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Synthesis and Crystal and Molecular Structure of (BEDT-TTF)$_2$[Pt(S$_2$C$_4$O$_2$)$_2$]: A Radical-Cation Salt of the Platinum(II) Dithiosquarate Complex

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Introduction

Bis(ethylenedithio)tetrathiafulvalene, BEDT-TTF, is an electron donor molecule, which in combination with several anions has provided more than 30 air-stable superconductors, although the observed critical temperatures, T_c, are below 13 K.[1] (BEDT-TTF)$_y$X$_x$ salts, where X is an inorganic anion, are very interesting solids owing to their broad range of structures, *i.e.*, α, β, and κ phases, and their differing BEDT-TTF's degree of charge, ρ.[2] The size, shape, and charge of the anion play an important role in the crystal structure packing and in the physical properties of this kind of derivative.[3] Several anions have been used, from the simple linear I$_3^-$ to the bulky inorganic clusters of the α-Keggin anion type, and many salts, whose behavior spans from superconductors to magnetic insulators, were isolated. In some cases radical-ion salts having formula (BEDT-TTF)$_n$[X^{n-}], with $n = 1$or 2, where the donor molecule has a degree of ionicity $\rho = +1$, have been isolated and characterized.[4] The latter is the simplest possible system for CT organic materials, *i.e.* a dimer of two open shell conjugated molecules interacting through their π-electron systems, and therefore, it represents a simple model for studying the coupling of electrons with molecular motions in these organic conducting materials.[5] A few square planar transition metal complexes are known to form radical-ion salts with BEDT-TTF, but only two were found to be superconductors.[6] In this regard transition metal dithiosquarate anions are good candidates, mainly because the molecular shape of these complexes resembles that of the donor molecule and because [M(S$_2$C$_4$O$_2$)$_2$]$^{n-}$ complexes of transition metals other than first row exhibit reversible redox behavior.[7] Here we wish to report on the synthesis and crystal structure of a new salt of formula (BEDT-TTF)$_2$[Pt(S$_2$C$_4$O$_2$)$_2$], obtained by combination of BEDT-TTF with the Pt(II) dithiosquarate anion.

Experimental Section

Synthesis. Elemental analyses were performed by the Laboratorio di Microanalisi del CNR, Area della Ricerca di Roma. All solvents were reagent grade and freshly distilled over CaH$_2$. Bis(ethylenedithio)-tetrathiafulvalene, BEDT-TTF, was prepared according to literature methods.[8] The product was recrystallized twice from chloroform. Potassium 3,4-dimercapto-1,2-cyclobutenedione (potassium dithiosquarate, K$_2$[S$_2$C$_4$O$_2$]) was prepared according to Krause and Mattes.[9] The synthesis of K$_2$[Pt(S$_2$C$_4$O$_2$)$_2$]·2H$_2$O was done as described elsewhere.[7] (Bu$_4$N)$_2$[Pt(S$_2$C$_4$O$_2$)$_2$] was obtained by adding solid [Bu$_4$N]Br to an aqueous solution of K$_2$[Pt(S$_2$C$_4$O$_2$)$_2$]·2H$_2$O. The yellow solid was filtered out, washed with ethanol and ether, and dried under vacuum. The compound was recrystallized from acetonitrile, and the purity of the complex was checked by elemental analyses and infrared spectroscopy.

Crystals of (BEDT-TTF)$_2$[Pt(S$_2$C$_4$O$_2$)$_2$] were obtained by the electrocrystallization technique performed in an H-shaped cell with platinum electrodes under an argon atmosphere. Good quality single crystals were obtained by starting from (Bu$_4$N)$_2$[Pt(S$_2$C$_4$O$_2$)$_2$] (0.25 g, 0.26 mmol) in the cathodic compartment and BEDT-TTF (0.030 g, 0.08 mmol) in the anodic one and then adding 170 mL of PhCN. Black hexagonal crystals were collected at the anode after 4 weeks, using a current density of 3 μA/cm^2. Anal. Calcd for C$_{28}$H$_{16}$S$_{20}$PtO$_4$: C, 26.85; H, 1.29; S, 51.18. Found: C, 26.67; H, 1.13; S, 50.87.

