Characterisation of Tridentate Macrocyclic Complexes of Molybdenum(0) with Tetra-aza Macrocycles; Crystal Structure of [Mo(CO)$_3$(tet *a*)] (tet *a* = C-*meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane)

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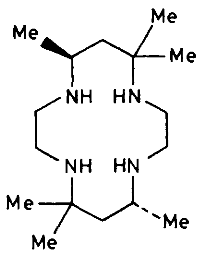
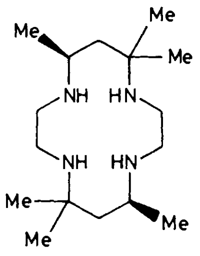
The tetra-aza macrocyclic ligands tet *a* (C-*meso*) (**1**) and tet *b* (C-racemic) (**2**) (tet = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotet-radecane), react with molybdenum hexacarbonyl in dry dimethylformamide to yield [Mo(CO)$_3$(tet *a*)] (**3**) and [Mo(CO)$_3$(tet *b*)] (**4**), respectively, in which the potentially tetradentate ligands are tridentate; the [Mo(CO)$_3$(tet *a*)] complex has been characterised by *X*-ray crystallography.

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 tet *a* (1) and tet *b* (2) have been well studied.[1] The tet *a* ligand is known to fold with difficulty, while tet *b* 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 tet *a* and *b*. We report the preparation of unique complexes[3] in which the tetra-aza macrocycle is found to be tridentate.



tet *a*
(C-*meso*)
(1)



tet *b*
(C-racemic)
(2)

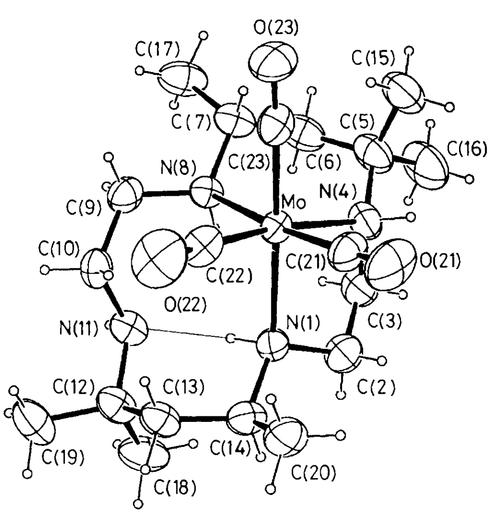


Figure 1. Single crystal *X*-ray structure of [$Mo(CO)_3$(tet *a*)].

Under gentle reflux conditions tet *a*·$2H_2O$ and tet *b*·H_2O (prepared as described in ref. 4) (1.89 mmol) reacted with $Mo(CO)_6$ (1.89 mmol) in deoxygenated dry dimethylformamide (15 cm^3) under N_2 for 5 h yielding dark brown solutions. On slow cooling to room temperature yellow crystals were deposited. {Yields [$Mo(CO)_3$(tet *a*)] (**3**), 0.63 g (72%); [$Mo(CO)_3$ (tet *b*)] (**4**), 0.60 g (68%).} The i.r spectra exhibited ν (CO) at 1886 and 1743 cm^{-1} for (**3**), and 1884 and 1741 cm^{-1} for (**4**). The fast atom bombardment spectra of both complexes display parent ion peaks at m/z^+ 464.

The (tet *a*) complex (**3**) was characterised by *X*-ray crystal structure analysis.† The molybdenum atom is in a distorted octahedral environment (see Figure 1). 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 tetradentate macrocycle. The structural study clearly shows that N(11) does not co-ordinate to the molybdenum atom [Mo–N(11) distance 3.862(2) Å], but there is evidence for intramolecular hydrogen bonding N(1)-H · · · N(11′).

