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Synthesis and structure of the neutral π-donor Me_3TTF-COOH and of its decarboxylated cation radical salt $[Me_3TTF^{\bullet}+][Re_6Se_5Cl_9^-]$

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Summary – Lithiation of Me_3TTF and subsequent reaction with CO_2 afforded the carboxylic acid Me_3TTF-COOH. The structure of the neutral π-donor was determined by X-ray diffraction, revealing the common hydrogen-bonded dimers pattern. Single crystals of the cation radical salt with the anion $Re_6Se_5Cl_9^-$ were obtained by electrocrystallization. The electrodecarboxylation or Kolbe reaction of the carboxylic acid, to form unsubstituted trimethyltetrathiafulvalene, is demonstrated by an analysis of the crystal structure of this cation radical salt.

tetrathiafulvalene / carboxylic acid / Kolbe reaction / rhenium cluster

Résumé – Synthèse et structure du donneur-π neutre Me_3TTF-COOH et de son sel de cation radical décarboxylé $[Me_3TTF^{\bullet+}][Re_6Se_5Cl_9^-]$. *L'acide carboxylique Me_3TTF-COOH est obtenu par lithiation du triméthyltétrathiafulvalène (Me_3TTF) et réaction avec CO_2. La structure de ce donneur π met en évidence l'association en dimères par liaison hydrogène. L'électrocristallisation de cet acide en présence de l'anion $Re_6Se_5Cl_9^-$ conduit au sel, $[Me_3TTF^{\bullet+}][Re_6Se_5Cl_9^-]$, ce qui démontre un processus d'électrodécarboxylation (réaction de Kolbe) de l'acide carboxylique Me_3TTF-COOH.*

tétrathiafulvalène / acide carboxylique / réaction de Kolbe / cluster de rhénium

Introduction

In the development of new conducting and superconducting organic cation radical salts, much effort has been devoted to the increase of solid-state intermolecular interactions by using non-planar donors [1] or by the introduction of heteroatoms such as S or Se in extended conjugated molecules [2], thus leading to structures of higher dimensionality. In addition, hydrogen bonds have been shown to play an important role in determining the structure of cation radical salts of TTF derivatives [3]. In this respect, a variety of functionalized TTF, containing oxygen-based functional groups (alcohols, ketones, esters) [4] as well as amines [5] have been synthesized for their potential to create hydrogen-bonded networks. In particular, since carboxylic acids are known to form hydrogen-bonded solid-state associations, the title donor Me_3TTF-COOH seems to be a good candidate for this. Moreover, the oxidation of the carboxylate anion $Me_3TTF\text{-}COO^-$ might lead to the zwitterionic radical $[Me_3TTF\text{-}COO^-]^{\bullet+}$ [6], thus giving access to a new class of organic conductors with a self-supported counter-anion. However, electrochemical studies have shown that anodic decarboxylation of the TTF-COOH/$TTF\text{-}COO^-$ system occurs in acetonitrile perchlorate medium [7].

We therefore report here an improved synthesis and the X-ray crystal structure of the π-donor Me_3TTF-COOH. The decarboxylation of the donor is demonstrated by the synthesis and the structural characterization of a cation radical salt with the rhenium cluster anion $Re_6Se_5Cl_9^-$.

Synthesis and crystal structure of the neutral donor Me_3TTF-COOH

Several tetrathiafulvalenes bearing a carboxylic acid functionality, which are precursors of further functionalized TTF, have been described [8], in particular by Green [9], who first prepared carboxytetrathiafulvalene from monolithio-TTF. This synthesis has recently been improved by Garin [10]. Following our study of functionalized trimethyltetrathiafulvalene derivatives [4a], we prepared the carboxylic acid Me_3TTF-COOH from the trimethyltetrathiafulvalene [4a] by lithiation and reaction with dry gaseous carbon dioxide (scheme 1) [8c]. The carboxylate $Me_3TTF\text{-}COO^-$ was isolated by filtration and converted to Me_3TTF-COOH by acidification of the suspension of the carboxylate in water by 1 M HCl. The carboxylic acid was then recrystallized from acetonitrile, affording red crystals. The

