

C4	0.7244 (5)	0.062 (1)	0.4417 (4)	0.028 (5)
C5	0.7534 (5)	0.021 (1)	0.3765 (4)	0.026 (5)
C6	0.8442 (5)	-0.012 (1)	0.3692 (5)	0.030 (6)
O6	0.8802 (3)	-0.0422 (8)	0.3146 (3)	0.041 (4)
N7	0.6784 (4)	0.0300 (9)	0.3254 (3)	0.034 (4)
C7	0.6752 (6)	-0.004 (1)	0.2478 (5)	0.050 (6)
C8	0.6100 (5)	0.071 (1)	0.3601 (5)	0.035 (5)
N9	0.6348 (4)	0.0918 (8)	0.4313 (3)	0.030 (4)

Table 2. Geometric parameters (Å, °)

Pd—S1	2.341 (2)	N1—C6	1.40 (1)
Pd—S2	2.338 (2)	C2—O2	1.217 (9)
Pd—S3	2.343 (2)	C2—N3	1.39 (1)
Pd—S4	2.331 (2)	N3—C4	1.352 (9)
S1—C1'	1.680 (9)	N3—C3	1.47 (1)
C1'—N1'	1.14 (1)	C4—C5	1.36 (1)
S2—C2'	1.675 (9)	C4—N9	1.371 (9)
C2'—N2'	1.13 (1)	C5—N7	1.407 (9)
S3—C3'	1.677 (9)	C5—C6	1.42 (1)
C3'—N3'	1.13 (1)	C6—O6	1.22 (1)
S4—C4'	1.662 (8)	N7—C8	1.31 (1)
C4'—N4'	1.14 (1)	N7—C7	1.46 (1)
N1—C2	1.37 (1)	C8—N9	1.35 (1)
S4—Pd—S2	89.22 (8)	C4—N3—C2	117.4 (7)
S4—Pd—S1	89.85 (8)	C4—N3—C3	122.2 (6)
S4—Pd—S3	179.08 (6)	C2—N3—C3	120.2 (6)
S2—Pd—S1	178.6 (1)	N3—C4—C5	124.6 (7)
S2—Pd—S3	89.89 (8)	N3—C4—N9	127.1 (7)
S1—Pd—S3	91.03 (8)	C5—C4—N9	108.3 (6)
C1'—S1—Pd	107.1 (3)	C4—C5—N7	106.2 (6)
N1'—C1'—S1	178.3 (8)	C4—C5—C6	121.8 (7)
C2'—S2—Pd	107.0 (3)	N7—C5—C6	131.9 (7)
N2'—C2'—S2	178.2 (7)	O6—C6—N1	120.7 (7)
C3'—S3—Pd	107.5 (3)	O6—C6—C5	129.2 (7)
N3'—C3'—S3	178.3 (9)	N1—C6—C5	110.1 (7)
C4'—S4—Pd	108.9 (3)	C8—N7—C5	107.6 (6)
N4'—C4'—S4	176.3 (8)	C8—N7—C7	125.3 (7)
C2—N1—C6	129.7 (6)	C5—N7—C7	127.1 (7)
O2—C2—N1	122.4 (7)	N7—C8—N9	110.8 (7)
O2—C2—N3	121.3 (8)	C8—N9—C4	107.0 (7)
N1—C2—N3	116.3 (7)		

The compound was prepared by the Spanish authors by the reaction of an aqueous solution (10 ml) of K_2PdCl_4 (0.33 g, 1 mmol) and KSCN (0.97 g, 10 mmol) with a suspension of theobromine (2 mmol) in 100 ml of ethanol under reflux for 1 h. The resulting red solution was allowed to stand at room temperature for three days, whereupon crystals of the complex formed. These were filtered off and dried with diethyl ether.

