

## The Use of Polyoxometallates as Acceptors in Charge Transfer Salts: Preparation, X-Ray Crystal Structures, and Preliminary Spectroscopic Characterizations of $D_3M_6O_{19}$ , $D = \text{TTF, TMTSF}^\dagger$ ; $M = \text{Mo, W}$

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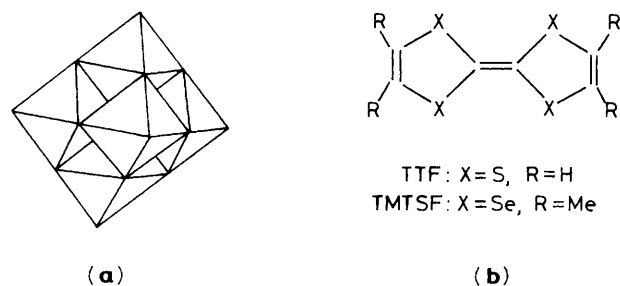
The preparation, X-ray crystal structures, conductivities, and preliminary spectroscopic characterization of new charge transfer salts of general formula  $(D)_3^{2+} P^{2-}$ , where D is an organic donor and P hexatungstate (or molybdate) acceptor dianions having the Lindquist structure, are given.

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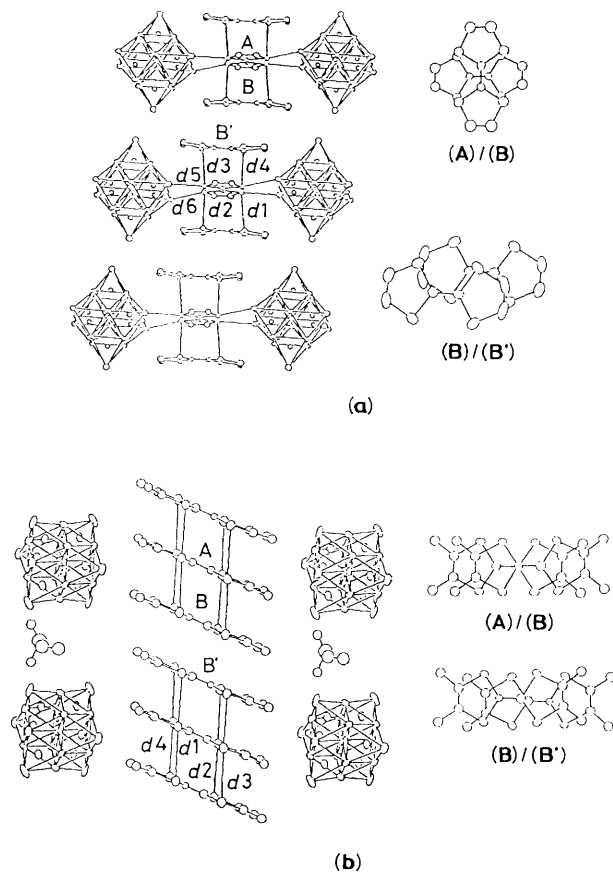
The  $\pi$ -molecular organic donor (D) and acceptor (A) based compounds have been classified into two families:<sup>1</sup> the ion-radical or 'organomineral'<sup>2</sup> salts of formulae  $D^+X^-$  and  $Y^+A^-$ , where X and Y represent inorganic anions and cations, respectively; and the charge transfer compounds

<sup>†</sup> TTF = tetrathiafulvalene, TMTSF = tetramethyltetraselenafulvalene.

$(D^+A^-)$  made with tetrathiafulvalene (TTF) and tetracyanoquinodimethane (TCNQ) derivatives. In the latter class, the use of *inorganic* donors or acceptors has not been investigated. In order to prepare *organic donor-inorganic acceptor* (ODIA) salts, we have chosen  $MO_6$  condensed octahedron polyoxometallate anions ( $M = \text{Mo, W, Nb}$ ) (see Figure 1). Known for over a century, these polyoxometallates are still of interest because of their high electron acceptor capabilities.<sup>3</sup> These



**Figure 1.** (a) Lindquist structure of  $M_6O_{19}^{n-}$  anions,  $M = Mo, W, Nb$ . (b) Organic donors.



**Figure 2.** Evidence of the stacking deformation. The thin lines indicate intra-trimer and anion-cation interactions. The intra- and inter-trimer overlaps are given. (a)  $(TTF)_3W_6O_{19}$  (1):  $d_1 = 3.315(3)$ ,  $d_2 = 3.528(3)$ ,  $d_3 = 3.392(3)$ ,  $d_4 = 3.358(3)$ ,  $d_5 = 3.051(4)$ ,  $d_6 = 3.091(5)$  Å. (b)  $(TMTSF)_3W_6O_{19}$  (3):  $d_1 = 3.731(5)$ ,  $d_2 = 3.753(4)$ ,  $d_3 = 3.745(5)$ ,  $d_4 = 3.807(5)$  Å.

