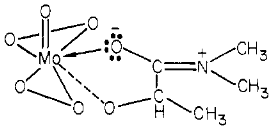
material (−)-(*S*)-ethyl lactate.[13]

Owing to steric constraints of the five-membered chelate ring $\overline{\mathrm{Mo{-}O7{-}C3{-}C2{-}O6}}$, 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]



8

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$(acac)_2$], $D_{\text{measd}} = 1.671$ (2) g cm^{-3}, and $D_{\text{calcd}} = 1.670$ 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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[1] (a) 3M Central Research Laboratories. (b) The Johns Hopkins University. (c) University of Mississippi. (d) Northwestern University.

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Table I. Final Nonhydrogen Atom Parameters

atom	x^a	y	z	$U_{11}{}^{b,c}$	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
(a) Pd(acac)$_2$ Complex									
Pd	0	0	0	244 (2)	216 (2)	435 (2)	−7 (7)	19 (2)	−21 (8)
O(2)	−1591 (4)	15 (4)	804 (6)	30 (2)	35 (2)	62 (2)	−1 (1)	14 (2)	−5 (1)
O(3)	164 (2)	−1688 (2)	58 (3)	37 (1)	23 (1)	63 (2)	−1 (1)	8 (1)	−1 (1)
C(4)	−648 (3)	−2359 (3)	493 (4)	43 (1)	28 (1)	36 (1)	−6 (1)	1 (1)	−0 (1)
C(5)	−1726 (3)	−2019 (3)	983 (5)	44 (1)	35 (1)	52 (2)	−14 (1)	10 (1)	−1 (1)
C(6)	−2138 (3)	−904 (3)	1126 (4)	35 (1)	43 (2)	45 (1)	−8 (1)	9 (1)	−3 (1)
C(7)	−324 (4)	−3615 (3)	490 (6)	69 (2)	29 (1)	61 (2)	−0 (1)	10 (2)	3 (1)
C(8)	−3307 (3)	−698 (4)	1778 (7)	55 (2)	56 (2)	106 (3)	−7 (2)	41 (2)	−1 (2)
(b) TTF Molecule									
S(9)	5510 (1)	3260 (1)	−645 (2)	639 (5)	548 (5)	709 (6)	−41 (4)	−8 (5)	−135 (5)
S(10)	6618 (1)	4887 (1)	2012 (2)	468 (7)	727 (6)	610 (7)	−92 (3)	−132 (6)	−48 (4)
C(11)	5441 (3)	4605 (3)	275 (4)	32 (1)	45 (2)	44 (2)	−7 (1)	5 (1)	−1 (1)
C(12)	7369 (4)	3613 (4)	1825 (7)	44 (2)	85 (3)	73 (2)	6 (2)	1 (2)	12 (2)
C(13)	6882 (4)	2862 (4)	651 (6)	62 (4)	63 (2)	84 (3)	12 (2)	15 (2)	13 (2)

[a] All coordinate parameters $\times 10^4$. [b] Pd and S atom parameters $\times 10^4$; O and C parameters $\times 10^3$. [c] The form of the anisotropic thermal ellipsoid is $\exp[-2\pi^2(a^*U_{11}h^2 + \ldots + 2a^*b^*U_{12}hk + \ldots)]$.

to the stable cation radical,[8] and, accordingly, its chemistry is dominated by electron-transfer processes.[9] Thus, **1** reacts with organic electron acceptors, e.g., tetracyanoquinodimethan,[10] and inorganic one-electron oxidants[5,11-13] to form completely or partially oxidized materials containing TTF$^{\rho+}$ where ρ ranges from about 0.6 to 2.0. X-ray studies of TTF–TCNQ[14] and (TTF)Br$_{0.79}$[15] have demonstrated columnar arrays of TTF whose constituent molecules have identical bond distances and angles. Recently, such compounds have been studied by resonance Raman spectroscopy,[16] and, in agreement with crystallographic data, the charge in TTF$^{\rho+}$ ($0 \le \rho \le 1$) was observed to be delocalized over all the TTF molecules and evidence for both neutral and cationic TTF was not found.

This paper reports the synthesis and spectroscopic and X-ray crystallographic characterization of (TTF)Pd(acac)$_2$ (acac = acetylacetonate), an unusual metallotetrathiaethylene which contains only neutral TTF.

