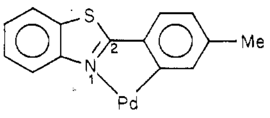
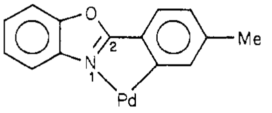
Within the pentaatomic heterocyclic thiazole ring of **1** the sulfur–carbon distances appear to be close to equivalent: S(3)–C(2) = 1.737 (6) Å, S(3)–C(9) = 1.721 (7) Å; S(3′)–C(2′) = 1.713 (6) Å, S(3′)–C(9′) = 1.719 (6) Å. In contrast to this, the nitrogen–carbon distances are decidedly nonequivalent, with N(1)–C(2) = 1.320 (7) Å vs. N(1)–C(8) = 1.397 (7) Å and N(1′)–C(2′) = 1.305 (7) Å vs. N(1′)–C(8′) = 1.398 (7) Å. Resonance forms such as **9** (with a formal double bond for N(1)–C(2)) are clearly favored.



9

It should be noted that the large size of the sulfur atom results in marked reduction of the C–S–C angles (to 90.7 (3)° for C(2)–S(3)–C(9) and 90.0 (3)° for C(2′)–S(3′)–C(9′)) relative to other internal angles within the planar thiazole rings.

In the oxazole rings of complex **2**, the oxygen–carbon distances are almost equivalent with O(3)–C(2) = 1.342 (11) Å, O(3′)–C(2′) = 1.351 (10) Å, O(3)–C(9) = 1.377 (12) Å, and O(3′)–C(9′) = 1.379 (12) Å. As with the thiazole ring (vide supra), the nitrogen–carbon distances are again inequivalent, with N(1)–C(2) = 1.305 (11) Å vs. N(1)–C(8) = 1.377 (12) Å and N(1′)–C(2′) = 1.299 (10) Å vs. N(1′)–C(8′) = 1.390 (11) Å. The resonance form **10** is thus favored.



10

The tolyl rings are regular, with carbon–carbon distances in **1** ranging from 1.369 (8) to 1.429 (8) Å in the C(10)→C(15) ring and from 1.376 (11) to 1.424 (8) Å in the C(10′)–C(15′) system. The C–Me linkages are C(13)–C(16) = 1.534 (8) Å and C(13′)–C(16′) = 1.570 (10) Å. The analogous distances in **2** are 1.384 (13)–1.428 (13) Å in the C(10)→C(15) ring, 1.364 (12)–1.413 (14) Å for the C(10′)–C(15′) system, and 1.543 (13) and 1.551 (14) Å for the C–Me distances.

Distances and angles within the acetate groups in **1** and **2** are all normal.

Finally we note that details of the ^{1}H NMR spectrum of the complex appear in Table IX.

Conclusions

We have shown that Pd(O_2CMe)$_2$ reacts with 2-*p*-tolylbenzthiazole, 2-*p*-tolylbenzoxazole, and their derivatives to provide dimeric cyclometalated products in which palladium is N,C bonded to a deprotonated 2-*p*-tolylbenzthiazole or 2-*p*-tolylbenzoxazole ligand. Dimerization is accomplished via two mutually cis acetate bridges. Interligand repulsions lead to the molecule "opening up" on the side opposite to the *cis*-bis(μ-acetato) systems. Unlike the situation in symmetrical binuclear $M_2(O_2CR)_4$ and $M(O_2CR)_4L_2$ complexes, the PdO_2NC coordination planes in the halves of the molecule are canted at ~24° to one another.

Acknowledgment. This work was supported by the National Science Foundation, through Grant CHE77-04981 (to M.R.C.).

Registry No. 1, 72509-65-0; **2**, 72509-64-9; **5**, 72509-63-8.

Supplementary Material Available: Listings of data-processing formulas and observed and calculated structure factors (32 pages). Ordering information is given on any current masthead page.

