Inorganica Chimica Acta, *112* (1986) 135–137

X-ray Crystal Structure and Properties of Tris(tetrathiafulvalenium) Hexachloroplatinate

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Received May 22, 1985

Abstract

The title salt has been prepared by the diffusion of tetrathiafulvalene (TTF) and $[NBu^n_4]_2[PtCl_6]$ in acetonitrile. Crystals (black plates) are tetragonal, space group *P*4/*mbm*, with $a = 11.757(2)$, $c = 11.707(2)$ Å, and $Z = 2$. The block-diagonal least-squares refinement, based on 804 independent reflections with $|F_o| > 3\sigma(F)$, yields an *R* factor of 0.11. The structure is comprised of TTF-trimer units which are arranged perpendicularly to each other, forming a two-dimensional layer with somewhat close sulfur–sulfur contact among the trimers. The salt exhibits the electrical resistivity of 87 Ω cm as a compacted pellet at 25 °C. Binding energies of platinum 4f electrons of the $[PtCl_6]^{2-}$ anion suggest an extreme reduction from the platinum(IV) state.

Introduction

Several electrically conductive tetrathiafulvalene (TTF) salts with metal halide anions have been prepared [1–6], some of which have been analyzed by X-ray crystallography [3–5]. Recently, we have reported a new type of TTF arrangement as the trimer unit in $[TTF]_3[SnCl_6]$ [4] and $[TTF]_3[SnMe_2Cl_4]$ [5].

Previously Siedle and co-workers [6] reported the reaction of TTF with K_2PtCl_4 to afford $[TTF]_2[PtCl_2]$. The crystal structure, however, has not been clarified. Although our several attempts to react TTF with K_2PtCl_4 have afforded no crystalline salts, the reaction of neutral TTF^0 with $[NBu^n_4]_2[PtCl_6]$ in acetonitrile has yielded black plates formulated as $[TTF]_3[PtCl_6]$, which has the same composition as $[TTF]_3[SnCl_6]$, with a high conductivity. This paper reports the crystal structure and properties of $[TTF]_3[PtCl_6]$.

Experimental

Preparation of $[TTF]_3[PtCl_6]$

Diffusion of TTF and $[NBu^n_4]_2[PtCl_6]$ in acetonitrile under nitrogen atmosphere using a conventional U-tube [7] gave black plates of $[TTF]_3[PtCl_6]$, m.p. (decomposition) > 300 °C. *Anal.* Calc. for $C_{18}H_{12}Cl_6S_{12}Pt$: C, 21.17; H, 1.18%. Found: C, 21.76; H, 1.38%.

Physical Measurements

Powder electronic reflectance [4] and X-ray photoelectron spectra [8] were recorded as described elsewhere. Electrical resistivities were measured as compacted samples by the conventional two-probe method [9].

X-ray Crystal Structure of $[TTF]_3[PtCl_6]$

Oscillation and Weissenberg photographs indicated a tetragonal system and possible space groups of *P*4*b*2, *P*4*bm*, and *P*4/*mbm*. The latter was proved to be correct from the successful analysis. Accurate unit-cell parameters were obtained from 25 reflections with 2θ values from 29–36° measured with a computer-controlled Rigaku four-circle diffractometer with Mo Kα (λ = 0.71069 Å) radiation.

Crystal Data

$C_{18}H_{12}Cl_6S_{12}Pt$, $M = 1020.8$, tetragonal, space group *P*4/*mbm*, $a = 11.757(2)$, $c = 11.707(2)$ Å, $U = 1618.2(4)$ Å^3, $Z = 2$, $D_c = 2.096(1)$ g cm^{-3}, $F(000) = 984$, and μ(Mo Kα) = 58.1 cm^{-1}.

Intensity data were collected for a crystal of size 0.50 × 0.35 × 0.08 mm by the ω–2θ scan technique up to $2\theta = 55°$ with the scan rate of 4°/min in 2θ; the scan width in ω was $(1.5 + 0.35 \tan\theta)°$. 1143 independent reflections were measured, of which 804 with $|F_o| > 3\sigma(F)$ were used in the subsequent calculations. The structure was solved by the Patterson method and positions of nonhydrogen atoms clarified from the successive Fourier syntheses. Positions of hydrogen atoms were not determined. Block-diagonal least-squares refinement with aniso-

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0020-1693/86/$3.50

TABLE I. Final Atomic Coordinates ($\times 10^4$) and Anisotropic Thermal Factors ($\times 10^3$)[a] for $[\mathrm{TTF}]_3[\mathrm{PtCl_6}]$ with e.s.d.s in Parentheses

