Condensation of *o*-Phenylenediamine and Phthalaldehyde using Molybdenum(0) as Template. Isolation and Crystal and Molecular Structure of an Intermediate Molybdenum Complex with an η^2-Bonded Aldehydic Group†

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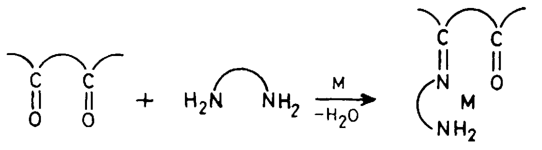
Reaction of $[Mo(CO)_3(C_6H_5Me)]$ with *o*-phenylenediamine and phthalaldehyde carried out in methanol at room temperature gives $[Mo(CO)_3L]$ {L = 2-[(2′-aminophenyl)iminomethyl]benzaldehyde}. The molecular structure determination of $[Mo(CO)_3L]$ shows the open-chain nature of L together with the η^2-co-ordination of the aldehydic group to the metal. The compound is an open-chain intermediate for a N_4 macrocyclic complex.

Most syntheses of macrocyclic nitrogen-donor ligands involve reactions between an amine and a carbonyl precursor in the presence of a suitable metal ion without isolation of any intermediate.

Nelson and Knox[1] have described how certain non-transition metal ions may be used to control the course of the condensation between dicarbonyl compounds and primary diamines. The initial intermediate product (I) in these types of reactions is presumed to be a monoimine complex[2] containing one unreacted carbonyl and one unreacted primary amine function. A complex containing the N_2O skeleton (I) has been obtained by reacting $PtCl_2$ with *o*-aminobenzaldehyde.[3] However, dimeric condensation of *o*-aminobenzaldehyde which produces the fragment (I) was accompanied by deprotonation of the terminal NH_2 group.

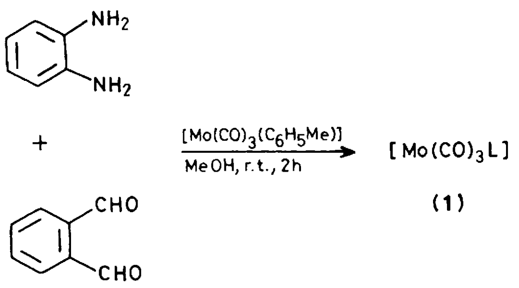


(I)

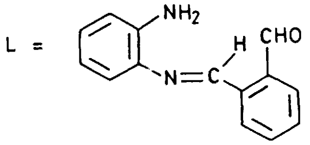
We report here the synthesis and *X*-ray structural determination of an open-chain intermediate similar to (I) which was obtained during the course of a study on the complexation of Mo^0 with macrocycles.[4]

Results and Discussion

The reaction of $[Mo(CO)_3(C_6H_5Me)]$[5] with *o*-phenylenediamine and *o*-phthalaldehyde (1:1:1 ratio) carried out in dry methanol at room temperature (r.t.) and under nitrogen gave a brown solution from which compound $[Mo(CO)_3L]$ (1) precipitated as a crystalline red-violet solid (75% yield)‡ [equation (1)].



(1)



The ^1H n.m.r. spectrum (in $[^2H_8]$tetrahydrofuran, $SiMe_4$ standard) of (1) shows bands due to the aromatic protons [δ 7.20—7.95 (m, 8 H)], the amino protons [2.98 (br t, 2 H)], the aldehydic proton [6.95 (s, 1 H)], and the methinic proton [8.65 (s, 1 H)]. The i.r. spectrum (Nujol mull) shows absorptions at 3 265m (ν_{NH}), 1 970s, 1 905s, 1 860vs (ν_{CO}), 1 615m, ($\nu_{C=N}$), and 1 565m cm^{-1} (ν_{CO}, aldehydic).

The molecular structure of (1) has been established by a single-crystal *X*-ray diffraction study. The complex is essentially octahedral (Figure) if the aldehydic group is assumed to be η^2 bonded to molybdenum. Such an assumption is justified by the Mo–C(17) and Mo–O(4) distances which are 2.276(5) and 2.120(3) Å respectively, and by the lengthening of the CO aldehydic bond (to 1.30 Å) (Table 1). Brunner *et al.*[6] reported similar values of Mo–C and Mo–O distances for a molybdenum complex with a η^2-co-ordinated benzaldehyde. Metal–nitrogen, metal–carbon and carbon–oxygen (terminal CO) bond lengths fall in the range of values reported for Mo^0 complexes.[7]

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† *Supplementary data available* (SUP No. 56430, 4 pp.): thermal parameters, H-atom co-ordinates. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

‡ Depending on the conditions of crystallization (1) contains variable amounts of solvent whose presence is inferred from spectroscopic data. Crystals utilized for the *X*-ray structural determination were solvent free.

