X-Ray Crystal Structure and Properties of Tetrathiafulvalenium Dicarbonyldichlororhodate(I) †

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A single crystal *X*-ray structure analysis of [ttf][Rh(CO)$_2$Cl$_2$] revealed the segregated columnar stackings both of tetrathiafulvalene radical cations, ttf$^{\bullet+}$, and of [Rh(CO)$_2$Cl$_2$]$^-$ anions with eclipsed overlaps. The crystals are orthorhombic, space group *Pbam*, with unit-cell dimensions $a = 14.596(3)$, $b = 12.487(3)$, $c = 3.584(1)$ Å, and $Z = 2$. Least-squares refinement, based on 804 independent reflections with $|F_o| > 3\sigma(F)$ converged at $R = 0.070$. The salt exhibits an electrical conductivity of 2.1×10^{-4} S cm^{-1} at 25 °C for a compacted pellet. Electronic states are discussed based on i.r., electronic powder reflectance, and e.s.r. spectra.

Arrangements of radical cations in crystalline organic salts with electrical conductivities are greatly influenced by the geometries and formal charges of the counter anions.[1] In the course of our structural study on radical cation salts with metal halide anions,[2,3] we have prepared a tetrathiafulvalene (ttf) salt with the planar *cis*-[Rh(CO)$_2$Cl$_2$]$^-$ anion. This anion is polarized with Rh–C and Rh–Cl bonds, and some metal–metal interactions may be possible, as observed for [Ir(CO)$_2$Cl$_2$]$^{\delta-}$ ($\delta < 1$) salts.[4] Although some ttf salts with planar metal halide anions have been prepared,[1] their crystal structures have never been reported. This paper reports the crystal structure of [ttf][*cis*-Rh(CO)$_2$Cl$_2$] and its electrical conductivity. The electronic interaction between the ions is discussed on the basis of i.r., e.s.r., and electronic reflectance spectra.

Table 1. Atomic co-ordinates ($\times 10^4$) for [ttf][Rh(CO)$_2$Cl$_2$] with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Rh	0	0	0
S(1)	4 368(3)	−1 571(3)	5 000
S(2)	3 588(3)	560(3)	5 000
Cl(1)	1 345(4)	1 177(5)	0
Cl(2)	−951(4)	1 548(5)	0
O(1)	1 659(13)	1 278(16)	0
O(2)	−1 165(14)	1 962(17)	0
C(1)	937(18)	849(17)	0
C(2)	−682(14)	1 279(16)	0
C(3)	4 560(10)	−219(9)	5 000
C(4)	2 824(10)	−497(11)	5 000
C(5)	3 192(10)	−1 487(12)	5 000

Experimental

Preparation of [ttf][Rh(CO)$_2$Cl$_2$].—An acetonitrile (10 cm^3) solution containing [Rh$_2$(CO)$_4$Cl$_2$][5] (32 mg, 0.082 mmol) and NEt$_4$Cl (26 mg, 0.16 mmol) was added with stirring to an acetonitrile (15 cm^3) solution of [ttf]$_3$[BF$_4$]$_2$[6] (60 mg, 0.076 mmol) under a nitrogen atmosphere. The solution was allowed to stand in a refrigerator overnight to afford dark green needles of [ttf][Rh(CO)$_2$Cl$_2$], which were collected by filtration and dried *in vacuo* {50% yield based on [Rh$_2$(CO)$_4$Cl$_2$]}, m.p. >300 °C (decomp.) (Found: C, 22.70; H, 1.10. Calc. for C$_8$H$_4$Cl$_2$O$_2$RhS$_4$: C, 22.15; H, 0.95%).

Physical Measurements.—I.r.,[6] Raman,[6] electronic powder reflectance,[7] and e.s.r. spectra[7] were recorded as described elsewhere. Electrical conductivity was measured for a compacted pellet by the conventional two-probe method.[8,9]

X-*Ray Crystal Structure of* [ttf][Rh(CO)$_2$Cl$_2$].—Oscillation and Weissenberg photographs indicated an orthorhombic system and possible space groups *Pba*2 and *Pbam*. The latter was confirmed from the successful analysis. Accurate unit-cell parameters were obtained from 25 reflections with 2θ values in the range 20—30° measured with a computer-controlled Rigaku four-circle diffractometer and using Mo-K_α ($\lambda = 0.710\,69$ Å) radiation.

