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Molybdenum carbonyl complexes of pendant-arm polyazamacrocycles

Monica Rossignoli,[a] **Paul V. Bernhardt**[b] **and Geoffrey A. Lawrance**[a]

[a] *Department of Chemistry, The University of Queensland, Brisbane 4072, Australia*
[b] *Department of Chemistry, The University of Newcastle, Callaghan 2308, Australia*

Molybdenum hexacarbonyl reacted with the pendant-arm macrocycles 10-methyl-1,4,8,12-tetraazacyclopentadecane-10-amine (L^1) and *trans*-6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane-6,13-diamine (L^2) in the absence of air to form complexes *fac*-$[MoL^1(CO)_3]$ and $[Mo_2L^2(CO)_8]$ respectively. The mononuclear complex has the macrocycle bound in a tridentate manner, including the pendant primary amine, whereas the dinuclear complex exhibits a bridging bis(didentate) co-ordination mode, again involving the pendant primary amines. Structures have been defined by crystal structure analyses. The preferential binding of the pendant primary amines rather than additional secondary amines parallels similar behaviour observed earlier with some mercury(II) and rhodium(III) complexes, and points to the important general role of this pendant, despite being fused directly to the macrocyclic ring, in metal-ion binding.

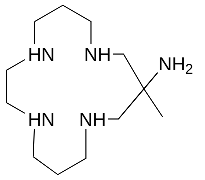
Present knowledge of polyamine complexation to molybdenum(0) *via* reaction with $[Mo(CO)_6]$ is limited to a few examples. Nevertheless, there is an obvious trend, also observed in parallel $[Cr(CO)_6]$ and $[W(CO)_6]$ chemistry, of ligand complexation in a facial tridentate manner irrespective of the polyamine (L) to yield *fac*-$[MoL(CO)_3]$ complexes. For example, 3-azapentane-1,5-diamine (dien),[1] 1,4,7-triazacyclononane (tacn)[2] and *meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (L′)[3] all form complexes of this type, despite the availability of four nitrogen donors in the latter case. With linear tetraamines 3,6-diazaoctane-1,8-diamine, 4,7-diazanonane-1,10-diamine and 4,8-diazaundecane-1,11-diamine the ligation of only three of the amines to form *fac*-$[MoL(CO)_3]$ complexes has been put to use, complexation being considered to provide 'temporary triprotection', leaving a primary amine free for N-alkylation.[4,5]

Macrocycles carrying a pendant primary amine attached to a polyamine macrocycle ring offer this group as a potential donor in addition to the secondary amine groups, and it was of some interest to examine donor selection by the metal in ligands which offer more than three potential donors such as 10-methyl-1,4,8,12-tetraazacyclopentadecane-10-amine (L^1). This ligand offers an $NHCH_2C(CH_3)(NH_2)CH_2NH$ unit which requires and readily achieves facial co-ordination with other metal ions,[6] and therefore co-ordination of this unit preferentially was anticipated as likely upon reaction with $[Mo(CO)_6]$. A related ligand is *trans*-6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane-6,13-diamine (L^2),[7] which has two triamine capping units on opposite sides of the macrocycle. This could in principle allow co-ordination of two *fac*-$Mo(CO)_3$ fragments on each side of the macrocycle, although steric considerations may limit this type of co-ordination. The chemistry of these reactions is examined herein.

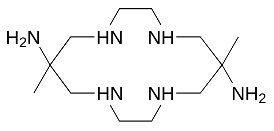
Experimental

Syntheses

The polyamine pendant-arm macrocycles L^1 and L^2 were prepared as hydrochloride salts as previously described,[7,8] and converted into the free base by reaction with an excess of concentrated sodium hydroxide solution, followed by rotary evaporation to dryness, extraction with chloroform and solvent evaporation, yielding the polyamine as a white solid. Molybdenum hexacarbonyl was used as supplied.



