Inorganica Chimica Acta, *122* (1986) 221–224

Synthesis and X-ray Crystal Structure of $Mo_2(CO)_6(C_{34}H_{32}N_{10})(C_3H_7NO)_8$

PAMELA CARR, BRIAN PIGGOTT* and SWEE FATT WONG

The Inorganic Chemistry Research Laboratory, Chemistry Department, School of Natural Sciences, The Hatfield Polytechnic, Hatfield, Herts AL10 9AB, U.K.

(Received July 5, 1986)

Abstract

The synthesis of $Mo_2(CO)_6L$ DMF_8 and Mo_2O_6-$L(H_2O)_4$ where L is *N,N,N',N'*-tetrakis(2-benzimidazolyl)1,2-ethanediamine ($C_{34}H_{32}N_{10}$) and DMF is dimethylformamide (C_3H_7NO) are described together with their spectroscopic properties. The X-ray structure of $Mo_2(CO)_6L$ DMF_8 is reported and seen to consist of two *fac* $Mo(CO)_3$ units bridged by the 1 and 2 amino nitrogen atoms of L. Six coordination about each molybdenum is completed by the imino nitrogen atoms of the benzimidazole rings of L.

Introduction

In previous papers we have described the synthesis, ^{95}Mo NMR and structure of Mo(VI) complexes with various substituted benzimidazoles [1–3]. Some of these complexes involve bridging between Mo atoms by ligand, oxo groups or both and their ^{95}Mo NMR properties have proved interesting. To extend this work and because of the known ability of L to form bridges [4] it was decided to synthesize and investigate some of its complexes with Mo.

Experimental

N,N,N',N'-Tetrakis(2-benzimidazolyl)1,2-ethanediamine was synthesized as described previously [5].

$Mo_2(CO)_6L$ DMF_8

L (1 mmol) in 50 ml of oxygen free diglyme and $Mo(CO)_6$ (1 mmol) were boiled under reflux in a dinitrogen atmosphere for 3 h. The bright yellow, air sensitive crystals that formed were filtered off and stored under dinitrogen.

Crystals suitable for an X-ray crystallographic study were obtained by recrystallisation from oxygen-free dimethylformamide. Because of rapid solvent loss from the crystal on exposure to air they were stored in their mother liquor under a dinitrogen atmosphere. *Anal.* Found: C, 49.14; H, 3.81; N, 14.68; Mo, 19.33. Calc. for $C_{40}H_{32}N_{10}O_6Mo_2$: C, 51.07; H, 3.43; N, 14.89; Mo, 20.40%.

$Mo_2O_6L(H_2O)_4$

MoO_2 (acetylacetonate)$_2$ (5 mmol) in 50 ml of ethanol was added with rapid stirring to 40 ml of a warm ethanolic solution of L (5 mmol). The off-white product which immediately formed was stirred for 1 h at 50 °C before filtering. It was not possible to recrystallise this compound because of its poor solubility. *Anal.* Found: C, 42.99; H, 4.35; N, 14.75; Mo, 19.90; weight loss 7.5. Calc. for $C_{34}H_{40}N_{10}O_{10}$-Mo_2: C, 43.40; H, 4.29; N, 14.89; Mo, 20.40; weight loss 7.6%.

X-ray Crystal Structure Data

$Mo_2C_{64}H_{88}N_{18}O_{14}$, $M_r = 1525.4$, triclinic, $a = 13.705(18)$, $b = 12.929(10)$, $c = 13.620(11)$ Å, $\alpha = 118.19(4)$, $\beta = 118.90(6)$, $\gamma = 66.84(6)°$, $U = 1819.16$ Å^3, space group $P\bar{1}$, $Z = 2$, μ(Mo Kα) = 7.95 cm^{-1}. A crystal of the title compound was mounted in a Lindemann tube with a small quantity of mother liquor. Intensity data were collected on a Phillips PW1100 four circle diffractometer using graphite monochromated Mo Kα radiation and a 2θ scan. A total of 3222 reflections were measured of which 2645 having $I > 2\sigma I$ were used. The data were corrected for Lorentz, polarization but not absorption. The structure was solved using Patterson and Fourier methods and least-squares refinement gave a final R value of 0.1106. The high R value is thought to be due to disorder of the DMF molecules. All computing was carried out using SHELX 76.

