Tetrathiafulvalenium Salts of Planar Pt^{II}, Pd^{II}, and Cu^{III} 1,2-Dithio-oxalato-*S,S'* Anions. Synthesis, Chemistry and Molecular Structures of Bis(tetrathiafulvalenium) Bis(1,2-dithio-oxalato-*S,S'*)palladate(II), $[ttf]_2[Pd(S_2C_2O_2)_2]$, and of Bis(tetrathiafulvalenium)tetrathiafulvalene Bis(1,2-dithio-oxalato-*S,S'*)platinate(II), $[ttf]_3[Pt(S_2C_2O_2)_2]$†

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Tetrathiafulvalenium (ttf) salts with inorganic dithio-oxalato anions, $[ttf]_2[Pd(S_2C_2O_2)_2]$ (**1**), $[ttf]_2[Pt(S_2C_2O_2)_2]$ (**2**), and $[ttf]_{1.0}[Cu(S_2C_2O_2)_2]$ (**3**) were prepared by reaction of $[ttf]_3[BF_4]_2$ and the corresponding $[A]_2[M(S_2C_2O_2)_2]$ (where A = NEt_4 or $AsPh_4$; M = Pd^{II}, Pt^{II}, or Cu^{II}) in acetonitrile, or by electrocrystallization of neutral ttf in acetonitrile containing $[NEt_4]_2[Pt(S_2C_2O_2)_2]$ in the case of $[ttf]_3[Pt(S_2C_2O_2)_2]$ (**4**). The crystal and molecular structures of compounds (**1**) and (**4**) were determined by single-crystal *X*-ray diffraction. Compound (**1**) crystallizes in the monoclinic space group $P2_1/c$ with unit-cell dimensions a = 9.447(2), b = 11.044(4), c = 12.299(2) Å, β = 113.52(2)°, and Z = 2. The ttf molecules exist as dimeric $(ttf^{\bullet +})_2$ and form mixed stacks with the anions along the b axis of the unit cell. Compound (**4**) crystallizes in the monoclinic space group $P2_1/c$ with unit-cell dimensions a = 9.754(2), b = 13.905(3), c = 13.733(3) Å, β = 119.21(1)°, and Z = 2. Two crystallographically independent ttf units are present: the first comprises dimerized $(ttf^{\bullet +})_2$, and the second is neutral (ttf^0) and perpendicular to the dimer. The compound is better formulated as $[(ttf^{\bullet +})_2(ttf^0)][Pt(S_2C_2O_2)_2]$. Electron spin resonance, infrared and *X*-ray photoelectron spectroscopic studies of the palladium and platinum derivatives indicate that, in each compound, the metal ion is in the oxidation state +2 and that ttf is present as $(ttf^{\bullet +})_2$ and ttf^0 as found in the crystal structure. The copper compound contains the metal ion in the uncommon oxidation state +3. Infrared, photoelectron, and electronic spectra suggest that the molecular structure of this compound consists of $(ttf^{\bullet +})_2$ dimers and planar diamagnetic $[Cu(S_2C_2O_2)_2]^-$.

In the past decade several electrically conductive molecular transition metal complexes have been synthesized and characterized.[1] and very recently the first transition metal complex which undergoes a transition to a superconducting state under pressure has been found.[2]

The known compounds of interest are inorganic complexes such as $K_2[Pt(CN)_4]Br_{0.3}\cdot 3H_2O$,[3] or donor–acceptor molecules, where the donor or the acceptor can be an organic molecule. In the latter compounds the electrical properties are a function of the nature of the constituent species.[1]

In this context, we decided to study the reaction between the prototypical organic donor molecule tetrathiafulvalene (ttf) [2-(1',3'-dithiol-2'-ylidene)-1,3-dithiole] and several square-planar inorganic metal(II) 1,2-dithio-oxalato-*S,S'* anions.[4] In the dithio-oxalato dianion the presence of four donor atoms and the possibility of charge delocalization on any two of these atoms results in a versatile ligand with peculiar co-ordination properties.[4,5]

This paper describes the synthesis, the chemical characterization and some spectroscopic studies of tetrathiafulvalenium salts of 1,2-dithio-oxalate-*S,S'* metalate anions, $[M(S_2C_2O_2)_2]^{n-}$, where M is Pt^{II}, Pd^{II}, or Cu^{III} and n = 2 or 1, and the crystal and molecular structures of $[ttf]_2[Pd(S_2C_2O_2)_2]$ and of $[ttf]_3[Pt(S_2C_2O_2)_2]$.

Experimental

Elemental analyses were performed by Malissa and Reuter Mikroanalytische Laboratorium, Elbach, West Germany, and by Laboratorio di Microanalisi dell'Area di Ricerca di Roma del C.N.R., Monterotondo (Roma), Italy.

Starting Materials.—The dithio-oxalate ligand was used as purchased from Eastman Kodak. The complexes $[NEt_4]_2[M(S_2C_2O_2)_2]$ (M = Pd or Pt) and $[AsPh_4]_2[Cu(S_2C_2O_2)_2]$ were prepared following the procedures described by Coucouvanis and co-workers[6] and the purity checked by elemental analysis. Tetrathiafulvalene was used as supplied from Fluka AG. The salt $[ttf]_3[BF_4]_2$ was prepared as described by Wudl.[7] All solvents were reagent grade, freshly distilled and deaerated prior to use.

Synthesis of $[ttf]_2[M(S_2C_2O_2)_2]$ *Complexes* (M = Pd *or* Pt).—Metathesis reaction under inert atmosphere of acetonitrile solutions of $[ttf]_3[BF_4]_2$ and $[NEt_4]_2[M(S_2C_2O_2)_2]$ in 1:1 molar ratio immediately give an insoluble, black, shiny microcrystalline powder (Found: C, 22.85; H, 0.90; O, 7.40; Pt, 22.05; S, 46.65. Calc. for $C_{16}H_8O_4PtS_{12}$: C, 22.75; H, 0.95; O, 7.60; Pt, 23.10; S, 45.60%. Found: C, 23.45; H, 1.15. Calc. for

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† A preliminary communication of this work has been presented to the N.A.T.O. Workshop: 'Organic and Inorganic Low-Dimensional Crystalline Materials,' held in Minorca (Spain), May 1987; see C. Bellitto, M. Bonamico, V. Fares, P. Imperatori, and S. Patrizio, in N.A.T.O. ASI Series, Plenum, New York, 1987, vol. B168, p. 337.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

Non-S.I. unit employed: eV $\approx 1.60 \times 10^{-19}$ J.

$C_{16}H_8O_4PdS_{12}$: C, 25.45; H, 1.05%). The analysis was confirmed by the crystal structure determination (see below).

Crystal Growth of $[ttf]_2[M(S_2C_2O_2)_2]$ *Complexes* (M = Pd *or* Pt).—The compounds are insoluble in common solvents. Single crystals suitable for *X*-ray investigations were obtained by slow interdiffusion of saturated solutions of $[ttf]_3[BF_4]_2$ and $[NEt_4]_2[M(S_2C_2O_2)_2]$. These experiments were carried out under purified N_2 gas in a three-compartment H-tube with a porous glass frit between the compartments.