The structure was solved by a combination of Patterson and Fourier methods. Positions of all H atoms, except for those of the water molecule, were observed in difference maps but they were placed at calculated positions. Two cycles of refinement including an extinction parameter resulted in an extinction coefficient not significantly different from zero. These refinement cycles were discarded.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55780 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HL1021]

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Acta Cryst. (1993). **C49**, 582–584

Structure of Tetracarbonyl[*N,N,N',N'*-tetramethylethylenediamine-*N,N'*]-molybdenum(0)

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(Received 24 July 1992; accepted 25 September 1992)

Abstract

The tetramethylethylenediamine ligand is bidentate to the Mo atom to give a distorted octahedral environment. The average Mo—C, Mo—N, N—C

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and C=O distances are 1.990 (3), 2.339 (2), 1.487 (4) and 1.146 (4) Å, respectively.

Comment

The tetracarbonyl-tetramethylethylenediamine (tmeda) complexes of Group 6 triad are all well known. A literature review on the single-crystal X-ray structure determination of these complexes reveals only the recent report on the chromium complex (Kruger, Garner, De Villiers, Raubenheimer & Swanepoel, 1980). We now report the X-ray structure determination of Mo(CO)₄(tmeda).

The complex was obtained by modification of the method employed by King & Fronzaglia (1966). Mo(CO)₆ and a stoichiometric amount of tmeda was refluxed in a 4:1 mixture of *n*-heptane/thf for 24 h under a nitrogen atmosphere. The yellow powder obtained was recrystallized from either acetone/*n*-hexane or dichloromethane/*n*-hexane. In this complex the Mo atom possesses a distorted octahedral geometry. The tetramethylethylenediamine (tmeda) ligand binds to the metal atom through the lone-pair orbitals of the two N atoms. These N atoms and the two carbonyl groups can be considered to occupy equatorial positions while the remaining two carbonyl groups are directed towards the axial positions. These axial carbonyl groups bend away from the tmeda ligand as a result of steric interactions and subtend a C(4)—Mo(1)—C(1) angle of 168.3 (1)°; the angles Mo(1)—C(1)—O(1) and Mo(1)—C(4)—O(4) [172.7 (3) and 171.3 (3)°, respectively] deviate considerably from linearity. Similar features are also observed in the isomorphous chromium complex (Kruger, Garner, De Villiers, Raubenheimer & Swanepoel, 1980). The Mo—C distances in the axial direction are slightly longer than those in the equatorial positions, as observed in other Mo complexes (Slot, Morrall & Welch, 1985; Graham, Akrigg & Sheldrick, 1983, 1985). The Mo—N bond distances

[2.334 (2), 2.345 (2) Å] and the N—C distances [average 1.487 (4) Å] of the ligand agree well with the values reported in Orpen *et al.* (1989).

Experimental

Crystal data

[Mo(C₄O₄)(C₄H₁₆N₂)]
M_r = 324.2
 Monoclinic
*P*2₁/*n*
a = 8.409 (3) Å
b = 12.087 (4) Å
c = 13.650 (4) Å
 β = 92.23 (2)°
V = 1386.3 (8) Å³
Z = 4
D_x = 1.553 Mg m⁻³

D_m = 1.540 Mg m⁻³
 Mo *K*α radiation
 λ = 0.71069 Å
 Cell parameters from 50 reflections
 θ = 7.5–17.5°
 μ = 0.950 mm⁻¹
T = 298 K
 Rectangular
 0.80 × 0.68 × 0.66 mm
 Yellow

Data collection

Siemens *P4* diffractometer
 2 θ / θ scans
 Absorption correction:
 empirical
 T_{\min} = 0.62, T_{\max} = 0.96
 3334 measured reflections
 3134 independent reflections
 2811 observed reflections
 $[F > 4.0\sigma(F)]$
 R_{int} = 0.0488

θ_{\max} = 55.0°
 h = 0 → 10
 k = 0 → 15
 l = -17 → 17
 2 standard reflections monitored every 200 reflections
 intensity variation: insignificant

Refinement

Refinement on *F*
 Final *R* = 0.0296
 wR = 0.0459
 S = 1.00
 2811 reflections
 218 parameters
 All H-atom parameters refined

$w = 1.0/[\sigma^2(F) + 0.0017F^2]$
 $(\Delta/\sigma)_{\max}$ = 0.297
 $\Delta\rho_{\max}$ = 0.63 e Å⁻³
 $\Delta\rho_{\min}$ = -0.67 e Å⁻³
 Atomic scattering factors from *SHELXTL/PC* (Siemens, 1990)

