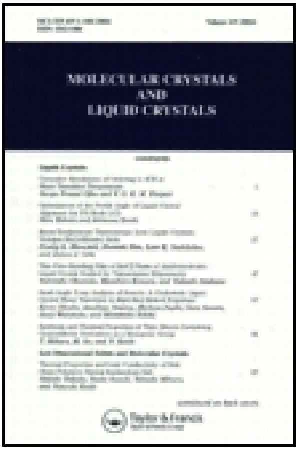

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Conductivity of Radical-Cation Salts of TTP Series Donors under High Pressure

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Version of record first published: 24 Sep 2006.

To cite this article: Tadashi Kawamoto , Takehiko Mori , Yohji Misaki , Kazuya Kawakami , Hideki Fujiwara , Tokio Yamabe , Hatsumi Mori & Shoji Tanaka (1996): Conductivity of Radical-Cation Salts of TTP Series Donors under High Pressure, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 284:1, 259-270

To link to this article: http://dx.doi.org/10.1080/10587259608037928

Mol. Cryst. Liq. Cryst., 1996, Vol. 284, pp. 259–270
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CONDUCTIVITY OF RADICAL-CATION SALTS OF TTP SERIES DONORS UNDER HIGH PRESSURE

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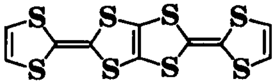
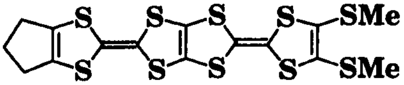
Abstract Anomalous conducting behavior in TTP series salts, particularly $(CPTM\text{-}TTP)_4PF_6$, where CPTM-TTP is 2-(4,5-cyclopenteno-1,3-dithiol-2-ylidene)-5-(4,5-dimethylthio-1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene, has been investigated in detail. This charge-transfer salt shows resistivity jumps around 100K, but is still metallic at low temperatures. These jumps are suppressed under applied pressures. Below 30K several sudden drops of resistivity like superconducting transitions are observed, but are not affected by magnetic fields. This anomalous behavior is discussed in view of hysteretic transitions between two metallic phases.

INTRODUCTION

Bis-fused tetrathiafulvalene, 2,5-bis(1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene (BDT-TTP, see below) and its derivatives (TTP (tetrathiapenetalene) series donors) are of considerable interest as a donor component for organic metals because several of them



BDT-TTP



CPTM-TTP

have afforded charge-transfer salts showing metallic conducting property down to low temperatures (≤4.2K).[1~3] In particular, we have recently found CPTM-TTP (2-(4,5-cyclopenteno-1,3-dithiol-2-ylidene)-5-(4,5-dimethylthio-1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene) (see above) forms several highly conducting salts.[4] A representative salt, $(CPTM\text{-}TTP)_4PF_6$ has the ß-type donor arrangement (Figure 1(a)), but shows complicated conducting behavior; the resistivity undergoes *upward* jumps at around 100 K, but furthermore exhibits *downward* jumps between 30K and 4K. Because we suspected that the latter might be associated with a superconducting transition, and also because (upward) resistivity jumps have been frequently observed in other TTP sereis salts, we have carried out somewhat detailed investigation of its resistivity, including measurements under applied pressures and under magnetic fields. The conclusion is negative about the superconductivity.

In the present paper, we first report the tight-binding energy band calculation, in order to explain the background of electronic structure of this compound, and second describe the conductivity measurements under various conditions. Finally we propose a model which explains the anomalous behavior of the conductivity. The model is based on hysteretic transitions between two metallic phases. This model is generally applicable to the salts of BDT-TTP derivatives.