NMR Data

The ^{95}Mo NMR spectrum was recorded using a Brucker WM-250 spectrometer, ^{95}Mo resonance frequency 16.3 MHz. Aqueous sodium molybdate (2 M) was used as an external chemical shift reference. All measurements were made using a 50 kHz sweep width and 40 ms data acquisition time. All free induction decays were multiplied by an expo-

---

*Author to whom correspondence should be addressed.

0020-1693/86/$3.50

nential window function selected to give a minimum line width of twice the digital resolution after Fourier transformation. Experimental parameters were selected to minimise the effects of acoustic ringing in the NMR probe head.

Infra-red spectra were recorded on a Pye Unicam SP3-300 spectrometer using nujol mulls.

Results

The structure of $Mo_2(CO)_6L$ DMF_8 is shown in Fig. 1 and bond lengths and angles in Table I. The DMF has been omitted from Fig. 1 to improve clarity and it is seen that the structure consists of two linked Mo octahedra. Six coordination about each Mo is achieved through two imino nitrogen atoms plus the ethane amino nitrogen atom and three mutually *cis* CO groups. The two halves of the molecule are related by a crystallographic centre of symmetry through the C(1)–C(1′) bond. Four of the DMF molecules are involved in hydrogen-bonding to the four NH groups of the ligands. 3×10^6 scans of a saturated DMF solution of $Mo_2(CO)_6L\,DMF_8$ resulted in a spectrum with a poor signal to noise ratio but with a definite signal at −1774 ppm. The solubility of $Mo_2O_6L(H_2O)_4$ was too low for its spectrum to be recorded.

Some of the infra-red spectral bands of *N,N,N′,N′*-tetrakis(2-benzimidazolyl)1,2-ethanediamine and the complexes are given in Table II. $Mo_2(CO)_6L$ DMF_8 shows two very strong bands, one at 1892 cm^{-1} and the other, broad and centred at 1750 cm^{-1}, which are assigned to ν(CO) stretching vibrations in the *cis* $Mo(CO)_3$ moiety. The strong band at 1650 cm^{-1} is attributed to the ν(CO) of DMF. $Mo_2(CO)_6LDMF_8$ readily oxidises to Mo_2O_6L which is also obtained by reaction of $MoO_2(acetylacetonate)_2$ with L. The infra-red spectrum of Mo_2O_6L shows strong bands at 922, 850 and 815 cm^{-1} assigned to ν(Mo=O) stretching vibrations.

Discussion

Table III lists selected bond lengths found in $Mo_2(CO)_6L$ DMF_8 (**A**) and *cis*(diethylenetriamine)-molybdenumtricarbonyl (**B**) [6]. It is seen from this table that the Mo–C bond lengths for **A** are significantly shorter than those for **B** and that within **A** Mo–C(18) is significantly shorter than Mo–C(19) and Mo–C(20). The average of the C–O bond lengths for **A** is significantly larger than that for **B** and within **A** O(1)–C(18) is significantly longer than O(2)–C(19) and O(3)–C(20). The shortness of Mo–C(18) bond is interesting since this bond is 'identical' to Mo–C(19) in that it is also *trans* to a benzimidazole imino nitrogen, the Mo–C(20) bond being 'different' since it is *trans* to an amino group. A stronger Mo–C(18) sigma/π interaction is suggested by the shortness of this bond which would be expected to lead to the observed increase in the O(1)–C(18) bond length

