical cell consisted of a planar platinum disc working

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

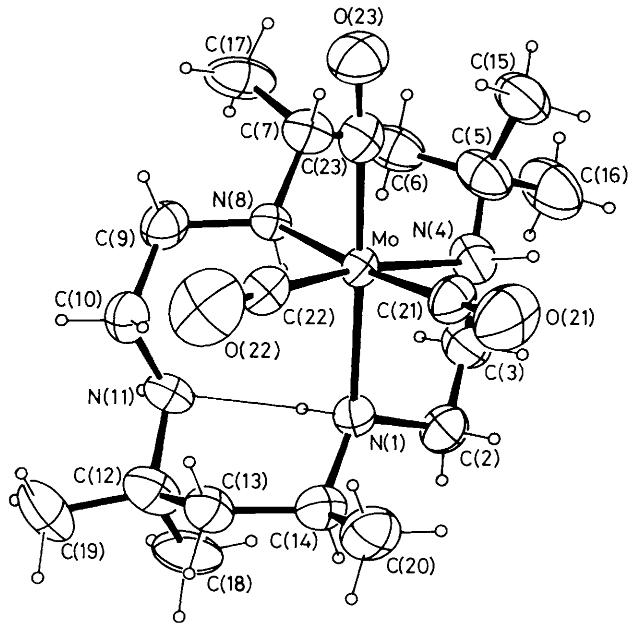


Figure 1. A view of [Mo(CO)$_3$L^1] with the crystallographic numbering scheme

electrode, a platinum pin counter electrode, and a saturated calomel reference electrode. After each experiment ferrocene was added to the solution and the $E_{\frac{1}{2}}$ values $[E_{\text{Pa}} + E_{\text{Pc}})/2]$ were referenced to the ferrocene–ferrocenium couple.

Fast atom bombardment (f.a.b.). mass spectra were determined at Swansea.

Crystal-structure Determination.—Crystal data. $C_{19}H_{36}MoN_4O_3$, $M = 464.46$, monoclinic, space group $P2_1(n$ (no. 14), $a = 8.699(2)$, $b = 19.839(4)$, $c = 12.518(2)$ Å, $\beta = 90.79(1)°$, $D_c = 1.43$ g cm^{-3}, $U = 2\,160(1)$ Å^3, $Z = 4$, μ(Mo-K_α) 6.2 cm^{-1}, λ(Mo-K_α) 0.710 73 Å, $F(000) = 976$.

A yellow needle crystal having approximate dimensions 0.10 × 0.13 × 0.31 mm was mounted on a glass fibre in a random orientation. Preliminary examination and data collection were performed with Mo-K_α radiation on an Enraf-Nonius CAD-4 diffractometer equipped with a graphite-crystal, incident-beam monochromator. A total of 3 680 reflections were collected of which 3 391 were unique and not systematically absent. As a check on crystal and electronic stability, three representative reflections were measured every 240 min. The intensities of these standards remained constant within experimental error throughout data collection. No decay correction was applied.

Lorentz and polarisation corrections were applied to the data. A numerical absorption correction was made. Relative transmission coefficients ranged from 92.675 to 94.405 with an average value of 93.800. A secondary extinction correction was applied.[6] The final coefficient, refined by least-squares, was 4.8×10^{-8} (in absolute units). Intensities of equivalent reflections were averaged. The agreement factors for the averaging of the 245 observed and accepted reflections was 2.7% based on intensity and 1.7% based on F_o.

Structure solution and refinement. The structure was solved using the Patterson heavy-atom method which revealed the position of the Mo atom. The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were included in the refinement but restrained to ride on the atom to which they were bonded.

All non-hydrogen atoms were assigned anisotropic displacement parameters. Scattering factors were taken from Cromer and Waber.[7] Anamalous dispersion effects were included in F_c. Only 2 243 reflections having intensities greater than 6.0 times their standard deviation were used in the refinements. The final cycle of refinement included 245 variable parameters and converged [largest parameter shift was <0.005 × the estimated standard deviation (e.s.d.)] with unweighted and weighted agreement factors of $R = 0.022$ and $R' = 0.030$. The standard deviation of an observation of unit weight was 1.09. The final difference Fourier map showed no significant electron density. Final atomic co-ordinates are given in Table 1.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates and thermal parameters.

