A new radical cation salt bis(ethylenedithio)tetrathiafulvalene with $[Pt(NO_2)_4]^{2-}$ anion: synthesis, structure, and conductivity

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A radical cation salt based on bis(ethylenedithio)tetrathiafulvalene (BEDT—TTF) containing the $[Pt(NO_2)_4]^{2-}$ anion was synthesized for the first time. The crystal and molecular structure of this salt, $(BEDT—TTF)_2Pt(NO_2)_4$, was established by X-ray diffraction analysis. The crystal structure consists of radical cation BEDT—TTF layers between which planar-square anions $[Pt(NO_2)_4]^{2-}$ are located. The layers are formed by BEDT—TTF stacks built of dimers. The interplanar distances within the dimers and between them are 3.41 and 3.96 Å, respectively. The distribution of the bond lengths and bond angles in BEDT—TTF corresponds to the charge of the cation +1. The room-temperature conductivity of $(BEDT—TTF)_2Pt(NO_2)_4$ is $3 \cdot 10^{-3}$ Ω^{-1} cm^{-1}, and the temperature dependence of the conductivity exhibits the semiconducting character.

Key words: radical cation salt, BEDT—TTF, X-ray diffraction analysis, conductivity.

Radical cation salts based on the organic electron donor bis(ethylenedithio)tetrathiafulvalene (BEDT—TTF) attract considerable attention because in their conducting properties many of these salts can be referred to as metals. At low temperature, some of these compounds turn into a superconducting state.[1,2] Salts of BEDT—TTF have layer structures, which consist of alternating radical cation BEDT—TTF layers and layers of counter-ions. The conducting properties of the salts are determined by the mode of packing of BEDT—TTF cations in layers, which, in turn, depends strongly on the nature, shape, and size of the anion. It was of interest to vary the anions in BEDT—TTF salts to establish a correlation between the structure of the cation layer, conductivity, and the nature of the anion. In this work, we report the synthesis, crystal structure, and conductivity of a new BEDT—TTF salt containing the metal-complex anion $[Pt(NO_2)_4]^{-2}$. Crystals of $(BEDT—TTF)_2Pt(NO_2)_4$ were prepared by electrocrystallization, which is widely used in the synthesis of conducting compounds based on radical-ionic salts.[3]

Results and Discussion

The projection of the structure of $(BEDT—TTF)_2Pt(NO_2)_4$ along the *b* axis is shown in Fig. 1. The structure is characterized by layers of BEDT—TTF radical cations between which $[Pt(NO_2)_4]^{2-}$ anions are located along the *c* axis. The projection of the radical cation layer along the *c* axis is shown in Fig. 2. The layer is formed by BEDT—TTF stacks arranged along the *a* axis. The stacks consist of centrosymmetrical dimers $I-I_i$. The interplanar distances within the dimer and between them are 3.41 and 3.96 Å ($I-I_{ia}$), respectively. (The distances were calculated for mean planes through 6 atoms of the central core of BEDT—TTF.) Dimerization within the radical cation stack is also clearly illustrated by different modes of overlapping of the adjacent cations $(BEDT—TTF)^+$, which is seen in Fig. 3. There are several shortened interionic contacts in the dimer $I-I_i$, *viz.*, S(1)...S(4), 3.497(3) Å; S(2)...S(3), 3.558(3) Å; C(1)...C(1), 3.41(1) Å; and C(1)...C(2), 3.48(1) Å. There are only two slightly shortened contacts in the stack: S(6)...S(6), 3.586(5) Å ($I-I_{i\bar{b}}$); and S(7)...S(7), 3.598(4) Å ($I-I_{iab}$) (see Fig. 2).

It should be noted that the mode of packing of BEDT—TTF found in $(BEDT—TTF)_2Pt(NO_2)_4$, namely, the presence of dimerized radical cation stacks with weak interactions, is typical of the so-called simple radical cation salts with complete charge-transfer.[4—9] These BEDT—TTF salts containing one-charge anions have the 1 : 1 stoichiometry, and salts containing two-charge anions have the 2 : 1 stoichiometry as is the case in the salt under consideration.