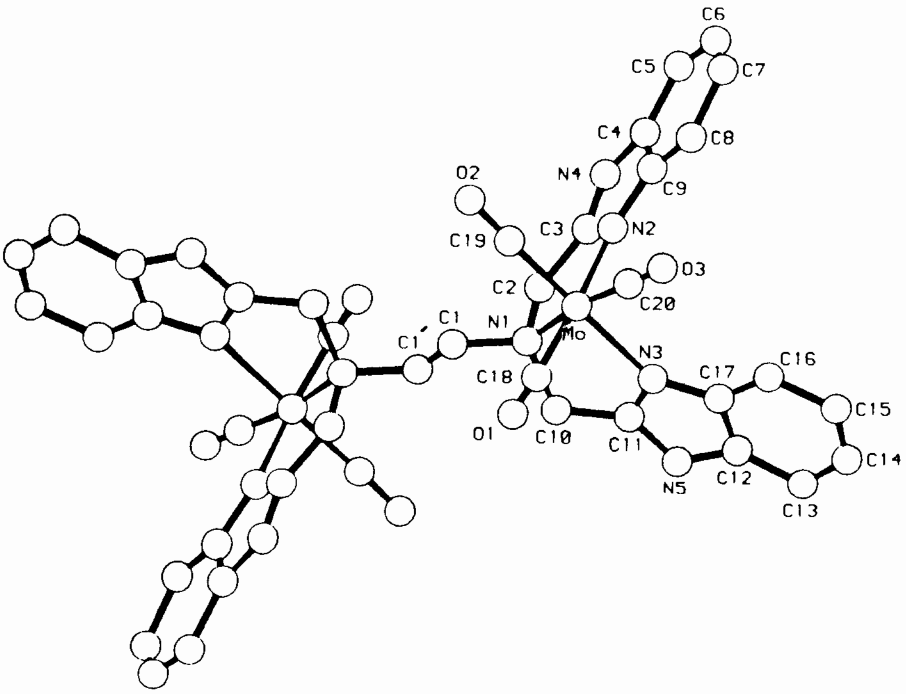

Fig. 1. The structure of $Mo_2(CO)_6LDMF_8$.