Crystal data. C$_8$H$_4$Cl$_2$O$_2$RhS$_4$, $M = 430.17$, orthorhombic, space group *Pbam*, $a = 14.596(3)$, $b = 12.487(3)$, $c = 3.584(1)$ Å, $U = 653.2(3)$ Å^3, $Z = 2$, $D_c = 2.208(1)$ g cm^{-3}, $F(000) = 422$, and μ(Mo-K_α) = 22.5 cm^{-1}.

Intensity data were collected for a specimen, 0.40 × 0.10 × 0.10 mm, by the ω—2θ scan technique up to 2θ = 55° with a scan rate of 8° min^{-1} in 2θ; the scan width in ω was (1.5 + 0.35 tanθ)°. No significant intensity variation was observed throughout the data collection. The intensities were corrected for Lorentz and polarization effects, but no correction was made for absorption. 1 615 Independent reflections were collected, of which 804 with $|F_o| > 3\sigma(F)$ were used in the solution and refinement of the structure.

Based on the reasonable calculated density with $Z = 2$ for the salt, the rhodium atom can be assumed to occupy special positions. By fixing the positions of the rhodium atom at the origin and ($\frac{1}{2}, \frac{1}{2}, 0$), subsequent Fourier syntheses revealed the positions of all the non-hydrogen atoms. However, the carbonyl groups and chlorine atoms of the anion were found to be disordered on the *ab* plane with an occupancy of 0.5. A block-diagonal least-squares refinement, assuming the disorder of the CO and Cl groups and anisotropic thermal parameters for all the non-hydrogen atoms, led to residual indices $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.070$ and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}} = 0.066$. The weighting scheme $1/w = \sigma^2(F_o)^2 + 0.0007(F_o)^2$ was

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† Tetrathiafulvalene = 2-(1′,3′-dithiol-2′-ylidene)-1,3-dithiole.

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

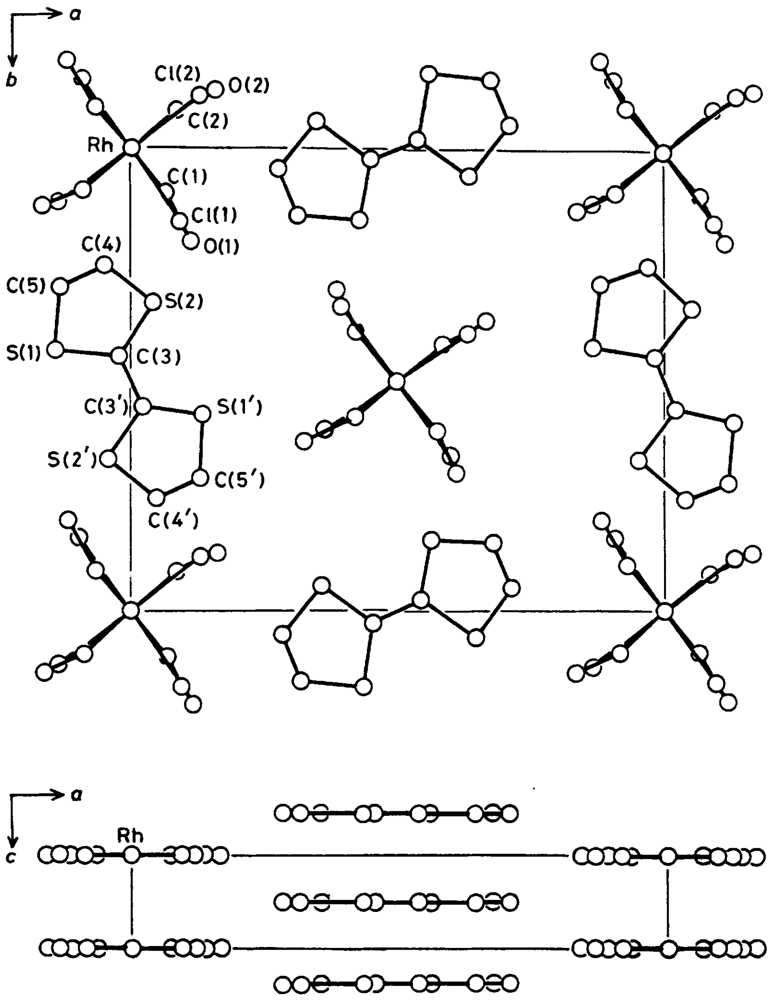


Figure 1. Projections of the crystal structure of [ttf][$Rh(CO)_2Cl_2$] along the *c* and *b* axes

Table 2. Selected bond distances (Å) and angles (°) for [ttf][$Rh(CO)_2Cl_2$] with estimated standard deviations in parentheses