In the case of the platinum derivative two compounds were isolated. The first one, of formula $[ttf]_2[Pt(S_2C_2O_2)_2]$, is prepared in higher yield and the synthesis has been described above. The second one, of formula $[ttf]_3[Pt(S_2C_2O_2)_2]$, was isolated as dark green platelets when the reaction was carried out by very low interdiffusion. The same salt was also obtained by electrolysis at constant current (4 μA) of an acetonitrile–1,1,2-trichloroethane (1:1) solution (30 cm^3) of ttf (0.027 g, 1.32×10^{-4} mol) and $[NEt_4]_2[Pt(S_2C_2O_2)_2]$ (0.046 g, 6.6×10^{-5} mol) for two weeks. The two compounds could be separated from the mixture by sedimentation on the basis of the different density of each compound. Both compounds were characterized by *X*-ray analysis.

Synthesis of $[ttf]_{1.0}[Cu(S_2C_2O_2)_2]$.—An acetonitrile solution (40 cm^3) of $[ttf]_3[BF_4]_2$ (0.100 g, 1.27×10^{-4} mol) was allowed to diffuse into a solution, in the same solvent (20 cm^3), of freshly prepared $[AsPh_4]_2[Cu(S_2C_2O_2)_2]$ (0.300 g, 2.8×10^{-4} mol) under an inert atmosphere and in the dark. Dark green, needle-like crystals were collected at the porous frit of the H-tube, after one night of diffusion (Found: C, 23.70; H, 0.95; Cu, 12.25; O, 12.55; S, 50.25. Calc. for $C_{10}H_4CuO_4S_8$: C, 23.65; H, 0.80; Cu, 12.50; O, 12.60; S, 50.50%). In our preliminary communication (see footnote on title page) the compound was incorrectly formulated as $[ttf]_{1.5}[Cu(S_2C_2O_2)_2]$.

Physical Measurements.—Infrared spectra were recorded on a Perkin-Elmer 621 spectrophotometer both on KBr and as Nujol mulls. A Beckmann DK 2A instrument was used to record diffuse-reflectance spectra on diluted samples with MgO. *X*-Band e.s.r. spectra were obtained at room temperature and at 110 K with a Varian E9 spectrometer, equipped with a standard variable-temperature accessory.

X-Ray photoelectron spectra were recorded on a VG ESCA 3M K II instrument, using Al-K_α (1 486.6 eV) radiation, of the Servizio ESCA, Area della Ricerca di Roma del C.N.R. Samples were mounted on a gold sample holder, whose Au $4f_{\frac{7}{2}}$ signal at 83.70 eV was used to check the instrumental scale. The data were corrected for charging effects by assigning the carbon 1*s* electrons a binding energy at 285.0 eV. In the case of $K_2[Pd(S_2C_2O_2)_2]$ and $K_2[Cu(S_2C_2O_2)_2]$ the K $2p_{\frac{3}{2}}$ binding energy was taken as a reference (292.9 eV). All measurements were made at ambient spectrometer temperature (*ca.* 35 °C). In the case of $[ttf]_{1.0}[Cu(S_2C_2O_2)_2]$ significant outgassing of the sample was observed and therefore several spectra were recorded as a function of time. Peak deconvolution was performed with a DuPont 310 curve resolver, using a Gaussian shape fit.

Electrical conductivities were determined on compressed pellets using the four-probe method of van der Pauw,[8] over the temperature range 100—300 K.

Crystal Structure Determinations.—*Crystal data for* $[ttf]_2[Pd(S_2C_2O_2)_2]$. $C_{16}H_8O_4PdS_{12}$, *M* = 755.41, monoclinic, space group $P2_1/c$, $a = 9.447(2)$, $b = 11.044(4)$, $c = 12.299(2)$ Å, $\beta = 113.52(2)°$, $U = 1\,176.6(6)$ Å^3, $Z = 2$, $D_c = 2.133$ g cm^{-3}, $D_m = 2.13$ g cm^{-3}, $F(000) = 748$, $\lambda(\text{Mo-}K_\alpha) = 0.710\,69$ Å, $\mu(\text{Mo-}K_\alpha) = 18.2$ cm^{-1}.

A prismatic crystal (dimensions $0.1 \times 1.0 \times 0.1$ mm) was used for the data collection on a Nicolet automated four-circle diffractometer at room temperature, by the θ–2θ scan technique with graphite-monochromated Mo-K_α radiation. A total of 5 872 independent reflections were collected, of which 3 844 with $I > 3\sigma(I)$ were used in the refinement. They were corrected for Lorentz-polarization factors; a semiempirical absorption correction, based on a 360° scan around the scattering vector of three selected reflections, was applied (ratio between maximum and minimum values 1.13). The structure was solved by Patterson and Fourier methods. Positional and anisotropic thermal parameters for non-hydrogen atoms were refined by full-matrix least squares minimizing $\Sigma w(|F_o| - |F_c|)^2$, $w = 1/\sigma(F_o)^2$. Hydrogen atoms were introduced in calculated positions with fixed isotropic thermal parameters equal to the B_{eq} of the carbon atoms to which they are linked. Refinement converted to $R = 0.030$ ($R' = 0.036$). Neutral scattering factors (f' and f'' values) were used.[9] Computations were performed on an IBM 4361/4 computer by using the SIR-CAOS crystallographic program system.[10] Atomic co-ordinates are listed in Table 1.

Crystal data for $[ttf]_2[Pt(S_2C_2O_2)_2]$. $C_{16}H_8O_4PtS_{12}$, *M* = 844.10, monoclinic, space group $P2_1/c$, $a = 9.446(2)$, $b = 11.036(3)$, $c = 12.293(2)$ Å, $\beta = 113.48(2)°$, $U = 1\,175.4(5)$ Å^3, $Z = 2$, $D_c = 2.386$ g cm^{-3}, $D_m = 2.37$ g cm^{-3}.

Crystal data for $[ttf]_3[Pt(S_2C_2O_2)_2]$. $C_{22}H_{12}O_4PtS_{16}$, *M* = 1 048.453, monoclinic, space group $P2_1/c$, $a = 9.754(2)$, $b = 13.905(3)$, $c = 13.733(3)$ Å, $\beta = 119.21(1)°$, $U = 1\,625.8(5)$ Å^3, $Z = 2$, $D_c = 2.142$ g cm^{-3}, $D_m = 2.14$ g cm^{-3}, $F(000) = 1\,020$, $\lambda(\text{Mo-}K_\alpha) = 0.710\,69$ Å, $\mu(\text{Mo-}K_\alpha) = 55.6$ cm^{-1}.

A prismatic crystal (dimensions $0.2 \times 0.3 \times 0.4$ mm) was used for the data collection. A total of 7 026 independent reflections were collected, of which 3 926 with $I > 3\sigma(I)$ were used in the refinement. A semiempirical absorption correction, based on a 360° scan around the scattering vector of three selected reflections, was applied (ratio between maximum and minimum values 1.08). Refinement converged to $R = 0.033$ ($R' = 0.035$). Details of the procedure are as given above for $[ttf]_2[Pd(S_2C_2O_2)_2]$. Atomic co-ordinates are listed in Table 2.