Table 1. Bond distances (Å) and angles (°) for [Mo(CO)$_3$L] (**1**)

Mo–C(1)	1.939(4)	C(6)–C(7)	1.368(9)
Mo–C(2)	1.990(5)	C(7)–C(8)	1.401(6)
Mo–C(3)	1.958(5)	C(8)–C(9)	1.368(3)
Mo–C(17)	2.276(5)	C(9)–N(2)	1.431(4)
Mo–O(4)	2.120(3)	C(10)–C(11)	1.407(6)
Mo–N(1)	2.274(4)	C(10)–C(15)	1.405(4)
Mo–N(2)	2.239(3)	C(10)–C(17)	1.475(7)
C(1)–O(1)	1.163(5)	C(11)–C(12)	1.380(8)
C(2)–O(2)	1.140(7)	C(12)–C(13)	1.362(5)
C(3)–O(3)	1.152(6)	C(13)–C(14)	1.393(6)
C(4)–C(5)	1.395(6)	C(14)–C(15)	1.391(7)
C(4)–C(9)	1.385(7)	C(15)–C(16)	1.465(6)
C(4)–N(1)	1.442(3)	C(16)–N(2)	1.275(7)
C(5)–C(6)	1.371(5)	C(17)–O(4)	1.300(6)
C(1)–Mo–C(2)	85.6(1)	C(9)–C(4)–N(1)	116.6(2)
C(1)–Mo–C(3)	88.7(1)	C(4)–C(5)–C(6)	118.7(3)
C(1)–Mo–C(17)	94.0(1)	C(5)–C(6)–C(7)	121.9(3)
C(1)–Mo–O(4)	94.3(1)	C(6)–C(7)–C(8)	119.1(3)
C(1)–Mo–N(1)	100.8(1)	C(7)–C(8)–C(9)	119.7(2)
C(1)–Mo–N(2)	169.6(1)	C(4)–C(9)–C(8)	120.5(2)
C(2)–Mo–C(3)	83.1(1)	C(4)–C(9)–N(2)	114.4(1)
C(2)–Mo–C(17)	158.1(1)	C(8)–C(9)–N(2)	125.1(1)
C(2)–Mo–O(4)	167.7(1)	C(11)–C(10)–C(15)	118.1(2)
C(2)–Mo–N(1)	85.2(1)	C(11)–C(10)–C(17)	116.2(2)
C(2)–Mo–N(2)	99.8(1)	C(15)–C(10)–C(17)	125.5(2)
C(3)–Mo–C(17)	75.0(1)	C(10)–C(11)–C(12)	121.4(3)
C(3)–Mo–O(4)	109.1(1)	C(11)–C(12)–C(13)	120.1(3)
C(3)–Mo–N(1)	164.3(1)	C(12)–C(13)–C(14)	120.0(3)
C(3)–Mo–N(2)	100.7(1)	C(13)–C(14)–C(15)	121.0(2)
C(17)–Mo–O(4)	34.2(1)	C(10)–C(15)–C(14)	119.2(2)
C(17)–Mo–N(1)	116.2(1)	C(10)–C(15)–C(16)	125.5(2)
C(17)–Mo–N(2)	84.3(1)	C(14)–C(15)–C(16)	115.3(2)
O(4)–Mo–N(1)	82.7(1)	C(15)–C(16)–N(2)	124.9(2)
O(4)–Mo–N(2)	78.5(1)	Mo–C(17)–C(10)	115.6(2)
N(1)–Mo–N(2)	71.0(1)	Mo–C(17)–O(4)	66.3(1)
Mo–C(1)–O(1)	179.3(2)	C(10)–C(17)–O(4)	121.3(2)
Mo–C(2)–O(2)	176.4(2)	Mo–O(4)–C(17)	79.5(1)
Mo–C(3)–O(3)	179.1(2)	Mo–N(1)–C(4)	108.6(1)
C(5)–C(4)–C(9)	119.9(2)	Mo–N(2)–C(9)	111.9(1)
C(5)–C(4)–N(1)	123.5(2)	Mo–N(2)–C(16)	128.9(1)
		C(9)–N(2)–C(16)	118.7(2)

Experimental

Preparation.—A solution of *o*-phenylenediamine (1.176 g, 0.0109 mol) in methanol (35 cm^3) and a solution of phthalaldehyde (1.459 g, 0.0109 mol) in methanol (35 cm^3) were added under nitrogen to a solution of [Mo(CO)$_3$(C$_6$H$_5$Me)] (2.96 g, 0.0109 mol) in methanol (50 cm^3). A red-violet crystalline solid began to precipitate from the brown solution a few minutes after the end of the addition. After leaving to stand for 2 h at room temperature the reaction mixture was cooled and filtered to yield 3.3 g (75%) of analytically pure (**1**). These crystals were suitable for *X*-ray analysis.

Crystallography.—A crystal of dimensions 0.15 × 0.20 × 0.15 mm was mounted on a computer-controlled Philips PW1100 single-crystal diffractometer, equipped with graphite-monochromatized Mo-K_α radiation.