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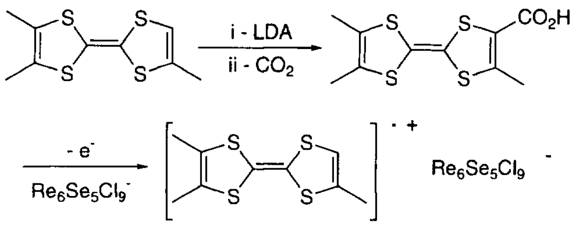

Scheme 1

electrochemical properties of this donor were determined by cyclic voltammetry at a platinum electrode in *N*,*N*-dimethylformamide. The cyclic voltammogram exhibits two well-defined oxidation waves at +0.43 and +0.66 V vs SCE to be compared with those for Me$_4$TTF [11] (+0.24 and +0.62 V vs SCE). The higher oxidation potential values result from the presence of the electron-withdrawing carboxylic substituent.

The structure of Me$_3$TTF-COOH was determined by single crystal X-ray diffraction. An Ortep drawing of the molecular structure of the carboxylic acid is given in figure 1. The donor molecules are quasi-planar and associated within hydrogen-bonded pairs (fig 2). The geometric features of the C=O···H–O bond (table I) are as expected for carboxylic acid derivatives [12] and impose the creation of a planar eight-membered ring including all atoms from O1 to H2, with its centroid located on an inversion center. This strong hydrogen bond alters the electronic structure of the H-bond donor and acceptor involved.

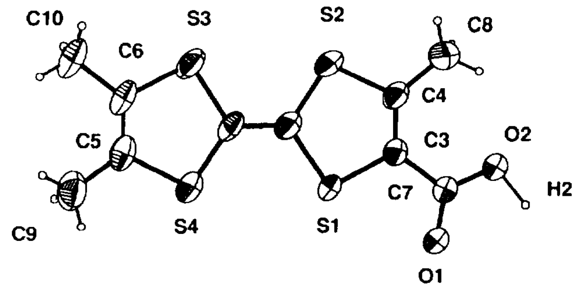

Fig 1. Ortep diagrams drawn at 50% enclosure ellipsoids for Me$_3$TTF-COOH showing atomic numbering.

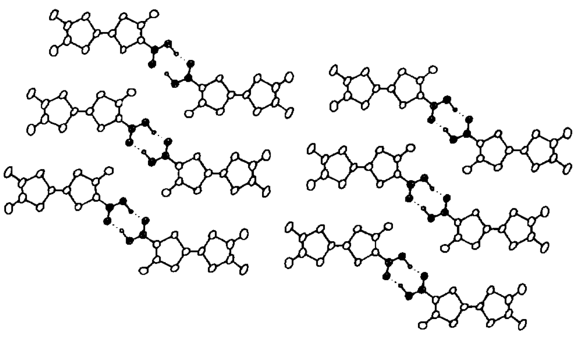

Fig 2. Packing diagrams of Me$_3$TTF-COOH showing the hydrogen-bonding schemes. For clarity, only the hydrogen atom H2 was drawn.

Table I. Hydrogen bonding schemes in Me$_3$TTF-COOH.

	O(C)···O (Å)	*H···O (Å)*	*O(C)-H···O (°)*
C8-H8b···O1	3.059(1)	2.570(1)	112.31(2)
O2-H2···O1	2.623(1)	1.618(1)	135.89(1)

We thus observe in Me$_3$TTF-COOH a lengthening of the acceptor C=O bond length, C7–O1 = 1.255(1) Å, to be compared with 1.214 Å for an unperturbed C(sp^2) = O bond [12], and a shortening of the donor C–OH bond length, C7–O2 = 1.281(1) Å, to be compared with 1.308 Å for a C(sp^2)–O bond [12]. In addition to this strong O–H···O hydrogen bond, there is a weaker C–H···O hydrogen bond [14] (table I) between the hydrogen atom H8b of a methyl group of a donor and the oxygen atom O1 of a neighboring dimer, which leads to the formation of an infinite chain of dimers. The chains are coplanar (fig 2) and no π–π interaction [14] is observed between layers, as exemplified by the lack of any short S···S contacts. Finally, on the basis of an Etter H-bond analysis [15], we assigned the first level graph set of this hydrogen-bonded network as $N_1 = C(6)R_2^2(8)$. The first motif C(6) represents the infinite chain of repeat unit six and the second, $R_2^2(8)$, the intermolecular eight-membered ring.