Results and Discussion

Complex Formation.—The compounds described in this paper were all synthesized by a direct mixing of an acetonitrile solution of Wudl's salt, $[ttf]_3[BF_4]_2$, and of a solution of the corresponding $R_2[M(S_2C_2O_2)_2]$ salts (M = Pd, Pt, or Cu; R = NEt_4 or $AsPh_4$), in the same solvent. In the case of the Pt derivatives, the direct mixing of the $[ttf]_3[BF_4]_2$ and $[NEt_4]_2[Pt(S_2C_2O_2)_2]$ gives two different species, $[ttf]_2[Pt(S_2C_2O_2)_2]$ and $[ttf]_3[Pt(S_2C_2O_2)_2]$, respectively. In the case of Pd and Cu only one type of compound could be isolated, *i.e.* $[ttf]_2[Pd(S_2C_2O_2)_2]$ and $[ttf]_{1.0}[Cu(S_2C_2O_2)_2]$. As described in the Experimental section, single crystals suitable for *X*-ray studies were obtained by slow interdiffusion of the solutions of the donors and of the acceptor molecules. The compounds are insoluble in common solvents. The copper derivative decomposes on exposure to light and to *X*-rays, preventing the resolution of the crystal structure and obtaining reliable Raman spectra. It is stable if stored dried and under nitrogen gas, in the dark.

The isolation of $[ttf]_{1.0}[Cu(S_2C_2O_2)_2]$ can be accounted for by the formation in solution of the $[Cu(S_2C_2O_2)_2]^-$ monoanion in equation (1) with the corresponding reduction of the

$$[Cu^{II}(S_2C_2O_2)_2]^{2-} \rightleftharpoons [Cu^{III}(S_2C_2O_2)_2]^- + e^- \quad (1)$$

$ttf^{\bullet+}$ radical cation present in solution. The compound decomposes in the presence of a solution of $[ttf]_3[BF_4]_2$,

Table 1. Atomic co-ordinates, with e.s.d.s in parentheses, for $[ttf]_2[Pd(S_2C_2O_2)_2]$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pd	0	0	0	C(3)	0.341 1(3)	0.406 5(2)	−0.021 9(2)
S(1)	0.230 7(1)	0.030 5(1)	0.160 8(1)	C(4)	0.385 0(3)	0.405 1(2)	0.095 8(2)
S(2)	0.124 8(1)	0.042 1(1)	−0.122 7(1)	C(5)	−0.288 3(3)	0.258 3(2)	0.027 5(2)
S(3)	0.147 6(1)	0.385 9(1)	−0.108 4(1)	C(6)	−0.334 8(3)	0.268 5(2)	−0.090 7(2)
S(4)	0.243 3(1)	0.382 5(1)	0.148 8(1)	C(7)	0.097 6(2)	0.365 0(2)	0.010 7(2)
S(5)	−0.101 3(1)	0.298 9(1)	0.112 8(1)	C(8)	−0.052 5(2)	0.331 1(2)	−0.004 6(2)
S(6)	−0.200 7(1)	0.319 6(1)	−0.142 0(1)	H(3)	0.417 6(3)	0.081 0(2)	0.441 7(2)
O(1)	0.488 9(2)	0.120 2(2)	0.166 3(2)	H(4)	0.495 5(3)	0.083 4(2)	0.650 8(2)
O(2)	0.401 3(2)	0.125 7(2)	−0.070 7(2)	H(5)	−0.359 4(3)	0.271 5(2)	0.563 9(2)
C(1)	0.360 4(3)	0.083 6(2)	0.104 2(2)	H(6)	−0.442 4(3)	0.252 6(2)	0.353 8(2)
C(2)	0.309 5(3)	0.088 0(2)	−0.032 7(2)				

Table 2. Atomic co-ordinates, with e.s.d.s in parentheses, for $[ttf]_3[Pt(S_2C_2O_2)_2]$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pt	0	0	0	C(4)	0.006 6(7)	0.370 6(5)	−0.213 9(5)
S(1)	0.211 0(2)	0.103 5(1)	0.074 0(1)	C(5)	0.009 7(7)	0.383 4(5)	0.253 8(5)
S(2)	0.168 2(2)	−0.126 2(1)	0.030 0(1)	C(6)	0.162 7(7)	0.381 5(5)	0.285 2(4)
S(3)	−0.201 7(2)	0.383 0(1)	−0.146 8(1)	C(7)	−0.013 1(6)	0.375 1(4)	−0.036 7(4)
S(4)	0.132 4(2)	0.369 1(1)	−0.072 6(1)	C(8)	0.023 3(6)	0.375 3(4)	0.074 7(4)
S(5)	−0.119 4(2)	0.381 1(1)	0.114 2(1)	C(9)	0.506 3(7)	0.271 8(4)	0.042 5(5)
S(6)	0.213 0(2)	0.375 3(1)	0.182 5(1)	C(10)	0.544 3(7)	0.306 9(4)	0.141 5(5)
S(7)	0.478 0(2)	0.351 8(1)	−0.063 2(1)	C(11)	0.508 4(6)	0.454 8(4)	0.019 5(4)
S(8)	0.567 0(2)	0.431 1(1)	0.159 4(1)	H(3)	−0.222 7(7)	0.377 0(5)	−0.325 5(4)
O(1)	0.506 0(5)	0.066 4(4)	0.140 9(4)	H(4)	0.044 9(7)	0.367 6(5)	−0.266 3(5)
O(2)	0.471 7(5)	−0.125 7(4)	0.116 9(4)	H(5)	−0.026 1(7)	0.385 8(5)	0.307 7(5)
C(1)	0.373 4(6)	0.033 1(5)	0.104 3(4)	H(6)	0.241 3(7)	0.383 7(5)	0.362 5(4)
C(2)	0.353 4(7)	−0.076 7(5)	0.087 5(4)	H(9)	0.494 1(7)	0.203 8(4)	0.028 8(5)
C(3)	−0.146 3(7)	0.376 5(5)	−0.247 6(4)	H(10)	0.559 5(7)	0.265 4(4)	0.201 8(5)

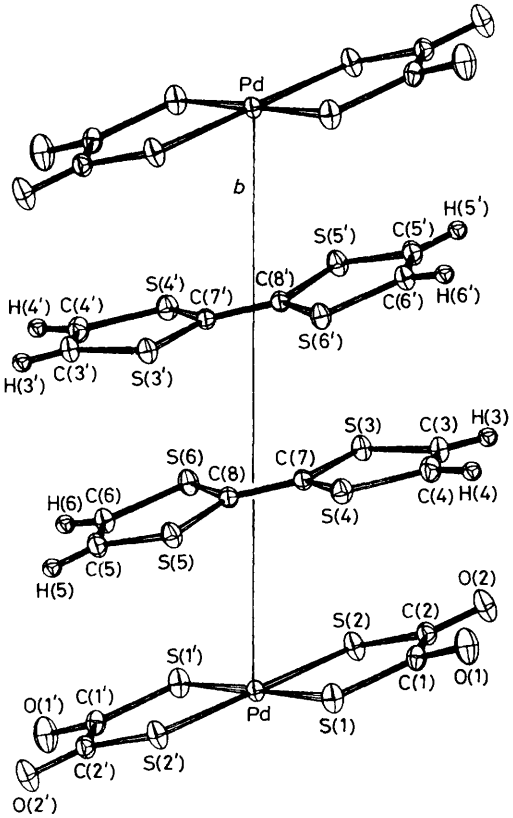
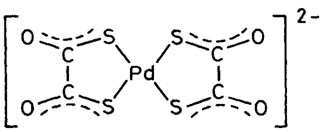


