which can operate more powerfully in this isopropyl ester derivative than in its ethyl analogue. These packing factors are reflected in the anomalously small slope of the Mössbauer resonance area vs. temperature plot. Interpretation of variable temperature Mössbauer data should take this possibility into account. So far as we are aware, the structure of the title compound is the first example of a monomeric tin species with the same expected dimensions as its corresponding polymeric form, although information concerning the location of the next-nearest molecule and the shortest contact distances are surprisingly difficult to obtain from published structure reports.[2]

Acknowledgment. Our work is supported by the Office of Naval Research and the National Science Foundation through Grant CHE-78-26548 (J.J.Z.) and the National Cancer Institute, DHEW, through Grant CA-17562 (D.v.d.H.). We thank the University of Oklahoma for providing computer time and M&T Chemicals, Inc., for the donation of organotin starting materials.

Registry No. $(C_6H_5)_2Sn[S_2P(OC_3H_7\text{-}i)_2]_2$, 73453-95-9.

Supplementary Material Available: Listing of structure factor amplitudes (13 pages). Ordering information is given on any current masthead page.

Contribution from the Institut für Organische Chemie
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Reagents for Asymmetric Epoxidations. Molecular Structure of a Molybdenum(VI)–Oxodiperoxo Complex Containing a Chiral Bidentate Lactamide Ligand

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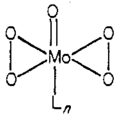
Received October 30, 1979

The molecular structure and absolute configuration of $MoO(O_2)_2\cdot(S)\text{-}MeCH(OH)CONMe_2$ have been determined from three-dimensional X-ray diffractometer data collected by counter methods. The molecule crystallizes in the orthorhombic space group $P2_12_12_1$ with four formula units per cell. The unit cell dimensions are a = 6.651 (2), b = 9.567 (3), and c = 15.504 (8) Å. The structure has been solved by the heavy-atom technique and refined to R = 0.0549 (3091 unique reflections). In the slightly distorted pentagonal-bipyramidal coordination sphere of molybdenum the two peroxo groups are located in equatorial positions; the chiral lactamide ligand is bidentate, being coordinated through the carbonyl oxygen at the fifth equatorial position and through the hydroxylic oxygen on the axial position opposite to the doubly bonded oxo group. The geometry of the amide group is significantly altered upon coordination to molybdenum. Crystal packing is determined by a three-dimensional network of hydrogen bonds between the hydroxyl group of the lactamide ligand and peroxo atoms of neighboring molecules. The absolute configuration at the asymmetric carbon atom of the coordinated lactamide derived from (−)-ethyl lactate has been determined by the Bijvoet method to be S in agreement with the classical assignment. The hydroxylic hydrogen was located and refined, establishing S chirality for the asymmetric oxygen atom which is formed upon coordination to molybdenum.

Introduction

Molybdenum(VI)–oxodiperoxo complexes of the general formula **1** (n = 1–2; L = H_2O, DMF, HMPA, pyr) are



1

stoichiometric reagents for the oxidation of various organic substrates such as sulfides, aliphatic amines, ketones, and olefins.[1] The epoxidation of olefins by **1** is of considerable interest since metal peroxo species of molybdenum are claimed to be involved as key intermediates in the hydroperoxide oxidation of olefins catalyzed by salts of this metal.[1] Recently, some of us have demonstrated that asymmetric epoxidation of simple prochiral olefins (e.g., propene, 1-butene, *trans*-2-butene) can be achieved with stoichiometric quantities of **1** in which L represents the chiral bidentate ligand (S)-N,N-dimethyllactamide. In order to clarify the exact molecular structure of the novel chiral oxidizing agent,[2] we have carried out an X-ray crystallographic analysis of the compound $MoO(O_2)_2\cdot N,N$-dimethyllactamide, **2**.