Cation radical salts

In order to prepare cation radical salts of the donor Me$_3$TTF-COOH, electrocrystallization experiments were conducted with different anions, including ClO_4^-, PF_6^- and larger molecular metal cluster anions such as $Re_6Q_5Cl_9^-$ and $Re_6Q_6Cl_8^{2-}$ (Q = S, Se). The chemistry of these chalcohalide octahedral rhenium cluster anions has been developed recently [16] and they have been incorporated into cation radical salts of different organic donors [3b, 17]. The mono- and dianions differ solely by the proportions of the disordered chalcogen and chlorine atoms in the eight face-capping inner ligand sites (L^i) surrounding the octahedral rhenium cluster. The intramolecular distances between the rhenium atoms and the apical chlorine atoms Re-Cl^a increase with and proved to be specific to the cluster anion charge [16c,d]. Single crystals of a cation radical salt with the monoanion $Re_6Se_5Cl_9^-$ were thus obtained and its structure was determined by X-ray diffraction, demonstrating the formulation of this salt as (Me$_3$TTF)(Re$_6$Se$_5$Cl$_9$).

The compound crystallizes in the triclinic system. There are two independent donor molecules and two independent cluster anions labeled A and B in the asymmetric unit (fig 3).

The analysis of the cluster inner ligand occupancy (μ, table II) and the Re-Cl^a distances (table III) for the cluster motif (see *Experimental section*) is in full agreement with the formulation $Re_6Se_5Cl_9^-$ for both anions A and B. Surprisingly, no peaks corresponding to the CO$_2$H functional group were found in the Fourier Difference map. Furthermore, the stoichiometry of one molecule of donor for one monovalent anion implies that the donors are fully oxidized. Therefore, it was concluded that the proper formulation of the

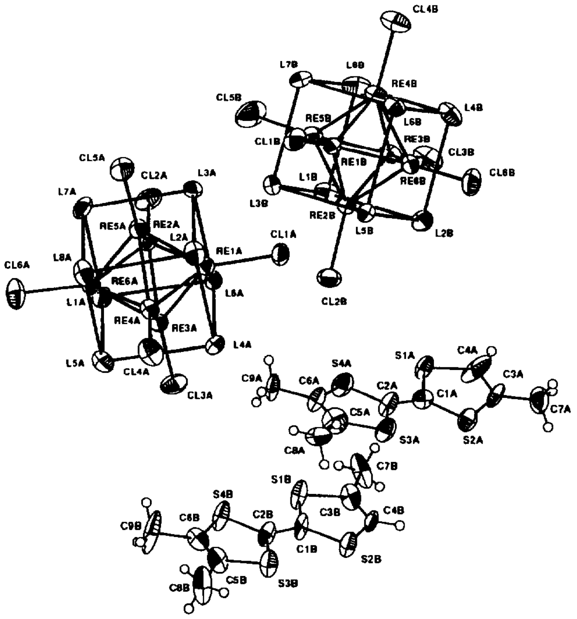

Fig 3. Ortep diagrams drawn at 50% enclosure ellipsoids for (Me_3TTF)-($Re_6Se_5Cl_9$) showing atomic numbering.

organic molecule was $Me_3TTF^{\bullet+}$. The intramolecular bond lengths within the mono-oxidized tetrathiafulvalene moieties in A and B are in the expected range for a fully oxidized TTF molecule, when compared with those in $Me_4TTF^{\bullet+}$, for example, in $(Me_4TTF)_2Re_6Se_6Cl_8$ [18]. The donor molecules are fully ordered with one position bearing a hydrogen atom and the other three methyl groups (fig 3), which is surprising, since we could have expected a structure similar to that of $(Me_4TTF)_2Re_6Se_5Cl_9$ [19] ie, with disordered donors.

Table II. Cluster inner-ligand occupancies in (Me_3TTF) ($Re_6Se_5Cl_9$).