Figure 1. View of the $[ttf]_2[Pd(S_2C_2O_2)_2]$ structure showing the mixed stack of anions and $(ttf^{•+})_2$ dimeric units along the *b* axis. Thermal ellipsoids for non-hydrogen atoms are at 30% probability level

probably due to reduction to Cu^I and cleavage of the C–C bond of the dithio-oxalate ligand.[6]

Crystal Structure of $[ttf]_2[Pd(S_2C_2O_2)_2]$.—The crystal structure consists of mixed stacks of donor $(ttf^{•+})_2$ dimers (D–D) and $[Pd(S_2C_2O_2)_2]^{2-}$ acceptors (A) developing along the *b* axis, according to the scheme ···A···D–D···A···D–D··· (see Figure 1). The A and D molecular best planes are at a distance of 3.60 Å and are almost parallel to each other, with a dihedral angle of *ca.* 4°, while their normals are tilted by 18° with respect to the *b* axis. The Pd atom occupies an inversion centre so that the PdS_4 chromophore is planar. The anion unit is not completely planar, the sulphur atoms S(1) and S(2) moving away from the best plane by 0.122 and 0.098 Å respectively. An overall 'chair' conformation is present with a dihedral angle between the PdS_4 central plane and the ligand $S_2C_2O_2$ planes of *ca.* 8°. The interatomic distances and angles are reported in Table 3 and are consistent with a partially delocalized structure (I), with a single C–C bond of 1.556(4) Å.



(I)

The Pd–S bond lengths of 2.302(1)—2.310(1) Å are slightly shorter than those of 2.334(1) Å found in dithio-oxalatobis(trimethylphosphine)palladium(II),[11] in agreement with a lower degree of strain within the five-membered ring,[12] the S–Pd–S and Pd–S–C angles being 88.7 and 106.6° *vs.* 87.9 and 105.4° respectively. Bond distances and angles within the

Table 3. Bond lengths (Å) and angles (°), with e.s.d.s in parentheses, for $[ttf]_2[Pd(S_2C_2O_2)_2]$

Pd–S(1)	2.310(1)	C(1)–O(1)	1.216(4)	S(4)–C(4)	1.725(2)	S(6)–C(8)	1.716(3)
Pd–S(2)	2.302(1)	C(2)–O(2)	1.212(3)	S(4)–C(7)	1.717(3)	C(3)–C(4)	1.337(5)
S(1)–C(1)	1.735(2)			S(5)–C(5)	1.716(3)	C(5)–C(6)	1.344(4)
S(2)–C(2)	1.728(3)	S(3)–C(3)	1.724(3)	S(5)–C(8)	1.718(2)	C(7)–C(8)	1.405(3)
C(1)–C(2)	1.556(4)	S(3)–C(7)	1.725(2)	S(6)–C(6)	1.720(2)		
S(1)–Pd–S(2)	88.66(2)	S(2)–C(2)–O(2)	123.3(2)	C(5)–S(5)–C(8)	95.5(1)	S(3)–C(7)–C(8)	121.7(2)
Pd–S(1)–C(1)	106.4(1)	S(2)–C(2)–C(1)	118.8(2)	C(6)–S(6)–C(8)	95.4(1)	S(4)–C(7)–C(8)	122.1(2)
Pd–S(2)–C(2)	106.8(1)	O(2)–C(2)–C(1)	117.9(3)	S(3)–C(3)–C(4)	117.5(2)	S(5)–C(8)–S(6)	115.2(1)
S(1)–C(1)–O(1)	123.2(2)			S(4)–C(4)–C(3)	117.3(2)	S(5)–C(8)–C(7)	122.5(2)
S(1)–C(1)–C(2)	118.8(2)	C(3)–S(3)–C(7)	94.3(1)	S(5)–C(5)–C(6)	116.8(2)	S(6)–C(8)–C(7)	122.4(2)
O(1)–C(1)–C(2)	118.0(2)	C(4)–S(4)–C(7)	94.6(1)	S(6)–C(6)–C(5)	117.0(2)		

dithio-oxalate group are comparable with those reported in the literature.[13]

As far as the $ttf^{\bullet +}$ unit is concerned, the bond lengths are in excellent agreement with those reported by Mahadevan[14] in bis(tetrathiofulvalenium) bis(maleonitrile-1,2-dithiolato)-nickelate(II).

The parameter most sensitive to the degree of charge transfer, the central C=C bond length,[15] is 1.405 Å, a value similar to that found in $[ttf][SnMe_2Cl_3]$[16] and in $[ttf][ClO_4]$[17] where a fully oxidized tetrathiafulvalene molecule is present. The $ttf^{\bullet +}$ ion shows a boat conformation, with a dihedral angle of *ca.* 9°, whereas in the neutral[18] and mixed-valence ttf compounds[19a,b] a chair conformation has been observed. The $ttf^{\bullet +}$ units are coupled in dimers and are nearly superimposed, with a lateral offset of 0.50 Å. The interplanar spacing between the members of the dimer of 3.48 Å suggests a significant bonding interaction as found in other $(ttf^{\bullet +})_2$ dimerized salts.[17] A short $S(4)\cdots S(6')$ intradimeric contact of 3.31 Å is present in the structure, owing to the particular distortion and cofacial arrangement of the two $ttf^{\bullet +}$ units within the dimer.

Crystal Structure of $[ttf]_3[Pt(S_2C_2O_2)_2]$.—The structure consists of $[Pt(S_2C_2O_2)_2]^{2-}$ anions, with the Pt atom lying on a centre of inversion (taken as origin), and two structurally distinct types of ttf molecules (A and B; see Figure 2). These three different molecules are almost mutually perpendicular, the angles between the anion and the two ttf types being *ca.* 82°, whereas that between the two ttf types is 90.4°. Two ttf of type A, related by a centre of inversion, form dimer units in an almost eclipsed configuration, with an offset of *ca.* 0.5 Å parallel to the long axis of the molecule. The ttf of type B is centrosymmetrical, being the centre of inversion in the middle of the C(11)–C(11′) bond at $\frac{1}{2},\frac{1}{2},0$. The PtS_4 chromophore is strictly planar, while the whole anion is almost planar with a root-mean-square (r.m.s.) deviation of 0.030(5) Å. Bond distances and angles are reported in Table 4. As far as the anion is concerned, they are as expected.[5,13] As shown in Table 5, distances in type A ttf molecules are, within the e.s.d.s, equal to the corresponding distances found in $[ttf]_2[Pd(S_2C_2O_2)_2]$, in which the ttf is present as $ttf^{\bullet +}$. As in the mentioned Pd compound, the $ttf^{\bullet +}$ radical cations form a dimer with a significant bonding interaction. The intradimeric distance is 3.50 Å and the shortest contact, between S(3) and S(6′), is 3.41 Å. The $ttf^{\bullet +}$ molecule is almost planar, the r.m.s. deviation being 0.030(5) Å. The type B ttf molecule shows interatomic distances typical of a neutral molecule, in agreement with the corresponding values found in the crystals of ttf by Cooper *et al.*;[18] the molecule is slightly distorted, having the two centrosymmetric halves of the fulvalene in an overall chair conformation; the central part of the molecule, defined by S(7), S(8), and C(11) and their symmetry-related atoms is planar and makes a dihedral angle of 6.7° with the planar exterior portion of the molecule S(7), S(8), C(9), and C(10). A similar, but smaller, distortion has been observed in other structures containing neutral ttf molecules.[20] This distortion may be related to the complex system of interactions present in the crystal packing (see Figure 3). In fact, the neutral ttf molecules are separated by only 3.33—3.38 Å from the $(ttf^{\bullet +})_2$ pairs, thus bridging these dimers together along the [100] direction. A similar arrangement, but with longer contacts (3.51 Å), was found by Interrante[21] in $(ttf)_2NiS_4C_4H_4$. In the latter case, the electrical conductivity along the bridge direction suggested ttf σ–π orbital interactions. Moreover, between the carbon atoms C(9) of the neutral ttf and the oxygen atoms of the anions there are short distances of 3.08 and 3.17 Å. The directions of these contacts are compatible with the theoretical position of the H atom linked to C(9) and are toward the oxygen lone-pair orbitals: this situation strongly suggests the existence of $CH\cdots O$ hydrogen bonds.[22] Finally, the oxygens of the anions are also involved in contacts of 2.98 and 3.08 Å with the cation atoms S(3) and S(6); the nature of such short distances is probably electrostatic in origin.

