$S = 1.16$
2167 reflections
199 parameters
H atoms: see below
Weighting scheme: see below
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| Sn1—O1 | 2.153 (2) | O2—C4 | 1.242 (4) |
| Sn1—O2$^{i}$ | 2.495 (2) | N1—C10 | 1.368 (4) |
| Sn1—C1 | 2.106 (3) | N1—C11 | 1.437 (4) |
| Sn1—C2 | 2.113 (4) | C4—C5 | 1.480 (4) |
| Sn1—C3 | 2.109 (3) | C5—C6 | 1.394 (4) |
| O1—C4 | 1.292 (4) | C5—C10 | 1.417 (4) |
| O1—Sn1—O2$^{i}$ | 173.60 (8) | C1—Sn1—C3 | 113.9 (2) |
| O1—Sn1—C1 | 97.5 (1) | C2—Sn1—C3 | 119.3 (1) |
| O1—Sn1—C2 | 96.3 (1) | Sn1—O1—C4 | 123.8 (2) |
| O1—Sn1—C3 | 88.1 (1) | Sn1$^{ii}$—O2—C4 | 162.3 (2) |
| O2$^{i}$—Sn1—C1 | 88.3 (1) | C10—N1—C11 | 125.9 (3) |
| O2$^{i}$—Sn1—C2 | 82.4 (1) | O1—C4—C5 | 117.1 (2) |
| O2$^{i}$—Sn1—C3 | 87.1 (1) | O2—C4—C5 | 121.8 (3) |
| C1—Sn1—C2 | 125.2 (1) | O1—C4—O2 | 121.1 (3) |

Symmetry codes: (i) $\frac{3}{2} - x, y - \frac{1}{2}, 2 - z$; (ii) $\frac{3}{2} - x, \frac{1}{2} + y, 2 - z$.

The weighting scheme used was $w = 4F^2/[\sigma(I)^2 + (0.04F^2)^2]$, if $F^2 < 4[\sigma(I)^2 + (0.04F^2)^2]^{1/2}$ then the reflection is omitted. All non-H atoms were refined with anisotropic displacement parameters. H atoms were placed geometrically 0.95 Å from their corresponding C atoms of the phenyl and xylyl rings, while the H atoms of N1, C17 and C18 were taken from a difference map and refined for a few cycles. For all H atoms, a riding model was used with $B_{eq}(H) = 1.3B_{eq}(C,N)$.

Data collection: *CAD-4 Express* (Enraf–Nonius, 1993). Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SIMPEL* in *MolEN*. Program(s) used to refine structure: *LSFM* in *MolEN*. Molecular graphics: *ORTEP*II (Johnson, 1976) in *MolEN*. Software used to prepare material for publication: *MolEN*.

The authors wish to acknowledge the purchase of the CAD-4 diffractometer under Grant DPT/TBAG1 of the Scientific and Technical Research Council of Turkey.

Lists of structure factors, anisotropic displacement parameters, atomic coordinates and complete geometry have been deposited with the IUCr (Reference: NA1265). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

## References

Danish, M., Ali, S., Mazhar, M., Badshah, A., Masood, T. & Tiekink, E. R. T. (1995). *Main Group Met. Chem.* **18**, 27–34.

Enraf–Nonius (1993). *CAD-4 Express Software*. Version 1.1. Enraf–Nonius, Delft, The Netherlands.

Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Lockhart, T. P. & Davison, F. (1987). *Organometallics*, **6**, 2471–2478.

Nowell, I. W., Brooks, J. S., Beech, G. & Hill, R. (1983). *J. Organomet. Chem.* **244**, 119–124.

Parulekar, C. S., Jain, V. K., Das, T. K., Gupta, A. R., Hoskins, B. F. & Tiekink, E. R. T. (1989). *J. Organomet. Chem.* **372**, 193–199.

Stocco, G., Guli, G., Giraslo, M. A., Bruno, G., Nicolo, F. & Scopelliti, R. (1996). *Acta Cryst.* C**52**, 829–832.

Tiekink, E. R. T., Sandhu, G. K. & Verma, S. P. (1989). *Acta Cryst.* C**45**, 1810–1811.

*Acta Cryst.* (1997). C**53**, 185–187

# Tetracarbonyl($\eta^{2:2}$-1,5-cyclooctadiene)-molybdenum(0)

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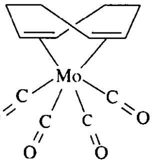
(*Received 16 May 1996; accepted 11 October 1996*)

## Abstract

In the title compound, tetracarbonyl[(1,2,5,6-$\eta$)-1,5-cyclooctadiene]molybdenum(0), $[Mo(C_8H_{12})(CO)_4]$, the coordination polyhedron around the metal atom is a distorted octahedron. The Mo—C bond distance for CO groups *trans* to a C=C unit is significantly shortened [average value 1.948 (8) Å], while the Mo—C bond distances for the *cis* groups are only slightly shortened [average value 2.031 (8) Å], compared with the values reported for $[Mo(CO)_6]$. The average distance of the Mo atom to the midpoints of the olefinic C=C bonds is 2.388 (8) Å.