The overall view of the BEDT—TTF radical cation is shown in Fig. 4. This radical cation is characterized by orientational disorder of the carbon atoms of the termi-

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Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\times 10^3$/Å^2) for the salt $(BEDT—TTF)_2Pt(NO_2)_4$

Atom	*x/a*	*y/b*	*z/c*	U_{eq}
S(1)	5275(2)	5261(2)	2600(2)	40(0)
S(2)	6418(2)	2522(2)	4721(2)	38(0)
S(3)	7180(2)	6865(2)	4203(2)	40(0)
S(4)	8292(2)	4214(2)	6390(2)	41(0)
S(5)	3620(3)	3968(3)	789(2)	52(1)
S(6)	4909(3)	794(2)	3268(2)	53(1)
S(7)	9062(3)	8545(3)	5340(3)	61(1)
S(8)	10363(3)	5404(3)	7948(3)	67(1)
C(1)	6364(8)	4350(8)	4155(7)	34(1)
C(2)	7187(8)	5065(7)	4849(7)	32(1)
C(3)	4737(8)	3735(8)	2313(7)	36(1)
C(4)	5270(8)	2478(8)	3299(7)	35(1)
C(5)	8516(9)	6916(9)	5494(8)	41(2)
C(6)	9043(9)	5682(9)	6516(8)	42(2)
C(7a)*	4675(29)	2250(20)	588(17)	60(4)
C(8a)*	4541(37)	966(51)	1498(44)	63(8)
C(7b)*	3702(41)	2163(32)	609(26)	75(8)
C(8b)*	5138(45)	841(70)	1607(66)	70(11)
C(9a)*	9357(30)	8555(28)	7024(28)	60(6)
C(10a)*	10658(23)	7261(26)	7810(24)	66(5)
C(9b)*	10072(43)	8320(49)	7012(39)	67(9)
C(10b)*	9843(33)	7160(26)	8198(23)	57(5)
Pt	10000	0	10000	30(0)
N(1)	8027(8)	1472(7)	9027(6)	43(1)
N(2)	11181(8)	1039(7)	8647(7)	41(1)
O(1)	7296(9)	1318(8)	8047(9)	81(2)
O(2)	7585(12)	2609(10)	9345(9)	105(4)
O(3a)*	12011(31)	242(31)	8177(27)	134(9)
O(4a)*	10910(25)	2276(23)	8467(26)	108(7)
O(3b)*	10990(30)	1119(29)	7630(22)	100(7)
O(4b)*	11956(38)	1789(32)	9091(25)	127(8)

* The occupancies of the C(7a), C(8a), C(9a), and C(10a) atoms are 0.57; the occupancies of the C(7b), C(8b), C(9b), and C(10b) atoms are 0.43; and the occupancies of the O(3a), O(4a), O(3b), and O(4b) atoms are 0.50.

Table 2. Bond lengths (*d*) in the structure of $(BEDT—TTF)_2Pt(NO_2)_4$

Bond	*d*/Å	Bond	*d*/Å
S(1)—C(1)	1.730(7)	S(8)—C(10a)	1.86(2)
S(1)—C(3)	1.745(8)	S(8)—C(10b)	1.76(2)
S(2)—C(1)	1.724(7)	C(1)—C(2)	1.39(1)
S(2)—C(4)	1.742(7)	C(3)—C(4)	1.35(1)
S(3)—C(2)	1.721(7)	C(5)—C(6)	1.36(1)
S(3)—C(5)	1.734(8)	C(7A)—C(8a)	1.42(5)
S(4)—C(2)	1.716(7)	C(7B)—C(8b)	1.66(6)
S(4)—C(6)	1.743(8)	C(9A)—C(10a)	1.51(3)
S(5)—C(3)	1.736(7)	C(9B)—C(10b)	1.54(5)
S(5)—C(7a)	1.81(2)	Pt—N(1)	2.008(7)
S(5)—C(7b)	1.80(2)	Pt—N(2)	2.093(7)
S(6)—C(4)	1.750(7)	N(1)—O(1)	1.222(9)
S(6)—C(8a)	1.82(4)	N(1)—O(2)	1.23(1)
S(6)—C(8b)	1.78(6)	N(2)—O(3a)	1.19(2)
S(7)—C(5)	1.743(8)	N(2)—O(4a)	1.14(2)
S(7)—C(9a)	1.77(3)	N(2)—O(3b)	1.05(2)
S(7)—C(9b)	1.83(4)	N(2)—O(4b)	1.25(2)
S(8)—C(6)	1.742(8)		