Physical Measurements. Electrochemical measurements were performed with an Amel electrochemistry system with two platinum electrodes and an Ag/AgCl reference electrode in dried and deoxygenated acetonitrile solution. Tetrabutylammonium hexafluorophosphate was used as a supporting electrolyte. Infrared spectra were recorded, at room temperature, with a Perkin-Elmer 621 spectrophotometer on powdered samples as KBr pellets. A Cary 5 spectrophotometer was used to record diffuse reflectance spectra on diluted samples in MgO. EPR spectra at room temperature were done by a Varian E9 spectrometer. Magnetization measurements were done by using a Quantum Design MPMS5 SQUID magnetometer.

X-ray Diffraction Crystallography. Data were collected on a Huber/Ital-Structure automated diffractometer fitted with a molybdenum source and graphite monochromator and corrected for Lorentz and polarization factors.

Selected crystal data are given in Table 1. The structure was found by Patterson and Fourier analysis. Refinement of all non-hydrogen atoms with anisotropic vibrational amplitude was performed; idealized locations for the hydrogen atoms positions were assigned. Atomic coordinates and equivalent isotropic thermal parameters are given in Table 2.

Results and Discussion

Electrochemical Oxidation. Tetrabutylammonium platinum(II) dithiosquarate shows one well-defined quasi-reversible wave at $E^{\circ\prime} = +0.58$ V which corresponds to the one-electron redox process $[\mathrm{Pt^{III}(S_2C_4O_2)_2}]^- + e^- \rightarrow [\mathrm{Pt^{II}(S_2C_4O_2)_2}]^{2-}$. The color of the solution changes from orange to brown. A cyclic voltammogram for BEDT-TTF recorded in the same conditions gives $E^{\circ\prime} = +0.59$ V for the first one-electron oxidation. In the electrochemical cell the oxidation of both BEDT-TTF^0 and the [Pt$^{\mathrm{II}}$(S$_2$C$_4$O$_2$)$_2$]$^{2-}$ anion could occur, but (BEDT-TTF$^{\bullet+}$)$_2$[Pt$^{\mathrm{II}}$(S$_2$C$_4$O$_2$)$_2$] only grows at the anode.

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Table 1. Crystallographic Data

empirical formula	$C_{28}H_{16}O_4PtS_{20}$
space group	$P2_1/c$ (No.14)
unit cell dimens	$a = 14.359(5)$ Å
	$b = 11.192(5)$ Å
	$c = 13.278(5)$ Å
	$\beta = 113.640(5)°$
V	1954.8(13) Å^3
Z	2
fw	1252.7
D(calc)	2.128 Mg/m^3
D(obs)	2.12 Mg/m^3
μ(Mo Kα)	4.696 mm^{-1}
radiation (λ)	Mo Kα (0.710 69 Å)
temp	20 °C
R^a	0.0329
$R_w{}^b$	0.0499

[a] $R = \sum|(F_o - F_c)|/\sum F_o$. [b] $R_w = \sum(|F_o - F_c|\sqrt{w})/\sum F_o\sqrt{w}$.

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients (Å^2 $\times$ 10^3)

