Molybdenum–tetracarbonyl complexes with Schiff base ligands

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Abstract

The single-crystal X-ray structure determinations of the title complexes, tetracarbonyl{2-[1-(methylimino)ethyl]-pyridine-N,N'}molybdenum(0), $[Mo(C_8H_{10}N_2)(CO)_4]$, and tetracarbonyl{2-[(methylimino)phenylmethyl]pyri-dine-N,N'}molybdenum(0), $[Mo(C_{13}H_{12}N_2)(CO)_4]$, show that the molybdenum complexes exhibit distorted octahedral geometry.

Comment

The title complexes, tetracarbonyl{2-[1-(methylimino)-ethyl]pyridine-N,N'}molybdenum(0), (1), and tetra-carbonyl{2-[(methylimino)phenylmethyl]pyridine-N,N'}-molybdenum(0), (2), have been prepared previously (bin Ali *et al.*, 1987). The charge-transfer spectra and solubilities of the complexes have been described (bin Ali & Burgess, 1993), but no IR, ¹H NMR, microanalytical or X-ray data have been reported.

(1) R=Me
(2) R=Ph
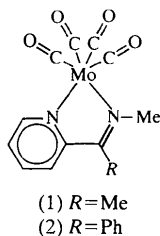
Complexes (1) and (2) have now been fully characterized and their crystal structures have been determined (Figs. 1 and 2, respectively). Complex (1) crystallizes with two independent molecules in the asymmetric unit. The geometries of the two independent molecules are very similar and the molecules may be superimposed with only a minor difference in the orientation of the ligand with respect to the $Mo(CO)_4$ unit. The Mo—C bond lengths of the carbonyl groups *trans* to nitrogen in (1) and (2) are shorter than those of the two carbonyl groups which are *trans* to each other, since the N-donor ligand is a poorer π-acceptor than the carbonyl. The axial Mo—CO groups are significantly non-linear [Mo1—C2—O2 170.0 (4) and Mo1—C4—O4 171.2 (4)° for

one of the independent molecules of (1), and Mo2—C2A—O2A 174.2 (4) and Mo2—C4A—O4A 173.1 (4)° for the second independent molecule; for (2), Mo1—C2—O2 170.9 (3) and Mo1—C4—O4 170.8 (3)°, with the O atom bent away from the diimine ligand in each case]. Similar observations have been made for the complexes [Mo(CO)₄(dmpipy)] (dmpipy = 3,3′-di-methyl-2,2′-bipyridine) [172.7 (3)–171.3 (2)°; Baxter *et al.*, 1992] and [Mo(CO)₄(phen)] (phen = 1,10 phenan-throline) [169.4 (3)–172.9 (3)°; Slot *et al.*, 1985]. The Mo—C distances of (1) and (2) compare well with the literature values for the complexes [Mo(CO)₄(dmpipy)] and [Mo(CO)₄(phen)]. The N1—Mo1—N2 angles in (1) and (2) [71.55 (12) and 71.47 (13)° for (1), and
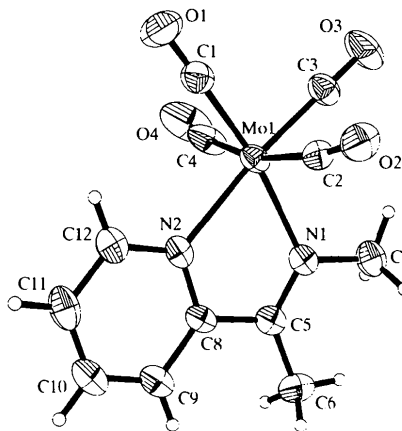
Fig. 1. The molecular structure of one of the independent molecules of (1), showing the atom-numbering scheme and 30% displacement ellipsoids. H atoms are drawn as spheres of arbitrary radii.
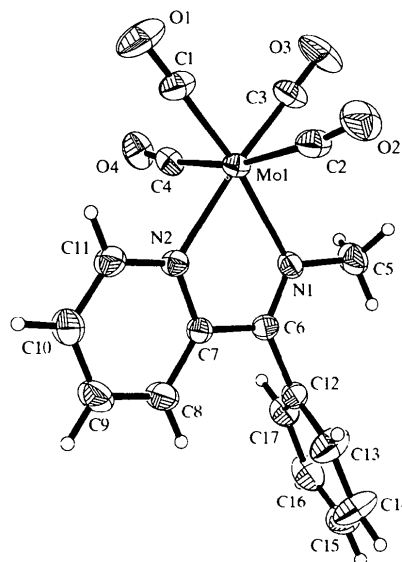
Fig. 2. The molecular structure of (2), showing the atom-numbering scheme and 30% displacement ellipsoids. H atoms are drawn as spheres of arbitrary radii.

71.92 (8)° for (2)] are smaller than those of the corresponding compounds [Mo(CO)$_4$(dmpipy)] [72.1 (1)°], [Mo(CO)$_4$(phen)] [73.62 (7)°] and [Mo(CO)$_4${(Me)(Ph)-C=N(CH$_2$)}$_2$] [75.7 (1)°] (Paz-Sandoval *et al.*, 1995).