Results and Discussion

Slow evaporation of an acetonitrile solution of **1** and Pd(acac)$_2$ (**2**) afforded chunky orange crystals of a 1:1 complex, (TTF)Pd(acac)$_2$ (**3**). The X-ray powder pattern of this compound was unique and did not show strong lines due to the starting materials. Likewise, the infrared spectrum was essentially a composite of the spectra of **1** and **2**, suggesting that a crystal complex had been obtained. In agreement with this, the ^{1}H NMR spectrum of **3** in acetonitrile-d_3 was indistinguishable from that of a mixture of **1** and **2**.

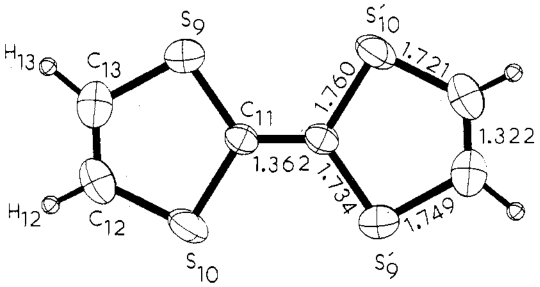

Figure 1. Molecular geometry and atomic numbering scheme for the TTF molecule. Primed atoms are related to unprimed atoms by the symmetry transform $(1 - x, 1 - y, -z)$. For the nonhydrogen atoms, the thermal ellipsoids are drawn at the 40% probability level; the isotropic thermal parameters of the hydrogen atoms here and in subsequent drawings have been artificially set to 1.0 Å.[2]

Table II. Nonhydrogen Atom Bond Angles (Deg)[a]

(a) Pd(acac)$_2$ Complex			
O(2)–Pd–O(3)	94.91 (6)	O(2)–Pd–O(3)′	85.09 (6)
Pd–O(2)–C(6)	122.6 (2)	Pd–O(3)–C(4)	123.0 (2)
O(2)–C(6)–C(5)	126.2 (2)	O(3)–C(4)–C(5)	126.0 (2)
O(2)–C(6)–C(8)	114.0 (2)	O(3)–C(4)–C(7)	114.1 (2)
C(5)–C(6)–C(8)	119.8 (2)	C(5)–C(4)–C(7)	119.9 (2)
		C(4)–C(5)–C(6)	127.3 (2)
(b) TTF Molecule			
C(11)–S(9)–C(13)	95.2 (2)	C(11)–S(10)–C(12)	94.6 (2)
S(9)–C(11)–C(11)′	123.9 (3)	S(10)–C(11)–C(11)′	121.6 (3)
S(9)–C(13)–C(12)	116.6 (3)	S(10)–C(12)–C(13)	118.9 (3)
		S(9)–C(11)–S(10)	114.6 (1)

[a] In the Pd(acac)$_2$ complex, the primed atoms are related to the unprimed atoms by the symmetry transform $(-x, -y, -z)$; in the TTF molecule, the symmetry transform is $(1 - x, 1 - y, -z)$.

Important information about the oxidation state of TTF in (TTF)Pd(acac)$_2$ was obtained from its Raman spectrum. The ν_3 mode in TTF, which is predominantly due to stretching of the central C=C bond, undergoes large frequency shifts on electron transfer. In solid, neutral **1**, ν_3 occurs at 1515 cm^{-1} [16,17] and this mode is seen at 1413 cm^{-1} in (TTF)Br.[5,16] In the Raman spectrum of (TTF)Pd(acac)$_2$, a strong band was observed at 1517 cm^{-1} by using 4579-Å excitation, which indicates the presence of neutral TTF. A weak band at 1421 cm^{-1}

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Table III. Some Least-Squares Planes and Deviations[a]