	x	y	z	U(eq)^a
Pt	0	0	0	35(1)
S(1)	−1122(1)	602(2)	−1729(1)	44(1)
S(2)	−1247(1)	131(2)	694(1)	45(1)
S(3)	−2788(1)	3619(2)	595(1)	51(1)
S(4)	−3433(2)	4463(2)	−2172(2)	58(1)
S(5)	−743(1)	3381(2)	650(1)	41(1)
S(6)	−1282(1)	4051(2)	−1635(1)	46(1)
S(7)	1547(1)	2806(2)	878(1)	41(1)
S(8)	956(1)	3510(2)	−1407(1)	44(1)
S(9)	3678(1)	2296(2)	1297(1)	54(1)
S(10)	3001(1)	3092(2)	−1406(1)	49(1)
O(1)	−3914(4)	1183(5)	−2952(4)	67(2)
O(2)	−4007(4)	836(5)	−575(4)	63(2)
C(1)	−2191(5)	727(6)	−1489(5)	41(2)
C(2)	−2252(5)	542(6)	−475(5)	40(2)
C(3)	−3283(5)	974(6)	−2014(6)	45(2)
C(4)	−3352(5)	801(6)	−913(6)	47(3)
C(5)	−4243(6)	3977(9)	−1535(7)	73(4)
C(6)	−3952(6)	4280(10)	−372(7)	75(4)
C(7)	−2016(4)	3720(5)	−121(5)	38(2)
C(8)	−2249(5)	4036(6)	−1186(5)	40(2)
C(9)	−369(4)	3584(5)	−421(5)	38(2)
C(10)	606(5)	3340(5)	−321(5)	38(2)
C(11)	2485(5)	2790(5)	374(5)	40(2)
C(12)	2217(5)	3120(6)	−691(5)	39(2)
C(13)	3726(5)	1779(6)	−747(5)	49(3)
C(14)	4385(4)	1957(7)	457(5)	49(3)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

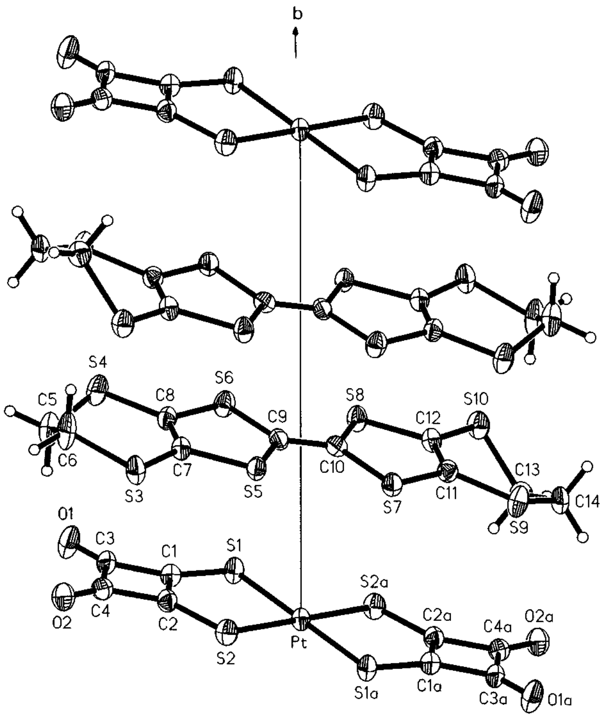

Figure 1. View of the (BEDT-TTF)$_2$[Pt(S$_2$C$_4$O$_2$)$_2$] structure showing the mixed stack of anions and (BEDT-TTF$^{\bullet+}$)$_2$ dimeric unit along the b axis. Thermal ellipsoids for non-hydrogen atoms are at the 30% probability level.

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg)a

Pt−S(1)	2.314(2)	Pt−S(2)	2.324(2)
S(1)−C(1)	1.694(8)	S(2)−C(2)	1.705(5)
S(5)−C(9)	1.723(8)	S(6)−C(8)	1.717(8)
S(6)−C(9)	1.702(5)	S(7)−C(10)	1.730(5)
S(8)−C(10)	1.716(7)	O(1)−C(3)	1.234(7)
O(2)−C(4)	1.194(11)	C(1)−C(2)	1.398(10)
C(1)−C(3)	1.464(9)	C(2)−C(4)	1.477(9)
C(3)−C(4)	1.517(12)	C(9)−C(10)	1.381(10)
S(1)−Pt−S(2)	92.0(1)	S(1)−Pt−S(2A)	88.0(1)
Pt−S(1)−C(1)	99.2(2)	Pt−S(2)−C(2)	99.2(3)
S(1)−C(1)−C(2)	125.4(4)	S(1)−C(1)−C(3)	143.5(5)
C(2)−C(1)−C(3)	91.1(6)	S(2)−C(2)−C(1)	124.1(5)
S(2)−C(2)−C(4)	142.4(6)	C(1)−C(2)−C(4)	93.5(5)
O(1)−C(3)−C(1)	136.9(8)	O(1)−C(3)−C(4)	133.8(7)
C(1)−C(3)−C(4)	89.3(5)	O(2)−C(4)−C(2)	137.6(7)
O(2)−C(4)−C(3)	136.4(6)	C(2)−C(4)−C(3)	86.0(6)
S(5)−C(9)−S(6)	116.4(4)	S(5)−C(9)−C(10)	122.3(4)
S(6)−C(9)−C(10)	121.2(5)	S(7)−C(10)−S(8)	115.4(4)
S(7)−C(10)−C(9)	123.0(5)	S(8)−C(10)−C(9)	121.6(4)