Crystal data. $C_{17}H_{12}MoN_2O_4$, $M = 404.2$, triclinic, space group $P\bar{1}$, $a = 10.225(3)$, $b = 9.881(2)$, $c = 9.046(2)$ Å, $\alpha = 103.59(2)$, $\beta = 114.46(2)$, $\gamma = 88.40(2)°$, $U = 806.14$ Å^3 (obtained by least-squares refinement for the setting angles of 25 reflections), $D_c = 1.664$ g cm^{-3}, $Z = 2$, μ(Mo-K_α) = 8.08 cm^{-1}, $F(000) = 404$.

Intensities were collected up to 2θ = 50° using the θ–2θ scan technique with a scan range of 1.7° and a scan speed of 0.05 s^{-1}. A total of 2 821 reflections were measured. Of these 1 995 with $I > 3\sigma(I)$ were used in the subsequent refinement. No intensity variations during the data collection were observed. The data were corrected for Lorentz and polarization factors. No absorption or secondary extinction correction was applied.

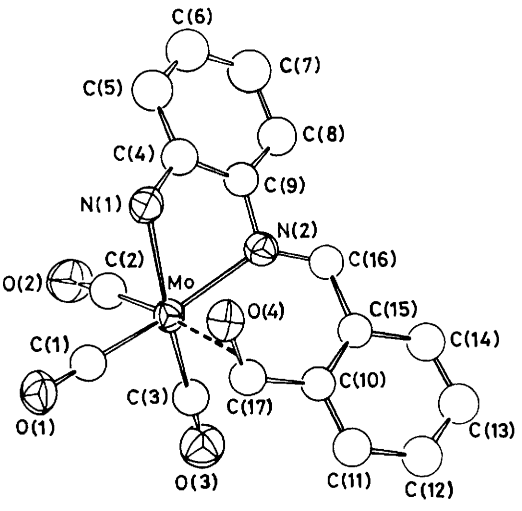

Figure. The structure of [Mo(CO)$_3$L] (**1**) showing the atomic-numbering scheme. Hydrogen atoms are omitted for clarity

Table 2. Fractional atomic co-ordinates for [Mo(CO)$_3$L] (**1**) with estimated standard deviations in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Mo	0.059 7(1)	0.221 5(1)	0.273 6(1)
C(1)	0.163 3(6)	0.176 7(6)	0.142 7(6)
C(2)	−0.056 3(6)	0.265 2(6)	0.083 3(7)
C(3)	0.191 0(6)	0.433 0(6)	0.278 8(6)
C(4)	−0.264 5(6)	0.027 9(6)	0.273 5(6)
C(5)	−0.412 6(7)	−0.058 5(7)	0.201 0(7)
C(6)	−0.519 4(8)	−0.022 1(8)	0.232 4(8)
C(7)	−0.485 1(7)	0.093 8(7)	0.335 1(7)
C(8)	−0.336 3(6)	0.179 9(6)	0.408 1(7)
C(9)	−0.228 0(5)	0.147 1(6)	0.375 9(6)
C(10)	0.252 1(6)	0.367 7(6)	0.609 0(6)
C(11)	0.395 2(7)	0.463 2(6)	0.692 6(7)
C(12)	0.416 6(7)	0.551 2(7)	0.819 6(7)
C(13)	0.297 9(7)	0.547 5(7)	0.866 2(7)
C(14)	0.154 6(6)	0.457 3(6)	0.783 5(6)
C(15)	0.130 1(6)	0.369 4(6)	0.653 7(6)
C(16)	−0.025 8(6)	0.283 8(6)	0.575 3(6)
C(17)	0.244 1(6)	0.265 5(6)	0.488 0(6)
O(1)	0.226 7(5)	0.151 3(6)	0.064 0(5)
O(2)	−0.117 1(5)	0.289 5(6)	−0.029 6(5)
O(3)	0.267 4(5)	0.557 7(5)	0.280 5(5)
O(4)	0.145 0(4)	0.128 1(4)	0.464 9(4)
N(1)	−0.143 2(5)	0.000 0(5)	0.249 0(5)
N(2)	−0.072 2(4)	0.230 8(4)	0.436 6(5)

The structure was solved by Patterson methods and refined by full-matrix least squares using the SHELX-76[8] package of programs. Hydrogen atoms H(1)–H(10) were included at calculated positions (C–H = 1.08 Å) with an overall isotropic thermal parameter of 0.14 Å^2. The positions of the amine hydrogens H(11) and H(12) were refined, constraining their bond lengths to N(1) to 1.00 ± 0.01 Å and the distance between them to 1.63 ± 0.05 Å. The Mo, O, and N atoms were refined with anisotropic thermal parameters. The refinement converged at $R = 0.036$ and $R' = 0.039$ for 139 parameters and 1 995 observed reflections $\{R' = [\Sigma w(|F_o| - |F_c|)^2/(\Sigma w F_o{}^2)]^{\frac{1}{2}}$, $w = [\sigma^2(F_o) + 0.000\,279 F_o{}^2]^{-1}\}$. Atomic scattering factors were taken from ref. 8 for O, N, C, and H and from ref. 9 for Mo; corrections for anomalous dispersion were included. The atomic positions are listed in Table 2.

Acknowledgements

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