	Cluster A	*Cluster B*
μ_{Se1}	0.95	0.94
μ_{Se2}	0.90	0.87
μ_{Se3}	0.79	0.84
μ_{Se4}	0.80	0.89
μ_{Se5}	0.85	0.73
μ_{Se6}	0.75	0.69
μ_{Se7}	0.73	0.64
μ_{Se8}	0.68	0.79
$\Sigma\mu$	6.45	6.39

Table III. Ranges and mean values of the Re-Cl^a distances (Å) for the cluster motif in (Me_3TTF)($Re_6Se_5Cl_9$) and comparison with the corresponding data for $(Bu_4N)Re_6Se_5Cl_9$ and $(Bu_4N)_2Re_6Se_6Cl_8$.

	Cluster A	*Cluster B*	$Re_6Se_6Cl_8^{2-}$	$Re_6Se_5Cl_9^{1-}$
Mean	2.350(20)	2.347(15)	2.378(6)	2.353(5)
Range	2.333(1)- 2.389(1)	2.320(1)- 2.356(1)	2.372(4)- 2.382(3)	2.347(3)- 2.360(4)

The cation radicals are stacked in infinite chains, which appear to be dimerized (fig 4). The dimeric unit is built from the association of molecules A and B. The configuration of the dimer is eclipsed with four S· · ·S intra-dimer contacts far shorter than the sum of the van der Waals radii, namely S1A· · ·S2B = 3.378(1) Å, S2A· · ·S1B = 3.422(1) Å, S3A· · ·S3B = 3.541(1) Å and S4A· · ·S4B = 3.396(1) Å, while there are no S· · ·S inter-dimer contacts shorter than 4.0 Å in the chain. The donor molecules, especially molecule A, are bent around the S-S axis, as is sometimes observed in fully oxidized dimers [9, 19]. This description of a dimerized organic chain is also consistent with the absence of an EPR signal for a single crystal of ($Me_3TTF^{\bullet+}$)($Re_6Se_5Cl_9^-$).

The organic dimers are surrounded by six cluster anions in an unusual pseudo-hexagonal environment (fig 5), associated with short inorganic ligand· · ·organic sulfur contacts (table IV). To our knowledge, the proximity of two cluster anion chains, depicted in figures 4 and 5, has never been observed before in cation radical salts with large anions such as $Re_6Se_5Cl_9^-$. This packing feature leads to $L^i\cdots L^i$ and $L^i\cdots Cl^a$ distances far shorter than the sum of the van der Waals radii (table IV). Such a situation is of course unexpected for intermolecular contacts between two negatively charged molecules.

Since the structural determination concludes the presence of trimethyltetrathiafulvalenium cation radicals $Me_3TTF^{\bullet+}$, it is likely that the electrogenerated $Me_3TTF\text{-}COOH^{\bullet+}$ is decarboxylated in the electrochemical cell. In order to confirm this result an isostructural compound has been synthesized by electrocrystallization of a solution of trimethyltetrathiafulvalene, under the same experimental conditions. Besides these electrocrystallization experiments, a preliminary study of the ability of Me_3TTF-COOH to form charge-transfer salts with tetracyanoquinodimethane (TCNQ) and tetrafluorotetracyanoquinodimethane ($TCNQF_4$) was conducted. Hot equimolar acetonitrile solutions of the donor Me_3TTF-COOH and the acceptor were mixed. When $TCNQF_4$ was used, dark-blue thin needles precipitated. The $TCNQF_4$ salt gave satisfactory analysis for the 1:1 charge-transfer salt (Me_3TTF)($TCNQF_4$). These results demonstrate that, whether the carboxylic donor Me_3TTF-COOH is chemically or electrochemically oxidized, the cation radical $Me_3TTF\text{-}COOH^{\bullet+}$ is decarboxylated. Me_3TTF-COOH does not form any charge-transfer salt with TCNQ, probably because of the presence of the carboxylic electron-withdrawing substituent.

Conclusions

In this paper, we have shown that, as expected, the structure of the carboxylic acid Me_3TTF-COOH is the result of the association of hydrogen-bonded dimers, a promising situation in the perspective of creating hydrogen-bonded networks within cation radical salts. However, the use of this donor as a building block in cation radical salts seems to be compromised because the donor proved to be decarboxylated in the conditions of the electrocrystallization experiments.