[a] Note: the designation A in the atomic numbering signifies the equivalent position −x, −y, −z.

Crystal and Molecular Structure. The crystal structure consists of mixed stacks of organic (BEDT-TTF$^{\bullet+}$)$_2$ dimers and [Pt(S$_2$C$_4$O$_2$)$_2$]$^{2-}$ anions, alternating along the b axis of the unit cell (see Figure 1). Table 3 summarizes the bond distances and angles. The platinum(II) atom occupies an inversion center and is in a square planar coordination; the Pt−S distances are similar to those observed in (TTF)$_3$[Pt(S$_2$C$_2$O$_2$)$_2$][10] and are shorter than those found in the palladium dithiosquarate.[11] The anion unit is almost planar, the mean deviation from the plane being 0.038 Å. As far as the BEDT-TTF is concerned, the ratio of the bond lengths between the sulfur atoms and the central carbon atoms distance b, with respect to the central carbon−carbon atom distance, a, is 1.24. The literature b/a values are 1.35 for neutral BEDT-TTF^0, 1.29 for BEDT-TTF$^{+0.5}$, 1.25 for BEDT-TTF$^+$, and 1.17 for BEDT-TTF^{2+}.[4,12] Therefore, the observed value indicates an ionicity degree of +1. The BEDT-TTF molecule within the dimer is almost planar, the mean deviation from the plane being 0.041 Å. The intradimeric distances between the sulfur atoms are in the range 3.67−3.88 Å, while that between the C(9)−C(9′) is 3.39 Å (see Figure 2). These values are of the same order of magnitude of the few examples reported in the literature.[4] The plane of the anion and those of the donor molecules are almost parallel (the dihedral angle being ca. 3.7°). More interesting are the contacts between neighboring chains: Figure 2 reports those having distances lower than 3.60 Å. The shortest distances are observed between the anion and BEDT-TTF molecules on the nearby

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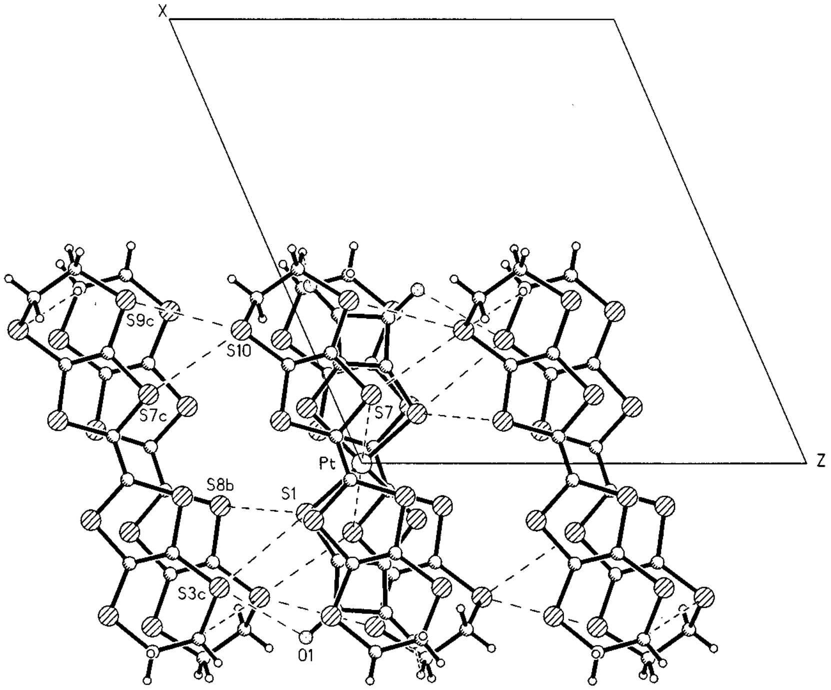