## Comment

Thermal or photochemical reactions between hexacarbonylmetal(0) and 1,5-cyclooctadiene (COD) form the olefin complexes of the group 6 metals $[M(CO)_4(\eta^{2:2}\text{-COD})]$ (Fischer & Fröhlich, 1959; Dixon, Kola & Howell, 1984). Olefin complexes have been used as powerful $[M(CO)_4]$ transfer reagents in the syntheses of many transition metal carbonyl derivatives due to the lability of the metal–diene bond (King & Fronzaglia, 1966). The stereochemistry of the rigid complexes has been studied by IR (Darensbourg, Tappan & Nelson, 1977) and $^{13}C$ NMR spectroscopy (Darensbourg, Nelson & Murphy 1977; Kotzian, Kreiter & Özkar, 1982; Gryf-Keller, Krawczyk & Szczecinski, 1991). Despite the extensive use of the $[Mo(CO)_4(\eta^{2:2}\text{-diene})]$ complexes, only the structure of the analogous tungsten compound with norbornadiene (Greveles, Jacke, Betz, Krüger & Tsay, 1989) appears to have been reported. The present paper deals with the structure determination of $[Mo(CO)_4(\eta^{2:2}\text{-COD})]$, (I), and the interpretation of the IR and $^{13}C$ NMR spectroscopic data.



(I)

As can be seen from Fig. 1, the Mo atom has basically a distorted octahedral coordination. The olefinic C5═C6 and C9═C10 bonds coordinate the metal atom in two *cis* sites and are oriented parallel to Mo—C1 and Mo—C4, respectively. The alternative orientation (90° rotation) is unlikely because the midpoints of the olefin bonds would then result in a severe distortion of the octahedral coordination and, more significantly, these bonds would also be incorrectly positioned for participation in the back-bonding interactions. The Mo—C2 and Mo—C3 bonds which are *trans* to the C═C units are significantly shortened, while the Mo—C bonds for the CO groups which are *cis* to both C═C units are only slightly shortened, compared with the average Mo—C distance reported for $[Mo(CO)_6]$ (Mak, 1984). This trend reflects the single-faced nature of the olefin ligand possessing only one $\pi^*$ orbital available for back bonding and can be rationalized in terms of the changes in the metal $d_\pi \rightarrow$ CO $\pi^*$ back donation to the individual CO groups. As a single-faced $\pi$-acceptor ligand, each C═C bond of the 1,5-cyclooctadiene ligand competes for $\pi$ back donation with the CO groups which are in the same plane. Thus, C2═O2 and C3═O3 compete with only one of the C═C bonds for $\pi$ back donation, while C1═O1 and C4═O4 compete with both. As a result, the distances of the Mo atom to both C2 and C3 are expected to be shorter than the distances to C1 and C4, which is as observed. The C2—Mo—C3 bond angle is 92.1 (3)°, a value anticipated for two *cis*-carbonyl groups in an octahedral complex. However, the C1—Mo—C4 bond angle is 165.4 (3)°, which is much smaller than the 180° expected for two *trans*-carbonyl ligands. This distortion is attributed to the steric repulsion between the C1═O1 or C4═O4 carbonyl ligands and the methylene groups of the 1,5-cyclooctadiene ligand.

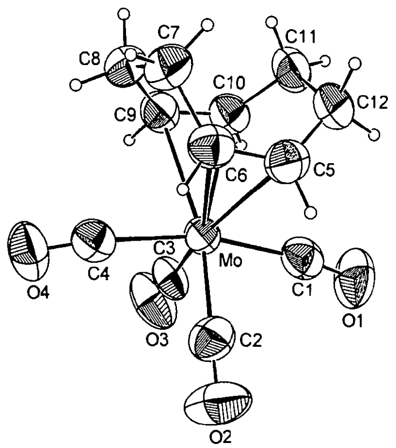


Fig. 1. The molecular structure of (I) with the atomic numbering scheme. The displacement ellipsoids are drawn at the 50% probability level. H atoms are shown as small spheres of arbitrary radii.