Table I. Crystal Data for **2** at 23 °C

cryst color: yellow
cryst size: 0.15 × 0.22 × 0.31 mm^3
cryst system: orthorhombic
space group: $P2_12_12_1$
cell dimensions: a = 6.651 (2) Å, b = 9.567 (3) Å,
c = 15.504 (8) Å, V = 986.52 $Å^3$, Z = 4, d_{calcd} = 1.973 g cm^{-3},
d_{exptl} = 1.94 g cm^{-3}
μ(Mo Kα): 12.04 cm^{-1}

Experimental Section

Preparation of 2. A solution of $H_2Mo_2O_{11}$ is prepared by dissolving MoO_3 (5 g, 34.7 mmol) in 30% H_2O_2 (25 mL) at 40 °C according to the general procedure.[1,3] (The necessary care when preparing and handling peroxometal compounds should be observed, although no incidence of a violent decomposition of **2** occurred during synthesis, storage, and use; cf. ref 3, p 189). (S)-N,N-Dimethyllactamide (4.1 g, 35 mmol) prepared from (−)-(S)-ethyl lactate[4] is added with stirring to the filtered solution of $H_2Mo_2O_{11}$. The solution is concentrated in vacuo at 40 °C to three-fourths its initial volume, and after addition of 15 mL of methanol, the compound crystallized at 20 °C. The crystals are collected by suction, washed with methanol and diethyl

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*Authors to whom correspondence should be addressed (W.W.: X-ray analysis).

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Table II. Atomic Parameters and Their Standard Deviations[a] for $MoO_5 \cdot (S)$-MeCH(OH)CONMe$_2$ (1)

	fractional coordinates			anisotropic thermal parameters[b] ($\times 10^4$)					
atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo	−0.0661 (1)	0.8746 (1)	0.6046	250 (2)	393 (2)	388 (2)	−46 (2)	3 (2)	−30 (2)
O1	0.0935 (8)	0.7077 (5)	0.5880 (3)	404 (26)	548 (28)	513 (30)	−29 (30)	−48 (22)	40 (23)
O2	−0.0257 (7)	0.7443 (6)	0.5124 (3)	374 (26)	563 (29)	384 (24)	−93 (22)	−27 (19)	0 (21)
O3	−0.1243 (7)	1.0722 (5)	0.6017 (4)	393 (23)	473 (25)	578 (29)	−97 (27)	−2 (25)	5 (19)
O4	−0.1875 (8)	0.9989 (6)	0.5243 (4)	430 (27)	558 (32)	516 (30)	16 (25)	−80 (23)	19 (25)
O5	−0.2602 (8)	0.8120 (6)	0.6611 (3)	380 (25)	588 (32)	449 (27)	−19 (24)	89 (21)	−94 (23)
O6	0.2465 (7)	0.9650 (6)	0.5596 (3)	288 (20)	505 (29)	293 (20)	−66 (20)	23 (17)	−19 (20)
O7	0.1070 (7)	0.9177 (5)	0.7124 (3)	355 (23)	617 (31)	287 (19)	−29 (19)	12 (17)	−107 (20)
C1	0.3235 (14)	1.1902 (8)	0.6175 (7)	645 (51)	459 (41)	707 (62)	8 (43)	−47 (48)	−153 (38)
C2	0.3579 (10)	1.0344 (8)	0.6256 (4)	270 (25)	489 (37)	329 (30)	−14 (26)	2 (21)	−26 (25)
C3	0.2769 (10)	0.9802 (7)	0.7109 (4)	337 (30)	443 (34)	294 (27)	−89 (25)	−70 (23)	19 (26)
C4	0.2771 (14)	0.9518 (10)	0.8640 (5)	612 (50)	771 (59)	306 (32)	−109 (36)	−82 (32)	166 (46)
C5	0.5685 (12)	1.0653 (9)	0.7920 (5)	413 (35)	684 (48)	599 (44)	−244 (37)	−236 (38)	120 (40)
N	0.3729 (8)	0.9973 (6)	0.7838 (4)	374 (27)	503 (33)	320 (25)	−117 (24)	−27 (21)	40 (24)
H6	0.301 (15)	0.907 (11)	0.542 (6)	$\bar{U} = 0.0721\ (361)$ Å^2					

[a] The number following each figure is the estimated standard deviation in the least significant figure. [b] The form of the thermal ellipsoid is $\exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{23}klb^*c^*)]$.