Notes

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Synthesis and Structure of the Binuclear Platinum(I)-Dimethyl Acetylenedicarboxylate Complex $Pt_2(CO)_2(PPh_3)_2(C_2(CO_2CH_3)_2)$

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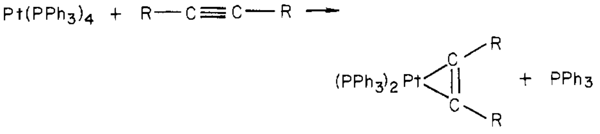
Brian J. Fitzgerald, and Cortlandt G. Pierpont*

Received April 18, 1979



(1)

Among the earliest examples of organometallic transition-metal complexes containing alkyne ligands were those prepared by the addition of an alkyne to Pt(PPh_3)$_4$ (eq 1).[1,2] We have recently found that the addition of dimethyl acetylenedicarboxylate to $Pt(CO)_2(PPh_3)_2$ under an atmosphere of carbon monoxide yields the binuclear complex $Pt_2(CO)_2(PPh_3)_2(MeO_2CC_2CO_2Me)$ (eq 2). Additionally, if the triphenyl-

$$Pt(PPh_3)_2(CO)_2 + R_2C_2 \xrightarrow{CO} Pt_2(CO)_2(PPh_3)_2(R_2C_2) \leftarrow Pt(PPh_3)_2(R_2C_2) + CO \quad (2)$$

$$R = CO_2CH_3$$

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Table I. Crystallographic Data for $Pt_2(CO)_2(PPh_3)_2(C_2(CO_2CH_3)_2)$

fw: 1112.89
monoclinic
space group *C*2/*c*
$a = 16.567$ (3) Å
$b = 10.915$ (2) Å
$c = 28.582$ (4) Å
$\beta = 127.77$ (2)°
$V = 4085.6$ (10) $Å^3$
Mo Kα radiation
$\mu = 73.23$ cm^{-1}
transmissn coeff: max = 0.271, min = 0.045
d(exptl) = 1.802 g cm^{-3}
d(calcd) = 1.809 g cm^{-3}
$Z = 4$
cryst size: 0.25 × 0.35 × 0.53 mm
bounding faces: {100}, {001}, {110}, {$\bar{1}$10}
aperture setting: 4.0 mm wide × 4.5 mm high
takeoff angle: 2.7°
scan rate: 2°/min
2θ limits: $4° \leqslant 50°$
scan range: ±0.8°, with allowance for the Kα_1-Kα_2 sepn
data collected: 3818
data used in refinement ($F_o^2 > 3\sigma(F_o^2)$): 2953
p: 0.04

phosphine complex of this acetylene prepared by reaction 1 is treated with carbon monoxide, the same product is formed. Bennett and Yoshida have recently reported a similar reaction with the cyclohexyne complex $Pt(PPh_3)_2(C_6H_8)$,[3] perhaps pointing to a general reaction for complexes of form $Pt(PPh_3)_2$(alkyne). The products of these reactions have been proposed to have an alkyne ligand bridging the Pt–Pt bond of the binuclear platinum(I) complex. Bridging alkyne ligands are known to form with the C–C bond either collinear or perpendicular to the metal–metal bond. To establish the mode of alkyne coordination for $Pt_2(CO)_2(PPh_3)_2(MeO_2CC_2CO_2Me)$, we determined the structure of the complex molecule by using crystallographic methods.

Experimental Section

Synthesis of $Pt_2(CO)_2(PPh_3)_2(C_2(CO_2CH_3)_2)$. Procedure 1. A solution prepared by dissolving 1.26 g (1.46 mmol) of $Pt(PPh_3)_2(C_2(CO_2CH_3)_2)$[2] in 30 mL of benzene was kept under an atmosphere of carbon monoxide at room temperature. The pale yellow product precipitated from solution over the period of 3 h.

