Synthesis, structure, and electroconductivity of new radical cation salt $[Pd(dddt)_2]_2GaBr_4$

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A new radical cation salt based on the dithiolate complex $Pd(dddt)_2$ (dddt = 5,6-dihydro-1,4-dithiine-2,3-dithiolate) with the tetrahedral anion $[GaBr_4]^-$ was synthesized. The crystal and molecular structure was determined by XRD analysis. The crystal structure of the salt contains $Pd(dddt)_2$ cation layers alternating with layers of $[GaBr_4]^-$ anions along the *c* axis of the unit cell. The cation layers contain stacks of $Pd(dddt)_2$, with a Pd...Pd distance of 3.011 Å. The electroconductivity of $[Pd(dddt)_2]_2GaBr_4$ single crystals at room temperature is 0.25 Ohm^{-1} cm^{-1} and decreases with temperature decrease, the activation energy being E_a = 0.66 eV.

Key words: radical cation salt; dithiolate complexes; palladium(II) 5,6-dihydro-1,4-dithiine-2,3-dithiolate; X-ray diffraction analysis.

Complexes $M(dddt)_2$ (dddt = 5,6-dihydro-1,4-dithiine-2,3-dithiolate; M = Ni, Pt, Pd, Au) are metal complex analogs of bis(ethylenedithio)tetrathiafulvalene (ET), which forms radical cation salts with metallic and superconducting properties.[1] Formal replacement of the central —C=C— bond in the ET molecule by metal results in the $M(dddt)_2^+$ complexes. Similarly to ET, these compounds form conducting radical cation salts in a partially oxidized state.[2–4] The salts of the $M(dddt)_2$ cation have a layered structure in which the $M(dddt)_2$ layers alternate with layers of counterions. The conducting properties of the salts are determined by the packing of the $M(dddt)_2$ cations in the layer, which depends on the nature of the metal M and anion. Variation of anions in the $M(dddt)_2$ salts is of interest for studying correlations between the structure of the cationic layer, electroconductivity, and the character of the anion. In this work, we synthesized a new salt of $Pd(dddt)_2$ with the tetrahedral $[GaBr_4]^-$ anion and studied its crystal structure and electroconductivity.

Experimental

Synthesis. Crystals of the $[Pd(dddt)_2]_2GaBr_4$ salt were prepared by electrochemical oxidation of neutral $Pd(dddt)_2$ (5 mg) in the presence of the electrolyte $[Bu^n_4N]_2GaBr_4$ (32 mg) in nitrobenzene (25 mL). Pt wire with a diameter of 0.5 mm was used as electrodes. Electrocrystallization was carried out in the d.c. regime (i = 1 μA cm^{-2}) at 25 °C for 2 weeks. The crystals were grown on the anode, filtered off, washed with acetone, and dried in air.

X-ray diffraction analysis. The composition of the $[Pd(dddt)_2]_2GaBr_4$ salt was established by XRD. A single crystal in the form of a thin plate close to a parallelepiped with a size of 0.15×0.4×0.05 mm was selected for analysis. The main crystallographic data: $(C_8H_8S_8Pd)_2GaBr_4$, molecular weight 1323.3, a = 15.569(3) Å, b = 6.545(1) Å, c = 34.752(7) Å, β = 91.82(3)°, V = 3539(1) $Å^3$, the crystals are monoclinic, space group $C2/c$, Z = 4, d_{calc} = 2.48 g cm^{-3}, μ = 23.25 cm^{-1}. Measurement of 3728 independent reflections (among them 3513 with $I > 2\sigma(I)$) was carried out on a KM-4 four-circle automated diffractometer (KUMA DIFFRACTION, Cu-Kα radiation, λ = 1.5418 Å, a graphite monochromator, θ/2θ scan mode, θ_{max} = 80.1°). The structure was solved by the direct method and a series of subsequent Fourier syntheses by the SHELX-86 program.[13] Absorption on crystal facing was applied by the SHELX-76 program.[14] The positions of hydrogen atoms in the $Pd(dddt)_2$ cations were determined by difference Fourier syntheses. The positions of all nonhydrogen atoms in the structure were refined by the full-matrix least-squares method in the anisotropic approximation, and those of hydrogen atoms were refined by the least-squares method in the isotropic approximation by the SHELX-93 program.[15] The final value of the R factor was 0.056.

Results and Discussion

The crystal structure of the $[Pd(dddt)_2]_2GaBr_4$ salt is layered: the layers of radical cations $Pd(dddt)_2$ alternate with the anionic layers in the direction of axis *c* of the unit cell (Fig. 1).