Table 3. Bond angles (ω) in the structure of $(BEDT—TTF)_2Pt(NO_2)_4$

Angle	ω/deg	Angle	ω/deg
C(1)—S(1)—C(3)	95.5(3)	S(3)—C(5)—S(7)	116.7(5)
C(1)—S(2)—C(4)	94.9(3)	S(3)—C(5)—C(6)	116.9(6)
C(2)—S(3)—C(5)	95.5(4)	C(6)—C(5)—S(7)	126.4(6)
C(2)—S(4)—C(6)	95.7(4)	S(4)—C(6)—S(8)	116.3(5)
C(3)—S(5)—C(7a)	93.8(7)	S(4)—C(6)—C(5)	116.1(6)
C(3)—S(5)—C(7b)	106.7(9)	S(8)—C(6)—C(5)	127.6(6)
C(4)—S(6)—C(8a)	102.0(1)	S(5)—C(7A)—C(8a)	116.0(2)
C(4)—S(6)—C(8b)	98.0(2)	S(6)—C(8A)—C(7a)	119.0(3)
C(5)—S(7)—C(9a)	99.9(9)	S(5)—C(7B)—C(8b)	115.0(2)
C(5)—S(7)—C(9b)	103.0(1)	S(6)—C(8B)—C(7b)	108.0(3)
C(6)—S(8)—C(10a)	102.8(7)	S(7)—C(9A)—C(10a)	110.0(2)
C(6)—S(8)—C(10b)	99.5(9)	S(8)—C(10A)—C(9a)	117.0(1)
S(1)—C(1)—S(2)	115.8(4)	S(7)—C(9B)—C(10b)	120.0(2)
S(1)—C(1)—C(2)	120.6(6)	S(8)—C(10B)—C(9b)	110.0(2)
S(2)—C(1)—C(2)	123.5(6)	N(1)—Pt—N(2)	89.7(3)
S(3)—C(2)—S(4)	115.6(4)	O(1)—N(1)—O(2)	118.1(7)
S(3)—C(2)—C(1)	121.9(6)	Pt—N(1)—O(1)	121.2(6)
S(4)—C(2)—C(1)	122.6(5)	Pt—N(1)—O(2)	120.4(6)
S(1)—C(3)—S(5)	117.3(4)	O(3A)—N(2)—O(4a)	131.0(2)
S(1)—C(3)—C(4)	116.1(6)	O(3B)—N(2)—O(4b)	120.0(2)
S(5)—C(3)—C(4)	126.7(6)	Pt—N(2)—O(3a)	115.0(1)
S(2)—C(4)—S(6)	116.9(4)	Pt—N(2)—O(4a)	114.0(1)
S(2)—C(4)—C(3)	117.7(6)	Pt—N(2)—O(3b)	124.0(1)
S(6)—C(4)—C(3)	125.4(6)	Pt—N(2)—O(4b)	114.0(1)

nal ethylene groups. The bond lengths and bond angles in the radical cation (see Table 2) correspond to $(BEDT—TTF)^+$ and are close to those observed in other BEDT—TTF radical cation salts:[4—8,10] compared to the neutral $(BEDT—TTF)^0$ molecule, the C(sp^2)—C(sp^2) double bonds are elongated, while the S—C(sp^2) bonds are shortened. For example, the C(1)—C(2) bond length is 1.39(1) Å, while the corresponding distance in the neutral molecule $(BEDT—TTF)^0$ is 1.319 Å (see Ref. 9).