Procedure 2. A solution of $Pt(PPh_3)_2(CO)_2$ (1.12 g, 1.44 mmol) dissolved in 20 mL of benzene was treated with dimethyl acetylenedicarboxylate (0.41 g, 2.89 mmol) under an atmosphere of CO. The color of the solution immediately changed from dark red to pale yellow, and after 5 h, 0.28 g (0.25 mmol) of pale yellow $Pt_2(CO)_2(PPh_3)(C_2(CO_2CH_3)_2)$ had precipitated from solution. The complex was recrystallized from an ether–dichloromethane solution: mp 196–198 °C dec; ν(CO) 2060, 2020 cm^{-1}; $\tau(CH_3)$ 7.3; λ_{max} 232 nm (ϵ 48 000 mol^{-1} L cm^{-1}), 295 (40 330), 310 (39 600). Anal. Calcd for $C_{44}H_{36}O_6P_2Pt_2$: C, 47.49; H, 3.26. Found: C, 47.30; H, 3.33.

Structure Determination of $Pt_2(CO)_2(PPh_3)_2(C_2(CO_2CH_3)_2)$. Crystals of the platinum complex were examined photographically and found to be in the monoclinic crystal system with extinctions consistent with space groups *Cc* and *C*2/*c*. The centrosymmetric space group was chosen for the structure determination and found to be correct. A suitable crystal was mounted and aligned on a Picker FACS-1 automated diffractometer equipped with a graphite crystal monochromator. The centered settings of 25 reflections with 2θ values greater than 18° (Mo Kα radiation) were refined by least-squares procedures and used to calculate the cell constants given in Table I. The structure was solved by using programs and procedures outlined previously.[4] Positions of the Pt and P atoms were determined from a Patterson function. Other nonhydrogen atoms were found from a subsequent difference Fourier map. Fixed-atom corrections were applied for phenyl-ring hydrogen atoms in the final cycle of least-squares refinement. The methyl hydrogen atoms could not be located. During refinement the quantity $\sum w(|F_o| - |F_c|)^2$ was minimized where w is the weighting factor defined as $4F_o^2/\sigma^2(F_o^2)$. The refinement converged with R and R_w values of 0.053 and 0.057, respectively. The error in an observation of unit weight is 1.73 electrons. Final positional and thermal parameters for all atoms are given in Table II. A table listing the observed and calculated structure factor amplitudes of the reflections used in the refinement is available as supplementary material.

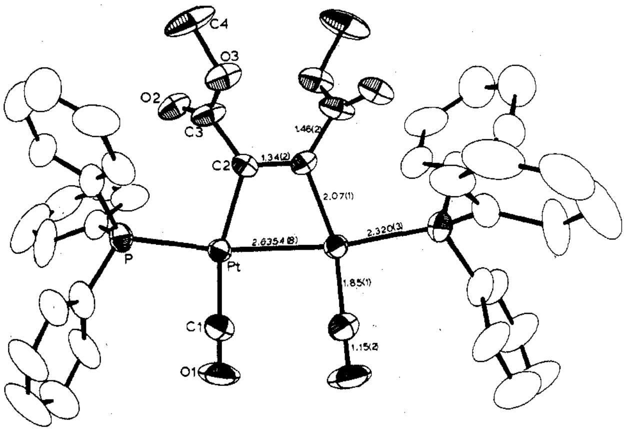
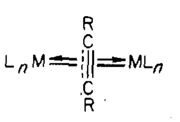


Figure 1. A perspective view of the $Pt_2(CO)_2(PPh_3)_2(C_2(CO_2CH_3)_2)$ molecule. The Pt–Pt′ and C(2)–C(2)′ bonds are bisected by a crystallographic twofold axis.

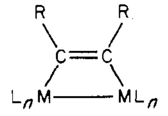
Description of the $Pt_2(CO)_2(PPh_3)_2(C_2(CO_2CH_3)_2)$ Molecule

The complex molecule is located about a crystallographic twofold axis which bisects the Pt–Pt and C(2)–C(2)′ bonds. A view of the molecule is shown in Figure 1. Bond distances and angles for the molecule are given in Table III.