Results and Discussion

Under gentle reflux conditions, $L^1 \cdot 2H_2O$ and $L^2 \cdot H_2O$ react with [Mo(CO)$_6$] in deoxygenated dry dmf to give yellow crystalline solids in yields of *ca.* 70%. The L^1 derivative exhibits ν(CO) at 1 886 and 1 743 cm^{-1}, while two bands at 1 884 and 1 741 cm^{-1} occur with the L^2 compound. The observation of two bands is expected for the *fac′*-[Mo(CO)$_3$L] structure (L = L^1 or L^2) with C_{3v} local symmetry. The very low ν(CO) frequencies of the terminal CO groups probably arise due to the high electron density on the molybdenum atom resulting from σ donation by the NH groups. This effect leads to strong back donation into the π^* orbitals of the CO ligands. The f.a.b. mass spectra of both compounds display parent ion peaks at *m/z* 464 ($C_{19}H_{36}{}^{96}MoN_4O_3 = 464$). Conductivity measurements establish that the complexes are non-electrolyes in nitromethane and magnetic susceptibility measurements at room temperature show them to be diamagnetic.

The complex [Mo(CO)$_3$L^1] was characterised by *X*-ray crystal structure analysis, Figure 1. The molybdenum atom is in a distorted octahedral environment. One octahedral face is occupied by three CO ligands and the other is bound by N(1), N(4), and N(8) of the potentially quadridentate macrocycle. The structural study clearly shows that N(11) does not co-ordinate to the molybdenum atom [Mo $\cdots$ N(11) distance 3.862(2) Å], but there is evidence for N(1)–H $\cdots$ N(11) intramolecular hydrogen bonding, Table 2. In addition the Mo–C(23) distance *trans* to N(1) is significantly longer [1.913(3) Å] than the Mo–C(21) and Mo–C(22) at 1.898(3) and 1.897(3) Å respectively. The geometry at N(1) differs from that at N(4) and N(8) allowing N(1)–H $\cdots$ N(11) intramolecular hydrogen bonding.

The complex [Mo(CO)$_3$L^1] can be regarded as an 'intermediate' in the formation of the 4N-co-ordinated macrocyclic complex [Mo(CO)$_2$L^1]. As such it provides interesting structural information regarding the sequence of events involved in the co-ordination of a tetra-aza-macrocycle to a metal. The binding of an N$_4$ macrocycle to an octahedral metal centre will initially result in the formation of a *cis* complex due to the required sequential loss of the labile monodentate ligands from ML$_6$ (L = CO or H$_2$O). In the case of the L^1 ligand, initial metal–nitrogen bond formation will probably occur *via* the less sterically hindered N(1) or N(8) donors, with second-bond formation taking place *via* N(4). Facial co-ordination will then be completed by N(1) or N(8). The final step involves the co-ordination of N(11) to give the *cis* complex M(N$_4$)L$_2$. The *cis*-[ML^{1}L$_2$] complex will have the macrocycle configuration (**I**) with the macrocycle folded along the axis shown (**II**). The macrocycle has the *trans* V chiral nitrogen configuration[8] with an N(4)–N(11) fold axis as previously observed[9] in *cis*-[NiL^1(acac)]$^+$ (acac = acetylacetonate). The almost identical physical properties of the two complexes leads us to believe that in [Mo(CO)$_3$L^2] the tetra-aza macrocycle is also acting as a

Table 1. Positional parameters and their estimated standard deviations of $[\mathrm{Mo(CO)_3L^1}]$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Mo	0.113 03(3)	0.224 27(1)	0.008 12(2)	C(10)	−0.226 9(3)	0.318 5(2)	0.057 9(3)
O(21)	0.429 9(3)	0.235 5(2)	−0.096 2(2)	C(12)	−0.099 3(4)	0.410 0(2)	0.164 2(3)
O(22)	0.055 0(3)	0.325 7(1)	−0.173 4(2)	C(13)	0.048 4(4)	0.412 9(2)	0.097 7(3)
O(23)	0.048 1(3)	0.125 5(1)	−0.178 4(2)	C(14)	0.188 5(4)	0.372 8(2)	0.136 2(3)
N(1)	0.149 4(3)	0.299 7(1)	0.149 3(2)	C(15)	0.163 1(5)	0.042 8(2)	0.078 7(3)
N(4)	0.187 7(3)	0.155 5(1)	0.155 0(2)	C(16)	0.175 9(6)	0.054 5(2)	0.274 8(3)
N(8)	−0.125 9(3)	0.202 6(1)	0.094 4(2)	C(17)	−0.322 9(4)	0.106 3(2)	0.099 5(3)
N(11)	−0.164 3(3)	0.340 6(1)	0.160 6(2)	C(18)	−0.064 0(4)	0.425 5(2)	0.280 8(3)
C(2)	0.252 7(4)	0.266 9(2)	0.227 1(3)	C(19)	−0.213 0(4)	0.462 7(2)	0.120 5(3)
C(3)	0.195 2(4)	0.197 8(2)	0.252 9(3)	C(20)	0.324 6(4)	0.383 0(2)	0.064 8(3)
C(5)	0.115 0(5)	0.087 5(2)	0.172 0(3)	C(21)	0.312 1(4)	0.231 0(2)	−0.051 2(3)
C(6)	−0.059 7(5)	0.093 3(2)	0.178 7(3)	C(22)	0.069 3(4)	0.287 9(2)	−0.101 4(3)
C(7)	−0.154 3(4)	0.127 4(2)	0.091 1(3)	C(23)	0.072 2(3)	0.161 1(2)	−0.104 2(3)
C(9)	−0.259 7(4)	0.243 4(2)	0.056 8(3)				