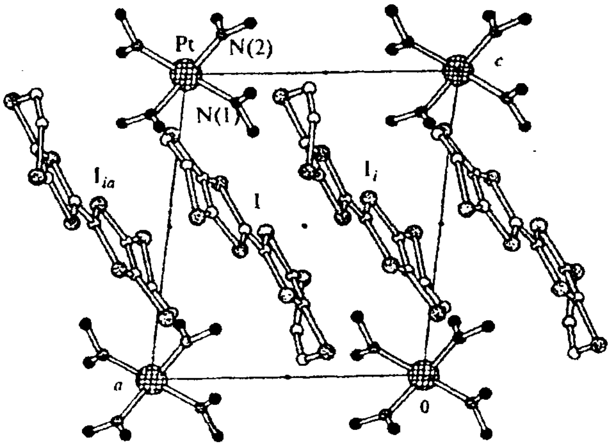

Fig. 1. Projection of the $(BEDT—TTF)_2Pt(NO_2)_4$ structure along the *b* axis. The symmetry operations for the radical cations BEDT—TTF are as follows: I (*x*, *y*, *z*), I_i (1 − *x*, 1 − *y*, 1 − *z*), and I_{ia} (2 − *x*, 1 − *y*, 1 − *z*).

The $[Pt(NO_2)_4]^{2-}$ anions occupy symmetry centers. The coordination about the Pt atom is a planar square. The interatomic Pt—N(1) and Pt—N(2) distances are 2.008(7) and 2.093(7) Å, respectively. The plane of the N(1)O(1)O(2) nitro group is approximately perpendicular to the PtN_4 plane (the dihedral angle is 86.5°). In the crystal, the N(2)O(3)O(4) nitro group is equally distributed over two sites (N(2)O(3a)O(4a) and N(2)O(3b)O(4b)). The dihedral angle between the planes of the nitro group in these two positions is 60°. The angles between these planes and the PtN_4 plane are 50° and 70°, respectively. The disorder of the two nitro groups related by a center of symmetry is due to a tendency to eliminate nonallowed short contacts of the oxygen atoms of the anion with the sulfur atoms and/or the terminal ethylene groups. The structures of Pt^{IV} octahedral nitro complexes, such as $K_2PtX_2(NO_2)_4$, where X = Cl or Br,[11] and *cis*-$K_2PtCl_3(NO_2)_3$ [12] were reported. It should be noted that the Pt—N bond length in the latter complex is substantially larger (2.20 Å) than that in the planar-square nitro complex of Pt^{II} studied by us.

The conductivity of crystals of $(BEDT—TTF)_2$ $Pt(NO_2)_4$, which was measured in the *ab* plane by the four-contact method, is $3 \cdot 10^{-3}$ Ω^{-1} cm^{-1}, and it decreased as the temperature decreased.

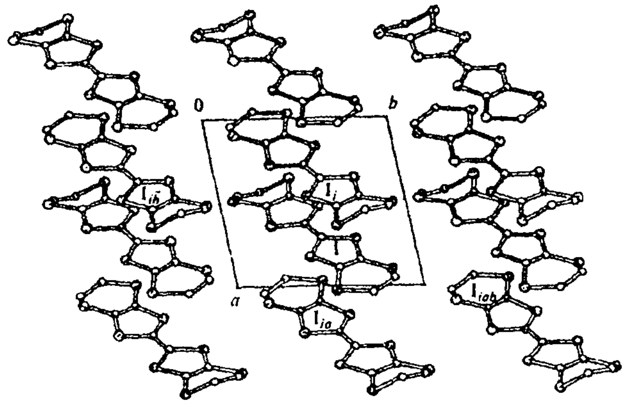

Fig. 2. Projection of the radical-cation layer along the *c* axis. The symmetry operations for $(BEDT—TTF)^+$ are as follows: $I_{i\bar{b}}(1-x, \bar{y}, 1-z)$ and I_{iab} $(2-x, 2-y, 1-z)$; see also the caption to Fig. 1.

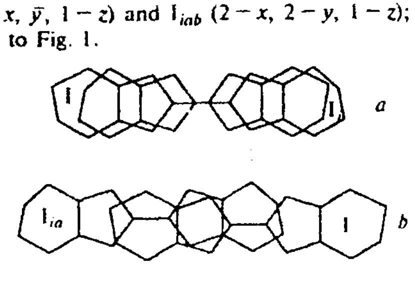

Fig. 3. Modes of overlapping of the adjacent BEDT—TTF molecules in the radical-cation stack: (*a*) in the dimer and (*b*) between the dimers.