Alkyne coordination in bimetallic complexes has been found to occur with the carbon–carbon bond oriented either perpendicular to the M–M bond (I) or collinear with the metal atoms (II). Structure I was first reported in 1959 for $Co_2(CO)_6(C_2Ph_2)$.[5] The dimetallacyclobutene ring (II) was observed in 1973 for the perfluorobenzyne complex $Fe_2(CO)_8(C_6F_4)$.[6] Within an isoelectronic series structure I appears favored for first-row metals while the dimetallacyclic ring is favored for second- and third-row metals.[7] This pattern is evident from the results of structural studies carried out on a number of binuclear alkyne complexes of group 8 metals. Day has found $Ni_2(Ph_2C_2)(COD)_2$ to have structure I[8] while the results of Stone and co-workers appear to indicate structure II for $Pt_2(Ph_2C_2)(COD)_2$.[7] A diplatinacyclobutene ring has been characterized structurally for $Pt_3(CF_3C_2CF_3)_2(C_4(CF_3)_4)(COD)$.[9] Within the cobalt triad $Co_2(CO)_6(C_2Ph_2)$ has been shown to have structure I while $Rh_2(C_5H_5)_2(CO)_2(C_2(CF_3)_2)$[10] and $Ir_4(CO)_8(C_2(CO_2Me)_2)_4$[11] both exhibit di-



I



II

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Table II. Positional and Thermal Parameters for the Atoms of $Pt_2(CO)_2(PPh_3)_2(C_2(CO_2CH_3)_2)$