L^1



L^2

Tricarbonyl(10-methyl-1,4,8,12-tetraazacyclopentadecane-10-amine)molybdenum(0), $[MoL^1(CO)_3]$. A mixture of $[Mo(CO)_6]$ (1.5 g) and L^1 (2.07 g) was heated at just below reflux in mesitylene (25 cm^3) under a dinitrogen atmosphere. Heating was continued for 45 min, during which a yellow precipitate formed. The solution was cooled in an ice-bath, filtered in air and the solid washed several times with small amounts of mesitylene, acetone and then diethyl ether. Working again under nitrogen, the solid was washed with water (100 cm^3) and taken up in acetonitrile (100 cm^3) and filtered. The volume of the solution was reduced gradually over a few weeks until a yellow crystalline solid precipitated (0.35 g) (Found: C, 42.2; H, 7.1; N, 16.2. Calc. for $C_{15}H_{29}MoN_5O_3$: C, 42.55; H, 6.9; N, 16.5%). IR (KBr disc): 1882, 1745, 1715 (CO), 1590 cm^{-1} (NH_2). NMR $[(CD_3)_2SO]$: ^1H, δ 1.00 (s, 3 H), 1.54 (m, 2 H), 1.82 (br s, 4 H), 2.00 (m, 2 H), 2.5–3.0 (m, 14 H), 3.58 (br s, 2 H) and 5.51 (br s, 2 H); ^{13}C (^1H-decoupled), δ 23.4, 26.0, 50.2, 51.3, 56.2, 58.5, 60.1, 229.8 and 230.4.

Octacarbonyl(*trans*-6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane-6,13-diamine)dimolybdenum(0), $[Mo_2L^2(CO)_8]$. A mixture of $[Mo(CO)_6]$ (0.82 g) and L^2 (0.4 g) in mesitylene (25 cm^3) was heated at gentle reflux under a nitrogen atmosphere for 25 min. On cooling, the yellow precipitate which had formed was filtered off in air and washed with small amounts of mesitylene and diethyl ether in turn. Working again under nitrogen, the solid was washed with water (100 cm^3), then acetonitrile (65 cm^3). The solid was taken up in dimethylformamide (dmf) (10 cm^3) and the solution filtered and refrigerated. Gradual removal of solvent and addition of a small amount of water produced bright yellow crystals (0.3 g) also containing 2 molecules of dimethylformamide per molecule of complex (Found: C, 37.9; H, 5.7; N, 13.4. Calc. for $C_{26}H_{44}Mo_2N_8O_{10}$: C, 38.05; H, 5.4; N, 13.65%). IR (KBr disc): 2004, 1885, 1840, 1715 (CO), 1600 cm^{-1} (NH_2). NMR

Table 1 The molybdenum environment in [MoL^1(CO)$_3$]

Atom	r	C(1C)	C(1B)	C(1A)	N(5)	N(2)
N(1)	2.334(5)	97.8(3)	100.8(3)	170.6(3)	74.3(2)	73.1(2)
N(2)	2.334(6)	101.7(3)	172.3(3)	98.0(3)	75.1(2)	
N(5)	2.287(6)	172.0(3)	99.0(3)	101.0(3)		
C(1A)	1.902(8)	86.6(3)	87.9(3)			
C(1B)	1.928(8)	83.5(3)				
C(1C)	1.928(9)					

r is the molybdenum–donor atom bond distance (Å); the other entries in the matrix are the angles (°) subtended at the molybdenum by the relevant atoms at the head of the row and column.

[(CD$_3$)$_2$SO]: ^{1}H, δ 1.14 (s, 6 H), 1.94 (br s, 2 H), 2.39 (m, 4 H), 2.6–2.9 (m, 12 H), 4.31, 3.91 (ABq, 4 H) and 5.02 (br s, 2 H); ^{13}C (^{1}H-decoupled), δ 26.0, 48.4, 54.7, 55.2, 59.7, 64.0, 206.7, 208.7, 220.8 and 222.0.

Physical methods

Nuclear magnetic resonance spectra were recorded on a Bruker Avance DPX300 spectrometer. Chemical shifts are cited *versus* the internal reference tetramethylsilane. Infrared spectra were recorded on a Bio-Rad FTS-7 spectrometer for compounds dispersed in KBr discs.

