X-Ray Crystal Structure of Tetra-acetatobis(tetrathiafulvalene)dirhodium(II) and the Properties of its Iodine-doped Complex†

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A single-crystal *X*-ray structure analysis of $[Rh_2(O_2CCH_3)_4(ttf)_2]$ (ttf = tetrathiafulvalene) revealed a tetra-acetatodirhodium(II) framework co-ordinated by two ttf molecules each through a sulphur atom. The essentially neutral ttf molecule assumes a boat conformation in which the four terminal carbon atoms deviate greatly from the central C_2S_4 plane. In the crystal phase the ttf molecules weakly interact with one another to form a two-dimensional network through sulphur–sulphur contacts. The complex crystallizes in the monoclinic system, space group $P2_1/n$ with unit-cell dimensions $a = 12.496(3)$, $b = 14.413(3)$, $c = 8.296(2)$ Å, $\beta = 104.27(2)°$, and $Z = 2$. The structure was solved by a standard heavy-atom method and refined, on the basis of 1 734 $[|F_o| > 3\sigma(F)]$ observed data, to an R value of 0.082. The complex was doped with iodine to afford $[Rh_2(O_2CCH_3)_4(ttf)_2]\cdot I_3$ which contains neutral ttf and the $ttf^{\bullet+}$ radical cation and exhibits a conductivity of 2.0×10^{-7} S cm^{-1} at 25 °C for a compacted pellet.

Tetrathiafulvalene (ttf) [2-(1′,3′-dithiol-2′-ylidene)-1,3-dithiole] is easily oxidized to the stable radical cation, and many electrically conducting molecular complexes with $ttf^{\bullet+}$ or $ttf^{\bullet+}$/ttf have been investigated.[1] The $ttf^{\bullet+}$ radical cation and partially oxidized ttf molecules in these complexes are almost planar in the crystal phase. On the other hand, a few reports have appeared on crystal structures of complexes containing the neutral ttf molecule; in $Pd(acac)_2\cdot ttf$ (acac = acetylacetonate)[2] and p-$C_6H_4(NO_2)_2\cdot ttf$,[3] as well as neutral ttf itself,[4] the ttf molecules are slightly distorted from a plane to form a chair conformation. In nematic liquid crystals, however, neutral ttf was reported to exist as a boat conformation greatly distorted from a planar structure.[5] We have isolated the tetra-acetatodirhodium–ttf adduct, which behaves as a semiconductor on its iodine oxidation. Thus, the ttf geometry and the crystal packing of this complex are of interest.

This paper reports the crystal structure of tetra-acetatobis-(tetrathiafulvalene)dirhodium(II) and the properties of its iodine-doped product.

Experimental

Preparation of $[Rh_2(O_2CCH_3)_4(ttf)_2]$ *and its Iodine-doped Complex.*—A methanol (40 cm^3) solution containing ttf (50 mg, 240 μmol) and $[Rh_2(O_2CCH_3)_4(CH_3OH)_2]$[6] (63 mg, 120 μmol) was refluxed for 6 h under a nitrogen atmosphere. The solution was gradually cooled and allowed to stand in a refrigerator overnight to yield green crystals of $[Rh_2(O_2CCH_3)_4(ttf)_2]$ (**1**), which were collected by filtration and dried *in vacuo* (29% yield), m.p. 245 °C (decomp.).

Finely powdered complex (**1**) (12 mg, 19 μmol) was suspended in a hexane (10 cm^3) solution containing iodine (7 mg, 28 μmol) and stirred for 18 h at room temperature. A black solid with the composition $[Rh_2(O_2CCH_3)_4(ttf)_2]\cdot I_3$ (**2**) was collected by filtration and dried *in vacuo* (78% yield), m.p. 204 °C (decomp.) (Found: C, 19.5; H, 1.7. Calc. for $C_{20}H_{20}I_3O_8Rh_2S_8$: C, 19.4; H, 1.65%).

X-Ray Crystal Structure of $[Rh_2(O_2CCH_3)_4(ttf)_2]$ (**1**).—Oscillation and Weissenberg photographs indicated a monoclinic system and the space group $P2_1/n$. Accurate unit-cell parameters were determined by least-squares treatment of angular co-ordinates of 25 reflections with $2\theta = 20$—$25°$, measured with a Rigaku four-circle diffractometer at the Crystallographic Research Centre, Institute for Protein Research, Osaka University.