atom	x	y	z	B_{11}[a]	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Pt	−0.00474 (3)	0.06890 (4)	0.20227 (2)	4.39 (2)	3.88 (2)	3.68 (2)	−0.33 (1)	2.30 (2)	−0.04 (1)
P	−0.0022 (2)	0.0343 (3)	0.3753 (1)	4.5 (1)	6.4 (1)	3.8 (1)	−0.3 (1)	2.4 (1)	−0.6 (1)
C(1)	0.0244 (10)	0.2363 (4)	0.3079 (6)	5.4 (6)	5.4 (7)	4.1 (6)	1.1 (5)	1.8 (5)	0.1 (5)
O(1)	0.0444 (12)	0.3390 (10)	0.3174 (6)	15.4 (10)	3.7 (5)	11.5 (9)	0.2 (6)	7.5 (8)	−1.3 (5)
C(2)	−0.0020 (8)	−0.1111 (10)	0.2727 (5)	4.2 (5)	4.1 (5)	4.6 (5)	0.2 (4)	2.6 (4)	−0.5 (4)
C(3)	−0.0091 (10)	−0.2238 (13)	0.2975 (6)	5.8 (7)	4.0 (7)	5.7 (8)	−0.3 (5)	2.0 (6)	1.4 (5)
O(2)	0.0499 (7)	−0.2495 (8)	0.3478 (5)	6.6 (5)	5.3 (4)	7.0 (6)	0.3 (4)	3.6 (5)	2.0 (4)
O(3)	−0.0829 (7)	−0.2948 (8)	0.2568 (4)	6.2 (4)	4.9 (4)	6.9 (5)	−0.5 (4)	3.0 (4)	1.0 (4)
C(4)	−0.894 (15)	−0.4117 (14)	0.2792 (10)	7.8 (10)	6.7 (9)	11.7 (15)	−3.5 (8)	2.9 (10)	2.9 (9)
R1C(1)	−0.0847 (11)	−0.0891 (13)	0.3638 (7)	6.2 (7)	8.0 (9)	5.2 (7)	0.2 (6)	3.9 (6)	0.1 (6)
R1C(2)	−0.0646 (13)	−0.1603 (15)	0.4116 (7)	8.3 (9)	8.5 (9)	7.4 (9)	−2.4 (8)	5.5 (8)	−0.6 (7)
R1C(3)	−0.1304 (18)	−0.2613 (21)	0.3997 (11)	11.8 (15)	12.5 (15)	12.0 (16)	−5.0 (12)	9.0 (14)	−1.7 (12)
R1C(4)	−0.2240 (15)	−0.2725 (22)	0.3408 (10)	7.3 (10)	13.8 (16)	9.3 (13)	−4.7 (11)	4.9 (10)	−2.5 (12)
R1C(5)	−0.2453 (13)	−0.2019 (16)	0.2919 (10)	6.7 (9)	7.1 (9)	11.8 (15)	−1.4 (7)	4.2 (10)	−2.4 (10)
R1C(6)	−0.1762 (9)	−0.1078 (14)	0.3046 (7)	3.5 (5)	8.0 (8)	6.5 (8)	−0.4 (5)	2.6 (5)	−2.1 (6)
R2C(1)	−0.0498 (9)	0.1651 (15)	0.3896 (5)	3.9 (5)	10.7 (10)	3.9 (5)	−1.4 (6)	2.0 (5)	−2.1 (6)
R2C(2)	−0.1517 (12)	0.1723 (16)	0.3694 (7)	6.4 (7)	9.5 (10)	6.6 (8)	−1.4 (7)	4.1 (7)	−2.8 (7)
R2C(3)	−0.1897 (14)	0.2769 (20)	0.3756 (10)	7.4 (9)	12.0 (13)	13.2 (16)	−0.6 (9)	7.0 (11)	−5.9 (12)
R2C(4)	−0.1314 (19)	0.3766 (24)	0.4029 (14)	12.4 (16)	12.5 (15)	22.7 (28)	−3.6 (14)	13.3 (20)	−10.3 (18)
R2C(5)	−0.0327 (15)	0.3815 (20)	0.4195 (11)	8.2 (11)	10.7 (12)	15.1 (18)	−3.9 (10)	8.2 (13)	−6.5 (13)
R2C(6)	0.0053 (14)	0.2757 (19)	0.4124 (9)	8.7 (10)	11.6 (12)	11.4 (13)	−4.5 (9)	7.7 (11)	−7.2 (11)
R3C(1)	0.1204 (9)	0.0051 (14)	0.4464 (5)	4.7 (5)	7.4 (9)	3.9 (5)	−1.1 (6)	2.3 (10)	0.0 (6)
R3C(2)	0.1412 (13)	0.0426 (21)	0.5008 (7)	6.7 (8)	19.7 (15)	3.6 (5)	−4.3 (8)	2.9 (11)	−0.6 (10)
R3C(3)	0.2367 (19)	0.0081 (30)	0.5554 (8)	10.3 (10)	22.1 (13)	4.8 (6)	−8.2 (10)	0.4 (7)	3.3 (11)
R3C(4)	0.3106 (15)	−0.0504 (19)	0.5559 (9)	6.3 (7)	11.9 (13)	7.2 (10)	−2.4 (10)	0.0 (10)	3.5 (12)
R3C(5)	0.2893 (12)	−0.0885 (16)	0.5125 (11)	3.8 (5)	8.9 (10)	12.6 (15)	−0.6 (11)	1.6 (12)	2.0 (5)
R3C(6)	0.1938 (12)	−0.0549 (13)	0.4460 (8)	5.2 (5)	6.2 (8)	6.9 (10)	0.1 (7)	1.0 (8)	0.9 (7)

[a] The form of the anisotropic thermal ellipsoid is $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$ and is expressed in units of Å².