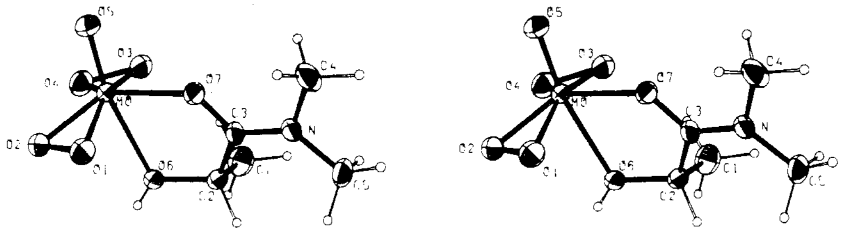

Figure 1. ORTEP stereoplot of the Mo complex **1**.

ether, and then dried over P_4O_{10} (10^{-2} mmHg); yield 6.9 g (67.8%). The crude product is analytically pure: mp 149 °C dec; mol wt calculated for $C_5H_{11}O_7NMo$ 293.09; IR ν_{O-O} 865, OMoO 540 (sym), 583 cm^{-1} (asym); ^{1}H NMR (CD_3OD) δ_{CH_3} 1.25, 1.32, 2.96, 3.08. Anal. Calcd: C, 20.49; H, 3.78; N, 4.78. Found: C, 20.49; H, 3.77; N, 4.72. A second crop of 1.2 g can be isolated by concentrating the mother liquor. The product is stored under refrigeration in 1-g portions in light-protected vials.

X-ray Crystallographic Procedure. Crystals of **2** suitable for X-ray crystallography were prepared by a vapor diffusion method with nitromethane/diethyl ether. The apparatus used was similar to that recently described by Brown and Trefonas.[5] Preliminary unit cell constants and space group information were obtained by precession photographs. The crystal was transferred to a Nonius CAD 4 automated diffractometer, and accurate cell constants were obtained by computer centering of 25 high-angle reflections. Least-squares refinement of the setting angles provided the figures listed in Table I.

Intensity data were collected in the range of $3° < \theta(\text{Mo K}\alpha) < 33°$ with a variable scan width of $\Delta\theta = (0.8 + 0.35 \tan \theta)°$ and the ω/θ-scanning mode. The scan rate was variable and was determined by a fast (20° min^{-1}) prescan. The scanning time for the weak reflections was limited to a maximum of 60 s; background counts were collected for 25% of the total scan time at each end of the scan range. An attenuator for decreasing the intensity of the diffracted beam by a factor of 21.8 was inserted into the beam when the prescan indicated an intensity too high for accurate counting ($I > 50\,000$ counts/s).

Intensities, relative structure factors, and standard deviations on relative structure factors were calculated according to

$$I = k[I_0 - 2(U_1 + U_2)]$$

$$F = (I/Lp)^{1/2}$$

$$\sigma(F) = \tfrac{1}{2}[I_0 + 2(U_1 + U_2) + 0.02I^2]^{1/2}[(Lp)I]^{1/2}$$

where k is a scaling constant which contains corrections for the scanning speed and the attenuator, I_0 is total integrated peak count, U_1 and U_2 are background counts, and Lp is the Lorentz and polarization correction.

A total of 3935 reflections were collected and as a check on crystal and electronic stability two reflections were measured periodically. No significant change has been observed until the end of data collection. A total of 3091 independent reflections were considered "observed" according to the criterion $I \geq 2\sigma(I)$. No absorption corrections were applied.

The structure was solved by the heavy-atom method. The location of the molybdenum atom was derived from a sharpened Patterson synthesis. Least-squares refinement of this first structural model ($R = 0.21$) and a succeeding difference Fourier synthesis led to the location of all remaining nonhydrogen atoms. After three full-matrix least-squares cycles, R was reduced to 0.10. The thermal parameters were converted to their anisotropic equivalent, and three further least-squares cycles led to $R = 0.078$. At this stage, all hydrogen atoms could be located in a difference Fourier synthesis. In the further refinement process, all CH_3 and CH groups were treated as "rigid groups" ($d_{C-H} = 0.96$ Å) with a common isotropic thermal parameter for all carbon-attached hydrogens. The hydroxylic hydrogen was refined isotropically without any constraints. Full-matrix least-squares refinement converged to $R = 0.0562$ and $R_G = 0.0571$. In order to establish the absolute configuration at the asymmetric carbon, we carried out the same refinement with inverse atomic coordinates. The resulting values of $R = 0.0549$ and $R_G = 0.0556$ showed at a probability level >99.5% that this latter model represented the correct absolute configuration.

Discrepancy indices used are defined as

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

$$R_G = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2} \quad \text{(unit weights)}$$

A final difference Fourier analysis showed only two peaks with an electron density <0.55 e/Å^3.