(a) TTF Molecular Plane ($0.6601 + 0.3939Y - 0.6396Z = 5.9703$ Å)			
S(9), S(9)′	–,+0.043	C(12), C(12)′	+,–0.030
S(10), S(10)′	–,+0.047	C(13), C(13)′	+,–0.020
C(11), C(11)′	–,+0.019		
(b) TTF Central Plane ($0.6794X + 0.3766Y - 0.6297Z = 5.9776$ Å)			
S(9), S(9)′	–,+0.000	C(12), C(12)′	+,–0.118*
S(10), S(10)′	+,–0.000	C(13), C(13)′	+,–0.107*
C(11), C(11)′	–,+0.000		
(c) TTF Exterior Plane ($0.6278X + 0.4234Y - 0.6531Z = 5.8429$ Å)			
S(9)	0.002	C(12)	0.006
S(10)	–0.002	C(13)	–0.006
(d) Pd(acac)$_2$ Complex Plane ($-0.3103X - 0.0432Y - 0.9497Z = 0.0$ Å)			
Pd	0.0	C(5), C(5)′	+,–0.012
O(2), O(2)′	–,+0.012	C(6), C(6)′	–,+0.002
O(3), O(3)′	–,+0.012	C(7), C(7)′	–,+0.048*
C(4), C(4)′	–,+0.001	C(8), C(8)′	–,+0.063*

[a] In each of the equations of the planes, X, Y, and Z are coordinates (Å) referred to the orthogonal axes a, b, and c^*. The atoms used to define a plane have been equally weighted; atoms indicated by an asterisk were given zero weight in defining the plane.

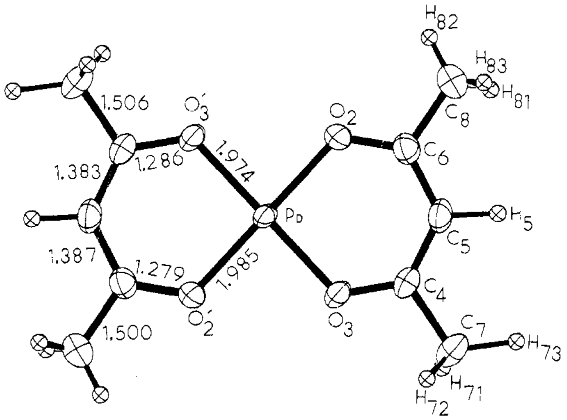

Figure 2. Molecular geometry and atomic numbering scheme for the Pd(acac)$_2$ complex. The thermal ellipsoids for the nonhydrogen atoms are drawn at the 40% probability level. Primed atoms are related to unprimed atoms by the transform ($-x$, $-y$, $-z$).

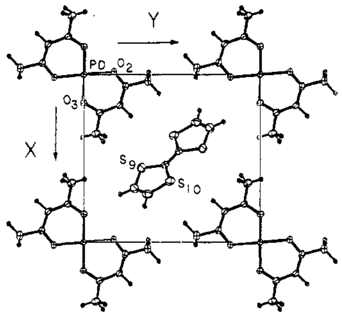

Figure 3. Projection of the crystal structure of (TTF)Pd(acac)$_2$ onto the *ab* plane.

was seen by using 50 mW of laser power; it is attributed to a trace of adventitious TTF$^{+\cdot}$. This impurity is very easily observed since the ν_3 mode in the cation radical is resonance enhanced.[16] Thus, the available spectroscopic data strongly suggested that **3** was a complex containing only neutral TTF. Since previously reported complexes containing **1** all contain partially or completely oxidized TTF, a single-crystal X-ray study was carried out to elucidate further the nature of this compound.

Description of the X-ray Structure

(A) The TTF Molecule. An illustration of the slightly asymmetric TTF molecule, along with its intramolecular, nonhydrogen atom bond lengths, is presented in Figure 1. Nonhydrogen atom positional parameters are given in Table I and the angles formed by them are given in Table II.

As found, for example, in the monoclinic form of neutral TTF[18] and in the TTF radical cation in TTF–TCNQ,[14] the TTF molecule in (TTF)Pd(acac)$_2$ is nonplanar; cf. Table III. The two halves of the fulvalene ring system are significantly distorted in antienvelope conformations, giving rise to an overall chair conformation for the molecule. The central portion of the molecule [defined by atoms S(9), S(10), and C(11) and their symmetry mates] is planar (plane b, Table III) and the planar exterior portion of the molecule [S(9), S(10), C(12), and C(13)] makes a dihedral angle of 4.3 (4)° [2.1° in TTF^0 and 2.2° in TTF–TCNQ] with this central plane. The exterior plane and its centrosymmetric mate lie some 0.27 Å apart; as for the dihedral angle noted above, TTF^0 and cationic TTF in TTF–TCNQ show significantly smaller mean separations of exterior planes—about 0.12 Å in each case. We presume that the slightly more distorted molecular geometry for TTF in **3** is a consequence of weak crystal packing forces and we note that there is no self-association of TTF molecules in this complex as is found in TTF^0 and TTF–TCNQ.