EXPERIMENTAL

Single crystals of $(CPTM\text{-}TTP)_4PF_6$ were electrochemically grown in chlorobenzene or 1,2-dichloroethane in the presence of the donor[4] and tetrabutylammonium hexafluorophosphate. The crystals were elongated thin plates with typical dimensions, 1.4x0.1x 0.05 mm^3. Electrical resistance was measured by the four-terminal method using low-frequency ac current (usually 10 μA). Resistance under applied pressures was measured by means of the clamp-cell technique. The values of the pressure was corrected to the low-temperature values. In order to apply moderate pressure, the samples were only coated by *Apiezon grease N*; this method is reported to equivalently afford a pressure in the order of a few hundred bars at low temperatures.[5] The electronic structure and the Fermi surface were calculated on the basis of the extended Hückel molecular orbital calculation and the tight-binding method.[6]

RESULTS

Donor arrangement of $(CPTM\text{-}TTP)_4PF_6$ is depicted in Figure 1(a).[7] The conducting sheet spreads in the *ac* plane, and is sandwitched by the anion layers along the *b* direction. There are two crystallographically independent donor molecules, and one unit cell contains four donor molecules. The donors are stacked along the $[10\bar{1}]$ direction, and four donors make one repeating period along this stacking direction. Because there is a stacking structure, this donor arrangement can be basically classified as the ß-type.[8] Table 1 lists the intermolecular overlap integrals S of the HOMO of the adjacent molecules, together with the angle of the intermolecular vector from the molecular plane ϕ, and the slip distance along the molecular long axis D.[6] Although the quatemerization along the stacking direction (the difference between p1, p2, and p3) is very weak, there are considerable interactions along the transverse q directions. As a result, the tight-binding band structure calculated from these overlap integrals has considerable dispersions along both k_a and k_c directions (Figure 1(b)), and the Fermi surface has a elliptical cross section just like ß-$(BEDT\text{-}TTF)_2I_3$ (BEDT-TTF: bis(ethylenedithio) tetrathiafulvalene).[8] It is noteworthy that the present salt has a 4:1 composition, in contrast to the 2:1 composition of ß-$(BEDT\text{-}TTF)_2I_3$. One unit cell, however, contains four donors in the present salt, whereas two in ß-$(BEDT\text{-}TTF)_2I_3$; there are four and two energy bands, respectively. Therefore in both cases the uppermost band is half-filled, giving rise to the similar elliptical Fermi surface.

Figure 2 shows the temperature dependence of the electrical resistivity at ambient pressure. At room temperature the resistivity in the conducting *ac* plane ($\rho_{//}$) is typically 4 mΩcm. In the cooling run $\rho_{//}$ is metal-like down to about 100K, but undergoes a few jumps, becoming more than two order larger than the room-temperature value. It is, however, not semiconductive even at liquid helium temperatures. Discontinuous resistance drops that are observed under applied pressures (*vide infra*) are not observed