Crystallography

The cell constants of a crystal of solvated [Mo$_2$L^2(CO)$_8$] and a twinned specimen of [MoL^1(CO)$_3$] were determined by a least-squares fit to the setting parameters of twenty independent reflections measured on an Enraf-Nonius CAD-4 four-circle diffractometer employing graphite-monochromated Mo-Kα radiation ($\lambda = 0.710\,73$ Å). Indexing was achieved using the program DIRAX,[9] and data reduction was applied with the XTAL package.[10] The structures were solved by heavy-atom methods with SHELXS 86,[11] and refined by full-matrix least-squares analysis with SHELXL 93.[12] All non-hydrogen atoms were refined anisotropically and hydrogen atoms were included at estimated positions.

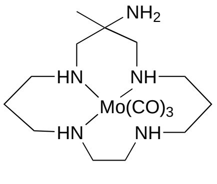
Crystal data. [MoL^1(CO)$_3$], C$_{15}$H$_{29}$MoN$_5$O$_3$, $M = 423.37$, monoclinic, space group $P2_1$, $a = 8.681(8)$, $b = 9.670(2)$, $c = 11.78(1)$ Å, $\beta = 106.31(4)°$, $U = 949(1)$ Å^3, D_c ($Z = 2$) = 1.481 Mg m^{-3}, μ(Mo-Kα) = 0.714 mm^{-1}, $F(000) = 440$, $T = 293$ K. Specimen: white prisms 0.50 × 0.27 × 0.27 mm; $N = 1777$, $N_o = 1777$ [$|F_o| > 2\sigma(|F_o|)$, $2 < \theta < 25°$], hkl 0 to 10, 0 to 11, −13 to 13. Final $R = 0.0420$, $wR2 = 0.1041$, $w^{-1} = \sigma(F_o)^2 + (0.0878P)^2 + 0.08P$ where $P = (F_o^2 + 2F_c^2)/3$, no. parameters = 217, goodness of fit = 1.061. Residual extrema +0.72, −1.7 e Å^{-3}.

[Mo$_2$L^2(CO)$_8$]·2dmf, C$_{26}$H$_{44}$Mo$_2$N$_8$O$_{10}$, $M = 820.57$, triclinic, space group $P\bar{1}$, $a = 8.4239(9)$, $b = 10.420(1)$, $c = 10.8869(9)$ Å, $\alpha = 86.620(8)$, $\beta = 84.078(7)$, $\gamma = 77.715(9)°$, $U = 928.1(2)$ Å^3, D_c ($Z = 1$) = 1.468 Mg m^{-3}, μ(Mo-Kα) = 0.734 mm^{-1}, $F(000) = 420$, $T = 293$ K. Specimen: white needles 0.6 × 0.07 × 0.05 mm; $N = 3498$, $N_o = 1787$[$|F_o| > 2\sigma(|F_o|)$, $2 < \theta < 25°$], hkl 0 to 9, −12 to 12, −12 to 12. Final $R1 = 0.0477$, $wR2 = 0.1006$, $w^{-1} = \sigma(F_o)^2 + (0.0533P)^2$ where $P = (F_o^2 + 2F_c^2)/3$, no. parameters = 203, goodness of fit = 1.027. Residual extrema +0.59, −0.58 e Å^{-3}.

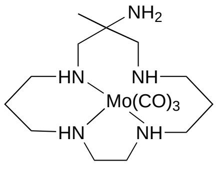
CCDC reference number 186/716.