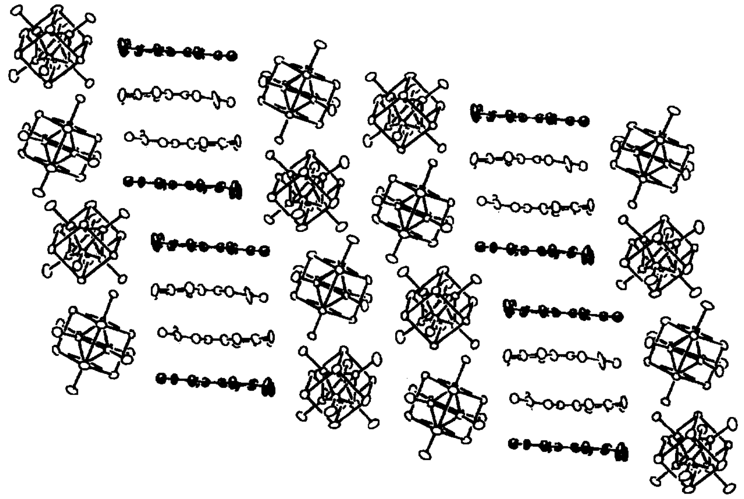

Fig 4. View of two adjacent stacks in $(Me_3TTF)(Re_6Se_5Cl_9)$. The ellipsoids of molecule A only have been drawn with a shading octant.

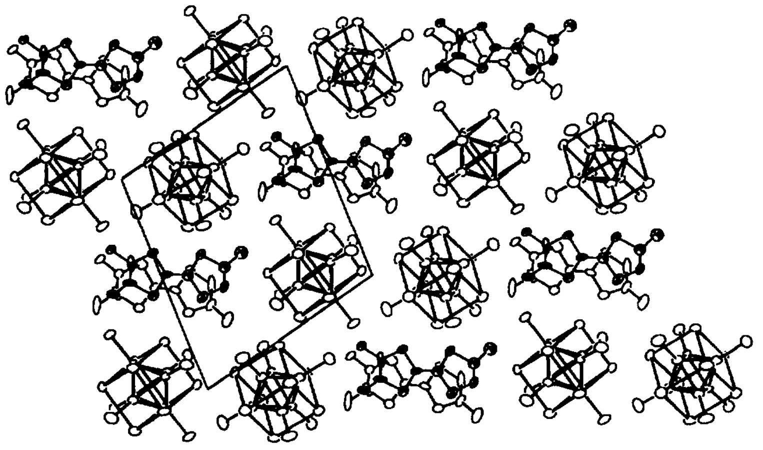

Fig 5. Projection of the structure of $(Me_3TTF)(Re_6Se_5Cl_9)$ on the (001) plane.

Table IV. Anion···anion and anion···donor contacts (Å) inferior to the sum of the van der Waals radii[a] in $(Me_3TTF)(Re_6Se_5Cl_9)$[b].

S(donor)···L^i(anion)	*S(donor)···Cl(anion)*	*Li(anion)···L^i(anion)*	*Li(anion)···Cl(anion)*
S1A···L1A = 3.462	S2A···Cl3A = 3.265	L2A···L6B = 3.809	L2A···Cl4A = 3.683
S2A···L2A = 3.588	S3A···Cl3B = 3.389	L3A···L3B = 3.580	L3A···Cl1B = 3.600
S4A···L1A = 3.572		L5A···L4B = 3.604	L5A···Cl3B = 3.507
S1B···L6A = 3.618		L6A···L3B = 3.570	L4B···Cl4A = 3.416
			L5B···Cl1A = 3.312
			L6B···Cl1B = 3.598

[a] With van der Waals radii of 2.00, 1.85 and 1.80 Å for Se, S and Cl, respectively. [b] The standard deviations are 0.001 to 0.002.