Scattering factors for neutral atoms were taken from tables of Cromer and Mann.[6] Anomalous dispersion effects were included in F_c; the values of f' and f'' were those of Cromer and Liberman.[7] All calculations were performed with the programs SHELX (G. M. Sheldrick), ORTEP (C. K. Johnson), and XANADU (P. Roberts and G. M. Sheldrick) on the TELEFUNKEN TR 440 at the Zentrum für

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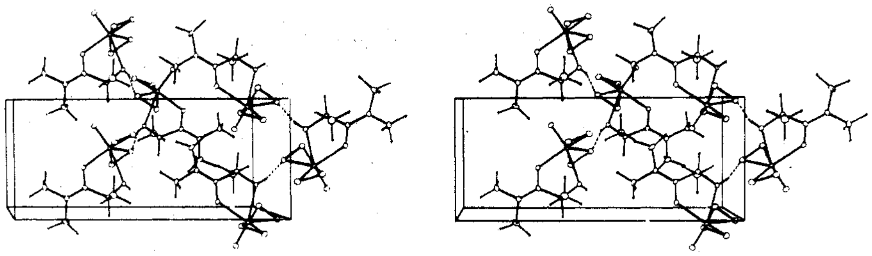

Figure 2. Packing diagram viewed along the *y* axis; dotted lines represent the hydrogen bonds. The origin of the unit cell lies in the upper left corner, the *x* axis is vertical, and the *z* axis goes to the right.

Table III. Bond Distances (Å) in $MoO_5 \cdot (S)$-MeCH(OH)CONMe$_2$

Mo-O1	1.935 (5)	C1-C2	1.512 (10)
Mo-O2	1.915 (5)	C2-O6	1.427 (7)
Mo-O3	1.930 (5)	C2-C3	1.520 (9)
Mo-O4	1.901 (5)	C3-O7	1.279 (7)
Mo-O5	1.671 (5)	C3-N	1.309 (8)
Mo-O6	2.357 (4)	N-C4	1.462 (10)
Mo-O7	2.072 (4)	N-C5	1.460 (10)
O1-O2	1.459 (6)	O6-H6	0.72 (10)
O3-O4	1.451 (7)		

Table IV. Bond Angles (Deg) in $MoO_5 \cdot (S)$-MeCH(OH)CONMe$_2$

O2-Mo-O1	44.5 (2)	O7-Mo-O3	86.3 (2)
O3-Mo-O1	156.3 (2)	O7-Mo-O4	129.8 (2)
O3-Mo-O2	130.4 (2)	O7-Mo-O5	94.4 (2)
O4-Mo-O1	131.5 (2)	O7-Mo-O6	71.1 (2)
O4-Mo-O2	88.8 (2)	Mo-O3-O4	66.7 (3)
O4-Mo-O3	44.5 (2)	Mo-O4-O3	68.8 (3)
O5-Mo-O1	101.4 (2)	Mo-O6-C2	114.6 (4)
O5-Mo-O2	105.4 (2)	Mo-O7-C3	124.7 (4)
O5-Mo-O3	102.0 (2)	C1-C2-O6	108.7 (6)
O5-Mo-O4	103.9 (2)	C1-C2-C3	110.8 (7)
O6-Mo-O1	77.3 (2)	C3-C2-O6	106.3 (5)
O6-Mo-O2	83.9 (2)	C2-C3-O7	119.3 (5)
O6-Mo-O3	79.1 (2)	C2-C3-N	122.5 (6)
O6-Mo-O4	87.2 (2)	N-C3-O7	118.2 (6)
O6-Mo-O5	165.4 (2)	C3-N-C4	119.0 (6)
O7-Mo-O1	88.1 (2)	C3-N-C5	124.4 (7)
O7-Mo-O2	130.8 (2)	C4-N-C5	116.5 (6)

Table V. Selected Least-Squares Planes in $MoO_5 \cdot (S)$-MeCH(OH)CONMe$_2$[a]

atoms	dev from plane, Å	atoms	dev from plane, Å
Plane 1: "Pentagonal Equator"; $5.4352x + 3.5907y - 6.7816z = -1.0080$			
Mo*	−0.311	O4*	0.020
O1*	0.070	O5	−1.974
O2*	0.066	O6	2.018
O3*	0.102	O7*	0.054
Plane 2: "Peroxo Plane"; $5.3425x + 3.5525y - 7.2205z = -1.2159$			
Mo	−0.396	O4*	−0.023
O1*	−0.016	O5	−2.063
O2*	0.023	O6	1.920
O3*	0.016	O7	−0.096
Plane 3: "*N,N*-Dimethyllactamide Plane"; $-2.9843x + 8.5219y + 1.1216z = 8.2887$			
Mo*	0.039	C3*	0.035
O6*	−0.174	N*	−0.013
O7*	0.011	C4*	−0.037
C1	1.580	C5*	−0.020
C2*	0.159		

[a] Coordinates of atoms marked with asterisk were used to define the planes. Angles between normals to planes: 1 and 2, 1.82°; 1 and 3, 93.67°; 2 and 3, 93.63°.