Electrochemical studies on the complexes were carried out at a platinum electrode using nitromethane solutions containing 0.1 M-tetra-n-butylammonium hexafluorophosphate as supporting electrolyte. Cyclic voltammograms of both (**3**) and (**4**) display a quasi-reversible one electron oxidation process corresponding to the Mo^0/Mo^I oxidation, with $E_{1/2} = -0.28$ and $E_{1/2} = -0.27$ V *vs.* ferrocene/ferrocenium, respectively.

The almost identical physical properties of (**3**) and (**4**) lead us to believe that in [$Mo(CO)_3$(tet *b*)], the tetra-aza macrocycle is also acting as a tridentate ligand. Pendant donor atoms in macrocycle complexes are not unknown. In the two reported complexes of platinum(II) containing potentially tridentate macrocycles which act as bidentate ligands,[8] oxidation of the metal centre to Pt^{III}[3b] or Pt^{IV}[3a] leads to the ligands adjusting their mode of co-ordination and becoming fully co-ordinated to the platinum centre. Weighardt and co-workers[5] have reported the oxidation of $LMo(CO)_3$ (L = 1,4,7-triazacyclononane) using concentrated HCl or $SOCl_2$–$CHCl_3$ to give $LMoCl_3$. These strategies for metal oxidation have proved unsuccessful with the complexes presented here. Neither (**3**) nor (**4**) reacts with hot concentrated HCl, and both complexes are destroyed when refluxed with $SOCl_2$ in $CHCl_3$.

Trimethylamine N-oxide (TMNO) has been found to replace CO selectively from transition metal carbonyl complexes and has been widely used as a decarbonylation reagent.[6] We are currently investigating the reactions of complexes (**3**) and (**4**) with TMNO.

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† *Crystal data:* $C_{19}H_{36}MoN_4O_3$, M = 464.46, monoclinic, space group $P2_1/n$, a = 8.699(2), b = 19.839(4), c = 12.518(2) Å, β = 90.79(1)°, D_x = 1.43 g cm^{-3}, U = 2160(1) $Å^3$, Z = 4, μ(Mo-K_α) 6.2 cm^{-1}, λ(Mo-K_α) 0.71073 Å. Reflections were measured using a Enraf-Nonius diffractometer. A yellow crystal (0.10 × 0.13 × 0.31 mm) was mounted in a random orientation. A total of 3680 reflections were collected. 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. 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 were restrained to ride on the atom to which they were bonded. The final cycle of refinement included 245 variable parameters and converged with R = 0.022 and R_w 0.030. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

References

1 See for example, D. A. House, R. W. Hay, and M. Akbar Ali, *Inorg. Chim. Acta*, 1983, **72**, 239.

2 See for example, P. O. Whimp, M. F. Bailey, and N. F. Curtis, *J. Chem. Soc.* (*A*), 1970, 19856; N. F. Curtis in 'Co-ordination Chemistry of Macrocyclic Compounds,' ed. G. A. Melson, Plenum Press, New York, 1979, p. 230, *et seq.*; H. Ito, M. Sugimoto, and T. Ito, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 1971.

3 Two platinum complexes containing potentially tridentate macrocycles have been reported: (a) K. Wieghardt, M. Koppen, W. Swiridoff, and J. Weiss, *J. Chem. Soc., Dalton Trans.*, 1983, 1869; (b) A. J. Blake, R. O. Gould, A. J. Holder, T. I. Hyde, A. J. Lavery, and M. O. Odulate, *J. Chem. Soc., Chem. Commun.*, 1987, 118.

4 R. W. Hay, G. A. Lawrence, and N. F. Curtis, *J. Chem. Soc., Perkin Trans. I*, 1975, 591.

5 G. Backes-Dahnann, W. Herrmann, K. Wieghardt, and J. Weiss, *Inorg. Chem.*, 1985, **24**, 485.

6 For a review of TMNO as a decarbonylation reagent, see T. Y. Luh, *Coord. Chem. Rev.*, 1984, **60**, 255.