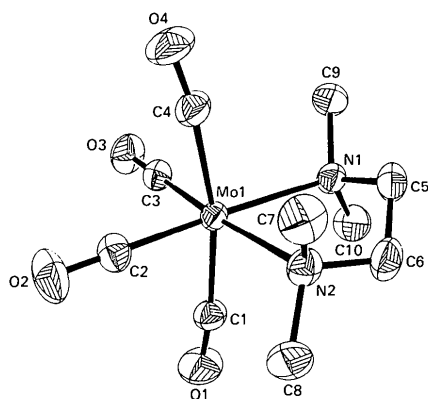


Fig. 1. View of the molecule showing the labelling of the non-H atoms. Thermal ellipsoids are drawn at 50% probability levels.

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (Å²)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Mo(1)	0.0341 (1)	0.8132 (1)	0.2278 (1)	0.042 (1)
O(1)	0.0821 (4)	1.0463 (2)	0.1294 (2)	0.104 (1)
O(2)	-0.0908 (4)	0.9543 (2)	0.3984 (2)	0.100 (1)
O(3)	0.3796 (3)	0.8458 (3)	0.3113 (2)	0.081 (1)
O(4)	0.0209 (4)	0.6198 (2)	0.3839 (2)	0.099 (1)
N(1)	0.1023 (3)	0.7028 (2)	0.0955 (2)	0.054 (1)
N(2)	-0.2150 (2)	0.7779 (2)	0.1509 (2)	0.058 (1)
C(1)	0.0626 (3)	0.9603 (2)	0.1584 (2)	0.060 (1)
C(2)	-0.0447 (3)	0.9015 (2)	0.3345 (2)	0.061 (1)
C(3)	0.2509 (3)	0.8335 (2)	0.2809 (2)	0.054 (1)
C(4)	0.0224 (4)	0.6832 (2)	0.3219 (2)	0.063 (1)
C(5)	-0.0513 (4)	0.6478 (3)	0.0617 (2)	0.072 (1)
C(6)	-0.1841 (4)	0.7284 (3)	0.0539 (2)	0.075 (1)
C(7)	-0.3124 (4)	0.7020 (4)	0.2092 (3)	0.084 (1)
C(8)	-0.3119 (4)	0.8799 (3)	0.1341 (3)	0.084 (1)
C(9)	0.2150 (4)	0.6122 (3)	0.1253 (3)	0.074 (1)
C(10)	0.1738 (6)	0.7638 (3)	0.0157 (3)	0.085 (1)

Table 2. Bond lengths (Å) and angles (°)

Mo(1)—N(1)	2.334 (2)	Mo(1)—N(2)	2.345 (2)
Mo(1)—C(1)	2.032 (3)	Mo(1)—C(2)	1.943 (3)
Mo(1)—C(3)	1.951 (3)	Mo(1)—C(4)	2.035 (3)
O(1)—C(1)	1.127 (4)	O(2)—C(2)	1.161 (4)
O(3)—C(3)	1.153 (3)	O(4)—C(4)	1.143 (4)
N(1)—C(5)	1.509 (4)	N(1)—C(9)	1.494 (4)
N(1)—C(10)	1.465 (5)	N(2)—C(6)	1.485 (4)
N(2)—C(7)	1.482 (5)	N(2)—C(8)	1.490 (5)
C(5)—C(6)	1.483 (5)		
N(1)—Mo(1)—N(2)	78.0 (1)	N(1)—Mo(1)—C(1)	95.9 (1)
N(2)—Mo(1)—C(1)	94.0 (1)	N(1)—Mo(1)—C(2)	174.3 (1)
N(2)—Mo(1)—C(2)	96.4 (1)	C(1)—Mo(1)—C(2)	85.3 (1)
N(1)—Mo(1)—C(3)	96.1 (1)	N(2)—Mo(1)—C(3)	174.1 (1)
C(1)—Mo(1)—C(3)	86.4 (1)	C(2)—Mo(1)—C(3)	89.6 (1)
N(1)—Mo(1)—C(4)	93.8 (1)	N(2)—Mo(1)—C(4)	94.5 (1)
C(1)—Mo(1)—C(4)	168.3 (1)	C(2)—Mo(1)—C(4)	85.7 (1)
C(3)—Mo(1)—C(4)	86.0 (1)	Mo(1)—N(1)—C(5)	104.8 (2)
Mo(1)—N(1)—C(9)	112.4 (2)	C(5)—N(1)—C(9)	106.7 (2)
Mo(1)—N(1)—C(10)	114.1 (2)	C(5)—N(1)—C(10)	111.5 (3)
C(9)—N(1)—C(10)	107.3 (3)	Mo(1)—N(2)—C(6)	106.7 (2)
Mo(1)—N(2)—C(7)	112.0 (2)	C(6)—N(2)—C(7)	110.4 (3)
Mo(1)—N(2)—C(8)	113.1 (2)	C(6)—N(2)—C(8)	108.0 (3)
C(7)—N(2)—C(8)	106.5 (3)	Mo(1)—C(1)—O(1)	172.7 (3)
Mo(1)—C(2)—O(2)	179.6 (3)	Mo(1)—C(3)—O(3)	179.2 (2)
Mo(1)—C(4)—O(4)	171.3 (3)	N(1)—C(5)—C(6)	111.4 (3)
N(2)—C(6)—C(5)	111.0 (3)		