Crystal data. $C_{20}H_{20}O_8Rh_2S_8$, $M = 850.67$, monoclinic, space group $P2_1/n$, $a = 12.496(3)$, $b = 14.413(3)$, $c = 8.296(2)$ Å, $\beta = 104.27(2)°$, $U = 1\,448.1(6)$ Å^3, $Z = 2$, $D_c = 1.951(1)$ g cm^{-3}, $F(000) = 844$, $\mu(\text{Mo-}K_\alpha) = 17.0$ cm^{-1}.

Intensities were collected in the range $3 < 2\theta < 55°$ for a crystal with approximate dimensions 0.33 × 0.12 × 0.07 mm, using graphite-monochromatized Mo-K_α ($\lambda = 0.710\,69$ Å) radiation and the ω–2θ scan technique at a 2θ scan rate of 8° min^{-1}. No significant intensity variation was observed throughout the data collection. Lorentz and polarization factors were applied, but no absorption correction was made. Of 3 529 unique reflections measured, 1 734 $[|F_o| > 3\sigma(F)]$ were used for the solution and refinement of the structure.

The structure was solved by the conventional heavy-atom method and atomic parameters were refined by the block-diagonal least-squares method. The final refinement, with anisotropic thermal parameters for non-hydrogen atoms, converged at $R = 0.082$ and $R' = 0.075$, using the weighting scheme, $1/w = \sigma^2(F_o) + 0.007F_o^2$. Atomic scattering factors used in the refinement were taken from ref. 7. The final atomic co-ordinates with standard deviations are given in Table 1.

Crystallographic calculations were performed using programs of Professor K. Nakatsu, Kwansei Gakuin University, on an ACOS 900S computer at the Crystallographic Research Centre, Osaka University. Figures 1 and 2 were drawn using a local version of the program ORTEP II.[8]

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

Physical Measurements.—Electrical resistivities were measured for compacted pellets by the conventional two-probe method. Powder electronic reflectance,[9] Raman,[10] e.s.r.,[11] and

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

Non-S.I. unit employed: eV ≈ 1.60×10^{-19} J.

Table 1. Atomic co-ordinates (× 10^4) for $[Rh_2(O_2CCH_3)_4(ttf)_2]$ (**1**) with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Rh	−385	720.5(8)	320(2)	C(2)	−2 634(12)	−1 419(12)	951(24)
S(1)	−1 232(3)	2 191(3)	1 084(5)	C(3)	1 083(12)	−162(10)	3 112(18)
S(2)	43(4)	3 982(3)	560(6)	C(4)	1 730(15)	−251(11)	4 904(18)
S(3)	1 174(4)	3 989(3)	4 367(6)	C(5)	−1 774(15)	2 825(11)	−776(23)
S(4)	141(4)	2 262(3)	5 098(6)	C(6)	−1 201(15)	3 583(12)	−950(23)
O(1)	−1 653(8)	−20(6)	795(13)	C(7)	−240(12)	3 023(10)	1 954(18)
O(2)	−939(8)	−1 379(7)	155(14)	C(8)	303(12)	3 062(10)	3 565(20)
O(3)	492(8)	544(7)	2 712(13)	C(9)	662(15)	3 011(12)	6 749(21)
O(4)	1 203(8)	−810(7)	2 137(13)	C(10)	1 136(15)	3 789(13)	6 430(24)
C(1)	−1 658(10)	−905(10)	627(20)				

Table 2. Selected bond lengths (Å) and angles (°) for $[Rh_2(O_2CCH_3)_4(ttf)_2]$ (**1**) with e.s.d.s in parentheses

