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Di(4,4′,5,5′-tetramethyl-2,2′-bi-1,3-diselenolyliden)ium Perrhenate, $C_{20}H_{24}Se_8^+.ReO_4^-$, $(TMTSF)_2ReO_4$. Detailed Superstructure at 120 K

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Abstract. $M_r = 1146\cdot3$, triclinic, space group $F\bar{1}$ ($P\bar{1}$ in conventional setting), $a = 14\cdot295$ (3), $b = 15\cdot419$ (2), $c = 26\cdot649$ (3) Å, $\alpha = 83\cdot96$ (1), $\beta = 88\cdot75$ (1), $\gamma = 69\cdot39$ (1)°, $V = 5467$ (2) Å^3, $Z = 8$, $D_x = 2\cdot785$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1\cdot54184$ Å, $\mu = 21\cdot21$ mm^{-1}, $F(000) = 4184$, $T = 120$ K, final $R = 0\cdot052$, $wR = 0\cdot070$, for 4042 observed reflections. Unlike the room-temperature structure the ReO_4^- anions are ordered and, in addition, the anions as well as the TMTSF molecules are displaced relative to their positions in the average structure previously reported. Bond distances and angles in TMTSF are the same as in the average structure. The ReO_4^- ion is an almost perfect tetrahedron.

Introduction. $(TMTSF)_2ReO_4$ belongs to a series of compounds $(TMTSF)_2X$ ($X = PF_6$, AsF_6, TaF_6, ClO_4, ReO_4, NO_3 *etc.*) which have been intensively studied in recent years because of their unusual physical properties (*e.g.* superconductivity of some members around 1 K). The structure of $(TMTSF)_2ReO_4$ at 295 and 120 K has previously been determined (Rindorf, Soling & Thorup, 1982). At 295 K ReO_4^- is situated at a site of inversion symmetry leading to orientational disorder of this anion. At 120 K a doubling of all three axial lengths is accompanied by an ordering of the ReO_4^- ions. The quality and size of the crystal used did not allow inclusion of the weaker superstructure reflections, *i.e.* only the average structure at 120 K was determined. Our data suggested no further distortion of the low-temperature phase, and the metal–insulator transition at 182 K in this material was described accordingly (Jacobsen, Pedersen, Mortensen, Rindorf, Thorup, Torrance & Bechgaard, 1982). Further measurements, however, indicated some additional displacements of Re atoms as well as TMTSF molecules below the phase transition (Moret, Pouget, Comes & Bechgaard, 1982; Guy, Boebinger, Marseglia, Friend & Bechgaard, 1983). An improved model for the metal–insulator transition has recently been proposed (Bruinsma & Emery, 1983), a model which also accounts for the transition in the analogous sulfur compound $(TMTTF)_2ReO_4$ taking place at approximately 160 K (Parkin, Mayerle & Engler, 1983).

Therefore, this redetermination using a better quality crystal now available in order to reveal the full superstructure at 120 K was initiated.

Experimental. Crystals of good quality prepared as described earlier (Bechgaard, Carneiro, Rasmussen, Olsen, Rindorf, Jacobsen, Pedersen & Scott, 1981) supplied by Dr K. Bechgaard. Crystal 0·05 × 0·1 × 0·2 mm. Enraf–Nonius CAD-4 diffractometer. Unit cell: least squares on 25 reflections, 24 < θ < 34°.

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ω–2θ scan ($\Delta = 1{\cdot}00° + 0{\cdot}14°\tan\theta$), graphite-monochromated Cu $K\alpha$ radiation, 4772 unique reflections ($h \le 17$, $k \le |18|$, $l \le |32|$, $h + k = 2n$, $k + l = 2n$), $0 < 2\theta < 70°$, max. $\sin\theta/\lambda = 0{\cdot}6094$ Å^{-1}. 3 standards, for intensity and orientation, every 200 reflections: no fading observed. Correction for absorption, transmission 0·1370 to 0·4171. 4042 reflections with $I > 3\sigma(I)$. Calculations by *SHELX* (Sheldrick, 1976). Neutral-atom scattering factors and anomalous-dispersion corrections for Se and Re from *International Tables for X-ray Crystallography* (1974). *ORTEP* (Johnson, 1965) was used for the illustrations.