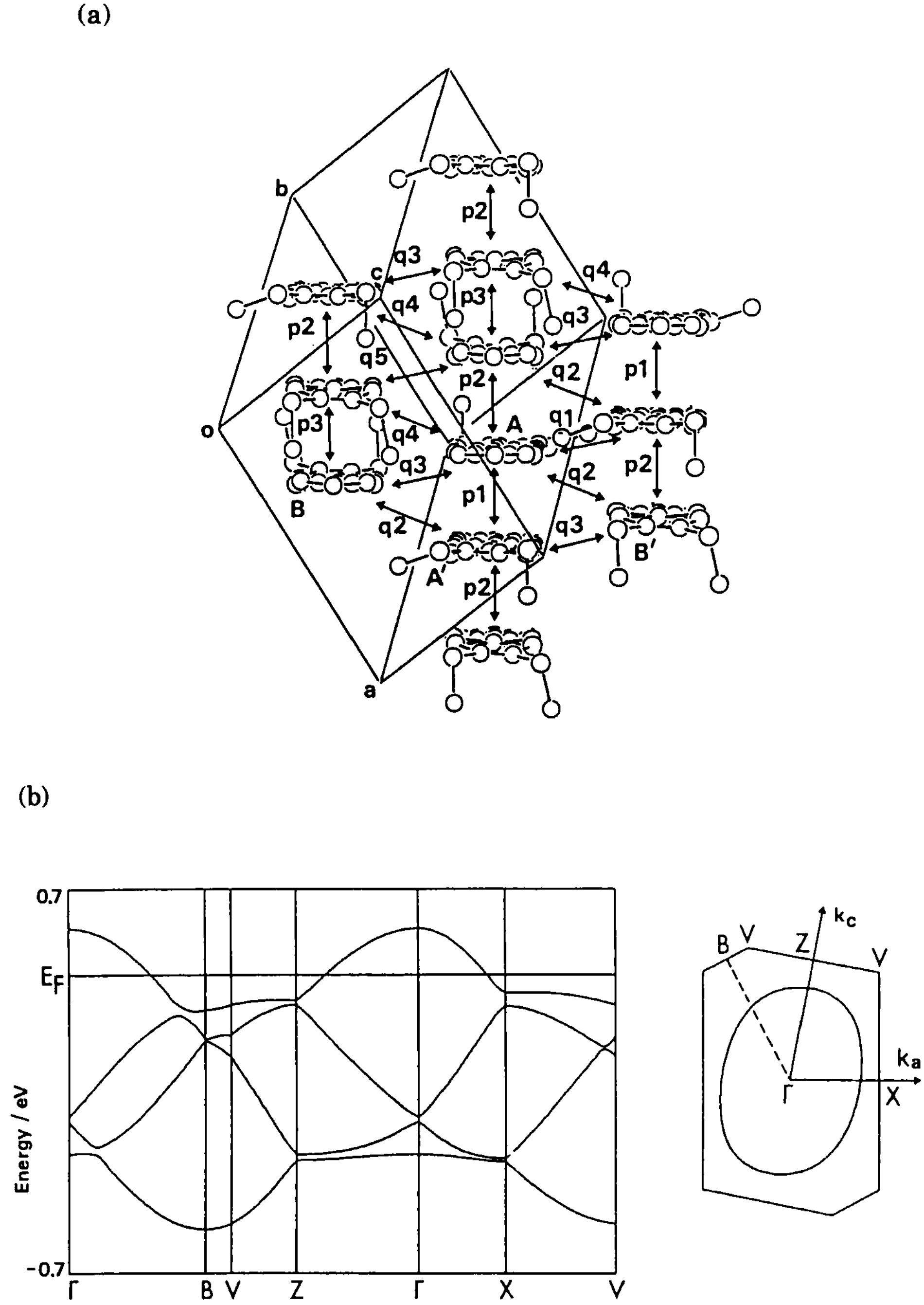


FIGURE 1 (a) Donor arrangement of $(\mathrm{CPTM\text{-}TTP})_4\mathrm{PF}_6$, viewed along the donor long axis. (b) Tight-binding energy band structure and Fermi surface of $(\mathrm{CPTM\text{-}TTP})_4\mathrm{PF}_6$.

TABLE 1 Intermolecular overlap integrals of the HOMO, S, and the parameters ϕ and D, which define the orientation of neighboring molecules (see text) in (CPTM-TTP)$_4$PF$_6$.

Direction	$S(\times 10^{-3})$	ϕ (°)	D(Å)
p1	21.3	89	1.56
p2	19.9	88	1.60
p3	19.7	88	4.75
q1	1.3	13	4.60
q2	-7.9	21	3.00
q3	0.2	12	1.43
q4	-6.5	20	3.23
q5	-0.2	13	1.40

at ambient pressure. In the heating run $\rho_{//}$ behaves like a metal at He temperatures, but in the region of 50-250K, it gradually goes back to the original room-temperature value.

When the current is applied perpendicularly to the conducting plane, the resistivity ($\rho_{\perp}$) is metal-like down to about 1.5K, and the resistance upward jumps are not prominent. Small low-temperature resistance drops (*vide infra*) are usually observed

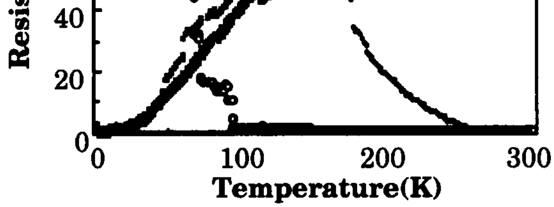


FIGURE 2 Temperature dependence of electrical resistance at ambient pressure; ⊥ refers to a current applied perpendicular to the *ac* plane, and // refers to a current applied parallel to the *ac* plane.

along this direction even at ambient pressure.