Rh–Cl(1)	2.452(7)	Rh–Cl(2)	2.380(6)
Rh–C(1)	1.730(24)	Rh–C(2)	1.882(20)
C(1)–O(1)	1.183(31)	C(2)–O(2)	1.107(29)
S(1)–C(3)	1.710(12)	S(1)–C(5)	1.719(15)
S(2)–C(3)	1.720(14)	S(2)–C(4)	1.727(15)
C(4)–C(5)	1.348(21)	C(3)–C(3′)	1.397(19)
Cl(1)–Rh–Cl(2)	88.9(2)	C(1)–Rh–C(2)	84(1)
Cl(1)–Rh–C(2)	85.1(6)	Cl(2)–Rh–C(1)	87.9(8)
Rh–C(1)–O(1)	169(2)	Rh–C(2)–O(2)	172(2)
S(1)–C(3)–S(2)	115.0(8)	C(3)–S(1)–C(5)	95.9(7)
S(1)–C(5)–C(4)	117.0(11)	S(2)–C(4)–C(5)	116.3(11)
C(3)–S(2)–C(4)	95.8(7)	S(1)–C(3)–C(3′)	122(1)

used. Atomic scattering factors were taken from ref. 10. The final atomic co-ordinates with estimated standard deviations are listed in Table 1.

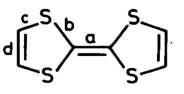
Crystallographic calculations were performed using the programs of Professor K. Nakatsu, Kwansei Gaukin University, on an ACOS 900S computer at the Crystallographic Research Centre, Institute for Protein Research, Osaka University.

Results and Discussion

Crystal Structure of [ttf][$Rh(CO)_2Cl_2$].—Figure 1 shows perspective views of the structure of the salt along the *c* and *b* axes. Bond lengths and angles are summarized in Table 2. The rhodium atom occupies the origin and $(\frac{1}{2}, \frac{1}{2}, 0)$ and all the atoms of the $[Rh(CO)_2Cl_2]^-$ anion lie on the *ab* plane, the carbonyl groups and chlorine atoms being disordered on the same plane with an occupancy of 0.5. On the other hand, the regularly planar $ttf^{\bullet +}$ radical cation is located on the (002) plane, the centre of the molecule lying on $(\frac{1}{2}, 0, \frac{1}{2})$ and $(0, \frac{1}{2}, \frac{1}{2})$. Since the closest chlorine–sulphur distance [3.812(4) Å] is larger than the sum of the van der Waals radii of these atoms (3.65 Å),[11] there is no appreciable cation–anion interaction.

Bond lengths of the ttf moiety of the salt are summarized in Table 3, together with those of neutral ttf and other ttf salts. In the salt studied here the exocyclic C–C bond (*a*) is somewhat lengthened and the C–S bonds (*b*) are shortened compared with the corresponding bonds of neutral ttf. They are rather close to those of [ttf][$HgCl_3$],[12] which suggests a complete one-electron oxidation of the ttf molecule in the present salt. In accordance with this, the Raman spectrum exhibits a band at 1 416 cm^{-1} which is attributable to the ν_3 mode of the $ttf^{\bullet +}$ radical cation [predominantly a stretching of the C–C bond (*a*)].[13] The $ttf^{\bullet +}$ radical cations are stacked with the regularly eclipsed overlap along the *c* axis. The interplanar distance of 3.584 Å is appreciably longer than those of the fully eclipsed $ttf^{\bullet +}$ radical

Table 3. Bond distances (Å) of the ttf molecule



	Bond			
	a	b	c	d
ttf[a]	1.349(3)	1.757(2)	1.726(4)	1.314(3)
[ttf][tcnq][b]	1.369(4)	1.743(4)	1.736(5)	1.323(4)
$[ttf]_3[SnCl_6]$[c]	1.357(24)	1.736(10)	1.717(16)	1.326(10)
	1.360(9)	1.737(5)	1.726(6)	1.345(9)
$[ttf]I_{0.71}$[d]	1.350	1.732	1.721	1.336
$[ttf][HgCl_3]$[e]	1.41(1)	1.72(1)	1.71(1)	1.31(1)
$[ttf][Rh(CO)_2Cl_2]$[f]	1.40(2)	1.72(1)	1.73(1)	1.35(2)

[a] T. E. Phillips, T. J. Kistenmacher, J. P. Ferraris, and D. O. Cowan, *J. Chem. Soc., Chem. Commun.*, 1973, 471. [b] T. J. Kistenmacher, T. E. Phillips, and D. O. Cowan, *Acta Crystallogr., Sect. B*, 1974, **30**, 763. [c] Ref. 2. [d] Ref. 19. [e] Ref. 12. [f] This work.