Results and Discussion

The pendant-arm macrocyclic pentaamine L^1 reacts readily with [Mo(CO)$_6$] to produce the complex *fac*-[MoL^1(CO)$_3$] in reasonable yield. The complex is stable to moisture and shows no sign of decomposition in air for several days. Assuming facial co-ordination only, there are several possible binding modes (such as **A**–**D**) for this ligand. Both **A** and **B** could exist as two isomeric forms depending on the location of the pendant primary amine, either above or below the plane of the co-ordinated secondary amines. Where pendant co-ordination is involved, as in **C** and **D**, this is not a consideration. The IR spectrum of the product shows three intense CO absorptions, at low frequency for terminal CO groups as a result of σ donation by co-ordinated amine groups. The pattern (two bands for C_{3v} local environment, one of which is broad and may be split into two bands) suggests facial tridentate co-ordination. Seven resonances in the ^{13}C NMR spectrum for L^1 and two for the CO groups are indicative of a mirror plane bisecting the five-membered ring and passing through the quaternary carbon, rendering each half of the molecule and two of the carbonyls equivalent. Isomers **A**, **B** and **D** do not satisfy this result, and thus **C** (the anticipated isomer) is formed. The spectroscopic results were confirmed by an X-ray analysis.



A



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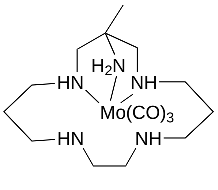
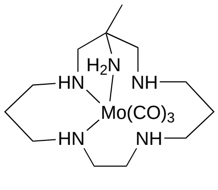


C



D

Views of the complex appear in Fig. 1, with pertinent angles and distances around the molybdenum given in Table 1. The molybdenum atom lies in a distorted octahedral environment, bound to three CO molecules on one face, with the pendant primary amines and adjacent secondary amines of the macrocycle on the other face. The molybdenum thus sits outside the macrocycle cavity. Non-co-ordinated secondary amines [N(3), N(4)] are hydrogen bonded to those co-ordinated [H(1) · · · N(4) 2.07(1) Å, H(2) · · · N(3) 2.11(1) Å], maintaining the integrity of the macrocycle in a structure similar to the one found with a metal ion co-ordinated in the cavity [Fig. 1(*b*)], except for the dispositions of the co-ordinated nitrogen bond pairs. Metal–carbon (average 1.916 Å) and nitrogen distances (average 2.318 Å) fall in the range found for similar structures, such as [Mo(dien)(CO)$_3$] (average Mo–C 1.943, Mo–N 2.323 Å) and [MoL′(CO)$_3$] (average Mo–C 1.902, Mo–N 2.368 Å).[1,3] However, in [MoL^1(CO)$_3$], there is a marked difference between the primary amine distance (2.287 Å) and the secondary amine distances (2.334 Å). This feature of a short M–N (primary) bond is replicated in other transition-metal complexes of ligands of this type containing the NHCH$_2$C(CH$_3$)(NH$_2$)CH$_2$NH 'capping' unit fully co-ordinated.[6] The secondary amine Mo–N distances are separately much closer to the average distances in