Table III. Bond Distances and Angles within the $Pt_2(CO)_2(PPh_3)_2(C_2(CO_2CH_3)_2)$ Molecule

	Distances (Å)		
Pt–Pt′	2.6354 (8)	C(3)–O(2)	1.172 (14)
Pt–P	2.320 (3)	C(3)–O(3)	1.306 (16)
Pt–C(1)	1.847 (12)	O(3)–C(4)	1.461 (15)
Pt–C(2)	2.070 (11)	P–R1C(1)	1.800 (14)
C(2)–C(2)′	1.341 (22)	P–R2C(1)	1.794 (15)
C(1)–O(1)	1.153 (18)	P–R3C(1)	1.816 (12)
C(2)–C(3)	1.461 (18)		
	Angles (Deg)		
Pt–Pt–C(2)	71.7 (3)	Pt–C(2)–C(2)′	108.1 (3)
Pt–Pt–C(1)	93.2 (4)	Pt–C(2)–C(3)	129.5 (9)
Pt–Pt–P	169.4 (1)	C(2)′–C(2)–C(3)	122.5 (8)
P–Pt–C(1)	96.6 (3)	C(2)–C(3)–O(2)	122.7 (13)
P–Pt–C(2)	78.1 (3)	C(2)–C(3)–O(3)	112.1 (11)
C(1)–Pt–C(2)	163.7 (5)	O(2)–C(3)–O(3)	124.9 (13)
Pt–C(1)–O(1)	174.9 (13)	C(3)–O(3)–C(4)	114.1 (12)

Table IV. Least-Squares Planes for $Pt_2(CO)_2(PPh_3)_2(C_2(CO_2CH_3)_2)$[a]

atom	dev, Å	atom	dev, Å
Plane 1: Coordination Plane of Pt Atom			
$13.20x - 0.85y - 0.42z = 0.21$			
Pt	0.000 (1)	C(2)	0.160 (11)
P	−0.009 (3)	C(3)	0.15
C(1)	0.198 (13)	O(1)	0.37
Plane 2: Methyl Carboxylate Substituent			
$14.65x - 4.81y - 18.98z = 4.67$			
C(2)	0.004 (10)	O(3)	0.005 (10)
C(3)	−0.028 (15)	C(4)	0.05
O(2)	0.006 (9)		
Dihedral Angle between Plane 1 and Plane 2: 49.8°			

[a] Least-squares plane is in crystal coordinates as defined by W. C. Hamilton, *Acta Crystallogr.*, **18**, 502 (1965).

metallacyclic rings. The Pd(I) complex $Pd_2(C_5Ph_5)_2(C_2Ph_2)$ with two additional electrons relative to $Pt_2(CO)_2(PPh_3)_2$(alkyne) has been shown to have structure I,[12] however.

The coordination geometry about the metal centers in $Pt_2(CO)_2(PPh_3)_2(C_2(CO_2CH_3)_2)$ could be viewed as a distorted square plane. The least-squares plane calculated for the Pt, C(1), C(2), and P atoms is contained in Table IV and shows no substantial deviations from planarity. Bond angles about the Pt are also consistent with this view with two significant distortions relating to the compressed Pt–Pt–C(2) angle at the interior of the diplatinacyclobutene ring (71.7 (3)°) and dislocation of the phosphorus atom from the site immediately trans to the Pt–Pt bond toward the acetylenic ligand. The C(1)–Pt–P angle is opened to 96.6 (3)° and the trans Pt–Pt–P angle is 169.4 (1)°. The Pt–Pt length of 2.6354 (8) Å is well within the range of values reported previously for a number of binuclear Pt(I) complexes. These values generally range upward from the 2.585 (1) Å value of $Pt_2((CF_3)_2CO)(COD)_2$ and average to approximately 2.63 Å.[13] The Pt–P length of 2.320 (3) Å found for $Pt_2(CO)_2(PPh_3)_2(C_2(CO_2CH_3)_2)$ is slightly longer than other Pt–P lengths reported for phosphine ligands at positions which are approximately trans to a Pt–Pt bond. Values of 2.218 and 2.246 Å have been reported for $Pt_2(PPh_3)_2(PPh_2)_2$,[14] a value of 2.219 (3) Å has been reported for $[Pt(SPEt_2)(P(OPh)_3)]_2$,[15] and values of 2.226 (9) and 2.318 (9) Å have been reported for $Pt_2(S)(CO)(PPh_3)_3$.[16]

The structural features of the organic ligand are consistent with a vinylic species with two Pt atoms occupying cis substituent positions. The C(2)′–C(2) length is 1.34 (2) Å, the C(2)′, C(3)′, C(2), C(3), Pt′, and Pt atoms are essentially

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planar, and the bond angles about C(2) have olefinic values. The methyl carboxylate substituents are also planar and have expected bond distances and angles.