The starting point of the crystal structure refinement was our previously determined average structure, ignoring O atoms of the ReO_4^- ions. A doubling of all three axial lengths to the present values leads to a face-centered triclinic cell, space group $F\bar{1}$. To facilitate comparisons with the room temperature as well as the average 120 K structure we have chosen to use this unconventional setting in our calculations and descriptions. It should be noted that we also had to shift the origin from a Re atom to a point midway between two Re atoms owing to the removal of the imposed inversion symmetry of ReO_4^- in the average structure. Subsequent difference electron density calculations confirmed the expected ordered arrangement of ReO_4^- ions. In the final stages some satisfactory methyl H positions were revealed. Since not all H positions could be found, however, none of them were included in the refinements. All Re, O, Se and C atoms were refined with anisotropic thermal parameters, 298 parameters in total. Full-matrix minimization of $\sum w(|F_o| - |F_c|)^2$, $w = 1/[\sigma(F_o)^2 + 0{\cdot}0004F_o^2]$. Max. Δ/σ 0·057, av. 0·008.

The superstructure reflections, *i.e.* the reflections with h odd, amount to 2349 unique reflections of which 1724 with $I > 3\sigma(I)$ yield $R = 0{\cdot}051$ (only scale factor refined). Calculation of the average structure based on the reflections with h even gave, within the experimental error, the same result as we found earlier (Rindorf *et al.*, 1982).

Discussion. Final positional and thermal parameters are given in Table 1.*

Table 1. *Fractional coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* (Å$^2 \times 10^3$)

$$U_{eq} = \tfrac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Re	2550·4 (3)	39·6 (2)	−20·2 (1)	15·6 (1)
O(1)	2614 (6)	881 (4)	329 (2)	29 (3)
O(2)	1908 (6)	569 (5)	−567 (3)	34 (3)
O(3)	1958 (6)	−614 (5)	312 (3)	42 (3)
O(4)	3734 (6)	−677 (5)	−167 (3)	37 (3)
Se(11)	4068·0 (7)	1692·2 (6)	3102·0 (3)	13·5 (3)
Se(21)	3311·7 (7)	3746·5 (6)	2569·1 (3)	13·0 (3)
Se(31)	3603·3 (7)	2925·0 (6)	1428·0 (3)	12·5 (3)
Se(41)	4367·6 (7)	862·4 (6)	1956·2 (3)	12·9 (3)
C(11)	3772 (7)	2475 (5)	2487 (3)	15 (3)
C(21)	3697 (7)	2694 (6)	3517 (3)	17 (3)
C(31)	3383 (7)	3562 (6)	3287 (3)	15 (3)
C(41)	3810 (7)	2403 (5)	4067 (3)	15 (3)
C(51)	3038 (7)	4449 (6)	3539 (3)	16 (3)
C(61)	3881 (7)	2138 (6)	2036 (3)	16 (3)
C(71)	4011 (7)	1928 (6)	1013 (3)	14 (3)
C(81)	4345 (7)	1044 (6)	1245 (3)	15 (3)
C(91)	3944 (8)	2207 (6)	456 (3)	21 (3)
C(01)	4698 (8)	180 (6)	973 (3)	21 (3)
Se(12)	4025·4 (7)	6679·4 (6)	3050·0 (3)	13·9 (3)
Se(22)	3271·0 (7)	8752·9 (6)	2535·7 (3)	14·1 (3)
Se(32)	3527·5 (7)	7946·1 (6)	1372·5 (3)	13·8 (3)
Se(42)	4351·9 (7)	5875·4 (6)	1899·2 (3)	13·6 (3)
C(12)	3741 (7)	7477 (6)	2437 (3)	16 (3)
C(22)	3662 (7)	7672 (6)	3476 (3)	17 (3)
C(32)	3346 (7)	8541 (6)	3251 (3)	15 (3)
C(42)	3771 (7)	7356 (6)	4029 (3)	18 (3)
C(52)	3017 (7)	9425 (6)	3515 (3)	19 (3)
C(62)	3857 (7)	7161 (6)	1988 (3)	15 (3)
C(72)	3963 (7)	6947 (6)	957 (3)	18 (3)
C(82)	4329 (7)	6069 (6)	1179 (3)	16 (3)
C(92)	3895 (8)	7247 (6)	400 (3)	27 (4)
C(02)	4740 (8)	5201 (6)	914 (3)	22 (3)