Some information about the degree of charge transfer should be obtainable from the charge-sensitive parameters in the TTF molecule.[19,20] It is known[19-21] that the most sensitive intramolecular bond length is the central C=C bond. Separation between these two carbon atoms is expected to increase as electron density is removed from the highest filled molecular orbital. The value observed for d(C=C) in **3** is 1.362 (7) Å, which is about midway between that found for TTF^0 [1.349 (3) Å] and that for ionic TTF [1.369 (4) Å] in TTF–TCNQ where the charge transfer is known to be about 0.59 e.[22] Thus, the observed geometry of the TTF molecule in (TTF)Pd(acac)$_2$ is indicative of low charge transfer, in qualitative accord with the zero charge transfer inferred from the Raman spectroscopic data (vide supra).

(B) The Pd(acac)$_2$ Complex. A view of the Pd(acac)$_2$ chelate normal to its mean molecular plane is presented in Figure 2. The core of the complex is essentially planar (plane d, Table III) with the methyl carbons nominally out of the molecular plane.

The molecular geometry of Pd(acac)$_2$ in **3** (cf. Figure 2 and Table II) is in good agreement with the relatively inaccurate values reported for Pd(acac)$_2$ itself.[23] The geometry within the acetylacetonate ligand is in excellent agreement with earlier reported structures for L$_2$Pd(acac) complexes,[24,25] although, of course, the Pd–O distances given here are about 0.1 Å

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shorter than those for L_2Pd(acac) compounds, where the ligating atom of the ligand L is carbon, owing to a trans influence.[26]

(C) Crystal Packing. The packing motif in (TTF)Pd(acac)$_2$ is illustrated in an *ab* plane projection in Figure 3. The Pd(acac)$_2$ chelate molecules occupy the vertices of the unit cell, while the TTF molecules assume positions at the center of the *ab* face. The intermolecular interactions are van der Waals in nature, consisting in the main of CH$_3$(acac)···CH$_3$(acac) and CH$_3$(acac)···S(TTF) contacts. The shortest contacts within these two groups are C(7)···C(7) $[-x, 1-y, -z]$ = 3.424 (8) Å and S(9)···C(8) $[-x, -y, -z]$ = 3.878 (5) Å.

Experimental Section

Tetrathiafulvalene, 0.20 g (1 mmol), and palladium bis(acetylacetonate), 0.30 g (1 mmol), were dissolved in 20 mL of hot acetonitrile. The solution was placed in a vacuum desiccator which was connected, via a short length of capillary tubing, to a vacuum source. As the solvent was slowly removed, the product separated as orange, nearly hexagonal prisms. These were collected on a filter, washed with a small amount of acetonitrile, and vacuum dried. The yield was 0.1 g. Anal. Calcd for $C_{16}H_{18}O_4PdS_4$: C, 37.80; H, 3.54; Pd, 20.87; S, 25.20. Found: C, 37.72; H, 3.71; Pd, 21.06; S, 25.06. IR (Nujol mull): 3055 (m), 1500 (br, s), 1450 (s), 1270 (w), 1030 (sh), 1020 (s), 935 (s), 790 (s), 780 (m), 730 (m), 700 (m), 680 (m), 660 (s), 615 (m), 470 (s), and 430 (w) cm^{-1}. Raman spectrum ($\Delta\nu$, relative intensity): 1517 (100), 1421 (13), 471 (62) cm^{-1} [4579 Å excitation]; 1565 (17), 1551 (15), 1519 (100), 1281 (9), 1122 (4), 1110 (8), 796 (6), 468 (36), 200 (15) cm^{-1} [5145 Å excitation]. Electronic spectrum (Nujol mull): λ_{max} at 275, 350 nm. The conductivity, measured by the microwave cavity perturbation technique on a compressed disk, was 1×10^{-4} (Ω cm)$^{-1}$.