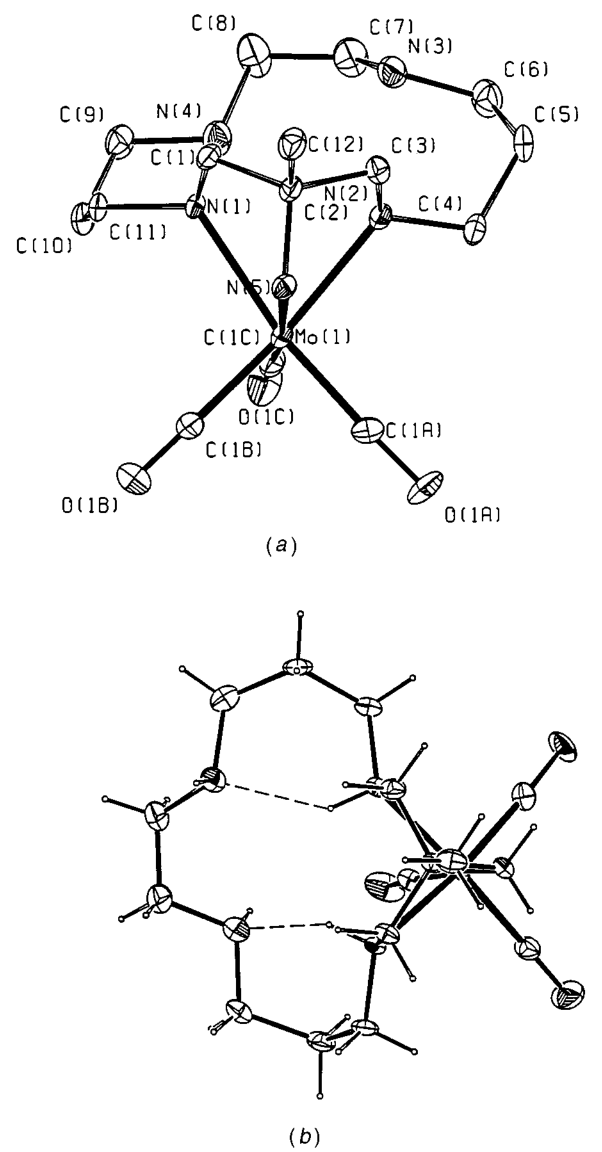


Fig. 1 Views of the [MoL^1(CO)$_3$] complex, including the atom numbering scheme

other complexes. The Mo–C bond *trans* to the primary amine [1.928(9) Å] is not markedly different from the other Mo–C bonds [1.902(8), 1.928(8) Å], so there is no general bond compression along that axis compared with the other two directions. The 'capping' tridentate unit is held in a boat conformation and the strain imposed by co-ordination is evident in the internal angles [*e.g.* C(3)–C(2)–N(1) 106.0°], but is even more pronounced at the molybdenum centre with the Mo–N(5) bond clearly pulled towards the ligand and the angles in the five-membered chelate rings involving N(1), N(2) and N(5) being particularly acute [N(1)–Mo–N(2) 73.1°, N(5)–Mo–N(2) 75.1°, N(5)–Mo–N(1) 74.3°]. The two 'compartments' of the molecule (MoN$_3$ *versus* MoC$_3$) are separated by opened-out N–Mo–C angles (99.0–101.7°).

Initial capture of a metal ion by the central NHCH$_2$-C(CH$_3$)(NH$_2$)CH$_2$NH unit of a larger polyamine has been observed previously in a rhodium(III) complex, also with a *fac*-N$_3$X$_3$ geometry.[13] The analogous behaviour in the present example, despite the obvious strain involved in co-ordination, indicates that the pendant primary amine is a strong competitor for co-ordination sites and suggests that it plays a role in the stepwise binding of such pendant-arm polyamines to metal ions.

Earlier, mercury(II) complexes of L^2 have been characterised structurally where the pendant primary amine binds either as the sole donor group or else as one of a didentate unit also involving an adjacent secondary amine group.[14] These mercury complexes also involve co-ordination of two metal ions, one on each side of the macrocycle. It was this observation which suggested that reaction of L^2 with [Mo(CO)$_6$] may lead to similar dimers, with the possibility of any of tri-, di- or uni-dentate co-ordination. Reaction of L^2 with [Mo(CO)$_6$] in refluxing mesitylene produced a good yield of a yellow product with a Mo : L ratio of 2 : 1. The IR spectrum shows four carbonyl resonances, unlike the three observed for *fac*-tridentate co-ordination. The ^{13}C NMR spectrum of the ligand exhibits six resonances, consistent with a centrosymmetric complex. This is itself consistent with symmetry-related co-ordination of a molybdenum at opposite 'ends' of the macrocycle. The observation, however, of four carbonyl group resonances in the ^{13}C NMR spectrum implies the presence of four groups in different magnetic environments. This could not arise if the molybdenum is bound by the ligand acting in a uni-, tri- or even a di-dentate manner involving co-ordination to equivalent secondary amine groups, but can be interpreted for didentate co-ordination *via* a secondary and primary amine. This was revealed as correct by a crystal structure determination.