Under a slight pressure applied by *Apiezon N*, the upward jumps of $\rho_{//}$ still remains (Figure 3), but there appears anomalously steep metallic behavior below 50 K, accompanied by a few small *downward* jumps (Figure 4). The resistance below 50K shows practically no hysteresis, and the same small anomalies are observed both in the cooling and heating runs. In the heating run, $\rho_{//}$ makes a peak at about 100 K, whose magnitude is five times as large as the room-temperature value, but again goes down to the original room-temperature value. Since the original room-temperature resistivity is recovered, this anomalous peak could not be attributed to some kind of irreversible process like formation of sample cracks.

Under applied pressures above 1 kbar, $\rho_{//}$ shows metallic behavior in the whole temperature range (Figure 3). Moreover $\rho_{//}$ exhibits large drops like superconducting transitions near 10K (Figure 4). The magnitude of these resistance drops are, however, largely dependent on the sample; typical sample shows several steps of small drops or shoulders at usually 8K, 13K, 18K, and 28K. Only one sample, Sample A in Figure 4, exhibited a large drop, where the resistance decreased to less than half of the "normal" value.

In order to determine whether these resistance drops are related to superconductivity or not, the resistance ($\rho_{\perp}$ at ambient pressure and $\rho_{//}$ with *Apiezon N*) is measured under magnetic fields (up to 9 T, perpendicular to the conducting plane). The magnetoresistance is, however, very small (<3% even at 9 T, 1.5K), and the resistance drops are not affected by the magnetic fields. Therefore these anomalies are not attributable to superconductivity (Figure 5).

The above resistivity measurements were repeated for a considerable number (several tens) of samples, and the reproducibility was sufficient, except the magnitudes of the low-temperature resistivity drops. Cooling speed dependence of the resistivity was practically not observed.

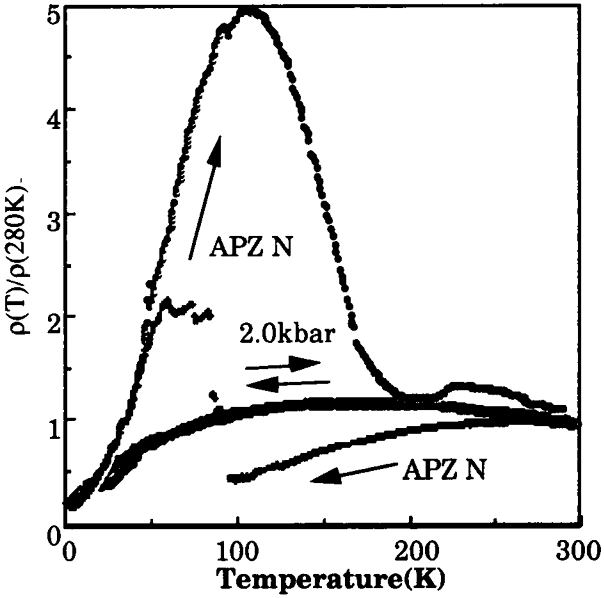


FIGURE 3 Electrical resistivity under applied pressures, normalized at 280 K.

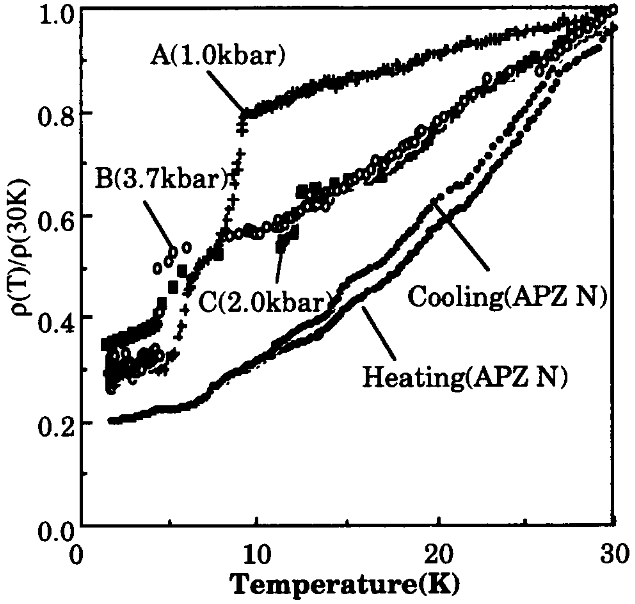


FIGURE 4 Low-temperature relative electrical resistivity, ρ(T)/ρ(30K) under applied pressures for different four samples.