The possibility of a general series of reactions between the relatively common $Pt(PR_3)_2$(alkyne) complexes and CO to give a dimetallacyclic product is interesting since it involves a formal one-electron oxidation of each metal. It is a reaction which is mediated by CO but where the alkyne ligand serves as the oxidizing agent. Bennett and Yoshida reported the formation of $Pt_2(PPh_3)_2(CO)_2(C_6H_8)$ by treating the platinum(0)–cyclohexyne complex with CO.[3] However, cyclic alkyne complexes prepared with less strained alkynes, cycloheptyne and cyclooctyne, were inert to CO addition. This was rationalized on the basis of the greater electrophilic character of the cyclohexyne ligand in complexes of form $Pt(PPh_3)_2$(alkyne). If complexes of electrophilic alkynes are indeed subject to CO addition and oxidation to Pt(I), the dimetallacyclic species may prove to be an important component of platinum–alkyne chemistry.

Registry No. $Pt_2(CO)_2(PPh_3)_2(C_2(CO_2CH_3)_2)$, 72207-39-7; $Pt(PPh_3)_2(C_2(CO_2CH_3)_2)$, 22853-55-0; $Pt(PPh_3)_2(CO)_2$, 15377-00-1.

Supplementary Material Available: A table of observed and calculated structure factor amplitudes (9 pages). Ordering information is given on any current masthead page.

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Structure and Spectral and Redox Properties of a Dioxomolybdenum(VI) Chelate of *N*-Methyl-*p*-tolylthiohydroxamic Acid, a Complex Containing a $\{O_2MoO_2S_2\}$ Donor Set

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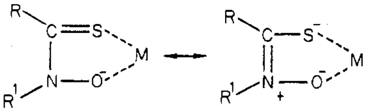
There is much current interest in complexes of molybdenum in which the metal is in oxidation states IV, V, and VI. Complexes with sulfur-containing ligands are of particular interest since they are useful for defining structural and spectroscopic features that can be used to understand the molybdenum active site in redox enzymes such as xanthine oxidase and sulfite oxidase. Recent comparisons of Mo–O and Mo–S distances in model systems (by crystallography or by extended X-ray absorption fine structure (EXAFS)) with those of the enzymes (by EXAFS) suggest that a number of sulfur atoms bind to an O_2Mo^{VI} moiety in the oxidized form of the enzymes.[1] In this paper we describe the first example of a mononuclear Mo(VI) chelate of the type MoO_2(chelate)$_2$ which possesses a donor set $MoO_2(S_2O_2)$. Other combinations such as $MoO_2(O_4)$, $MoO_2(N_2O_2)$, $MoO_2(S_2N_2)$, and $MoO_2(S_4)$ are known.[2] The ligand used in the present work is an N-substituted thiohydroxamic acid which binds to metals in the form of a uninegative bidentate anion via S and O donor atoms:



We have recently investigated a wide range of thiohydroxamate chelates of iron[3,4] and copper.[5] The present study is part of a systematic study of molybdenum complexes with thio ligands ranging from simple unidentate thiolates $\{RS^-\}$[6] to other chelate groups {SX}, where X = S, N, or O.

Experimental Section

The complex $MoO_2(p\text{-}CH_3C_6H_4C({=}S)N(CH_3)O)_2$ was obtained by reacting $(pyH)_2MoOCl_5$, ligand, and sodium methoxide in 1:2:2 mole ratio in dry methanol under nitrogen. The initial green/black solution lightened on stirring and a yellow/green solid deposited which formed yellow columnar crystals when recrystallized in the air from acetone; mp 140 °C. Anal. Calcd for $C_{18}H_{20}MoN_2O_4S_2$: C, 44.3; H, 4.1; N, 5.7. Found: C, 45.0; H, 4.4; N, 5.9.