An orange monoclinic prism with approximate dimensions 0.4 × 0.3 × 0.2 mm was selected for an X-ray diffraction investigation. Unit cell data, based on a least-squares fit to the setting angles for 25 reflections measured on an Enraf–Nonius CAD-4 automated diffractometer operating at room temperature and employing graphite monochromatized Cu Kα radiation, are as follows: a = 11.142 (3) Å, b = 11.642 (3) Å, c = 7.920 (3) Å, β = 99.97 (2)°, V = 1011.9 Å^3, Z = 2 (for $C_{16}H_{18}O_4PdS_4$), D_{calcd} = 1.670 g cm^{-3}, D_{measd} = 1.671 (2) g cm^{-3}, μ(Cu Kα, λ = 1.5418 Å) = 114.8 cm^{-1}. The observed systematic absences [$h0l$, $l = 2n + 1$; $0k0$, $k = 2n + 1$] are consistent with the monoclinic space group $P2_1/c$. The presence of two formula units per cell in this space group requires $\bar{1}(C_i)$ molecular symmetry for both the TTF and Pd(acac)$_2$ molecules.

Intensity data[27] were collected on the diffractometer operating in the bisecting geometry mode and employing the θ–2θ scan technique. A set of 2295 unique reflections were surveyed, of which 2101 were considered to be observed and subsequently utilized in the structure solution and refinement. The raw intensity data were corrected for the usual geometrical factors, including absorption by the method of ψ scans.[28,29]

A trial model was obtained by standard methods, with the Pd atom placed at the origin of the unit cell and the center of mass of the TTF molecule coincident with the symmetry point ($^1/_2$, $^1/_2$, 0). At an intermediate stage in the analysis, a difference Fourier synthesis allowed the positioning of the hydrogen atoms. Full-matrix, least-squares refinement [including positional and anisotropic thermal parameters for the nonhydrogen atoms, positional and isotropic thermal parameters for hydrogen atoms, a secondary extinction parameter ($g = 5.27 \times 10^{-6}$), and an overall scale factor] led to convergence. On the basis of the final derived parameters, the normal discrepancy values are $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.056$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum|F_o|^2]^{1/2} = 0.089$. The goodness-of-fit value, $[(\sum w(|F_o| - |F_c|)^2/(\mathrm{NO} - \mathrm{NV})]^{1/2}$, where NO = 2101 independent observations and NV = 152 parameters, was 2.3. The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = 4F_o^2/\sigma^2(F_o^2)$ and $\sigma^2(F_o^2)$ was derived from counting statistics plus a correction term proportional to I^2. Final parameters for nonhydrogen atoms are collected in Table I; the parameters for the hydrogen atoms have been deposited as supplementary material.

Most of the crystallographic calculations were performed on a PDP 1134 computer employing the Molecular Structure Corporation's Enraf-Nonius structure determination package of programs.[30] The structure illustrations were obtained with the aid of the ORTEP program.[31]

(TTF)Pt(acac)$_2$ was prepared, after the structure of the palladium analogue had been solved, by the cocrystallization of TTF and platinum(II) acetylacetonate. Anal. Calcd for $C_{16}H_{18}O_4PtS_4$: C, 32.16; H, 3.02; Pt, 32.66; S, 21.44. Found: C, 32.10; H, 2.98; Pt, 33.27; S, 21.24. Preliminary powder and single-crystal photographs of the golden yellow platelets indicated that the compound is isomorphous with (TTF)Pd(acac)$_2$. Unit-cell data, determined from the angular settings for 15 high-angle reflections measured on a Syntex P$\bar{1}$ automated diffractometer [λ(Mo Kα) = 0.71069 Å] are a = 11.152 (2) Å, b = 11.644 (4) Å, c = 7.904 (2) Å, β = 99.98 (2)°, V = 1010.8 Å^3, Z = 2 (for $C_{16}H_{18}O_4PtS_4$, space group $P2_1/c$). We are greatly indebted to Mr. T. J. Emge of Johns Hopkins for these data.

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Registry No. (TTF)Pd(acac)$_2$, 73296-18-1; (TTF)Pt(acac)$_2$, 73296-20-5; Pd(acac)$_2$, 14024-61-4; Pt(acac)$_2$, 15170-57-7; TTF, 31366-25-3.

Supplementary Material Available: Tables of hydrogen atom parameters and observed and calculated structure factor amplitudes (19 pages). Ordering information is given on any current masthead page.

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