Rh–Rh′	2.408(2)	Rh–S(1)	2.519(4)	S(1)–C(5)	1.777(17)	S(1)–C(7)	1.746(15)
Rh–O(1)	2.029(10)	Rh–O(3)	2.033(9)	S(2)–C(6)	1.719(17)	S(2)–C(7)	1.754(16)
O(1)–C(1)	1.283(17)	O(2)–C(1)	1.266(19)	S(3)–C(8)	1.748(14)	S(3)–C(10)	1.748(21)
O(3)–C(3)	1.253(17)	O(4)–C(3)	1.268(18)	S(4)–C(8)	1.765(17)	S(4)–C(9)	1.740(17)
C(1)–C(2)	1.506(22)	C(3)–C(4)	1.512(20)				
O(1)–Rh–O(3)	90.2(4)	O(1)–Rh–Rh′	87.8(3)	Rh–S(1)–C(5)	107.9(6)	Rh–S(1)–C(7)	112.5(6)
O(1)–Rh–S(1)	89.8(3)	O(3)–Rh–S(1)	91.1(3)	C(5)–S(1)–C(7)	94.9(7)	C(6)–S(2)–C(7)	94.2(8)
O(2)–Rh′–O(4)	90.6(4)	O(2)–Rh′–Rh	88.3(3)	C(8)–S(3)–C(10)	94.7(9)	C(8)–S(4)–C(9)	94.3(8)
O(1)–C(1)–O(2)	125.8(13)	O(1)–C(1)–C(2)	116.8(13)	S(1)–C(5)–C(6)	114.6(13)	S(2)–C(6)–C(5)	120.3(14)
O(2)–C(1)–C(2)	117.3(13)	O(3)–C(3)–O(4)	125.7(13)	S(3)–C(10)–C(9)	117.1(14)	S(4)–C(9)–C(10)	117.9(15)
O(3)–C(3)–C(4)	117.8(13)	O(4)–C(3)–C(4)	116.5(12)				

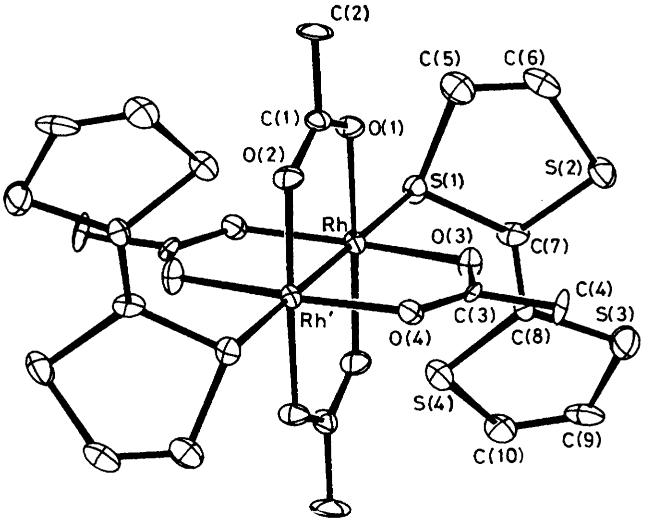

Figure 1. Molecular structure of $[Rh_2(O_2CCH_3)_4(ttf)_2]$ (**1**) with the atom-labelling scheme

X-ray photoelectron spectra (x.p.s.)[11] of the complexes were recorded as described elsewhere.

Results and Discussion

Crystal Structure of $[Rh_2(O_2CCH_3)_4(ttf)_2]$ (**1**).—The molecular structure of (**1**) is illustrated in Figure 1 with the atom-labelling scheme. Selected bond lengths and angles are summarized in Table 2. The structure consists of the well known tetra-acetatodirhodium(II) framework[12] with ttf molecules binding to each axial position of the rhodium atom through a sulphur atom. The molecule is located on an inversion centre. The Rh–Rh′ distance of 2.408(2) Å and the Rh–S(1) distance of 2.519(4) Å are close to those of tetra-acetatodirhodium analogues with sulphur ligands: $[Rh_2(O_2CCH_3)_4(tht)_2]$ [tht = tetrahydrothiophene; Rh–Rh 2.413(1), Rh–S 2.517(1) Å] and $[Rh_2(O_2CCH_3)_4(dmso)_2]$ [dmso = dimethyl sulphoxide; Rh–Rh 2.406(1), Rh–S 2.451(1) Å].[13]

The ttf molecule in the present complex is appreciably non-planar; although S(1), S(2), S(3), S(4), C(7), and C(8) form a plane (±0.008 Å), C(5) and C(6), as well as C(9) and C(10), deviate greatly from this plane to afford an overall boat conformation of the molecule. The S(1)–S(2)–C(5)–C(6) and S(3)–S(4)–C(9)–C(10) planes make dihedral angles of 17.2 and 21.5°, respectively, with the central plane. This conformation is rather analogous to that of neutral ttf in nematic liquid crystals (the above dihedral angle is 13 ± 2°).[5]

It is known[14–16] that the distance of the central C=C bond of the ttf molecule is the most sensitive to the formal charge of the molecule; the C=C bond distance is expected to increase with decreasing electron density in the highest occupied (bonding) molecular orbital. The value [1.34(2) Å] for the present complex is close to that [1.349(3) Å] of neutral ttf.[4] Hence, charge transfer from ttf to the dirhodium moiety may be small, although ttf co-ordinates to the rhodium atom.