The $^{13}C\{^1H\}$ NMR spectrum of $[Mo(CO)_4(\eta^{2:2}\text{-COD})]$ gives two signals for the CO groups and two signals for the COD ligand. The observation of two carbonyl signals with relative intensities of 1:1 indicates a symmetrical bidentate coordination by the ligand. The $[M(CO)_4]$ moiety thus has $C_{2v}$ symmetry. This is also supported by the observation of two signals for the COD ligand. The CO signal at lower magnetic field is assigned to the carbonyl groups *trans* with respect to the olefin ligand (Kotzian, Kreiter & Özkar, 1982), which can be rationalized in terms of the increased $d_\pi \rightarrow$ CO $\pi^*$ back donation to C2═O2 and C3═O3. However, the chemical shift difference between the carbonyl signals is quite small. This parallels the observation of three absorption bands in the CO stretching vibrational region of the IR spectrum, instead of the typical four-band pattern ($2A_1 + B_1 + B_2$) commonly observed for a $[M(CO)_4]$ moiety with $C_{2v}$ symmetry. One of the $A_1$ bands overlaps with $B_1$.

## Experimental

The title compound was prepared by refluxing a solution of $[Mo(CO)_6]$ and COD in *n*-heptane for 24 h according to the method of Fischer & Fröhlich (1959). The reaction mixture was filtered to remove the colloidal decomposition products. The excess solvent and unreacted COD ligand were removed by evaporation under vacuum. The residue was dissolved in *n*-hexane and the solution allowed to stand for one day at 238 K for crystallization. The solvent was decanted and crystals dried in a vacuum. IR [$\nu$(CO) in hexane]: 2032, 1950 and 1906 cm$^{-1}$. $^{13}C$ NMR chemical shifts [$\delta$ (p.p.m.), ref. TMS in toluene-$d_8$, 100.613 MHz]: 216.5 for *trans*-CO, 216.4 for *cis*-CO, 94.4 for ═CH, 29.6 for $CH_2$.

*Crystal data*

$[Mo(C_8H_{12})(CO)_4]$
$M_r = 316.167$
Orthorhombic
*Pbca*
$a = 12.3560 (11)$ Å
$b = 13.6240 (12)$ Å
$c = 14.7050 (15)$ Å
$V = 2475.4 (3)$ Å$^3$
$Z = 8$
$D_x = 1.697$ Mg m$^{-3}$
$D_m$ not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 20 reflections
$\theta = 9.9$–$18.2°$
$\mu = 1.03$ mm$^{-1}$
$T = 295$ K
Prismatic
0.35 × 0.20 × 0.15 mm
Dark brown

*Data collection*

Enraf–Nonius CAD-4 diffractometer

1350 reflections with $I > 3\sigma(I)$

$\omega/2\theta$ scans
Absorption correction: empirical *via* $\psi$ scans (*MolEN*; Fair, 1990)
$T_{\min} = 0.833$, $T_{\max} = 0.857$
2092 measured reflections
2018 independent reflections

$R_{\rm int} = 0.037$
$\theta_{\max} = 26.0°$
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 14$
$l = 0 \rightarrow 18$
3 standard reflections
frequency: 120 min
intensity decay: 0.26%

*Refinement*

Refinement on $F$
$R = 0.029$
$wR = 0.034$
$S = 0.74$
1350 reflections
154 parameters
H atoms: see below
Weighting scheme: see below

$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.561$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.291$ e Å$^{-3}$
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| Mo—*M*1 | 2.392 (7) | Mo—C9 | 2.462 (6) |
| Mo—*M*2 | 2.385 (9) | Mo—C10 | 2.496 (6) |
| Mo—C1 | 2.030 (7) | O1—C1 | 1.151 (9) |
| Mo—C2 | 1.952 (6) | O2—C2 | 1.176 (8) |
| Mo—C3 | 1.945 (6) | O3—C3 | 1.166 (8) |
| Mo—C4 | 2.032 (6) | O4—C4 | 1.156 (7) |
| Mo—C5 | 2.476 (6) | C5—C6 | 1.360 (8) |
| Mo—C6 | 2.497 (6) | C9—C10 | 1.348 (8) |
| C1—Mo—*M*1 | 94.9 (3) | C3—Mo—*M*2 | 94.2 (3) |
| C1—Mo—*M*2 | 96.8 (2) | C3—Mo—C4 | 86.1 (3) |
| C1—Mo—C2 | 84.3 (3) | C3—Mo—C5 | 160.6 (2) |
| C1—Mo—C3 | 84.4 (3) | C3—Mo—C6 | 162.0 (2) |
| C1—Mo—C4 | 165.4 (2) | C3—Mo—C9 | 92.8 (2) |
| C1—Mo—C5 | 79.0 (2) | C3—Mo—C10 | 95.2 (2) |
| C1—Mo—C6 | 110.7 (2) | C4—Mo—*M*1 | 96.4 (3) |
| C1—Mo—C9 | 112.5 (2) | C4—Mo—*M*2 | 94.9 (2) |
| C1—Mo—C10 | 81.4 (2) | C4—Mo—C5 | 112.1 (2) |
| C2—Mo—*M*1 | 97.7 (3) | C4—Mo—C6 | 80.8 (2) |
| C2—Mo—*M*2 | 173.7 (3) | C4—Mo—C9 | 79.0 (2) |
| C2—Mo—C3 | 92.1 (3) | C4—Mo—C10 | 110.6 (2) |
| C2—Mo—C4 | 84.9 (3) | C5—Mo—C6 | 31.8 (2) |
| C2—Mo—C5 | 96.0 (2) | C5—Mo—C9 | 84.6 (2) |
| C2—Mo—C6 | 98.9 (2) | C5—Mo—C10 | 72.7 (2) |
| C2—Mo—C9 | 162.9 (2) | C6—Mo—C9 | 72.7 (2) |
| C2—Mo—C10 | 163.2 (2) | C6—Mo—C10 | 78.1 (2) |
| C3—Mo—*M*1 | 170.0 (3) | C9—Mo—C10 | 31.6 (2) |