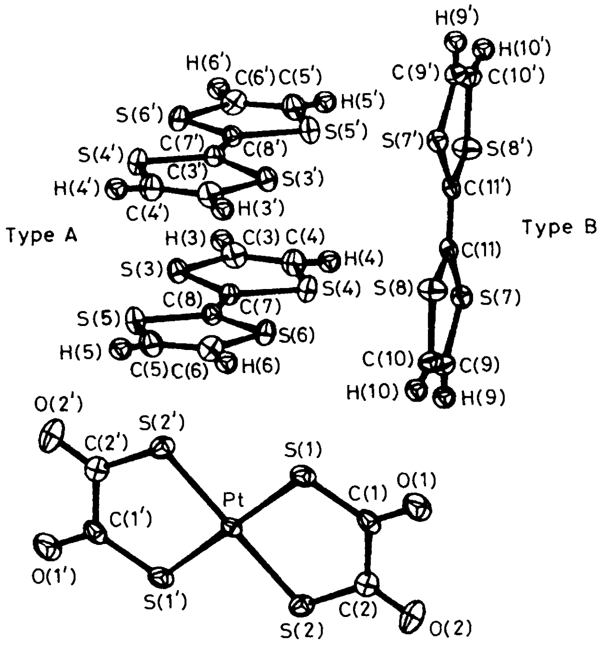


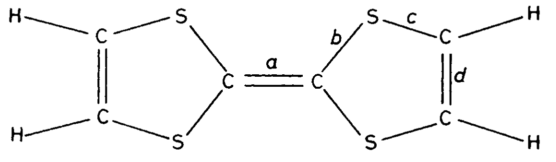
Figure 2. Perspective drawing of the $[ttf]_3[Pt(S_2C_2O_2)_2]$ structure with thermal ellipsoids (30% probability level) for non-hydrogen atoms, showing the anions, the $(ttf^{\bullet +})_2$ (type A) dimeric unit, and the ttf^0 molecule (type B)

Table 4. Bond lengths (Å) and angles (°), with e.s.d.s in parentheses, for $[ttf]_3[Pt(S_2C_2O_2)_2]$

Pt–S(1)	2.313(2)	S(3)–C(3)	1.717(5)	S(6)–C(6)	1.707(5)	S(7)–C(9)	1.744(7)
Pt–S(2)	2.308(2)	S(3)–C(7)	1.730(8)	S(6)–C(8)	1.722(8)	S(7)–C(11)	1.766(5)
S(1)–C(1)	1.738(7)	S(4)–C(4)	1.721(9)	C(3)–C(4)	1.336(12)	S(8)–C(10)	1.753(6)
S(2)–C(2)	1.731(8)	S(4)–C(7)	1.719(5)	C(5)–C(6)	1.342(11)	S(8)–C(11)	1.749(6)
C(1)–C(2)	1.550(9)	S(5)–C(5)	1.709(10)	C(7)–C(8)	1.393(8)	C(9)–C(10)	1.317(10)
O(1)–C(1)	1.233(10)	S(5)–C(8)	1.726(5)			C(11)–C(11^{I})	1.351(7)
O(2)–C(2)	1.231(9)						
S(1)–Pt–S(2)	89.57(6)	S(2)–C(2)–C(1)	119.4(5)	S(4)–C(4)–C(3)	117.3(5)	C(9)–S(7)–C(11)	94.5(3)
Pt–S(1)–C(1)	105.6(2)	O(2)–C(2)–C(1)	118.1(7)	S(5)–C(5)–C(6)	117.4(5)	C(10)–S(8)–C(11)	94.7(3)
Pt–S(2)–C(2)	105.9(2)			S(6)–C(6)–C(5)	117.4(6)	S(7)–C(9)–C(10)	118.1(5)
S(1)–C(1)–O(1)	122.9(5)	C(3)–S(3)–C(7)	94.6(3)	S(3)–C(7)–C(8)	123.7(4)	S(8)–C(10)–C(9)	117.9(5)
S(1)–C(1)–C(2)	119.4(5)	C(4)–S(4)–C(7)	94.9(3)	S(4)–C(7)–C(8)	120.7(5)	S(7)–C(11)–S(8)	114.5(3)
O(1)–C(1)–C(2)	117.8(6)	C(5)–S(5)–C(8)	94.8(3)	S(5)–C(8)–S(6)	115.4(3)	S(7)–C(11)–C(11^{I})	123.9(4)
S(2)–C(2)–O(2)	122.4(5)	C(6)–S(6)–C(8)	95.0(3)	S(5)–C(8)–C(7)	122.1(5)	S(8)–C(11)–C(11^{I})	121.6(4)
		S(3)–C(3)–C(4)	117.5(6)	S(6)–C(8)–C(7)	122.5(4)		

Superscript I: $1 - x, 1 - y, -z$.

Table 5. Comparison between averaged bond distances (Å) of the two ttf types in $[ttf]_3[Pt(S_2C_2O_2)_2]$ and the ttf of $[ttf]_2[Pd(S_2C_2O_2)_2]$



Parameter	ttf (type A)	ttf (type B)	ttf$^{\cdot +}$ in $[ttf]_2[Pd(S_2C_2O_2)_2]$
a	1.393(8)	1.351(7)	1.405(3)
b	1.724(7)	1.758(5)	1.719(3)
c	1.714(7)	1.748(6)	1.721(3)
d	1.339(11)	1.317(10)	1.340(5)
$\bar{B}$/Å^2 *	3.3	3.2	2.3

* Note the difference in the ttf averaged thermal motion between the Pt and the Pd compounds, responsible for the higher e.s.d.s in the Pt derivative.

X-Ray Photoelectron Spectra.—*X*-Ray photoelectron spectroscopy provides useful information on the electronic structure of transition metal complexes. It is well known that core binding energies generally increase with increasing positive oxidation state of the emitting atom. Further, it has been shown that shake-up satellites are present in the spectra of paramagnetic but not diamagnetic copper complexes.[23] So, in the present case the ESCA data gave the possibility of assessing the oxidation state of the metal ion in the compounds and the degree of fraction oxidation state, if any, of the donor molecule.