Experimental

cis-[Mo(CO)$_4$(N–N)] complexes of molybdenum were prepared by treatment of *cis*-[Mo(CO)$_4$(pip)$_2$] (pip = piperidine) (Darensbourg & Kump, 1978) with the appropriate α-diimine ligands in refluxing propan-2-ol (bin Ali *et al.*, 1987). The complexes were characterized by ^{1}H NMR, IR and FAB–MS spectroscopy, and microanalysis. The complexes are stable at room temperature and give strong violet solutions in chloroform. Dark-red crystals were obtained from toluene at room temperature. Complex (1): *cis*-[Mo(CO)$_4$(pip)$_2$] (2 g, 5.3 mmol), 2-acetylpyridine (1 ml, 5.3 mmol) and methylamine (1 ml) in propan-2-ol (25 ml) gave (1) [yield: 0.92 g (50%)]. Analysis found: C 41.9, H 2.7, N 8.1%; calculated for C$_{12}$H$_{10}$MoN$_2$O$_4$: C 41.9, H 2.9, N 8.1; ^{1}H NMR (300 MHz, CDCl$_3$): δ 2.47 (3H, *s*, C—CH$_3$), 3.89 (3H, *s*, N—CH$_3$), 7.40–9.10 (4H, *m*, aromatic); IR [NaCl plates in nujol; cm^{-1}, ν(CO)]: 2015, 1895, 1852, 1820; FAB–MS: [*M*]$^+$ 344. Complex (2): *cis*-[Mo(CO)$_4$(pip)$_2$] (1.13 g, 3 mmol), 2-benzoylpyridine (0.55 g, 3 mmol) and methylamine (1 ml) in propan-2-ol (25 ml) gave (2) [yield: 0.67 g (55%)]. Analysis found: C 50.9, H 2.8, N 6.7%; calculated for C$_{17}$H$_{12}$MoN$_2$O$_4$: C 50.3, H 3.0, N 6.9%; ^{1}H NMR (300 MHz, CDCl$_3$): δ 3.74 (3H, *s*, N—CH$_3$), 7.23–9.16 (9H, *m*, aromatic); IR [NaCl plates in nujol; cm^{-1} ν(CO)]: 2020, 1910, 1865, 1825; FAB–MS: [*M*]$^+$ 406.

Compound (1)

Crystal data

[Mo(C$_8$H$_{10}$N$_2$)(CO)$_4$]
M_r = 342.16
Triclinic
$P\bar{1}$
a = 8.951 (2) Å
b = 12.802 (2) Å
c = 12.879 (2) Å
α = 107.62 (1)°
β = 104.61 (1)°
γ = 90.31 (1)°
V = 1355.7 (4) Å^3
Z = 4
D_x = 1.676 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 35 reflections
θ = 4.9–12.5°
μ = 0.978 mm^{-1}
T = 293 (2) K
Block
0.48 × 0.24 × 0.18 mm
Dark red

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction:
  ψ scan (*XEMP* in *SHELXTL/PC*; Sheldrick, 1996)
  T_{min} = 0.75, T_{max} = 0.86
5077 measured reflections
4175 independent reflections

3482 reflections with
  $I > 2\sigma(I)$
R_{int} = 0.022
θ_{max} = 24°
$h = -1 \rightarrow 10$
$k = -13 \rightarrow 13$
$l = -14 \rightarrow 14$
3 standard reflections
  every 100 reflections
  intensity decay: <1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.085
S = 1.071
4175 reflections
343 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.035P)^2 + 0.830P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.68 e Å^{-3}
$\Delta\rho_{min}$ = -0.30 e Å^{-3}
Extinction correction: none
Scattering factors from
  International Tables for Crystallography (Vol. C)

Table 1. *Selected bond lengths (Å) for (1)*

Mo1—C1	1.958 (6)	Mo2—C1A	1.959 (5)
Mo1—C2	2.018 (4)	Mo2—C2A	2.033 (4)
Mo1—C3	1.947 (5)	Mo2—C3A	1.947 (5)
Mo1—C4	2.052 (5)	Mo2—C4A	2.031 (4)
Mo1—N1	2.236 (3)	Mo2—N1A	2.233 (3)
Mo1—N2	2.242 (3)	Mo2—N2A	2.234 (3)

Compound (2)

Crystal data

[Mo(C$_{13}$H$_{12}$N$_2$)(CO)$_4$]
M_r = 404.23
Monoclinic
$P2_1/n$
a = 11.529 (2) Å
b = 11.879 (1) Å
c = 12.661 (4) Å
β = 96.21 (1)°
V = 1723.8 (6) Å^3
Z = 4
D_x = 1.558 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 22 reflections
θ = 4.9–12.5°
μ = 0.783 mm^{-1}
T = 293 (2) K
Block
0.54 × 0.24 × 0.18 mm
Dark red

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction:
  ψ scan (*XEMP* in *SHELXTL/PC*; Sheldrick, 1996)
  T_{min} = 0.737, T_{max} = 0.863
7643 measured reflections
3391 independent reflections