Experimental section

3-Carboxy-3′,4,4′-trimethyltetrathiafulvalene *Me_3TTF-COOH*

To a solution of trimethyltetrathiafulvalene Me_3TTF (1 g, 4.06 mmol) in dry Et_2O (100 mL) at −78 °C under dinitrogen was added $NH(i\text{-}Pr)_2$ (0.64 mL, 4.46 mmol) followed by BuLi (2.5 M in hexane, 1.8 mL, 4.46 mmol). The suspension was stirred for 1 h. From a round flask containing solid CO_2, dry gaseous carbon dioxide was bubbled into the suspension for 30 min. The orange solution was slowly warmed to room temperature, 100 mL water was added to the solution, the organic layer was dried over $MgSO_4$ and concentrated, affording the unreacted trimethyltetrathiaful-

Table V. Crystal data, experimental and refinement parameters.

Compound	*Me$_3$TTF-COOH*	*(Me$_3$TTF)(Re$_6$Se$_5$Cl$_9$)*
Crystal data		
Molecular formula	$C_{10}H_{10}O_2S_4$	$C_9H_{10}Cl_9Re_6S_4Se_5$
Molecular weight, g mol^{-1}	290.4	2 077.5
Space group	*P*-1	*P*-1
a, Å	5.802(2)	13.005(2)
b, Å	7.147(1)	15.452(3)
c, Å	15.133(2)	16.972(2)
α, °	85.66(1)	107.08(1)
β, °	81.45(2)	92.42(1)
γ, °	87.73(2)	101.18(1)
V, Å^3	618.6(2)	3 180(1)
Z	2	4
D_c, g cm^{-3}	1.56	4.34
μ(Mo-$K\alpha$), cm^{-1}	72.2	295.0
Data collection		
Crystal dimensions	0.06 × 0.30 × 0.45	0.20 × 0.20 × 0.23
Ranged scanned θ, °	1–26	1–26
Range of indices h, k, l	±7, +8, ±18	+16, ±19, ±20
No of reflections collected (unique)	2 426	12 439
No of reflections observed with $I > 3\sigma(I)$	1 308	5 815
Final refinement		
No of parameters	145	597
Weighting scheme	$w = 1$	$w = 4F_0^2/[\sigma^2(I) + (0.03F_0^2)^2]$
R^a	0.046	0.058
Rw^b	0.046	0.070
S^c	0.85	1.47
Maximum height in difference Fourier map, e Å^{-3}	0.52	5.3

[a] $R = \Sigma||F_0| - |F_c||/\Sigma|F_0|$. [b] $R_w = [\Sigma w(|F_0| - |F_c|)^2/\Sigma w|F_0|^2]^{1/2}$. [c] $S = [\Sigma w(F_0^2 - F_c^2)^2/(N_{\text{observations}} - N_{\text{variables}})]^{1/2}$.

valene Me$_3$TTF. The carboxylic acid precipitated from the aqueous layer treated with 10 mL of 1 M HCl. The acid was recrystallized from acetonitrile affording Me$_3$TTF-COOH as red crystals; m = 0.7 g, yield 59%; mp 188–190 °C.

^{1}H NMR (200 MHz, DMSO): $\delta = 1.94$ (s, 6H, CH$_3$), $\delta = 2.34$ (s, 3H, CH$_3$), $\delta = 3.31$ (s, 1H, COOH).

Anal calc for $C_{10}H_{10}O_2S_4$ (found): C, 41.36 (40.67); H, 3.47 (3.38); S, 44.16 (44.31) O, 11.02 (10.87).

(Me$_3$TTF)(Re$_6$Se$_5$Cl$_9$)

Experiments were conducted at 30 °C. The solvents were dried over basic activated alumina before use. A solution of 8 mg of Me$_3$TTF-COOH and 20 mg of the tetrabutylammonium salt of $Re_6Se_5Cl_9^-$ in a solvent mixture CH$_3$CN/DMF (7 mL/2 mL) was electrolyzed at platinum wire electrodes under constant current (I = 0.5 μA). Black shiny platelets grown at the bottom of the electrochemical cell were collected after one week.

(Me$_3$TTF)(TCNQF$_4$)

To a solution of Me$_3$TTF-COOH (10 mg, 0.035 mmol) dissolved in 10 mL of dry acetonitrile was slowly added a solution of TCNQF$_4$ (9.5 mg, 0.035 mmol) in the same solvent. The mixture immediately turned green. Dark-blue crystals were collected after one week.