In addition, the geometry around the co-ordinating sulphur atom [Rh–S(1)–C(5) 107.9(6), Rh–S(1)–C(7) 112.5(6)°] is very close to that of $[Rh_2(O_2CCH_3)_4(tht)_2]$ [Rh–S–C 107.3(2)° (av.)];[13] both geometries are derived from the sp^3 configuration around the sulphur atom. The ligation of one of four sulphur atoms of ttf to the metal ion has been compared with the geometry of tetrathiafulvalene *S*-oxide.[17,18]

In the crystal phase the ttf molecules are located closely to one another with sulphur–sulphur contacts [S(2)··· S(2′) 3.361(6), S(1′)··· S(3″) 3.627(6) Å] (Figure 2). Thus, among the ttf molecules there seems to exist a weak, two-dimensional, attractive molecular interaction approximately parallel to the $(10\bar{1})$ plane. This molecular arrangement may be responsible for the semiconductive properties of the iodine-doped complex $[Rh_2(O_2CCH_3)_4(ttf)_2]\cdot I_3$ (**2**), as described below.

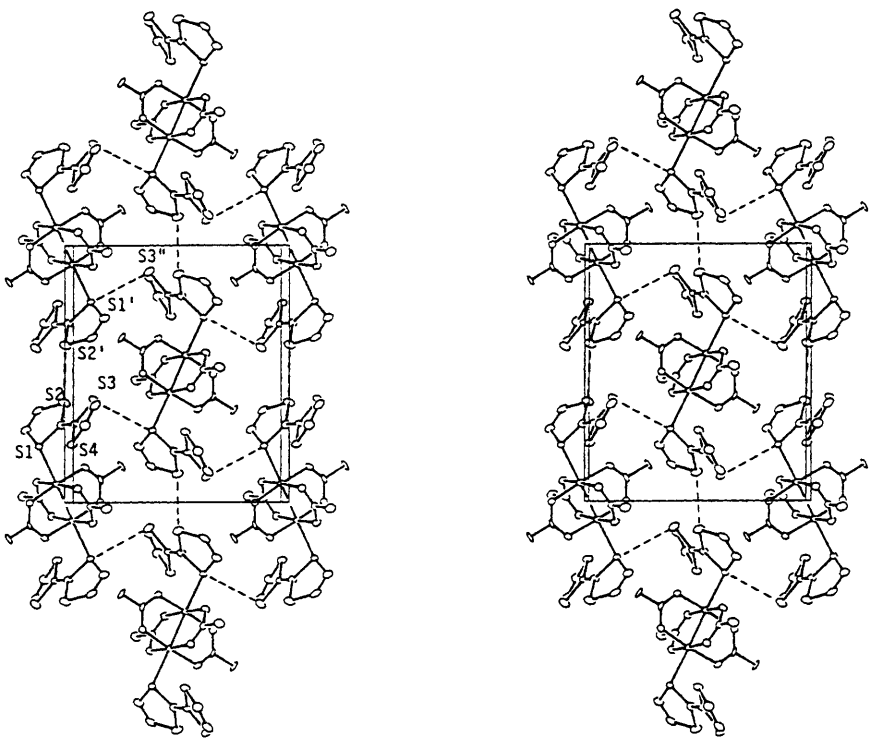

Figure 2. Stereoscopic packing diagram for $[Rh_2(O_2CCH_3)_4(ttf)_2]$ (**1**). The origin of the cell is at the bottom left-hand corner. The *x* axis is horizontal, the *y* axis is vertical, and the *z* axis points out from the origin