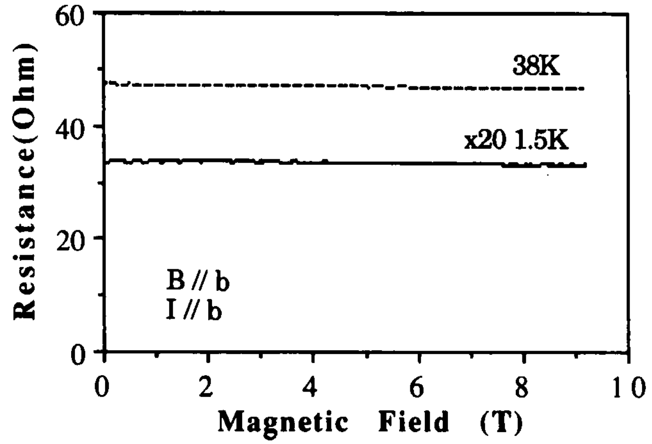


FIGURE 5 Electrical resistance $\rho_{\perp}$ under magnetic field applied perpendicularly to the ac plane.

DISCUSSION

In order to explain the anomalous behavior of the resistivity, we shall propose a phenomenological model, which are based on existence of two metallic phases, M1 and M2. First we deal with $\rho_{//}$ under a slight applied pressure (*Apiezon N*). M1 is assumed to be the stable phase at high temperatures, and M2 is the stable phase at low temperatures (Figure 6(a)). The crossover of the free energy occurs at around 100 K, and this temperature is supposed to be essentially independent of the pressure. In addition, resistance of M1 is smaller than that of M2, but this relation is inverted below 50K (Figure 6(b)). The transition between M1 and M2 is supposed to be considerably slow.

When the sample is cooled, the M1 phase gradually changes to the M2 phase below 100K, accompanied by the *upward* resistivity jumps, but the same process gives rise to the *downward* resistance drops below 50 K, because the resistivity of M2 is smaller than that of M1 at these temperatures. This is, we think, the origin of anomalous resistance drops like superconducting transitions at low temperatures. In the heating run, the M2 phase gradually goes back to the M1 phase above 100K, making a

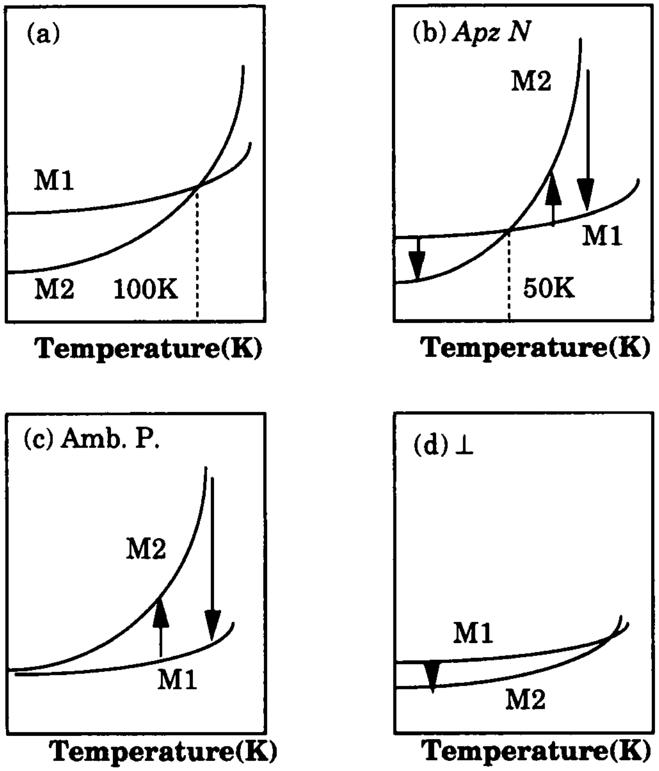


FIGURE 6 Schematic representation of (a) free energy and (b)-(d) resistivity of the M1 and the M2 phases. (a) The free energy crosses around 100 K. (b) With *Apiezon N* coated, the resistivity crosses around 50 K. (c) At ambient pressure, M2 is always more resistive than M1. (d) As for $\rho_{\perp}$, M2 is not much larger than M1 at high temperatures.

resistance peak at this temperature. Because the resistance jumps step by step, we have to assume that the M1 and the M2 phases coexist with making domains.