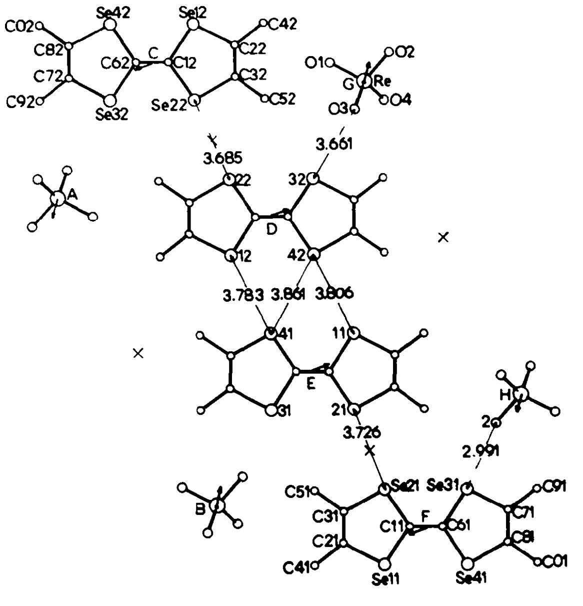

Fig. 1. View of $(TMTSF)_2ReO_4$ along the a axis with atom labels as in Tables 1 and 2. Intermolecular Se–Se and Se–O distances in Å; e.s.d.'s for Se–Se 0·002 and for Se–O 0·007 Å. The directions of the displacements are marked with arrows from the Re atoms and from the middle of the TMTSF molecules. Centers of symmetry are marked with a cross. Symmetry operations are given in Table 3.

Geometry of the constituents. In Fig. 1 is shown the numbering of the atoms. Every other TMTSF molecule has a short Se–O distance, 2·991 (7) Å, to an O atom in ReO_4^-; in these molecules all atom numbers terminate in '1' [henceforth TMTSF(1)]. The remaining TMTSF molecules have a longer distance, 3·661 (8) Å to an O atom and the atom numbers terminate in '2' [henceforth

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* Lists of structure factors, anisotropic thermal parameters and bond lengths and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39311 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

TMTSF(2)]. Distances and angles in both types of TMTSF molecules are alike and within experimental error the same as those reported for the average structure (Rindorf *et al.*, 1982); the actual values have been deposited. The ReO_4^- ion has an almost perfect tetrahedral shape; bonds and angles are given in Table 2.

Packing. In Fig. 2 is shown a side view of the TMTSF stack and the ReO_4^- array with interstack Se–Se distances and interplanar distances indicated. The TMTSF stack consists of two molecules of TMTSF(1) alternating with two molecules of TMTSF(2). The angles between the *a* axis and the lines perpendicular to the best plane through TMTSF(1) and to that through TMTSF(2) are 0·87 (1) and 0·99 (1)°, respectively, while the angle between the two perpendiculars is 0·81 (1)°. The distance between two TMTSF molecules is defined as the perpendicular distance from the centroid of the atoms defining the plane through one molecule to the plane through the next molecule. As the TMTSF(1) is not strictly parallel to TMTSF(2), the distance from TMTSF(1) to TMTSF(2), 3·59 Å, is not the same as the distance from TMTSF(2) to TMTSF(1), 3·61 Å. In Fig. 2 is given the average, 3·60 (1) Å, the same as the distance between two TMTSF(2) molecules. Between two TMTSF(1) molecules the distance is 3·50 (1) Å.

Fig. 1 shows a section of the structure projected along the stacking direction with the interstack Se–Se distances as well as the shortest Se–O distances.