Figure 2. Main interactions and packing (partial view). The designation b in the atomic numbering signifies the equivalent positions $-x$, $-^1/_2 + y$, $-^1/_2 - z$; the designation c signifies the equivalent positions x, $^1/_2 - y$, $-^1/_2 + z$.

chain, *i.e.* 2.98 Å between the O(1) and S(3c) atoms; other short distances are S(1)···S(8b) (3.48 Å) and S(1)···S(3c) (3.51 Å). Between BEDT-TTF molecules on neighboring chains contacts of 3.51 Å for S(10)···S(7c) and 3.58 Å for S(10)···S(9c) are observed. Contacts of 3.26−3.36 Å between the oxygen atoms of the platinum dithiosquarate molecule and the terminal carbon atoms C(13) and C(14) of the BEDT-TTF molecules can explain the higher stability of these atoms with respect to the other terminal C(5) and C(6) atoms. The last two carbon atoms, in fact, show a high thermal motion and an (apparently) short bond distance of 1.47 Å: a similar situation is observed in (BEDT-TTF)$_4$[Pt(C$_2$O$_4$)$_2$].[13] Magnetic susceptibility measurements showed a diamagnetic behavior for the compound, and the weak single transition of Lorentzian shape (peak to peak line of 50 G at room temperature) observed in the EPR spectrum can be ascribed to impurities or stacking faults. From stoichiometry, crystal structure, and magnetism, an average charge ρ of +1 is therefore assessed for the BEDT-TTF molecule. The solid-state diffuse reflectance spectrum of the salt at room temperature is characterized by having the three highest energy bands at 32 470, 23 350, and 17 430 cm^{-1}, which can be assigned to electronic excitations of the platinum(II) dithiosquarate anion, while the others at 11 630, 7670, 6320, and 4950 cm^{-1} arise from *inter*- and *intra*molecular excitations in the organic moiety.[14] The infrared spectrum of the title compound shows vibrations arising from the anion which can be easily identified and assigned: 1722 (s), 1680 (m), 1662 (m), 1419 (s), 1160 (w), 1025 (vw) cm^{-1}. BEDT-TTF vibrational modes are located in the range of frequency between 1400 and 1200 cm^{-1}. The most prominent are observed at 1358 (s) and 1278 (s) cm^{-1}; these are vibrational modes, *i.e.* $\nu_3(a_g)$ and $\nu_5(a_g)$, respectively, involving the central C=C bond of the molecule. These modes are infrared inactive in the neutral molecule, while in ionized systems they couple strongly to the charge oscillating between molecules of each dimer, becoming infrared active.[5b] The intensity of these modes is strongly enhanced, similarly to that found in (BEDT-TTF)$_2$[Mo$_6$O$_{19}$],[15] where dimerized (BEDT-TTF$^{\bullet+}$)$_2$ ions form κ-phase layers, alternating with layers of the inorganic cluster along the [100] direction of the unit cell.[4d]

Conclusion

A new 1:1 radical-ion salt of BEDT-TTF with a platinum(II) dithiosquarate anion has been prepared and the crystal and molecular structure solved. This is one of a few examples reported in the literature where BEDT-TTF is +1e and dimerized and where the molecular structure of the Pt(II) dithiosquarate complex has been determined. The packing motif has not previously been observed in similar dimerized (BEDT-TTF$^{\bullet+}$)$_2$ salts, and it features S···S interactions between molecules residing on neighboring mixed-stacked chains. A correlation between the optical and structural properties has also been observed.

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Supporting Information Available: Tables containing a full summary of the crystal data and structure determination, bond lengths and angles, anisotropic thermal parameters for the non-hydrogen atoms, and hydrogen atoms coordinates with isotropic coefficients (6 pages). Ordering information is given on any current masthead page.

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