Anal calc for $C_{21}H_{10}S_4N_4F_4$ (found): C, 48.27 (48.50); H, 1.93 (2.25); S, 24.54 (24.00) N, 10.72 (10.60).

Structure determination and refinement

Crystal data and parameters of the data collection are compiled in table V. Unit cell parameters were determined by accurate centering of 25 strong independent reflections. The data were collected on an Enraf-Nonius CAD4-F diffractometer, using the $\omega/2\theta$ scan. The structure was solved using direct methods. The non-hydrogen atoms were refined anisotropically by full-matrix least-squares methods. All the calculations were performed on an IBM RS/6000 computer using the Xtal 3.2 [20] systems of programs. Hydrogen atoms were included in structure factor calculations at ideal positions and not refined. In Me$_3$TTF-COOH the hydrogen atom belonging to the carboxylic group was found in the ΔF map. In (Me$_3$TTF)(Re$_6$Se$_5$Cl$_9$), due to the presence of heavy atoms (Re, Se, S), the absorption phenomena are particularly significant. Absorption corrections were thus applied using analytical procedures, assuming that the crystal geometry is close to that of a sphere. Despite these corrections, the refinement is not completely satisfactory and the residual peak density remains somewhat high. Note however that these peaks are localized near the cluster anions.

The structural characterization of the cluster anion in (Me$_3$TTF)(Re$_6$Se$_5$Cl$_9$) was supported by two major features [16c]. First a proper treatment of the core chalcogen occupancy is required along the refinement procedure. Thus after isotropic refinement, using the selenium scattering factor for all eight inner ligands, the occupancy of these ligands was refined. The results are given in table II. The actual chalcogen/halogen ratio for each cluster was deduced from the comparison of the quantity $\Sigma\mu$, as determined for the cluster A and B, with the theoretical values, $\Sigma\mu$, corresponding to the cluster anion formulations $Re_6Se_5Cl_9^-$ and $Re_6Se_6Cl_8^{2-}$; since chlorine has 17 electrons against 34 for selenium, a chlorine atom should appear as a selenium atom with 0.5 occupancy in the refinements. Therefore one obtains $\Sigma\mu = 5 + (0.5 \times 3) = 6.5$ for $Re_6Se_5Cl_9^-$ and $\Sigma\mu = 6 + (0.5 \times 2) = 7$ for $Re_6Se_6Cl_8^{2-}$. The occupancy

μ_{Se} was converted into $\mu'_{Se} + \mu_{Cl}$, a chlorine atom (with the occupancy μ_{Cl}) was placed at the same position as the selenium atom (with the occupancy μ'_{Se}); constraints on the position, the anisotropic thermal factor, and the occupancy of the chlorine atom were subsequently imposed.

In addition, the Re–Cl^a distances increase with the amount of negative charge on the cluster anion [16c,d]. Therefore a comparison of the Re–Cl^a distances with those for the reference structures $(Bu_4N)Re_6Se_5Cl_9$ and $(Bu_4N)_2Re_6Se_6Cl_8$ complements the former chalcogen core occupancy analysis (table III).

Supplementary material data have been deposited with the British Library, Document Supply Centre at Boston Spa, Wetherby, West Yorkshire, UK as supplementary publication No = SUP 9405 and is available on request from the Document Supply Centre; material available: atomic coordinates and anisotropic thermal parameters for non-hydrogen atoms, hydrogen atom parameters, bond lengths and angles, observed and calculated structure factors for Me_3TTF-COOH (11 pages) and $(Me_3TTF)(Re_6Se_5Cl_9)$ (50 pages).