Datenverarbeitung at the University of Tübingen.

Atomic coordinates and thermal parameters for the nonhydrogen atoms and the hydroxylic hydrogen are listed in Table II. The numbering scheme of these atoms is that given in Figure 1. Interatomic distances, intramolecular angles, and deviations of atoms from selected planes are listed in Tables III–V, respectively.

Results and Discussion

Only a few single-crystal structural determinations of molybdenum(VI)–oxodiperoxo complexes containing group 5 and 6 donor ligands have been reported thus far, e.g., compounds of the composition $MoO(O_2)_2(C_2O_4^{2-})$ (**2**),[8] $MoO(O_2)_2 \cdot$HMPA$\cdot$L (**3**, L = H_2O; **4**, L = pyr),[9] and $MoO(O_2)(F)$-(pyridine-2,6-dicarboxylate) (**5**),[10] and more recently $MoO(O_2)(H_2O)$(pyridine-2,6-dicarboxylate) (**6**) and $MoO(O_2)_2$-(pyridine-2-carboxylate) (**7**).[11] The main structural features of compounds **2**–**7** are also observed in the present chiral reagent $MoO(O_2)_2 \cdot (S)$-*N,N*-dimethyllactamide, **1** (see Figure 1).

The molybdenum atom is surrounded by seven oxygen atoms in a nearly pentagonal-bipyramidal coordination geometry with the bidentate peroxo groups O1–O2 and O3–O4 lying in the equatorial plane and the doubly bonded oxo group O5 occupying one apical position. The fifth coordination site of the pentagonal plane and the remaining apical position are occupied by the oxygen atoms O6 and O7 of the bidentate *N,N*-dimethyllactamide ligand. The arrangement of the oxygens in the pentagonal plane is not entirely coplanar (see Table V). The molybdenum atom and the oxygen atom O7 of the lactamide group are situated 0.40 and 0.10 Å, respectively, above the best plane defined by the peroxo atoms O1–O2–O3–O4 in the direction toward O5. This arrangement, which has been observed in the molybdenum complexes cited above, confirms the previous prediction that this deviation from planarity represents a common phenomenon for peroxo complexes of group 5B and 6B metals.[11]

The invariance of the MoO_5 geometry with respect to the metal and the organic ligand is clearly seen from the data of Tables III and IV; all bonding distances and angles are (within the ranges of ±0.02 Å and ±1°, respectively) nearly identical with those observed in the structure of the complexes mentioned above. In a valence-bond description, the Mo–O5 bond and the Mo–O1, Mo–O2, Mo–O3, and Mo–O4 bonds can be represented as a triple bond and as single bonds, respectively, according to the correlation of bond order vs. bond distance given by Cotton and Wing.[12]

As depicted in Figure 1, the lactamide ligand has *S* configuration at C2; the determination of the absolute configuration with the use of anomalous dispersion effects (see the Experimental Section) agrees with the classical assignment of absolute configuration for the optically active starting

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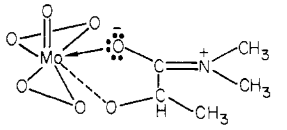
material (−)-(*S*)-ethyl lactate.[13]

Owing to steric constraints of the five-membered chelate ring Mo–O7–C3–C2–O6, the pentagonal-bipyramidal coordination geometry of molybdenum is significantly distorted. The two pyramidal axes Mo–O5 and Mo–O6 include an angle of 165.4°. The bonding strength of molybdenum to the carboxylic oxygen O7 differs appreciably from that to the hydroxylic oxygen O6. The former bond is much stronger (2.07 Å) than the relatively weak Mo–OH bond (2.36 Å) which resembles the weak Mo–OH_2 bond in the molybdenum–aquo complexes **3** and **6**.[9,11] Obviously, this lenghthening of the axial Mo–O6 bond is due to the strong trans influence of the multiple Mo–O5 bond. In the related complex **5** the axial Mo–F bond trans to the multiple Mo–O bond exhibits an analogous weakening.[10]