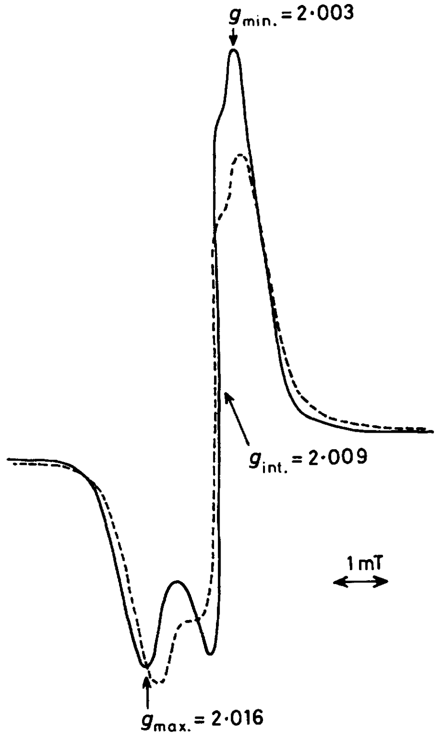


Figure 2. Powder e.s.r. spectra of $[ttf][Rh(CO)_2Cl_2]$ at 77 K (——) and at room temperature (– – –)

cation dimers reported for [ttf]Br (3.34 Å),[14] [ttf][dftcnq] (dftcnq = 2,5-difluoro-7,7,8,8-tetracyano-*p*-quinodimethane) (3.34 Å),[15] $[ttf]ClO_4$ (3.42 Å),[16] and $[ttf]_2[Ni(S_2C_2H_2)_2]$ (3.48 Å).[17] However, it is rather close to those of other mixed-valence ttf salts: $[ttf]Br_{0.71-0.76}$ (3.57 Å),[18] $[ttf]I_{0.71}$ (3.55 Å),[19] and $[ttf]SCN_{0.57}$ (3.607 Å).[20]

The electronic powder reflectance spectrum of the salt shows a broad band at 12 400 cm^{-1} which is due to the ttf$^{\bullet+}$–ttf$^{\bullet+}$ charge-transfer transition.[21] The spin-pairing interaction between the ttf$^{\bullet+}$ radical cations, however, may be weak, as suggested from the e.s.r. spectrum of the polycrystalline sample of the salt, which exhibits three kinds of signals with anisotropic g values of $g_{max.}$ = 2.016, $g_{int.}$ = 2.009, and $g_{min.}$ = 2.003, as shown in Figure 2. Similar e.s.r. signals were reported for $[ttf]_2[M(C_2O_4)_3]$ (M = Si or Ge)[22] and for $[dbttf][SnEt_2Cl_3]$ [dbttf = dibenzotetrathiafulvalene = 2-(1′,3′-benzodithiol-2′-ylidene)-1,3-benzodithiole].[3]

Although the *X*-ray structure analysis has not revealed the geometry of the anionic moiety of the salt because of the disorder, it may reasonably assume a *cis* configuration, since the salt in Nujol mull displayed pairs of ν(Rh–C) bands at 484 and 455 cm^{-1} and ν(Rh–Cl) bands at 295 and 270 cm^{-1} as well as two intense ν(C–O) bands at 2 055 and 1 975 cm^{-1} in the i.r. spectrum. This appearance is very similar to the spectrum of $[NBu^n_4][cis\text{-}Rh(CO)_2Cl_2]$ which exhibits ν(C–O) at 2 050 and 1 965 cm^{-1}, ν(Rh–C) at 495 and 465 cm^{-1}, and ν(Rh–Cl) at 320 and 290 cm^{-1}.[23] The ν(C–O) frequencies of the present salt, however, are somewhat higher, and the ν(Rh–C) and ν(Rh–Cl) frequencies are appreciably lower than those of the tetrabutylammonium salt. Thus, the present anion may be oxidized by the ttf$^{\bullet+}$ radical cation to some extent, resulting in a decrease of the back-bonding character of the rhodium atom thereby weakening the Rh–C and Rh–Cl bonds and strengthening the C–O bond owing to some removal of electrons from the carbonyl π^* orbital.

The salt behaves as a semiconductor with the electrical conductivity 2.1×10^{-4} S cm^{-1} at 25 °C and the activation energy E_a = 0.26 eV (*ca.* 0.4×10^{-19} J) for a compacted pellet. The electrical conduction may occur through the columnar structure of the ttf$^{\bullet+}$ radical cations with the eclipsed overlap. Conduction through the anion columns seems unlikely because of the long Rh–Rh distance in the salt.

Acknowledgements

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