Table 2. Molecular dimensions (distances in Å, angles in °)

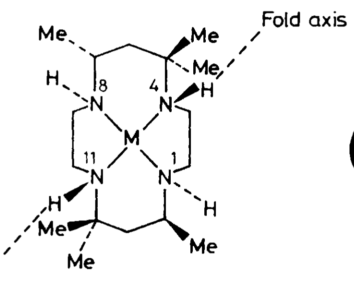
Mo–N(1)	2.335(2)	O(22)–C(22)	1.178(4)	N(11)–C(10)	1.457(4)	C(7)–C(17)	1.531(5)
Mo–N(4)	2.373(3)	O(23)–C(23)	1.184(4)	N(11)–C(12)	1.489(4)	C(9)–C(10)	1.516(5)
Mo–N(8)	2.395(2)	N(1)–C(2)	1.468(4)	C(2)–C(3)	1.496(5)	C(12)–C(13)	1.542(5)
Mo···N(11)	3.862(2)	N(1)–C(14)	1.498(4)	C(5)–C(6)	1.528(6)	C(12)–C(18)	1.519(5)
Mo–C(21)	1.898(3)	N(4)–C(3)	1.485(4)	C(5)–C(15)	1.529(5)	C(12)–C(19)	1.536(5)
Mo–C(22)	1.897(3)	N(4)–C(5)	1.507(4)	C(5)–C(16)	1.532(6)	C(13)–C(14)	1.528(5)
Mo–C(23)	1.913(3)	N(8)–C(7)	1.513(4)	C(6)–C(7)	1.520(5)	C(14)–C(20)	1.508(5)
O(21)–C(21)	1.180(4)	N(8)–C(9)	1.488(4)				

N(1)–Mo–N(4)	75.46(9)	C(21)–Mo–C(23)	85.4(1)	N(4)–C(3)–C(2)	110.5(3)	N(11)–C(12)–C(13)	109.7(3)
N(1)–Mo–N(8)	83.28(8)	C(22)–Mo–C(23)	82.6(1)	N(4)–C(5)–C(6)	111.1(3)	N(11)–C(12)–C(18)	106.8(3)
N(1)–Mo–C(21)	97.9(1)	Mo–N(1)–C(2)	107.0(2)	N(4)–C(5)–C(15)	107.0(3)	N(11)–C(12)–C(19)	112.2(3)
N(1)–Mo–C(22)	98.3(1)	Mo–N(1)–C(14)	124.5(2)	N(4)–C(5)–C(16)	111.1(3)	C(13)–C(12)–C(18)	110.6(3)
N(1)–Mo–C(23)	176.7(1)	C(2)–N(1)–C(14)	111.4(2)	C(6)–C(5)–C(15)	111.7(3)	C(13)–C(12)–C(19)	108.6(3)
N(4)–Mo–N(8)	77.13(9)	Mo–N(4)–C(3)	108.9(2)	C(6)–C(5)–C(16)	108.6(3)	C(18)–C(12)–C(19)	109.0(3)
N(4)–Mo–C(21)	95.9(1)	Mo–N(4)–C(5)	120.9(2)	C(15)–C(5)–C(16)	107.4(3)	C(12)–C(13)–C(14)	118.5(3)
N(4)–Mo–C(22)	172.7(1)	C(3)–N(4)–C(5)	113.8(3)	C(5)–C(6)–C(7)	121.5(3)	N(1)–C(14)–C(13)	110.9(3)
N(4)–Mo–C(23)	103.9(1)	Mo–N(8)–C(7)	107.9(2)	N(8)–C(7)–C(6)	109.4(3)	N(1)–C(14)–C(20)	112.1(3)
N(8)–Mo–C(21)	172.4(1)	Mo–N(8)–C(9)	116.1(2)	N(8)–C(7)–C(17)	115.1(3)	C(13)–C(14)–C(20)	111.9(3)
N(8)–Mo–C(22)	106.2(1)	C(7)–N(8)–C(9)	113.7(2)	C(6)–C(7)–C(17)	109.8(3)	Mo–C(21)–O(21)	174.5(3)
N(8)–Mo–C(23)	93.5(1)	C(10)–N(11)–C(12)	116.2(2)	N(8)–C(9)–C(10)	112.6(3)	Mo–C(22)–O(22)	173.8(3)
C(21)–Mo–C(22)	81.1(1)	N(1)–C(2)–C(3)	110.3(3)	N(11)–C(10)–C(9)	111.9(3)	Mo–C(23)–O(23)	175.6(3)