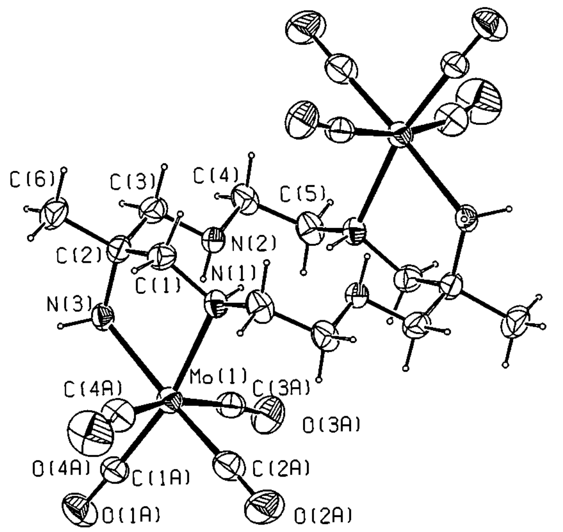


Fig. 2 A view of the [Mo$_2$L^2(CO)$_8$] complex, including the atom numbering scheme

A view of the complex [Mo$_2$L^2(CO)$_8$] appears in Fig. 2, with pertinent angles and distances around the molybdenum given in Table 2. The complex lies on a centre of symmetry in the crystal structure. Each molybdenum atom is in a distorted octahedral environment, bound to four CO molecules and to the pendant primary amine and an adjacent secondary amine of the macrocycle. The molybdenum thus sits outside the macrocycle cavity, and an equivalent molybdenum is bound in a *trans* disposition on the opposite side and end of the macrocycle. The unit cell includes two half-dimer units and also incorporates two dimethylformamide molecules which sit together in the centre of the unit cell and are involved in some weak contacts with the carbonyl groups. The primary and secondary amines exhibit similar bonding distances to the molybdenum [Mo–N(1) and Mo–N(3) 2.304(5) and 2.312(5) Å respectively], although perhaps slightly different *trans* carbonyl distances [Mo–C(2A) 1.935(9) and Mo–C(1A) 1.952(8) Å] are found. The other Mo–CO distances [Mo–C(3A) 2.026(8), Mo–C(4A) 2.012(9) Å] are similar also, suggesting that their magnetically different environments with the Mo–C(3A) carbonyl group placed below (or above for the opposite centre) the macrocycle cavity and the Mo–C(4A) carbonyl disposed away from the macrocycle are not sterically differentiated. Differences in Mo–CO distances as a result of the differing *trans* effects of the CO and amine ligands (0.075 Å) is apparent, however. Unlike [MoL^1(CO)$_3$], where there is a marked difference (0.047 Å) between the primary amine and the secondary amine distances, the difference

Table 2 The molybdenum environment in $[Mo_2L^2(CO)_8]$

Atom	*r*	C(4A)	C(3A)	C(2A)	C(1A)	N(3)
N(1)	2.312(5)	93.2(3)	93.5(2)	102.1(2)	168.0(2)	74.2(2)
N(3)	2.304(5)	95.3(3)	97.0(2)	176.2(3)	94.2(2)	
C(1A)	1.952(8)	84.8(3)	90.8(3)	89.5(3)		
C(2A)	1.935(9)	84.0(3)	83.9(3)			
C(3A)	2.026(8)	167.2(3)				
C(4A)	2.012(9)					

here (0.008 Å) is negligible (within experimental error) as a result of greater flexibility resulting from di- as compared with tri-dentate ('cap') co-ordination.

Each complex unit is related by an S_2 axis, with all four carbonyl groups in different environments, consistent with the NMR results. The angle at the metal centre involving the chelate, N(3)–Mo–N(1), is significantly reduced to 74.2(2)°, which can be compared with the opposite C(1A)–Mo–C(2A) angle which is close to normal at 89.5(3)°, reflecting the small bite angle of the chelate groups. The distortion also shows up in the N(1)–Mo–C(1A) and N(3)–Mo–C(2A) angles which are less than ideal at 168.0(2) and 176.2(3)° respectively. However, the octahedron is significantly less distorted than is the other structure where tridentate co-ordination occurs, possibly because unique MoN_3 and $Mo(CO)_3$ octahedral faces do not exist in the present example. Notably, the macrocycle adopts the geometry found when bound in a tetradentate manner with a metal ion in the cavity, with the exception that the lone pairs of the co-ordinating amines are placed out of the cavity, directing two secondary amine protons into the centre of the cavity. This appears to be the first report of this type of co-ordination of a cyclic polyamine to zerovalent molybdenum. Tridentate co-ordination of each molybdenum involving the third adjacent amine group may be disfavoured because this would bring each $Mo(CO)_3$ unit into close proximity with the macrocycle ring and also lead to closer proximity of the molybdenum centres to each other, with unfavourable steric consequences. Full facial co-ordination may possibly be enforced by extended reaction, but we found no evidence for this occurring.