$[ttf]_2[Pt(S_2C_2O_2)_2]$ *and* $[ttf]_3[Pt(S_2C_2O_2)_2]$. Table 6 lists the binding energies of Pt $4f_{\frac{7}{2}}$ and $4f_{\frac{5}{2}}$ electrons of the two ttf platinum salts and of the related Pt^{II} complexes as obtained from *X*-ray photoelectron spectra. The most important feature is that the platinum atoms are all equivalent in each compound. The full-width at half-maximum (f.w.h.m. < 2 eV) is the same for all the compounds and this value is comparable to that found for $K_2[PtCl_4]$. No appreciable shift in the Pt 4*f* binding energies is observed and the absolute values are typical of Pt^{II} compounds.[24] The present results are therefore quite consistent with the structural data and indicate that the oxidation state of the Pt atoms, *i.e.* Pt^{II}, has not changed in these ttf salts. The S 2*p* spectra of both compounds have been recorded. In both cases, the observed spectrum shows a peak corresponding to S $2p_{\frac{3}{2}}$ and a shoulder to S $2p_{\frac{1}{2}}$. The overall f.w.h.m. is >2.0 eV, suggesting the presence of a different type of sulphur atom in agreement with the chemical composition of the compounds where one can expect contributions from the sulphur of the donor molecule and the anion molecule. In particular, the S 2*p* peak analysis, obtained by deconvolution, gives two binding energy values, *i.e.* 162.6 and 164.7 eV (see Table 6) in the case of $[ttf]_2[Pt(S_2C_2O_2)_2]$ and three values, *i.e.* 162.5, 163.8, and 164.8 eV, in the case of $[ttf]_3[Pt(S_2C_2O_2)_2]$. The first value (162.5 eV) can be assigned to the S 2*p* orbital of the anion {*cf.* $[NEt_4]_2[Pt(S_2C_2O_2)_2]$} and the value at 164.7 eV is attributable to S 2*p* of ttf$^{\cdot +}$. In the second compound there is

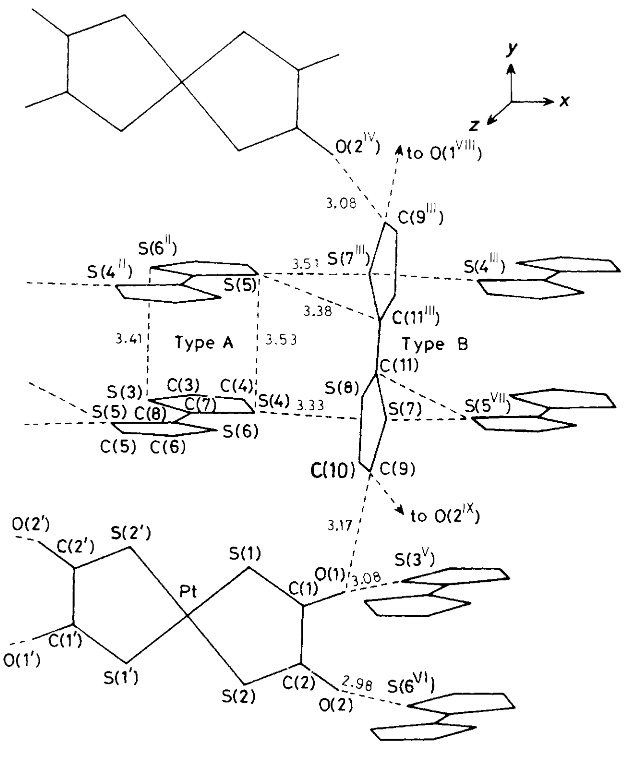


Figure 3. Main interactions and packing (partial view) in $[ttf]_3[Pt(S_2C_2O_2)_2]$. Superscript roman numerals refer to the following equivalent positions: I, $-x, -y, -z$; II, $-x, 1 - y, -z$; III, $1 - x, 1 - y, -z$; IV, $x, 1 + y, z$; V, $1 + x, \frac{1}{2} - y, \frac{1}{2} + z$; VI, $1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$; VII, $1 + x, y, z$; VIII, $1 - x, y, z$; IX, $1 - x, 1 + y, z$

Table 6. Electron binding energies of various $[ttf]_x[M(S_2C_2O_2)_2]$ compounds (M = Pd, Pt, or Cu)[a]

	Pt		S 2*p*			
Compound	$4f_{\frac{5}{2}}$	$4f_{\frac{7}{2}}$	Anion[b]	ttf^{0}[b]	ttf$^{\bullet+}$[b]	
$[NEt_4]_2[Pt(S_2C_2O_2)_2]$	75.55	72.20	162.8			
	(1.9)	(1.9)				
$[ttf]_2[Pt(S_2C_2O_2)_2]$	75.45	72.25	162.6		164.7	
	(1.8)	(1.8)	[*ca.* 35][c]		[*ca.* 65][c]	
$[ttf]_3[Pt(S_2C_2O_2)_2]$	75.40	72.10	162.5	163.8	164.8	
	(1.6)	(1.6)	[*ca.* 25][c]	[*ca.* 25][c]	[*ca.* 50][c]	
	Pd					
	$3d_{\frac{3}{2}}$	$3d_{\frac{5}{2}}$				K $2p_{\frac{3}{2}}$
$K_2[Pd(S_2C_2O_2)_2]$	342.65	337.4	162.4			292.9
	(1.6)	(1.6)				
$[ttf]_2[Pd(S_2C_2O_2)_2]$	342.2	337.4	161.8		164.0	
	(1.6)	(1.6)	[*ca.* 35][c]		[*ca.* 65][c]	
	Cu					
	$2p_{\frac{1}{2}}$	$2p_{\frac{3}{2}}$				
$[ttf][Cu(S_2C_2O_2)_2]$	955.8	935.6	162.1		164.0	

[a] Energies in eV; full-width at half-maximum (f.w.h.m.) are in parentheses. [b] Obtained by deconvolution of the experimental peak. [c] Percentage of the total intensity.

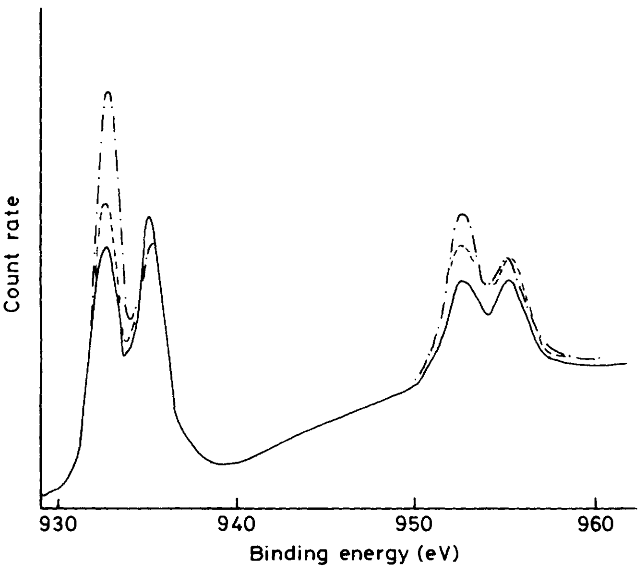


Figure 4. *X*-Ray photoelectron spectra of $[ttf]_{1.0}[Cu(S_2C_2O_2)_2]$ in the Cu $2p_{\frac{3}{2},\frac{1}{2}}$ region: (——) immediately after the introduction of the sample into the vacuum chamber, (- - -) after 30 min, (· · · -) after 1 h

another peak, the binding energy value of which is intermediate (*i.e.* 163.8 eV) and this can be reasonably assigned as due to the neutral molecule. In both cases the intensity ratios of the deconvoluted peaks are roughly in agreement with the stoicheiometric ratios of the anion and of the donor molecules in the compounds.