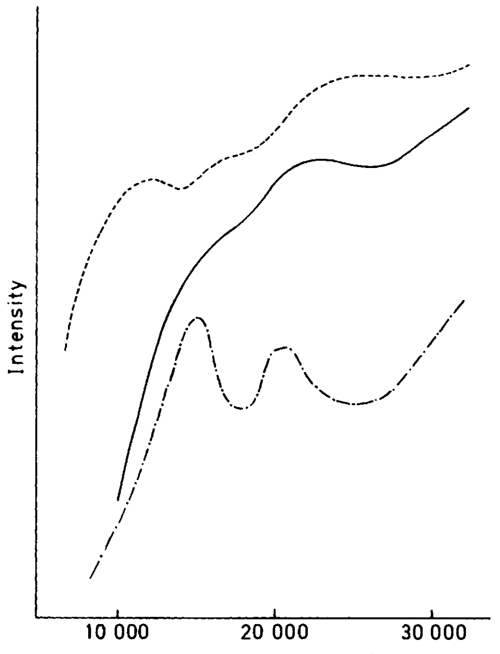

Figure 3. Powder reflectance spectra of (**1**) (——), (**2**) (– – – –), and $[Rh_2(O_2CCH_3)_4(CH_3OH)_2]$ (– · – · –)

Spectroscopic and Electrical Properties of (**1**) *and* (**2**).—The Raman spectrum of (**1**) shows a band at 1 520 cm^{-1}, which is assigned to the ν_3 mode of neutral ttf (a stretching of the central C=C bond).[19] Figure 3 shows the powder reflectance spectra of (**1**) and its iodine-doped complex (**2**), together with that of $[Rh_2(O_2CCH_3)_4(CH_3OH)_2]$. These spectra show two distinct bands around 17 000 and 22 000 cm^{-1}, which are ascribed to $\pi^*(Rh-Rh) \rightarrow \sigma^*(Rh-Rh)$ and $\pi^*(Rh-Rh) \rightarrow \sigma^*(Rh-O)$ transitions, respectively.[12] Since the low-energy band is associated with a transition to a $\sigma^*(Rh-Rh)$ orbital located along the L–Rh–Rh–L axis (L = ligand), its position may be sensitive to an axial ligand L. Such a band seemingly appears at a higher frequency for (**1**) than for $[Rh_2(O_2CCH_3)_4(CH_3OH)_2]$, suggesting the occurrence of charge transfer from ttf sulphur to rhodium being somewhat stronger than that from CH_3OH oxygen to rhodium in the latter. Thus, the π^* energy level of the CH_3OH adduct may be raised compared with that in the ttf adduct. In accordance with this, the binding energies of the Rh $3d_{3/2}$ and $3d_{5/2}$ electrons of (**1**) (312.7 and 307.9 eV) determined from the *X*-ray photoelectron spectra are somewhat lower than those of $[Rh_2(O_2CCH_3)_4(CH_3OH)_2]$ (313.5 and 308.8 eV), indicating some reduction of the rhodium atoms of (**1**) compared with the CH_3OH adduct. In addition, complex (**1**) shows no e.s.r. signal, indicating a very weak charge transfer between ttf sulphur and the rhodium atoms.

The Raman spectrum of the iodine-doped complex (**2**) reveals strong bands at 1 519 and 1 421 cm^{-1}, which are ascribed to the neutral ttf and $ttf^{\bullet +}$ radical cation, respectively.[19] In addition, the spectrum of (**2**) exhibits a sharp band at 108 cm^{-1} which can be assigned to the I_3^- ion.[20] The presence of the $ttf^{\bullet +}$ radical cation has been confirmed also by the powder e.s.r. spectrum which shows a signal at $g = 2.009$.[21] The binding energies of the Rh $3d_{3/2}$ and $3d_{5/2}$ electrons (313.3 and 308.6 eV) of (**2**) are larger than those of (**1**), while they are close to those of $[Rh_2(O_2CCH_3)_4(CH_3OH)_2]$. This reflects a decreased interaction between the rhodium atom and the ttf moiety due to some oxidation of ttf by iodine. The occurrence of such an oxidation may be consistent with the reflectance spectrum of (**2**), which shows an intense broad band around 12 300 cm^{-1} (Figure 3) assignable to ttf$^{\bullet +}$/ttf$^{\bullet +}$ and/or ttf/ttf$^{\bullet +}$ charge-transfer transition.

Although (**1**) is an insulator ($\sigma_{25\,°C} < 10^{-11}$ S cm^{-1}), (**2**) behaves as a semiconductor in the temperature range measured (−40 to 40 °C): $\sigma_{25\,°C} = 2.0 \times 10^{-7}$ S cm^{-1}, $E_a = 0.31$ eV. This may be due to the ttf$^{\bullet +}$/ttf$^{\bullet +}$ and/or ttf/ttf$^{\bullet +}$ interaction, as suggested from the ttf molecular interactions in the crystal phase for complex (**1**).

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