References

1 a) Fourmigué M, Huang YS, *Organometallics* (1993) 12, 797-802
b) Fourmigué M, Batail P, *J Chem Soc, Chem Commun* (1991) 1370
c) Fourmigué M, Batail P, *Bull Soc Chim Fr* (1992) 129, 29

2 Sallé M, Jubault M, Gorgues A, Boubekeur K, Fourmigué M, Batail P, Canadell E, *Chem Mater* (1993) 5, 1196-1198

3 a) Blanchard P, Boubekeur K, Sallé M, Duguay G, Jubault M, Gorgues A, Martin JD, Canadell E, Auban-Senzier P, Jérome D, Batail P, *Adv Mater* (1992) 4, 579-581
b) Pénicaud A, Boubekeur K, Batail P, Canadell E, Auban-Senzier P, Jérôme D, *J Am Chem Soc* (1993) 115, 4101

4 a) Dolbecq A, Fourmigué M, Batail P, Coulon C, *Chem Mater* (1994) 6, 1417
b) Bryce MR, Cooke G, Dhindsa AS, Lorcy D, Moore AJ, Petty MC, Hursthouse MB, Karaulov AI, *J Chem Soc, Chem Commun* (1990) 816
c) Bryce MR, Marshallsay G, *Tetrahedron Lett* (1991) 32, 6033
d) Moore AJ, Bryce MR, *J Chem Soc, Chem Commun* (1991) 1638
e) Bryce MR, Marshallsay G, Moore AJ, *J Org Chem* (1992) 57, 4859

5 Fabre JM, Garin J, Uriel S, *Tetrahedron Lett* (1991) 32, 6407

6 Kreitsberga JN, Neiland OJ, *J Org Chem*, USSR (1987) 2131, Engl Transl of *Zh Org Khim* (1986) 22, 2372

7 Idriss KA, Chambers JQ, Green DC, *J Electroanal Chem* (1980) 109, 341

8 a) Fabre JM, Giral L, Montginoul C, Mungroo A, Sagnes R, Schué F, *Makromol Chem* (1989) 190, 2747
b) Mora H, Fabre JM, Giral L, Montginoul C, *Bull Soc Chim Belge* (1992) 101, 741
c) Pittman CU, Jr, Narita M, Liang YF, *J Org Chem* (1976) 41, 2855
d) Sudmale IV, Tormos GV, Khodorkovsky VY, Edzina AS, Neilands OJ, Cava MP, *J Org Chem* (1993) 58, 1355

9 Green DC, *J Org Chem* (1979) 44, 1476

10 Garin J, Orduna J, Uriel S, Moore AJ, Bryce MR, Wegener S, Yufit DS, Howard JAK, *Synthesis* (1994) 489

11 Schukat G, Richter AM, Fanghanel E, *Sulfur Reports* (1987) 7, 155

12 Bernstein J, Etter MC, Leiserowitz L, in: *Structure Correlation*, Bürgi HB, Dunitz JD Eds, VCH, New York, 1994, vol 2

13 Donohue J, *Acta Crystallogr Sect B* (1968) 24, 1558

14 Krishnamohan Sharma CV, Panneerselvam K, Pilati T, Desiraju GR, *J Chem Soc Perkin Trans 2* (1993) 2209

15 Etter MC, *Acc Chem Res* (1990) 23, 120

16 a) Batail P, Ouahab L, Penicaud A, Lenoir C, Perrin A, *C R Acad Sci, Paris* (1987) 304, 81
b) Yaghi OM, Scott MJ, Holm RH, *Inorg Chem* (1992) 31, 4778
c) Gabriel JC, Boubekeur K, Batail P, *Inorg Chem* (1993) 32, 2894
d) Uriel S, Boubekeur K, Batail P, Orduna J, Canadell E, *Inorg Chem* (1995) 34, 5307

17 a) Batail P, Livage C, Parkin SSP, Coulon C, Martin JD, Canadell E, *Angew Chem Int Ed Engl* (1991) 30, 1498
b) Boubekeur K, Lenoir C, Batail P, Carlier R, Tallec A, LePaillard MP, Lorcy D, Robert A, *Angew Chem Int Ed Engl* (1994) 33, 1379
c) Dolbecq A, Boubekeur K, Batail P, Canadell E, Auban-Senzier P, Coulon C, Lerstrup K, Bechgaard K, *J Mater Chem* (1995) 5, 1707

18 Boubekeur K, PhD Thesis, 1989, University of Rennes, France

19 Batail P, Ouahab L, *Mol Cryst Liq Cryst* (1985) 125, 205

20 Hall RS, Flack HD, Stewart JM, *XTAL 3.2 Reference Manual*, Universities of Western Australia, Geneva and Maryland, 1992