$[ttf]_2[Pd(S_2C_2O_2)_2]$. Similar observations can be made for the palladium derivative. In Table 6 are reported the Pd $3d_{\frac{5}{2},\frac{3}{2}}$ binding energies. No shift is observed in the Pd 3*d* core-electron binding energies going from $K_2[Pd(S_2C_2O_2)_2]$ to $[ttf]_2[Pd(S_2C_2O_2)_2]$. The values measured are typical of Pd atoms in the oxidation state +2, the values being in good agreement with literature data for palladium(II) complexes.[25]

$[ttf]_{1.0}[Cu(S_2C_2O_2)_2]$. The core binding energies determined for $[ttf]_{1.0}[Cu(S_2C_2O_2)_2]$ are reported in Table 6. The Cu $2p_{\frac{1}{2},\frac{3}{2}}$ photoelectron spectrum of this compound is peculiar. First, it does not show shake-up satellites,[23] denoting that the copper ions in the ttf salt must be diamagnetic, *i.e.* Cu^{I} or spin-paired Cu^{III} ($3d^8$ configuration). Second, the spectrum recorded immediately after the introduction of the sample into the vacuum chamber shows two peaks each for the Cu $2p_{\frac{3}{2}}$ and Cu $2p_{\frac{1}{2}}$ (see Figure 4). The peaks at higher energies disappear after *ca.* 2 h of *X*-ray source exposure and a typical Cu^{I} 2*p* spectrum is present eventually. The difference in binding energies between the two peaks for each group is 2.6 eV. The relatively high chemical shift is consistent with the Cu^{III} oxidation state.[26] A reasonable explanation of this behaviour is the reduction on the surface after *X*-ray exposure of the Cu^{III} compound to Cu^{I} with the formation of carbonyl sulphide gas. This process is confirmed by the change of the pressure in the vacuum chamber of the instrument during the experiment. The +3 oxidation state of Cu in the ttf salt was confirmed by e.s.r. measurements, which show that the weak paramagnetism of the compound is due to the ttf$^{\bullet+}$ radical ion.

Infrared Spectra.—Infrared assignments of the constituent species have been made previously[27,28] and a comparison of these results with the observed spectra of the reported compounds leads to the assignments described below.

$[ttf]_2[M(S_2C_2O_2)_2]$ (M = Pt *or* Pd). The i.r. spectrum of the platinum derivative in the 2 000—300 cm^{-1} region is given in Figure 5. Typical vibrational modes of the square-planar $[Pt(S_2C_2O_2)_2]^{2-}$ anion can be identified and assigned. The i.r. spectrum reveals the presence of sulphur-co-ordinated dithiooxalate ligands ($\nu_{C=O}$ at 1 586 cm^{-1} and M–S stretching at 317 cm^{-1}). The i.r. spectrum also provides information on the nature of the ttf molecule in charge-transfer compounds. It is well known that vibrational modes of ttf molecules in these

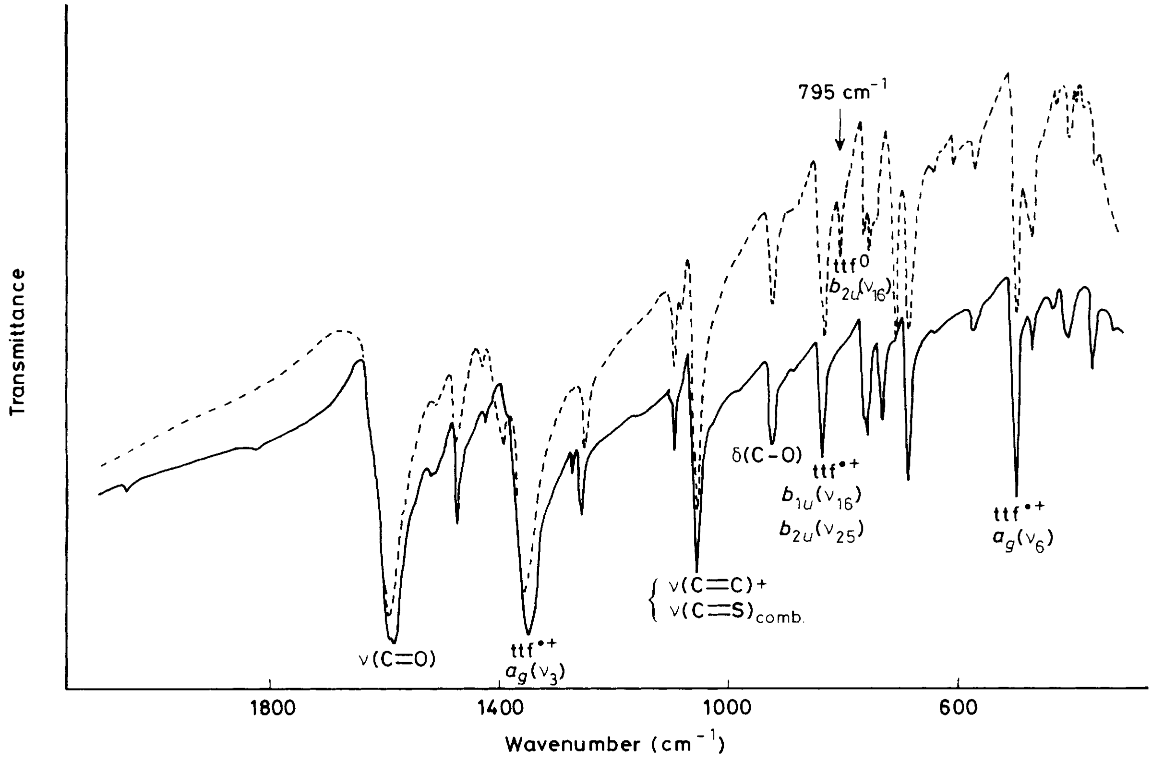


Figure 5. Infrared spectra (cm^{-1}) of [ttf]$_3$[Pt(S$_2$C$_2$O$_2$)$_2$] (- - -) and [ttf]$_2$[Pt(S$_2$C$_2$O$_2$)$_2$] (——) in the KBr region