The data were collected with a variable scan speed of 5.33–29.3° min⁻¹ in ω . The structure was solved by direct methods and refined by full-matrix least squares. No correction for extinction was required. All H atoms were located from the difference Fourier map. *SHELXTL/PC* was used for all calculations.

The authors would like to thank the Malaysian Government and Universiti Sains Malaysia for research grants R&D Nos. 122/0250/0070 and 123–3417–2201.

Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55620 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: LI1027]

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Acta Cryst. (1993). **C49**, 584–587

Structures of 2-Amino-3-methylpyridinium Bis(1,2-dithiooxalato-*S,S'*)metallates(II) (*M* = Ni, Pd and Pt)

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(Received 21 April 1992; accepted 6 October 1992)

Abstract

Three 2-amino-3-methylpyridinium salts of planar inorganic dithiooxalato anions, (C₆H₉N₂)₂[Ni(S₂C₂O₂)₂] (1), (C₆H₉N₂)₂[Pd(S₂C₂O₂)₂] (2) and (C₆H₉N₂)₂[Pt(S₂C₂O₂)₂] (3) have been prepared. Complexes (1) and (3) are isomorphous with (2) which crystallizes in the monoclinic space group *P*2₁/*c* with *Z* = 2 so that the anion straddles a crystallographic centre of symmetry. The crystal structure of (2) is built by mixed layers of quasi-planar complex [Pd(S₂C₂O₂)₂]²⁻ anions and (C₆H₉N₂)⁺ cations linked through electrostatic interactions, an extensive network of hydrogen bonds of types N—H...O and C—H...O, and weak π – π interactions. It is clear that the packing in this type of compound is affected by the cation shape and by the hydrogen-bonding network since it is the nature of the cation rather than the metal which determines the geometry of the interactions.

Comment

The structural studies of these metal complexes were undertaken in order to obtain a deeper insight into the effects of the cation and metal on the crystal packing, and the strength of the intermolecular interactions in compounds containing square-planar inorganic metal(II) 1,2-dithiooxalato-*S,S'* anions. The compounds (C₆H₉N₂)₂[*M*(S₂C₂O₂)₂] (*M* = Ni, Pd and Pt) were obtained by reaction of the potassium bis(dithiooxalato)metallate(II) salts, prepared according to the procedure of Cox, Wardlaw & Webster (1935), and 2-amino-3-methylpyridinium base in aqueous solution. Crystals were grown by the slow evaporation of an *N,N*-dimethylformamide solution of the complexes at room temperature. Table 1 summarizes the crystal data for the three compounds and shows that they are isostructural. Only the structure determination of the Pd complex was undertaken as a result of the poor quality of the crystals of the Ni compound and since all compounds are isostructural.