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt	0	0	0	21.8(4)	21.8(4)	21.0(6)	0	0	0
Cl(1)	0	0	1986(6)	32(2)	32(2)	28(3)	0	0	0
Cl(2)	1952(5)	323(5)	0	27(3)	42(3)	39(3)	−1(20)	0	0
S(1)	1221(3)	2026(4)	3620(4)	30(2)	30(2)	39(2)	−9(2)	0(2)	−2(2)
S(2)	4125(6)	875(6)	3584(19)	42(3)	42(3)	36(2)	1(4)	−15(6)	15(6)
C(1)	1751(17)	2435(19)	2322(15)	42(10)	53(12)	42(9)	−6(8)	−3(8)	−10(9)
C(2)	2084(12)	2917(12)	4439(19)	18(5)	18(5)	44(11)	−1(8)	3(6)	−3(6)
C(3)	4579(47)	422(47)	2284(68)	102(28)	102(28)	332(98)	−22(37)	6(43)	−6(43)
C(4)	5000	0	4437(68)	29(11)	29(11)	214(74)	0	0	0

[a] The form of the anisotropic thermal ellipsoid is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

tropic thermal factors for all the nonhydrogen atoms gave the final indices $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.11$ and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0.13$, with the weighting scheme $1/w = \sigma^2(F_o) + 0.01(F_o)^2$. Atomic scattering factors were taken from the tabulation [10]. The final atomic coordinates with the standard deviations are listed in Table I. Observed and calculated structure factors have been deposited with the Editor-in-Chief.

Crystallographic calculations were performed on an ACOS 900S computer at the Crystallographic Research Center, Institute for Protein Research, Osaka University. Figures 1 and 2 were drawn by the local version of ORTEP-II program [11].

Results and Discussion

Since TTF has a low oxidation potential (0.33 V *vs.* SCE) [12] and the $[\mathrm{Pt^{IV}Cl_6}]^{2-}$ anion has a very low reduction potential (0.68 V *vs.* NHE; corresponds to 0.44 V *vs.* SCE) [13], $[\mathrm{TTF}]_3[\mathrm{PtCl_6}]$ may be obtained by the redox reaction between TTF and the $[\mathrm{Pt^{IV}Cl_6}]^{2-}$ anion forming the $\mathrm{TTF}^{\cdot+}$ radical cation and the $[\mathrm{Pt^{II}Cl_4}]^{2-}$ anion, as formulated in the following equation.

$$2[\mathrm{Pt^{IV}Cl_6}]^{2-} + 3\mathrm{TTF}^0 \longrightarrow \underbrace{[\mathrm{Pt^{IV}Cl_6}]^{2-} + 2\mathrm{TTF}^{\cdot+} + \mathrm{TTF}^0}_{[\mathrm{TTF}]_3[\mathrm{PtCl_6}]} + [\mathrm{Pt^{II}Cl_4}]^{2-} + 2\mathrm{Cl}^-$$

The crystal structure of the salt is illustrated in Figs. 1 and 2. Bond lengths and angles as well as relevant intermolecular atom-atom contacts are summarized in Table II. The octahedral $[\mathrm{PtCl_6}]^{2-}$ anion occupies the origin and $(\frac{1}{2}\ \frac{1}{2}\ 0)$. The Pt–Cl distances (2.325(7) and 2.337(6) Å) are very close to that of $\mathrm{K_2PtCl_6}$ (2.33 Å) [14]. TTF molecules are arranged co-facially; the molecular planes are parallel to the c axis to form a trimer unit with the equal intermolecular spacing of 3.500(9) Å, and are overlapped in the eclipsed form within the trimer unit. All the atoms of the central TTF molecules in the trimeric unit have large thermal factors, particularly along the c axis. This is due to a loose positioning of this molecule compared with the other two TTF molecules, which are more rigidly positioned through the sulfur–chlorine (S(1)–Cl(1)) electrostatic interaction, as mentioned later. These findings are the same as reported for $[\mathrm{TTF}]_3[\mathrm{SnCl_6}]$ [4] and $[\mathrm{TTF}]_3[\mathrm{SnMe_2Cl_4}]$ [5]. Since we have also observed the tetragonal systems of $[\mathrm{TTF}]_3[\mathrm{SnEt_2Cl_4}]$ [15] and $[\mathrm{TTF}]_3[\mathrm{SnBr_6}]$ [16], we conclude that the trimeric $[\mathrm{TTF}]_3^{2+}$ units stack stably with octahedral $[\mathrm{MX_2Y_4}]^{2-}$ anions ($\mathrm{X^-}$, $\mathrm{Y^-}$ = alkyl groups or halide ions).