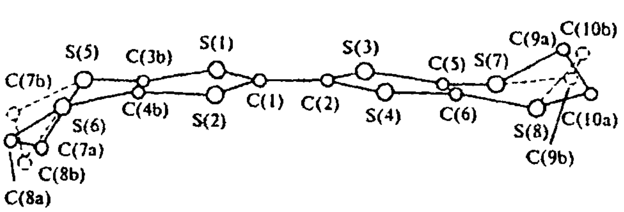

Fig. 4. Overall view of the radical cation $(BEDT—TTF)^+$ and the atomic numbering scheme.

The stoichiometry of the $(BEDT—TTF)_2$ $Pt(NO_2)_4$ salt (2 : 1) differs fundamentally from the stoichiometry (4 : 1) of high-conductivity BEDT—TTF salts containing other planar-square two-charge anions, $Pt(CN)_4$ or $Pt(C_2O_4)$.[15,16] Unlike the last-mentioned salts, in the crystals of $(BEDT—TTF)_2$ $Pt(NO_2)_4$, the positive charge (+1) is located on each BEDT—TTF molecule, which leads to pronounced dimerization of BEDT—TTF cations in stacks and, as a result, to low conductivity of the crystals.

Experimental

Synthesis of the salt $(BEDT—TTF)_2[Pt(NO_2)_4]$. Bis(ethylenedithio)tetrathiafulvalene (Aldrich) was recrystallized from 1,1,2-trichloroethane; $[(C_4H_9)_4N]_2Pt(NO_2)_4$ was recrystallized from anhydrous ethanol. 1,1,2-Trichloroethane (Fluka) was distilled over P_2O_5 and passed through a column with neutral alumina before use. BEDT—TTF (11 mg, $2.8 \cdot 10^{-4}$ mol) and the electrolyte $[(C_4H_9)_4N]_2Pt(NO_2)_4$ (60 mg, $7.8 \cdot 10^{-4}$ mol) were placed in an H-shaped electrochemical cell with a porous glass membrane and dissolved in 1,1,2-trichloroethane (25 mL) with stirring under an atmosphere of argon. Then the cell was sealed, placed into an air-dried thermostat, and connected to a constant-current source; 1-mm platinum wire electrodes were used. Electrocrystallization was carried out at 25 °C for 1.5—2 weeks in the constant current mode (i = 0.5 μA, j = 1 μA cm^{-2}). Black brilliant platelet-like crystals of dimensions 1×0.5×0.06 mm were grown on the anode. The crystals were filtered off and washed with 1,1,2-trichloroethane and acetone. The composition of the crystals was established by complete X-ray diffraction analysis.

X-ray diffraction study. Crystals of $(BEDT—TTF)_2Pt(NO_2)_4$ are triclinic, a = 9.089(1) Å, b = 9.737(2) Å, c = 10.566(1) Å, α = 76.19(1), β = 96.73(1), γ = 76.99(1), V = 870.2(2) Å^3, space group $P\bar{1}$, Z = 1, $C_{20}H_{16}N_4O_8PtS_{16}$, $F(000)$ = 562, M = 1148.42, d_{calc} = 2.19 g cm^{-3}, μ(Mo—Kα) = 50.4 cm^{-1}. The unit cell parameters and intensities of 3039 reflections were measured on an automated four-circle Nonius CAD-4F diffractometer (293K, (λMo-Kα) radiation, graphite monochromator, ω scanning technique to $2\theta_{max}$ = 50°). The structure was solved by the heavy-atom method and refined by the full-matrix least-squares method with anisotropic thermal parameters for nonhydrogen atoms using the SHELXL-93 program[10] to R = 0.045 for 2839 independent reflections with $F_0 \geq 4\sigma(F)$. The positions of the hydrogen atoms were calculated geometrically and were not refined. The final coordinates of the nonhydrogen atoms and their thermal parameters are given in Table 1. The bond lengths and bond angles in the BEDT—

TTF radical cation and in the [Pt(NO$_2$)$_4$]$^{2-}$ anion are listed in Tables 2 and 3, respectively.

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