For the weighting scheme, if $F \geq 90.55$, then $w = 90.55/F^2$, otherwise $w = 1$, or $w = 0$ if $F^2 < 3\sigma(F^2)$. All non-H atoms were refined with anisotropic displacement parameters. H atoms were placed geometrically 0.95 Å from their parent C atoms. For all H atoms, a riding model was used with $B_{\rm iso}({\rm H}) = 1.3B_{\rm eq}({\rm C})$.

Data collection: *CAD*-4 *Express* (Enraf–Nonius, 1993). Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SIMPEL* in *MolEN*. Program(s) used to refine structure: *LSFM* in *MolEN*. Molecular graphics: *ORTEP*II (Johnson, 1976) in *MolEN*. Software used to prepare material for publication: *MolEN*.

The authors wish to acknowledge the purchase of the CAD-4 diffractometer under Grant DPT/TBAG1 of the Scientific and Technical Research Council of Turkey, and support under Grant TBAG-1226 is gratefully acknowledged.

Lists of structure factors, anisotropic displacement parameters, atomic coordinates and complete geometry have been deposited with the IUCr (Reference: AB1394). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

## References

Darensbourg, D. J., Nelson III, H. H. & Murphy, M. A. (1977). *J. Am. Chem. Soc.* **99**, 896–903.
Darensbourg, D. J., Tappan, J. E. & Nelson III, H. H. (1977). *Inorg. Chem.* **16**, 534–540.
Dixon, D. T., Kola, J. C. & Howell, J. A. S. (1984). *J. Chem. Soc. Dalton Trans.* pp. 1307–1315.
Enraf–Nonius (1993). *CAD*-4 *Express Software*. Version 1.1. Enraf–Nonius, Delft, The Netherlands.
Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.
Fischer, E. O. & Fröhlich, W. (1959). *Chem. Ber.* **92**, 2995–2998.
Greveles, F.-W., Jacke, J., Betz, P., Krüger, C. & Tsay, Y.-H. (1989). *Organometallics*, **8**, 293–298.
Gryf-Keller, A. G., Krawczyk, H. & Szczecinski, P. (1991). *J. Organomet. Chem.* **402**, 77–82.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
King, R. B. & Fronzaglia, A. (1966). *Inorg. Chem.* **5**, 1837–1846.
Kotzian, M., Kreiter, C. G. & Özkar, S. (1982). *J. Organomet. Chem.* **229**, 29–42.
Mak, T. C. W. (1984). *Z. Kristallogr.* **166**, 277–281.

*Acta Cryst.* (1997). C**53**, 187–189

# Diaquabis(*N*,*N*-diethylnicotinamide-*N*$^1$)bis(2-hydroxybenzoato-*O*)cobalt(II)

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(*Received 27 June 1996; accepted 21 October 1996*)

## Abstract

The title monomeric centrosymmetric cobalt complex, $[{\rm Co}({\rm C}_7{\rm H}_5{\rm O}_3)_2({\rm C}_{10}{\rm H}_{14}{\rm N}_2{\rm O})_2({\rm H}_2{\rm O})_2]$, contains two water molecules, two 4-hydroxybenzoate ligands and two diethylnicotinamide (DENA) ligands. All ligands are coordinated to the Co atom as monodentate ligands. The four nearest O atoms around the Co atom form a slightly distorted square-planar arrangement, with the distorted octahedral coordination completed by the pyridine N atoms of the DENA ligand at a distance of