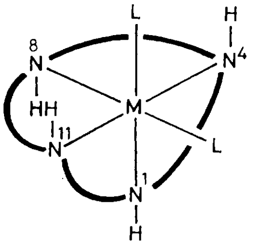
Hydrogen-bond dimensions

Type	Distance (Å)		Angle (°)	
N(1)–H···N(11)	N···N	2.851(3)	N–H···N	158
N(11)–H···O(23)[I]	N···O	3.303(3)	N–H···O	159

Equivalent position: I $-\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$.



(I)



(II)

tridentate ligand. In this compound the ligand will also fold across the N(4)–N(11) axis and will only differ from the $\mathrm{L^1}$ compound in that the configuration of the methyl group at C(7) is reversed.

Electrochemistry and Reactivity.—Electrochemical studies on the complexes were carried out at a platinum electrode using nitromethane solutions containing 0.1 mol $\mathrm{dm^{-3}}$ tetra-*n*-butylammonium hexafluorophosphate as supporting electrolyte. Both $[\mathrm{Mo(CO)_3L^1}]$ and $[\mathrm{Mo(CO)_3L^2}]$ display quasi-reversible one-electron oxidation processes corresponding to the $\mathrm{Mo^0}$–$\mathrm{Mo^I}$ oxidation with $E_{\frac{1}{2}} = -0.28$ and -0.27 V *vs.* ferrocene–ferrocenium, respectively, Figure 2.

Pendant donor atoms in macrocyclic complexes are not unknown. In the two reported complexes of platinum(II) containing potentially tridentate macrocycles which act as bidentate ligands, oxidation of the metal centre to $\mathrm{Pt^{IV}}$[4a] or $\mathrm{Pt^{III}}$[4b] leads to the ligands adjusting their mode of co-ordination and becoming fully co-ordinated to the platinum centre. Weighardt and co-workers[10] have reported the oxidation of $[\mathrm{Mo(CO)_3L}]$ (L = 1,4,7-triazacyclononane) using concentrated HCl or $\mathrm{SOCl_2}$–$\mathrm{CHCl_3}$ to give $[\mathrm{MoCl_3L}]$. These strategies for metal oxidation have proved unsuccessful with the complexes presented here. Neither $[\mathrm{Mo(CO)_3L^1}]$ nor

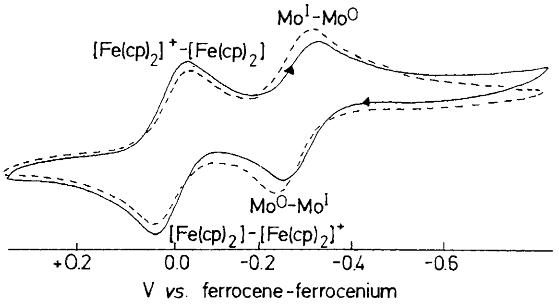


Figure 2. Cyclic voltammograms of $[Mo(CO)_3L^1]$ (————) and $[Mo(CO)_3L^2]$ (. . . .) in $MeNO_2$ (0.1 mol dm^{-3} $NBu^n{}_4PF_6$) at platinum electrodes. Scan rate 100 mV s^{-1}. cp = η^5-Cyclopentadienyl

$[Mo(CO)_3L^2]$ reacts with hot concentrated HCl, and both complexes are destroyed when refluxed with $SOCl_2$ in $CHCl_3$.

Trimethylamine *N*-oxide has been found to replace CO selectively from transition-metal carbonyl complexes, and has been widely used as a decarbonylation reagent.[11] However, no characterisable products were obtained on reaction of it with the present complexes. It appears that at least three CO ligands are required to stabilise Mo^0 when three strong sigma donors are also present in the co-ordination sphere. Characterisation of the complex $[Mo(CO)_2L]$ where L is quadridentate appears unlikely.

Acknowledgements

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