Molybdenum and Tungsten Carbonyl Complexes with a 14-Membered Macrocyclic Ligand, Dibenzo[*b*,*i*][1,4,8,11]tetra-azacyclotetradecine

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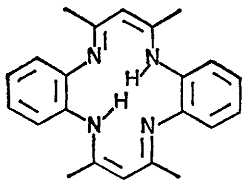
Summary The synthesis and characterization of molybdenum and tungsten carbonyl complexes with a macrocyclic Schiff base are described.

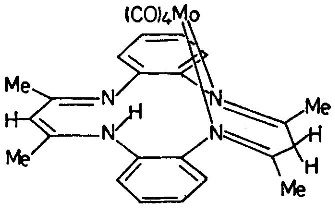
Particular interest has recently been shown in the preparation of metal carbonyl complexes of porphyrins in which the metal is either π-bonded to the phenyl ring of a phenylporphyrin,[1] or situated out of the porphyrin plane and bonded directly to the nitrogen donor atoms.[2] We report the synthesis and characterization of a molybdenum and tungsten carbonyl complex with the title synthetic macrocyclic ligand, (I)[3] formed from acetylacetone and *o*-phenylenediamine. Although cyclic Schiff base ligands have been complexed with a variety of metal ions, their involvement in metal carbonyl chemistry has not been previously reported. Molecular models and a number of physical measurements suggest that the metal is bonded to only two of the four possible sites afforded by the macrocyclic ligand [see (II)].



(I)

The reaction of equimolar quantities of (I) and [$M(CO)_6$], (M = Mo, W) in diglyme–light petroleum (10:1) gave yellow air-stable crystalline complexes.† Nearly quantitative yields of the new compounds were obtained by heating the reaction mixture (Mo, 100 °C; W, 115 °C) for 5 h under argon. Chemical analyses for C, H, N, and M were consistent with the stoicheiometry of (II).

Both complexes exhibited a single broad electronic absorption band in benzene solution; Mo, λ_{max} 345 (ϵ 2900), W, λ_{max} 355 (ϵ 9500). I.r. spectra showed four intense absorptions in the terminal CO region; Mo, ν_{max} (Nujol) 2002, 1895, 1872, and 1837 cm^{-1}; W, ν_{max} (Nujol), 2000, 1880, 1862, and 1830 cm^{-1}. By analogy with other systems,[4] these i.r. absorptions suggest a *cis* $ML_2(CO)_4$ configuration for the complexes. A strong imine (C=N) absorption due to the macrocyclic framework was observed at 1615 cm^{-1}. The mass spectra contained parent-molecular ion peaks (P^+) with the correct isotope distributions. In addition, both complexes exhibited signals for the fragmentions (I) and $(P - 4CO)^+$.



Proposed structure of the metal carbonyl complex (II)

N.m.r. spectra supported the structure of (II). The 100 MHz ^1H n.m.r. spectrum of (II; M = Mo) in $(CD_3)_2O$ (Figure) shows a complex series of phenyl resonances at δ 7·1 (8H). The methyl groups are in different chemical environments, (II), and give two sharp singlets at δ 1·99 (6H) and 1·86(6H). An AB quartet, δ 4·19 and 3·59 (each 1H, d, J 13·5 Hz) is due to the methylene protons of the six membered chelate ring. One of the NH protons has migrated to the methine carbon atom and has been replaced by the $Mo(CO)_4$ unit.

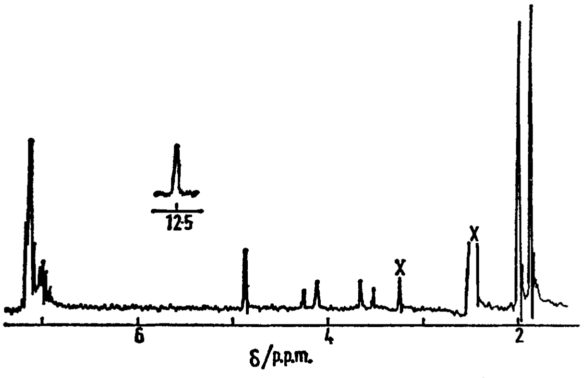


Figure. All shifts relative to Me_4Si. X; δ|3·25, H_2O; δ|2·48, Me_2SO.

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† The presence of light petroleum (b.p. 90—110 °C) prevents decomposition.

There is also a singlet resonance at δ 4·86 (1H) corresponding to the remaining olefinic hydrogen, and an NH peak at higher field, δ 12·50 (1H, s). The extreme deshielding of this type of NH proton has been previously noted.[5]

Similar ^{1}H n.m.r. results were obtained for (II; M = W); [$(CD_3)_2SO$] 1·88 (6H, s, Me), 2·02 (6H, s, Me), 4·22 and 3·62 (each 1H, d, *J* 14 Hz, CH_2), 4·88 (1H, s, CH), 7·1 (8H, m, Ar-H), and 12·64 (1H, s, NH).

Thus far attempts to prepare the analogous chromium complex have resulted in the isolation of the free ligand and decomposition products.

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[1] N. J. Cogan and Z. U. Siddiqui, *J.C.S. Chem. Comm.*, 1970, 284; *Canad. J. Chem.*, 1972, **50**, 720.

[2] D. Cullen, E. Meyer, T. S. Srivastava, and M. Tsutsui, *J. Amer. Chem. Soc.*, 1972, **94**, 7603; D. Ostfield, M. Tsutsui, C. P. Hrung, and D. C. Conway, *J. Co-ord. Chem.*, 1972, **2**, 101; *J. Amer. Chem. Soc.*, 1971, **93**, 2548; M. Tsutsui and C. P. Hrung, *ibid.*, 1974, **96**, 2638.

[3] V. L. Goedken, J. M. Case, and Y. Whang, *J.C.S. Chem. Comm.*, 1973, 339.

[4] C. S. Kraihanzel and F. A. Cotton, *Inorg. Chem.*, 1963, **2**, 533; R. St. L. Bruce, M. K. Cooper, and B. G. McGrath, *Chem. Comm.*, 1970, 69.

[5] T. J. Truex and R. H. Holm, *J. Amer. Chem. Soc.*, 1972, **94**, 4529.