In the conducting layer, the $Pd(dddt)_2$ radical cations form dimeric stacks in the direction of axis *c* of the unit cell (see Fig. 1). The dimers are connected with one another by a short Pd...Pd contact 3.01 Å (the van der Waals radius of the palladium atom is 2.1 Å),[5] six shortened Pd...S contacts 3.677(1)—3.799(1) Å, and eight

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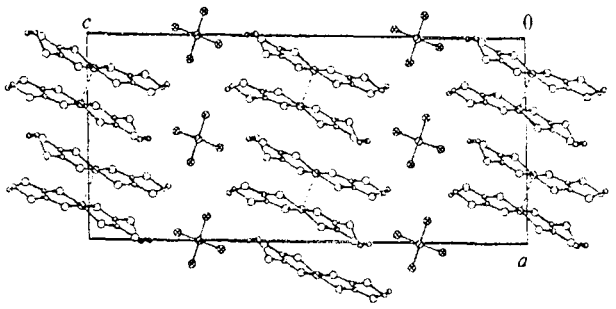

Fig. 1. Projection of the crystal structure of $[Pd(dddt)_2]_2GaBr_4$ on the *ac* plane of the unit cell.

shortened S...S distances 3.238(1)—3.676(1) Å (the van der Waals radius of the S atom is 1.85 Å).[5] The distance between mean planes of the radical cations in the dimers is equal to 3.440(2) Å, and that between the dimers is 4.189 Å. The $Pd(dddt)_2$ radical cations of adjacent dimers are shifted relative to one another by ~2.80 Å. Each radical cation possesses 18 shortened S...S contacts 3.536(1)—3.677(1) Å with radical cations of the adjacent stacks.

The bond lengths and bond angles in the radical cation are close to those observed previously[6,7] in $Pd(dddt)_2$ complexes with a formal charge of +0.5. The radical cation is nonplanar. In addition to the standard shift of the terminal C atoms from the mean plane of the radical cation, we observed a shift of the Pd atom from the plane of four S atoms connected to Pd (0.14 Å). The Pd atoms in the dimer are directed opposite to each other, which may indicate Pd...Pd interaction. The coordinates of atoms are presented in Table 1, and the bond lengths and bond angles are presented in Tables 2 and 3, respectively.

The $[GaBr_4]^-$ anion has the standard structure, and the Ga—Br bond lengths (2.315(1)—2.317(1) Å) and Br—Ga—Br bond angles (108.35(7)—110.98(4)°) are close to the parameters characteristic of tetrahedral anions.[8,9] A strong interaction between the anions and cations was observed in the $[Pd(dddt)_2]_2GaBr_4$ crystal. Each anion possesses two shortened Br...S contacts 3.661(1) Å (the van der Waals radius of the Br atom is 1.9 Å)[5] and two Br...H contacts 2.87(4) Å, which indicate the presence of C—H...Br hydrogen bonds.

The $[Pd(dddt)_2]_2GaBr_4$ crystals are isostructural to $[Pd(dddt)_2]_2FeCl_4$ salt,[10] but they are not isostructural to $(ET)_2GaCl_4$.[11] However, there are many common features in the structures of ET salts and $Pd(dddt)_2$ with GaX_4^- anions (X = Cl or Br): the layered packing, dimeric stacks in the cationic layer, and a great number of shortened interstack S...S contacts. A difference is observed in character of dimerization in stacks: in $Pd(dddt)_2$ salt dimerization is more pronounced due to the Pd...Pd interaction.

The electroconducting properties of $[Pd(dddt)_2]_2GaBr_4$ and $(ET)_2GaCl_4$ salts are close. The conductivity of $[Pd(dddt)_2]_2GaBr_4$ crystals measured in plane *ab* by the four-contact method is 0.25 Ohm^{-1} cm^{-1} at room temperature and decreases with an activation energy of 0.066 as the temperature decreases. The relatively low conductivity at room temperature and the semiconducting (nonmetallic) character of conductivity of $[Pd(dddt)_2]_2GaBr_4$ crystals are related to the substantial dimerization of the radical cations in stacks. The $Pd(dddt)_2$ and $Pt(dddt)_2$ salts with tetrahedral and linear anions ($[BF_4]^-$, $[FeCl_4]^-$, $[AuBr_4]^-$, and $[IBr_2]^-$), in which the $M(dddt)_2^+$ cations are dimerized,

Table 1. Coordinates of atoms ($\times 10^4$; for H atoms, $\times 10^3$) and isotropic thermal parameters (B_{iso}) in $[Pd(dddt)_2]_2GaBr_4$