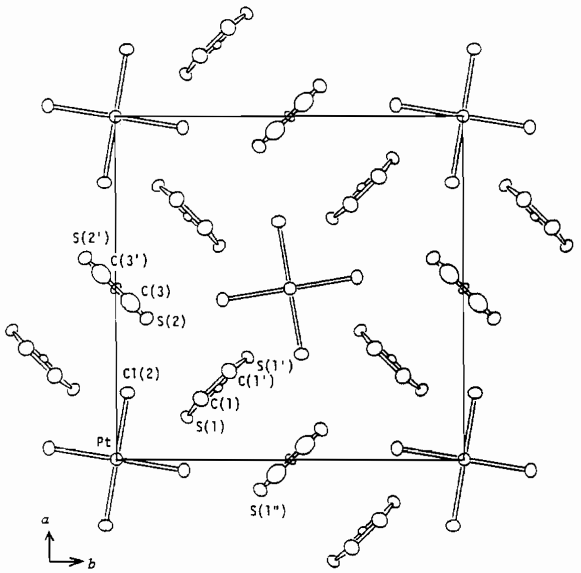

Fig. 1. Crystal structure of $[\mathrm{TTF}]_3[\mathrm{PtCl_6}]$ projected along the c axis.

The powder electronic reflectance spectrum exhibited a broad band at 8900 $\mathrm{cm^{-1}}$ due to the

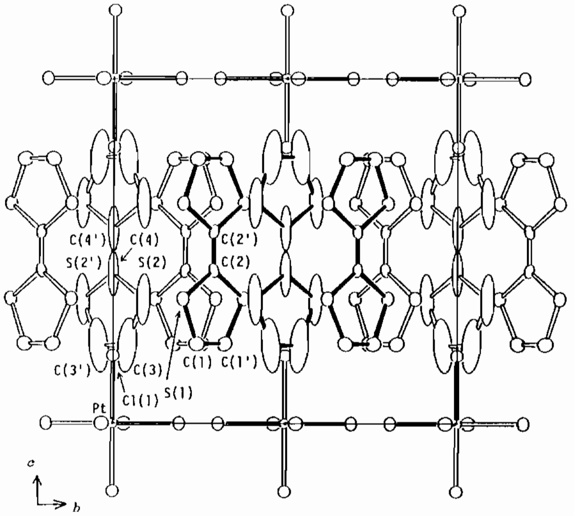

Fig. 2. Crystal structure of $[TTF]_3[PtCl_6]$ projected along the *a* axis.

TABLE II. Selected Bond Lengths (Å) and Angles (°)[a] together with the Non-bonded Contacts (Å) for $[TTF]_3$-$[PtCl_6]$ with e.s.d.s in Parentheses

Pt–Cl(1)	2.325(7)	C(1)–C(1')	1.35(3)
Pt–Cl(2)	2.337(6)	C(2)–C(2')	1.31(3)
S(1)–C(1)	1.71(2)	C(3)–C(3')	1.40(8)
S(1)–C(2)	1.75(2)	C(4)–C(4')	1.32(11)
S(2)–C(3)	1.70(8)		
S(2)–C(4)	1.77(5)		
Cl(1)–Pt–Cl(2)	90	S(2)–C(3)–C(1')	116(6)
C(1)–S(1)–C(2)	96(1)	S(1)–C(2)–C(2')	123(1)
C(3)–S(2)–C(4)	98(3)	S(2)–C(4)–C(4')	124(2)
S(1)–C(1)–C(1')	117(1)		
Non-bonded contacts[b]			
S(1)---S(2)	3.672(9)	Cl(1)---S(1)	3.375(6)
S(1)---S(1'')	3.500(9)		

[a] The atoms with the prime are in mirror symmetry with respect to the atoms with the same number (see Figs. 1 and 2). [b] See Figs. 1 and 2.

$TTF^{\dot{+}}/TTF^0$ charge transfer transition [17, 18], which is compatible with the above-mentioned trimer arrangement. As is apparent from the Figures, the TTF trimers are perpendicular to each other with the sulfur-sulfur contact of 3.672(9) Å to form a two-dimensional layer parallel to the *c* plane. The S–S distance is somewhat smaller than the sum of van der Waals radii of the sulfur atoms (3.70 Å) [19]. The small electrical resistivity and the low activation energy of the present salt (87 Ω cm as a compacted pellet at 25 °C and 0.05 eV, respectively) may result from the electrical conduction through the two-dimensional TTF layer.

The closest chlorine–sulfur contact (Cl(1)--- S(1), 3.375(6) Å) is appreciably shorter than the sum of van der Waals radii of chlorine and sulfur atoms (3.65 Å) [19], indicating an electrostatic interaction between those two atoms. Binding energies of Pt $4f_{7/2}$ and Pt $4f_{5/2}$ electrons have been determined to be 70.9 ± 0.2 and 74.1 ± 0.2 eV, respectively, from the X-ray photoelectron spectra; these values are considerably smaller than those for $[NBu^n{}_4]_2[PtCl_6]$ (73.9 ± 0.2 and 77.1 ± 0.2 eV) and rather close to those for $[NBu^n{}_4]_2[PtCl_4]$ (71.2 ± 0.2 and 74.2 ± 0.2 eV). This suggests the occurrence of an appreciable reduction of the Pt(IV) valence state of the $[PtCl_6]^{2-}$ anion of the present salt, as a result of the transfer of negative charge from the TTF molecules to the anion through the chlorine–sulfur interaction.

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