Cyclic voltammetric measurements were made on a PAR 170 instrument. $Et_4N(ClO_4)$ supporting electrolyte, Pt wire working electrode, and Ag/AgCl reference electrode were used with dry acetone as solvent. $Bu_4N(ClO_4)$ supporting electrolyte and the SCE were used with dichloromethane as solvent.

X-ray Crystallographic Data. For $Mo(C_{18}H_{20}N_2O_4S_2)$ (mol wt 488.5): monoclinic, $a = 12.674\ (7)$ Å, $b = 12.762\ (7)$ Å, $c = 13.058\ (8)$ Å, $\beta = 91.83\ (5)°$, $V = 2111.0$ Å^3, $\rho_{obsd} = 1.53\ (2)\ g{\cdot}cm^{-3}$, $Z = 4$, $\rho_{cald} = 1.54\ g{\cdot}cm^{-3}$, $F(000) = 991.7$, space group $P2_1/c$ (No. 14), systematic presences $h0l$, $l = 2n$, $0k0$, $k = 2n$, Mo Kα radiation, $\lambda = 0.7107$ Å, μ(Mo Kα) = 7.5 cm^{-1}.

Diffraction data were collected from a columnar crystal of approximate dimensions 0.08 × 0.08 × 0.27 mm at 290 K on a Philips PW 1100 diffractometer, using graphite-monochromated Mo Kα radiation. One quadrant of data was collected (6661 reflections) by the ω-scan technique, with a scan speed of 0.04° s^{-1}, with a symmetric scan range of ±0.65° in θ (with an allowance for dispersion) to the limit $2\theta < 60°$. The intensities of three standard reflections, monitored at regular intervals, showed no significant fluctuation during the data collection period. The raw intensity data were corrected for Lorentz, polarization, and absorption ($\mu = 7.5$ cm^{-1}) effects (absorption because of marked variation in crystal dimensions, transmission coefficients range from 0.88 to 0.95). After averaging of equivalent reflections, a total of 2170 independent reflections ($F^2 > 3\sigma(F^2)$) were used for solution and refinement. The estimated variances in the intensities (used to derive the weights for least-squares refinement) were obtained from counting statistics plus an additional term (0.04 × scan count)^2 to account for errors dependent upon intensity.

Solution and Refinement of the Structure. The position of the molybdenum atom was determined from a three-dimensional Patterson function calculated from intensity data; the remainder of the molecule was located from a difference Fourier map. Full-matrix least-squares refinement[7] was based on minimization of the function $\sum w(|F_o| - |F_c|)^2$, with the weights w taken as $(4F_o^2/\sigma^2(F_o^2))$, where F_o and F_c are the observed and calculated structure factor amplitudes, respectively. Atomic scattering factors and both the real, $\Delta f'$, and imaginary, $\Delta f''$, components of anomalous dispersion were taken from the "International Tables of X-ray Crystallography", Vol. 4. Anisotropic temperature factors were introduced for all nonhydrogen atoms. Hydrogen atoms were included in the refinement in their geometrically calculated positions, with the methyl groups free to rotate about the $C\text{–}C_{Me}$ bond (C–H = 1.08 Å).

The final agreement factors are

$$R = \sum||F_o| - |F_c||/\sum|F_o| = 0.047$$

and

$$R_w = \sum w^{1/2}(|F_o| - |F_c|)/\sum w^{1/2}|F_o| = 0.041$$

and the estimated standard deviation of an observation of unit weight is 1.47. The ratio of data to parameters is 8.4:1. Atomic coordinates and thermal parameters for all nonhydrogen atoms are listed in Table I. Some pertinent interatomic distances and angles are listed in Table II. A table of observed and calculated structure factor amplitudes is available.[8]

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