At ambient pressure, M2 has higher resistivity in the whole temperature region (Figure 6(c)), and the low-temperature drops do not occur. On the contrary under high pressures M2 always shows lower resistivity below 100K, resulting in no *upward* jumps.

When the current is applied perpendicularly to the conducting plane, the difference of the resistivity between M1 and M2 is supposed to be small at high temperatures

(Figure 6(d)). Then the resistivity does not jump at high temperatures, but the resistance drops at low temperatures.

The *upward* resistance jumps have been very frequently observed in the salts of BDT-TTP derivatives.[1] For example, the resistivity of $(TMEO\text{-}TTP)_2Au(CN)_2$,[2] where TMEO-TTP is 2-(4,5-dimethylthio-1,3-dithiol-2-ylidene)-5-(4,5-ethylenedioxy-1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene), shows a few jumps near 100 K, but exhibits a steep metallic behavior at low temperatures, and in the heating run the resistivity makes a broad peak at around 150 K. This behavior has a close resemblance to the ambient-pressure behavior of the present salt, and can be explained by Figure 6(c). $(BDT\text{-}TTP)_2ClO_4$ also exhibits a similar behavior.[3] On the contrary to these cases, in the present salt the M2 phase happens to have lower resistivity than the M1 phase at low temperatures under applied pressures, resulting in anomalous *downward* drops of the resistivity.

Because $(TMEO\text{-}TTP)_2Au(CN)_2$ has open Fermi surface, the M2 phase has been attributed to a semimetallic phase caused by the imperfect nesting of the Fermi surface.[2] The Fermi surface of the present salt is closed (Figure 1(b)), and a similar semimetallic phase is not likely. However, even ß-$(BEDT\text{-}TTF)_2I_3$, which has a similar Fermi surface to the present salt,[8] suffers from incommensurate lattice modulation, resulting in the reduction of the superconducting transition temperature from 8K to 1.5 K,[9] though the resistivity is not clearly influenced by the modulation. Therefore it is quite likely that the present salt has a similar lattice modulation, which causes the M1 to M2 transition. The modulation of ß-$(BEDT\text{-}TTF)_2I_3$ is associated with the vibration of the terminal ethylene groups of BEDT-TTF. The present salt has methylthio groups, which show even larger thermal vibration.[4] Then we suspect that the freezing of vibration of the methylthio groups, possibly with some lattice modulation, may be associated with the M1 to M2 transition. It should be pointed out that TMEO-TTP has also the methylthio groups.

The temperature dependence of the resistivity in the M2 phase is anomalously large. In particular with *Apiezon N*, $\rho_{//}$ drops more than 20 times from 100 K to 1.5 K (Figure 3). This suggests that there is quite large thermal vibrations which cause the scattering of conduction electrons. In other words, there exist low-energy phonons (or low Debye temperature), which are thermally excited even at low temperatures. It is likely that the soft thermal rotation of the methylthio groups is the origin of these soft phonons.

The salts of BDT-TTP derivatives generally have two-dimensional electronic structure, because the extended donor molecules prefer packings where the donors are arranged parallel to each other. Therefore such metal-insulator transitions as frequently occur in the TTF salts are not common in the BDT-TTP derivatives. However, some kind of structural instability still remains, where the low-temperature phase is not insulating but metallic (or semimetallic). The anomalous conducting behavior observed in the present salt can be regarded as a special case of this general tendency.

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Å^3, and Z=1. This salt is isostructural to the corresponding AsF_6 salt, (CPTM-TTP)$_4$$AsF_6$, reported in Ref. 4.

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