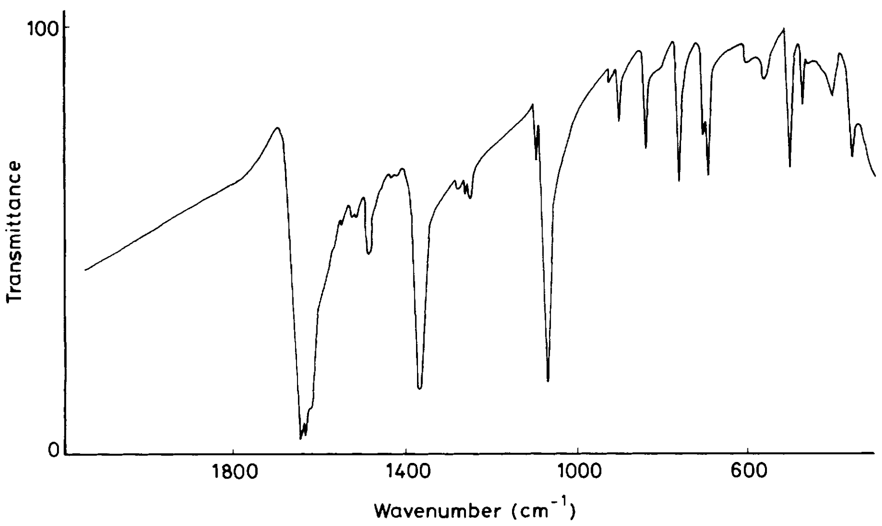


Figure 6. Infrared spectrum (cm^{-1}) of [ttf]$_{1.0}$[Cu(S$_2$C$_2$O$_2$)$_2$] in the KBr region

compounds show a frequency shift that is dependent on the charge occupation of the molecule.[28] Here the $b_{1u}(\nu_{16})$ mode (arising mainly from the C–S stretch) is diagnostic of the presence of the ttf$^{\bullet +}$ radical cation because it does show a large ionization shift, *i.e.* $b_{1u}(\nu_{16})$ = 829 cm^{-1}. The other important information comes from the presence of a_g modes at 1 347 and 490 cm^{-1}. Such absorptions have been demonstrated to be due to an 'intensity borrowing' from a charge-transfer absorption band *via* coupling with electrons of the totally symmetric $a_g(\nu_3)$ and $a_g(\nu_6)$ modes of the ttf$^{\bullet +}$ radical.[28] These bands are therefore an indication of the presence of (ttf$^{\bullet +}$)$_2$ dimers.

The i.r. spectrum of [ttf]$_2$[Pd(S$_2$C$_2$O$_2$)$_2$] is superposable on that of the platinum derivative, which can be accounted for on the basis of the molecular structure described above.

[ttf]$_3$[Pt(S$_2$C$_2$O$_2$)$_2$]. The i.r. spectrum of this compound is given in Figure 5. Previous considerations can be applied to these systems. The presence of two bands, at 829 and 795 cm^{-1}, suggests that both ttf$^{\bullet +}$ and neutral ttf^0 units occur in this compound. Further ttf$^{\bullet +}$ is dimerized as revealed from a_g modes at 1 347 and 490 cm^{-1}. In conclusion, ttf^0 and (ttf$^{\bullet +}$)$_2$ are constituent species of the title compound.

[ttf]$_{1.0}$[Cu(S$_2$C$_2$O$_2$)$_2$]. The i.r. spectrum of the title compound is reported in Figure 6. As previously discussed, also in this case we can identify bands typical of the anion and those of the donor

Table 7. Electronic spectra (diffuse reflectance; energies in 10^3 cm^{-1})

$[ttf]_2[Pd(S_2C_2O_2)_2]$	12.4	$[ttf]_{1.0}[Cu(S_2C_2O_2)_2]$	13.3
	19.2		19.2
	25.6		28.8
$[ttf]_2[Pt(S_2C_2O_2)_2]$	12.4	$[ttf]_3[Pt(S_2C_2O_2)_2]$	12.4
	19.2		19.2
	24.1		24.1

Table 8. Electrical conductivity of the salts at r.t.

Compound	Colour	$\Lambda/S\ cm^{-1}$
$[ttf]_2[Pd(S_2C_2O_2)_2]$	Dark brown	Insulator
$[ttf]_2[Pt(S_2C_2O_2)_2]$	Dark brown	Insulator
$[ttf]_3[Pt(S_2C_2O_2)_2]$	Black	4.0×10^{-7}
$[ttf]_{1.0}[Cu(S_2C_2O_2)_2]$	Dark green	1.1×10^{-6}

molecule. The spectrum is similar to that of $[ttf]_2[Pt(S_2C_2O_2)_2]$, suggesting that (*a*) $(ttf^{\bullet +})_2$ dimers are present; (*b*) the structure of the CuS_4 group is square-planar.

Optical Spectra.—The powder electronic reflectance spectra of the salts studied are reported in Table 7. The first observation to be made is the presence of the band at 12 400 cm^{-1} in the Pd and both of the Pt derivatives and at 13 300 cm^{-1} in the Cu compound. This band is absent in the spectra of the starting metal complexes and it corresponds to charge transfer within the $(ttf^{\bullet +})_2$ dimers[29] as illustrated in equation (2). The absence

$$(ttf^{\bullet +})(ttf^{\bullet +}) \longrightarrow (ttf^0)(ttf^{2+}) \qquad (2)$$

of a strong broad electronic band in the region 5 000—8 000 cm^{-1} together with the low electrical conductivity shown by these compounds, excludes a mixed-valence formulation. At higher energy there is another band at 19 200 cm^{-1}, which is present in all the compounds. This band has been assigned as an intramolecular excitation of the $ttf^{\bullet +}$ radical.[29]

Finally, the copper derivative features a band at 27 000 cm^{-1}, which has been previously observed in benzyltriphenylphosphonium bis(dithio-oxalato-*S,S'*)cuprate(III)–dichloromethane.[6]

Electrical Conductivity.—As expected from the *X*-ray crystal structure these compounds behave as semiconductors or insulators (see Table 8).

Electron Spin Resonance.—The room temperature e.s.r. spectra of powdered samples of the compounds are all characterized by a weak narrow signal with a *g* value of *ca.* 2.003, typical of ttf radical cations.

Conclusions

The chemical reaction of $[ttf]_3[BF_4]_2$ with square-planar dithio-oxalato complexes of Pd^{II}, Pt^{II}, and Cu^{II} has resulted in the formation of new charge-transfer salts. $[ttf]_2[Pd(S_2C_2O_2)_2]$ is an integrated 'stack' material with integral formal oxidation states. As in the case of 1:1 ttf–halide systems, the structural motif consists of integrated stacks of alternating $(ttf^{\bullet +})_2$ dimers and $[Pd(S_2C_2O_2)_2]^{2-}$ anions. Not surprisingly, such a structure gives rise to high electrical resistivity. $[ttf]_2[Pt(S_2C_2O_2)_2]$ has been found to be isomorphous and isostructural with the palladium analogue.

The molecular structure of $[ttf]_3[Pt(S_2C_2O_2)_2]$ consists of two crystallographically distinct types of donor molecules. The first one forms a fully eclipsed $(ttf^{\bullet +})_2$ unit, while the second one is the neutral ttf^0. Thus the compound can be better formulated as $[(ttf^{\bullet +})_2(ttf^0)][Pt(S_2C_2O_2)_2]$. According to this structure there should be no strong broad absorption in the region 5 000—8 000 cm^{-1}, excluding therefore a mixed-valence formulation of the salt. The observed higher electrical conductivity of this compound compared with $[ttf]_2[Pt(S_2C_2O_2)_2]$ can be explained by invoking a degree of electron delocalization in this compound due to an orbital interaction between the $(ttf^{\bullet +})_2$ unit and ttf^0 molecules. The copper compound is peculiar because it contains the ion in the unusual oxidation state +3. Previously, ttf copper–halide salts were found to contain the copper ion in the oxidation state +1 or +2. The i.r. and electronic spectra suggest that the molecular structure of this compound consists of $(ttf^{\bullet +})_2$ dimers and diamagnetic square-planar $[Cu(S_2C_2O_2)_2]^-$ anions.

Acknowledgements

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