The co-ordination of the Mo to L^2 is very like the co-ordination observed in a mercury complex of the same ligand, where an equivalent dimer featuring in that case chelated tetrahedral $HgCl_2$ units has been characterised by a crystal structure analysis.[14] We have already noted above examples of tridentate cap co-ordination also. The preferential binding of the pendant primary amines rather than additional secondary amines is becoming a feature of certain complexes of this type of ligand, and points to the important general role of the amine pendant, despite being fused directly to the macrocyclic ring, in metal-ion binding. The role the pendant amine group may play in capturing metal ions which eventually are inserted into the macrocycle ring has been developed in extensive mechanistic studies of formation reactions.[15] Compounds albeit unlikely to lead to metal-ion insertion into the ring characterised by X-ray structural analyses may nevertheless represent intermediates along the path by which metal ions are stepped into the ring *via* uni-, di- and tri-dentate co-ordination,[13,14] leading eventually to incorporation in the macrocycle cavity. The molybdenum complexes described here also extend the range and type of structures known for complexes of polyamines with molybdenum carbonyls.

Acknowledgements

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References

1 F. A. Cotton and R. M. Wing, *Inorg. Chem.*, 1965, **4**, 314.
2 P. Chaudhuri, K. Wieghardt, Y.-H. Tsai and C. Krüger, *Inorg. Chem.*, 1984, **23**, 427.
3 R. W. Hay, I. Fraser and G. Ferguson, *J. Chem. Soc., Dalton Trans.*, 1989, 2183.
4 J.-J. Yaouanc, N. Le Bris, J.-C. Clément, H. Handel and H. des Abbayes, *J. Chem. Soc., Chem. Commun.*, 1993, 696.
5 N. Le Bris, J.-J. Yaouanc, J.-C. Clément, H. Handel and H. des Abbayes, *Tetrahedron Lett.*, 1993, **34**, 5429; V. Patinec, J.-J. Yaouanc, J.-C. Clément, H. Handel and H. des Abbayes, *Tetrahedron Lett.*, 1995, **36**, 79.
6 P. V. Bernhardt and G. A. Lawrance, *Coord. Chem. Rev.*, 1990, **104**, 297.
7 P. V. Bernhardt, G. A. Lawrance and T. W. Hambley, *J. Chem. Soc., Dalton Trans.*, 1989, 1059.
8 G. A. Lawrance, T. M. Manning, M. Maeder, M. Martinez, M. A. O'Leary, W. C. Patalinghug, B. W. Skelton and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1992, 1635.
9 A. J. M. Duisenberg, DIRAX, Utrecht University, 1994.
10 S. R. Hall, H. D. Flack and J. M. Stewart (Editors), *The XTAL3.2 User's Manual*, Universities of Western Australia, Geneva and Maryland, 1992.
11 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.
12 G. M. Sheldrick, SHELXL 93, Program for Crystal Structure Determination, University of Göttingen, 1993.
13 T. W. Hambley, G. A. Lawrance, M. Maeder, K. J. Molloy and M. Rossignoli, *Aust. J. Chem.*, 1994, **47**, 829.
14 P. G. Lye, G. A. Lawrance, M. Maeder, B. W. Skelton, H. Wen and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1994, 793.
15 P. G. Lye, Doctoral thesis, The University of Newcastle, 1994.

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