TABLE I. Bond Lengths (Å) and Bond Angles (°) for $Mo_2(CO)_6L(DMF)_8$

Mo–N(1)	2.423(2)	N(5)–C(11)	1.32(2)
Mo–N(2)	2.171(2)	N(5)–C(12)	1.35(3)
Mo–N(3)	2.178(1)	C(1)–C(1)	1.53(4)
Mo–C(18)	1.775(3)	C(2)–C(3)	1.45(2)
Mo–C(19)	1.860(2)	C(4)–C(5)	1.38(4)
Mo–C(20)	1.876(3)	C(4)–C(9)	1.35(4)
O(1)–C(18)	1.25(4)	C(5)–C(6)	1.36(4)
O(2)–C(19)	1.19(3)	C(6)–C(7)	1.30(6)
O(3)–C(20)	1.17(3)	C(7)–C(8)	1.36(4)
N(1)–C(1)	1.47(2)	C(8)–C(9)	1.42(3)
N(1)–C(2)	1.48(4)	C(10)–C(11)	1.50(3)
N(1)–C(10)	1.44(3)	C(12)–C(13)	1.40(3)
N(2)–C(3)	1.33(3)	C(12)–C(17)	1.37(2)
N(2)–C(9)	1.38(2)	C(13)–C(14)	1.34(3)
N(3)–C(11)	1.30(2)	C(14)–C(15)	1.41(3)
N(3)–C(17)	1.42(3)	C(15)–C(16)	1.39(3)
N(4)–C(3)	1.31(4)	C(16)–C(17)	1.39(3)
N(4)–C(4)	1.36(2)		
N(1)–Mo–N(2)	74(1)	N(2)–C(3)–N(4)	114(2)
N(1)–Mo–N(3)	72(1)	N(2)–C(3)–C(2)	122(3)
N(1)–Mo–C(18)	97(1)	N(4)–C(3)–C(2)	124(3)
N(1)–Mo–C(19)	103(1)	N(4)–C(4)–C(5)	133(3)
N(1)–Mo–C(20)	171(1)	N(4)–C(4)–C(9)	104(2)
N(2)–Mo–N(3)	82(1)	C(5)–C(4)–C(9)	123(2)
N(2)–Mo–C(18)	171(1)	C(4)–C(5)–C(6)	117(4)
N(2)–Mo–C(19)	96(1)	C(5)–C(6)–C(7)	121(3)
N(2)–Mo–C(20)	101(1)	C(6)–C(7)–C(8)	125(3)
N(3)–Mo–C(18)	96(1)	C(7)–C(8)–C(9)	115(3)
N(3)–Mo–C(19)	175(1)	N(2)–C(9)–C(4)	113(2)
N(3)–Mo–C(20)	99(1)	N(2)–C(9)–C(8)	129(3)
C(18)–Mo–C(19)	86(1)	C(4)–C(9)–C(8)	119(2)
C(18)–Mo–C(20)	88(1)	N(1)–C(10)–C(11)	110(1)
C(19)–Mo–C(20)	85(1)	N(3)–C(11)–N(5)	116(2)
Mo–N(1)–C(1)	110(1)	N(3)–C(11)–C(10)	119(2)
Mo–N(1)–C(2)	110(1)	N(5)–C(11)–C(10)	125(2)
Mo–N(1)–C(10)	107(2)	N(5)–C(12)–C(13)	131(2)
C(1)–N(1)–C(2)	108(2)	N(5)–C(12)–C(17)	107(2)
C(1)–N(1)–C(10)	111(1)	C(13)–C(12)–C(17)	123(2)
C(2)–N(1)–C(10)	111(2)	C(12)–C(13)–C(14)	116(2)
Mo–N(2)–C(3)	119(1)	C(13)–C(14)–C(15)	123(2)
Mo–N(2)–C(9)	139(2)	C(14)–C(15)–C(16)	120(2)
C(3)–N(2)–C(9)	102(2)	C(15)–C(16)–C(17)	117(2)
Mo–N(3)–C(11)	120(1)	N(3)–C(17)–C(12)	109(2)
Mo–N(3)–C(17)	138(1)	N(3)–C(17)–C(16)	130(2)
C(11)–N(3)–C(17)	102(1)	C(12)–C(17)–C(16)	121(2)
C(3)–N(4)–C(4)	108(2)	Mo–C(18)–O(1)	173(2)
C(11)–N(5)–C(12)	106(1)	Mo–C(19)–O(2)	174(3)
N(1)–C(2)–C(3)	114(2)	Mo–C(20)–O(3)	178(2)

as a consequence of enhanced Mo(4d) → CO(π^*) back donation. However the differences between complexes **A** and **B** in their C–O bond distances are not reflected in their infra-red spectra since both complexes show absorption bands in very similar positions, *i.e.* **A** 1892 and 1750 cm^{-1} (mull spectrum) and **B** 1898 and 1758 cm^{-1} (solution spectrum). These are claimed to be very similar since it is observed that mull spectra are usually 10–20 cm^{-1} lower than solution spectra [7]. But in both complexes the ν(CO) stretching frequencies are appreciably lower than the values found for *cis* $Mo(CO)_3(PCl_3)_3$, for example [8]. This can be interpreted in terms of the weaker π acceptor (or greater π donor ability) of L and diethylenetriamine compared to PCl_3.

TABLE II.

Compound	νN–H (cm^{-1})	$\nu(Mo–O_t)$ (cm^{-1})	ν(Mo–CO) (cm^{-1})
L	3150	–	–
$Mo_2(CO)_6L\ DMF_8$	3380		1892 1750 1650 (νCO of DMF)
$Mo(CO)_3(dien)$ [a]			1898 1758
$Mo_2O_6L(H_2O)_4$	3360	922 850 815	
$Na_4[Mo_2O_6(edta)]\cdot 8H_2O$ [b]		900 860 826	

[a] Ref. 6. [b] Ref. 9. dien = diethylenetriamine. edta = ethylenediaminetetraacetic acid.