Atom	*x*	*y*	*z*	$B_{iso} \cdot 10^3/Å^2$
Ga(1)	5000	6861(2)	2500	51(1)
Br(1)	4594(1)	4814(2)	3006(1)	87(1)
Br(2)	6154(1)	8918(2)	2681(1)	82(1)
Pd(1)	621(1)	945(1)	4839(1)	31(1)
S(1)	6518(1)	1020(2)	5185(1)	37(1)
S(2)	5748(1)	3436(2)	5273(1)	40(1)
S(3)	7307(1)	356(2)	4351(1)	36(1)
S(4)	6588(1)	4839(2)	4472(1)	37(1)
S(5)	5901(1)	−2255(2)	5923(1)	43(1)
S(6)	5128(1)	2613(2)	6016(1)	47(1)
S(7)	7735(1)	1185(3)	3572(1)	52(1)
S(8)	6923(1)	6038(2)	3704(1)	45(1)
C(1)	5978(3)	−340(8)	5578(1)	33(1)
C(2)	5642(3)	1671(8)	5619(1)	33(1)
C(3)	7301(3)	2095(9)	3991(1)	34(1)
C(4)	6987(3)	4113(8)	4046(1)	33(1)
C(5)	4920(4)	−1520(10)	6147(2)	47(1)
C(6)	4974(4)	524(11)	6342(2)	54(2)
C(7)	7365(5)	3002(11)	3206(2)	58(2)
C(8)	7540(4)	5157(11)	3315(2)	55(2)
H(1)	431(5)	−173(10)	598(2)	57(19)
H(2)	481(6)	−224(13)	629(3)	86(27)
H(3)	536(4)	43(10)	6654(2)	50(18)
H(4)	432(3)	58(8)	645(1)	24(12)
H(5)	674(4)	334(9)	315(2)	34(14)
H(6)	778(6)	311(13)	296(2)	100(26)
H(7)	802(6)	562(14)	343(3)	100(29)
H(8)	748(8)	648(17)	312(4)	142(42)

Table 2. Bond lengths (*d*) in $[Pd(dddt)_2]_2GaBr_4$

Bond	*d*/Å	Bond	*d*/Å
Ga(1)—Br(1)	2.315(1)	Ga(1)—Br(1)*	2.315(1)
Ga(1)—Br(2)	2.317(1)	Ga(1)—Br(2)*	2.317(1)
Pd(1)—S(1)	2.291(1)	Pd(1)—S(2)	2.281(1)
Pd(1)—S(3)	2.284(1)	Pd(1)—S(4)	2.284(1)
S(1)—C(1)	1.686(5)	S(2)—C(2)	1.678(5)
S(3)—C(3)	1.690(5)	S(4)—C(4)	1.692(5)
S(5)—C(1)	1.739(5)	S(5)—C(5)	1.802(6)
S(6)—C(2)	1.730(5)	S(6)—C(6)	1.796(7)
S(7)—C(3)	1.733(5)	S(7)—C(7)	1.821(7)
S(8)—C(4)	1.733(5)	S(8)—C(8)	1.779(6)
C(1)—C(2)	1.425(7)	C(3)—C(4)	1.423(8)
C(5)—C(6)	1.500(10)	C(7)—C(8)	1.484(10)

* Symmetry operations for obtaining coordinates of equivalent atoms: $-x + 1, y, -z + 1/2$.

Table 3. Bond angles (ω) in $[Pd(dddt)_2]_2GaBr_4$

Angle	ω/deg
Br(1)—Ga(1)—Br(1)*	109.24(7)
Br(1)—Ga(1)—Br(2)	110.98(4)
Br(1)—Ga(1)—Br(2)*	108.35(4)
S(1)—Pd(1)—S(2)	87.84(5)
S(1)—Pd(1)—S(4)	174.31(5)
S(2)—Pd(1)—S(4)	90.62(5)
C(1)—S(1)—Pd(1)	104.3(2)
C(3)—S(3)—Pd(1)	104.5(2)
C(1)—S(5)—C(5)	100.6(3)
C(3)—S(7)—C(7)	103.9(3)
C(2)—C(1)—S(1)	121.2(4)
S(1)—C(1)—S(5)	114.4(3)
C(1)—C(2)—S(6)	126.1(4)
C(4)—C(3)—S(3)	121.3(3)
S(3)—C(3)—S(7)	113.4(3)
C(3)—C(4)—S(8)	126.5(3)
C(6)—C(5)—S(5)	113.4(4)
C(8)—C(7)—S(7)	112.9(4)
Br(1)—Ga(1)—Br(2)**	108.35(4)
Br(1)*—Ga(1)—Br(2)*	110.98(4)
Br(2)—Ga(1)—Br(2)*	108.94(7)
S(1)—Pd(1)—S(3)	92.68(5)
S(2)—Pd(1)—S(3)	171.24(5)
S(3)—Pd(1)—S(4)	88.01(5)
C(2)—S(2)—Pd(1)	104.6(2)
C(4)—S(4)—Pd(1)	104.7(2)
C(2)—S(6)—C(6)	107.8(3)
C(4)—S(8)—C(8)	105.4(3)
C(2)—C(1)—S(5)	124.3(4)
C(1)—C(2)—S(2)	121.3(4)
S(2)—C(2)—S(6)	112.6(3)
C(4)—C(3)—S(7)	125.2(4)
C(3)—C(4)—S(4)	121.0(4)
S(4)—C(4)—S(8)	112.4(3)
C(5)—C(6)—S(6)	113.7(4)
C(7)—C(8)—S(8)	113.9(5)

* Symmetry operations for obtaining coordinates of equivalent atoms: $-x + 1, y, -z + 1/2$. ** $-x + 3/2, -y + 1/2, -z + 1$.

also exhibit a semiconducting character of electroconductivity,[3,10] whereas the $[Ni(dddt)_2]_3(AuBr_2)_2$ and $[Pd(dddt)_2]Ag_{1.54}Br_{3.50}$ salts, in which dimerization in stacks is absent, are molecular metals.[6,12]

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