The coordinates of the Re atom show that the phase transition of $(TMTSF)_2ReO_4$ involves not simply an ordering of the O atoms. In addition, the position of the Re atom is shifted, 7·20 (4) $\times 10^{-2}$ Å along the *a* axis, 6·11 (3) $\times 10^{-2}$ Å along the *b* axis and −5·38 (3) $\times 10^{-2}$ Å along the *c* axis, in total 0·1185 (1) Å from the point (0·25, 0·0, 0·0). Only rigid displacements of TMTSF molecules are observed since the geometry of TMTSF is unchanged relative to the average structure, as mentioned above. The displacements are mainly translations, which for TMTSF(1) amount to 2·2 (2) $\times 10^{-2}$, −0·2 (2) $\times 10^{-2}$, and 6·2 (2) $\times 10^{-2}$ Å along the *a*, *b* and *c* axes, respectively, in total 0·068 (5) Å from the position in the average structure. TMTSF(2) is displaced by the same distances in the opposite directions. The directions of the displacements from the average structure are marked with arrows in Figs. 1 and 2.

Table 2. *Bond lengths* (Å) *and angles* (°) *in the* ReO_4^- *anion*

O(1)–Re	1·702 (7)	O(1)–Re–O(2)	108·3 (3)
O(2)–Re	1·707 (8)	O(1)–Re–O(3)	109·6 (4)
O(3)–Re	1·702 (9)	O(1)–Re–O(4)	110·6 (4)
O(4)–Re	1·727 (7)	O(2)–Re–O(3)	110·4 (4)
		O(2)–Re–O(4)	108·9 (4)
		O(3)–Re–O(4)	109·0 (4)

Table 3. *Symmetry operations* (*Figs.* 1 *and* 2)

A: (x, y, z)
B: $(-x, 1-y, -z)$
C: $(x, y-1, z)$
D: $(0{\cdot}5-x, 1-y, 0{\cdot}5-z)$
E: $(x-0{\cdot}5, y+0{\cdot}5, z)$
F: $(-x, 1{\cdot}5-y, 0{\cdot}5-z)$
G: $(0{\cdot}5-x, -y, 0{\cdot}5-z)$
H: $(x-0{\cdot}5, y+1, z+0{\cdot}5)$
J: $(1-x, 0{\cdot}5-y, 0{\cdot}5-z)$
K: $(x, 0{\cdot}5+y, 0{\cdot}5+z)$
L: $(1{\cdot}5-x, 1-y, 0{\cdot}5-z)$
M: $(x+0{\cdot}5, y-0{\cdot}5, z)$
N: $(1+x, y, z)$
P: $(1-x, -y, -z)$

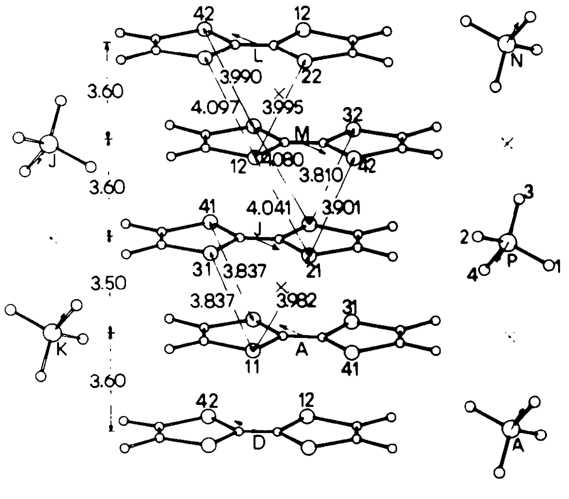

Fig. 2. Side view of stacks (tilted 20°). Intermolecular Se–Se distances in Å; e.s.d.'s 0·002 Å. The directions of the displacements are marked with arrows from the Re atoms and from the TMTSF molecules. Centers of symmetry are marked with a cross. Symmetry operations are given in Table 3.

These results are in good accord with the displacements given by Moret *et al.* (1983), which were based on a few crude measurements, and thus support their conclusions with respect to the nature of the metal–insulator transition.

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