TABLE III. Selected Bond Lengths (Å) for $Mo_2(CO)_6L(DMF)_8$, **A** and $Mo(dien)(CO)_3$ [a], **B**

A		**B**	
Mo–C(18)	1.773(3)	Mo–C(1)	1.933 ± 0.021
Mo–C(19)	1.860(2)	Mo–C(2)	1.953 ± 0.019
Mo–C(20)	1.876(3)	Mo–C(3)	1.942 ± 0.021
O(1)–C(18)	1.25(4)	O(1)–C(1)	1.158 ± 0.027
O(2)–C(19)	1.19(3)	O(2)–C(2)	1.135 ± 0.026
O(3)–C(20)	1.17(3)	O(3)–C(3)	1.166 ± 0.030
Mo–N(1)	2.423(2)	Mo–N(1)	2.311 ± 0.019
Mo–N(2)	2.171(2)	Mo–N(2)	2.310 ± 0.019
Mo–N(3)	2.178(1)	Mo–N(3)	2.348 ± 0.018

dien = diethylenetriamine. [a] Ref. 6.

The Mo–N bond lengths, Table III, are interesting in that the bond to the imino nitrogen in **A**, at 2.422 Å, is longer than any of the Mo–N bonds in **B**, mean 2.323 Å. The Mo to imino nitrogen bond distances in **A** are both very short, Table III, which suggests a greater sigma interaction for these donors compared to those in **B**. The mean Mo–N bond length in **A** is 2.257 Å.

The ^{95}Mo NMR signal at –1774 ppm in **A** indicates substantially greater shielding of the Mo nucleus than is observed in **B** which gives a signal at –1088 ppm; it is more comparable in magnitude to that found for $Mo(CO)_3(POMe)_3$, –1756 ppm [8]. Given the differences in bond lengths between **A** and **B** as detailed above, it is suggested that the differences in ^{95}Mo NMR chemical shifts are a result of a greater sigma electron density on the Mo nucleus in **A** compared to **B**.

From the similarity in infra-red spectra and elemental analysis it is claimed that the product obtained by the reaction of MoO_2(acetylacetone)$_2$ with L and that obtained by oxidation of $Mo_2(CO)_6L$ are identical and their structure similar to that of $Mo_2(CO)_6L$ (Fig. 1) with the CO replaced by O^{2-}, the Mo being formally Mo(VI). This type of structure is found in $Na_4[MoO_3(EDTA)MoO_3]\cdot 8H_2O$ where EDTA is ethylenediaminetetraacetic acid [9]. The infra-red spectra of the EDTA complex and Mo_2O_6L are very similar in the Mo=O stretching region, Table II.

Supplementary Material

The atomic coordinates for this work are available on request from the Director of Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EWK. Any request should be accompanied by the full literature citation for this communication.

References

1 B. Piggott, R. N. Sheppard and D. J. Williams, *Inorg. Chim. Acta, 86* (3), L65 (1984).
2 M. V. Capparelli, B. Piggott, S. D. Thorpe, S. F. Wong and R. N. Sheppard, *Inorg. Chim. Acta, 106,* 19 (1985).
3 B. Piggott, S. F. Wong and R. N. Sheppard, *Inorg. Chim. Acta, 107,* 97 (1985).
4 H. M. J. Hendriks, P. J. M. W. L. Birker, J. Van Rijn, G. C. Verschoor and J. Reedijk, *J. Am. Chem. Soc., 104,* 3607–3617 (1982).
5 H. M. J. Hendriks, ten Bokkel Huinink and W. O. Reedijk, *J. Recl. Trav. Chim. Pays Bas, 98,* 499–500 (1979).
6 F. A. Cotton and R. M. Wing, *Inorg. Chem., 3,* 314 (1965).
7 C. S. Kraihanzel and F. A. Cotton, *Inorg. Chem., 2,* 533 (1963).
8 F. A. Cotton, *Inorg. Chem., 3,* 702 (1964).
9 J. J. Park, M. D. Glick and J. L. Hoard, *J. Am. Chem. Soc., 91,* 301 (1969).