The strong bond Mo–O7 alters significantly the geometry of the *N*,*N*-dimethyllactamide entity: the lengthening of the keto group C3–O7 to 1.28 Å and the shortening of the C3–N amide bond to 1.31 Å suggest that the "zwitterionic" resonance form **8** shows an increased contribution in comparison to uncoordinated amides.[14]



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The crystal structure of **2** is governed by chains of hydrogen-bonded molecules parallel to the *x* axis (see below), which may explain the hardness of single crystals which we have observed at cutting. Whereas all intermolecular distances in the unit cell are equal or greater than the sum of the van der Waals' radii, the oxygen of the hydroxy group O6 comes close to the O2 peroxo atom of a neighboring molecule by 2.75 Å (symmetry relation: $0.5 + x$, $1.5 - y$, $1 - z$), the corresponding distance of H6 to this atom being 2.03 Å. The latter value is clearly of limited physical significance, because O–H distances found by X-ray analysis are often too short (0.7–0.9 Å).[15,16] The angle of the intermolecular hydrogen bond O6–H6–O2′ is 180 ± 10° and is based on a realistic O–H distance of 1.00 Å (derived from neutron diffraction[15]); the intermolecular bond H6···O2′ can be estimated to approximate 1.75 Å in length.

As shown in Figure 2, the hydrogen-bonding scheme in the unit cell forces the H6 hydrogen in a position by which the coordination geometry of O6 becomes nearly tetrahedral. Taking into account that the angles Mo–O6–H6 (106°) and C2–O6–H6 (112°) are of reduced precision ($\sigma = 8°$) of course, the nearly tetrahedral bond direction toward H6 is highly significant according to Cruickshank and Robertson.[17] So, upon complexation to molybdenum, O6 constitutes an additional chiral center. In the present crystal structure its absolute configuration is *S* according to the Cahn, Ingold, and Prelog convention.[18]

Registry No. **1**, 70355-53-2; $H_2Mo_2O_{11}$, 59250-18-9.

Supplementary Material Available: A table of hydrogen coordinates and a table with observed and calculated structure factors (19 pages). Ordering information is given on any current masthead page.

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(Tetrathiafulvalene)bis(acetylacetonato)palladium(II), (TTF)Pd$(acac)_2$, a Metallotetrathiaethylene Containing Neutral Tetrathiafulvalene

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The synthesis, Raman spectrum, and crystal and molecular structure of (TTF)Pd$(acac)_2$, $(C_6H_4S_4)Pd(C_5H_7O_2)_2$, are reported. The ν_3 mode for the TTF molecule in the complex occurs at 1517 cm^{-1}, indicative of the presence of only neutral TTF. An X-ray diffraction study is in accord with the Raman evidence of low charge transfer. Pertinent crystallographic data for (TTF)Pd$(acac)_2$ are space group $P2_1/c$, $a = 11.142$ (3) Å, $b = 11.642$ (3) Å, $c = 7.920$ (3) Å, $\beta = 99.97$ (2)°, $V = 1011.9$ Å^3, $Z = 2$ [requiring $\bar{1}(C_i)$ molecular symmetry for both TTF and Pd$(acac)_2$], $D_{measd} = 1.671$ (2) g cm^{-3}, and $D_{calcd} = 1.670$ g cm^{-3}. The structure was solved by standard crystallographic methods and refined, on the basis of 2101 observed data, to an *R* value of 0.056. The crystal packing is pseudo-*C* centered with the Pd$(acac)_2$ species occupying the vertices of the unit cell and the TTF molecules assuming positions at the center of the *ab* face. The interactions between molecular components are solely van der Waals in nature. Neither of the molecular constituents are self-associated in the solid. The platinum analogue (TTF)Pt$(acac)_2$ is isomorphous, and unit cell data are space group $P2_1/c$, $a = 11.152$ (2) Å, $b = 11.644$ (4), Å, $c = 7.904$ (2) Å, $\beta = 99.98$ (2)°, $V = 1010.8$ Å^3, and $Z = 2$.

Introduction

Tetrathiafulvalene (TTF), **1**, is a constituent of numerous materials which exhibit a one-dimensional metallic state and a concomitant high, anisotropic electrical conductivity,[2-4] and, on this account, it has attracted considerable interest. Recent work in these laboratories has focused on metallotetrathiaethylenes, compounds containing **1**, or its analogues, and metallic elements.[5-7] Tetrathiafulvalene is easily oxidized

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