2768 reflections with
  $I > 2\sigma(I)$
R_{int} = 0.029
θ_{max} = 26°
$h = -1 \rightarrow 14$
$k = -14 \rightarrow 14$
$l = -15 \rightarrow 15$
3 standard reflections
  every 100 reflections
  intensity decay: <1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.083
S = 1.096
3391 reflections
217 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0373P)^2 + 0.3537P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = -0.53 e Å^{-3}
Extinction correction: none
Scattering factors from
  International Tables for Crystallography (Vol. C)

Table 2. *Selected bond lengths (Å) for (2)*

Mo1—C1	1.960 (3)	Mo1—C4	2.051 (3)
Mo1—C2	2.025 (3)	Mo1—N1	2.228 (2)
Mo1—C3	1.946 (3)	Mo1—N2	2.241 (2)

For both (1) and (2), H atoms were included in calculated positions (C—H = 0.96 Å) with isotropic displacement parameters set to $1.5U_{eq}$(C) for methyl H atoms and $1.2U_{eq}$(C) for all other H atoms. All non-H atoms were refined with anisotropic displacement parameters.

For both compounds, data collection: *XSCANS* (Fait, 1991); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structures: *XS* in *SHELXTL/PC* (Sheldrick, 1996); program(s) used to refine structures: *XL* in *SHELXTL/PC*; molecular graphics: *XP* in *SHELXTL/PC*; software used to prepare material for publication: *XCIF* in *SHELXTL/PC*.

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Aquatetrakis[(4-chlorobenzoato)(μ3-2-dimethylaminoethanolato)copper(II)] hydrate

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Abstract

A cubane-type core has been found in the tetrameric title complex, aqua-1κ*C*-tetrakis(4-chlorobenzoato)-1κ*C*,2κ*C*,3κ*C*,4κ*C*-tetrakis[μ3-(2-dimethylaminoethanolato)-κ³*O:O:O*]-*tetrahedro*-tetracopper(II) hydrate, [Cu$_4$-

(C$_7$H$_4$ClO$_2$)$_4$(C$_4$H$_{10}$NO)$_4$(H$_2$O)]·H$_2$O. The structure of the complex molecule is composed of two ethanolate O-bridged dimers, with Cu—O bond lengths in the range 1.919 (5)–1.979 (5) Å, and Cu···Cu distances of 2.855 (2) and 2.890 (2) Å. The dimers are bridged into the tetrameric unit by triply bridging ethanolate O atoms, with Cu—O distances in the range 2.417 (5)–2.618 (5) Å. Of the four Cu atoms, three are five-coordinated and one is six-coordinated.

Comment

Monomeric, dimeric, tetrameric, hexameric and nonameric complexes have been obtained from reactions between 2-dimethylaminoethanol and Cu^{II}–carboxylates (Turpeinen *et al.*, 1980, 1985, 1987, 1988, 1995; Turpeinen, Hämälänen *et al.*, 1996; Turpeinen, Klinga *et al.*, 1996). The present structure, (I), is composed of two dimers, which are bridged into a tetrameric cubane-type unit by ethanolate O atoms, with Cu—O distances in the range 2.417 (5)–2.618 (5) Å. Within the

(I)
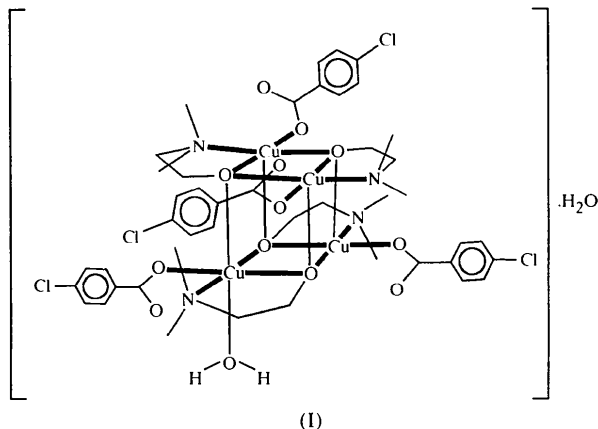
ethanolate O-bridged dimers, the Cu···Cu distances are 2.855 (2) and 2.890 (2) Å, and the Cu—O—Cu angles vary between 93.2 (2) and 95.9 (2)°. The Cu1, Cu2 and Cu3 atoms are five-coordinated in a square-pyramidal environment, while the Cu4 atom is six-coordinated. The two ethanolate O atoms, a carboxyl O atom and an amino N atom form the basal plane, with Cu—O bond lengths in the range 1.904 (6)–1.982 (5) Å and Cu—N distances in the range 2.007 (8)–2.047 (7) Å. The apical positions of the Cu1, Cu2 and Cu3 atoms are occupied by the ethanolate O atoms, with Cu—O distances in the range 2.417 (5)–2.611 (5) Å. The axial sites of the Cu4 atom are occupied by the ethanolate and water O atoms, with Cu—O distances of 2.618 (5) and 2.671 (12) Å, respectively. The structure is stabilized by hydrogen bonds between the water O and the non-coordinated carboxyl O atoms, with distances O1···O13 of 2.798 (9) Å and O2···O43(−*x*+1, −*y*, −*z*+1) of 2.604 (15) Å.