properties are exploited in catalysis<sup>4</sup> for instance. The presence of inorganic acceptor anions in charge transfer salts can induce the coexistence of mixed valence states in the organic and inorganic systems. The stabilization of a mixed valence state is one of the prerequisites for electron delocalization (electrical conductivity) and unpaired spin localization on the metal d-orbitals (magnetic properties). We have recently characterized<sup>5</sup> the first material obtained with the phosphododecatungstate anion  $[PW_{12}O_{40}]^{3-}$ , which has the Keggin

structure.<sup>6</sup> We report here new conducting charge transfer salts using hexametallate acceptor dianions  $(M_6O_{19})^{2-}$  ( $M = Mo, W$ ) having the Lindquist structure.<sup>7</sup>

New conducting salts,  $(TTF)_3W_6O_{19}$  (1),  $(TTF)_3Mo_6O_{19}$  (2), and  $(TMTSF)_3W_6O_{19}(DMF)_2$  (3) (DMF = *N,N*-dimethylformamide), have been obtained on a platinum wire electrode by anodic oxidation of the organic donor ( $2 \times 10^{-3}$  M) under low constant current ( $I = 1 \mu A$ ) in the presence of tetrabutylammonium salts of the dianions ( $10^{-2}$  M) as supporting electrolyte. The latter were prepared according to the literature procedures.<sup>8</sup> Acetonitrile was used for (1) and (2) and DMF- $CH_2Cl_2$  (ratio 3:1) was used for (3). The compounds have the same 3:1 stoichiometry but differ in their stacking mode (see below).

In all compounds, the unit cell contains two independent organic molecules, noted (A) and (B) in Figure 2. Molecules (A) are positioned in the  $(1/2, 1/2, 1/2)$  and  $(0, 0, 1/2)$  centres of symmetry for (1) and (3), respectively. One molecule (A) and two molecules (B) stack together to form trimers.

In compounds (1)‡ and (2) [Figure 2(a)], the TTF molecules form stacks of trimers. Molecules (A) and (B) overlap in a 'criss-cross' fashion. Strong intra-trimer S  $\cdots$  S contacts (3.31–3.59 Å) are observed. The distance between (B) and (B') (inter-trimer separation) is 3.57 Å, but because of the slipping of one trimer relative to the other (Figure 2a), the inter-trimer S  $\cdots$  S contacts are longer than the corresponding van der Waals separations ( $>3.8$  Å). Short S  $\cdots$  S separations (3.43 Å) between chains are also observed. The compound (3)‡ [Figure 2(b)] crystallizes with two DMF solvent molecules. In this salt the TMTSF molecules form stacks of trimers with intra- and inter-trimer zig-zag overlaps identical to those observed in the  $(TMTSF)_2X$  series.<sup>9</sup> The intra-trimer Se  $\cdots$  Se contacts (3.73–3.81 Å) are shorter than those commonly observed in the 2:1 series.<sup>10</sup> The inter-trimer Se  $\cdots$  Se contacts (4.05–4.12 Å) are in the range of the van der Waals separation (4 Å). Short  $S_{TTF} \cdots O_{anion}$

‡ *Crystal data* for (1):  $(TTF)_3W_6O_{19}$ ,  $C_{18}H_{12}O_{19}S_{12}W_6$ ;  $M = 2020.15$ , triclinic,  $P\bar{1}$ ,  $a = 9.965(3)$ ,  $b = 10.503(3)$ ,  $c = 10.634(3)$  Å,  $\alpha = 71.93(2)$ ,  $\beta = 78.63(2)$ ,  $\gamma = 63.38(3)^\circ$ ,  $U = 943.8$  Å<sup>3</sup>,  $Z = 1$ ,  $D_c = 3.554$  g cm<sup>-3</sup>,  $\mu = 193.23$  cm<sup>-1</sup>,  $F(000) = 908$ ,  $\lambda(Mo-K\alpha) = 0.71073$  Å. Enraf-Nonius CAD4 diffractometer. Data were collected in the range  $2 \leq 2\theta \leq 56^\circ$  with the  $\theta$ - $2\theta$  scan mode. 4525 Independent reflections were observed. Intensities were corrected for Lorentz and polarization effects. 3380 Absorption corrected data with  $I \geq 3\sigma(I)$  were obtained. The structure was solved by direct methods. Full matrix least squares refinement was used (non-hydrogens anisotropic, hydrogen in idealized positions not refined); 251 variables, weights  $w = [\sigma^2(F_o) + (0.07F_o)^2]^{-1}$ ,  $R = 0.020$ ,  $R_w = 0.031$ . For (2):  $(TTF)_3Mo_6O_{19}$ , triclinic,  $P\bar{1}$ ,  $a = 9.942(3)$ ,  $b = 10.417(3)$ ,  $c = 10.601(3)$  Å,  $\alpha = 72.33(2)$ ,  $\beta = 78.77(2)$ ,  $\gamma = 63.52(3)^\circ$ ,  $U = 933.9$  Å<sup>3</sup>,  $D_c = 2.291$  g cm<sup>-3</sup>.

*Crystal data* for (3):  $(TMTSF)_3W_6O_{19}(DMF)_2$ ,  $C_{36}H_{50}N_2O_{21}Se_{12}W_6$ ;  $M = 2897.42$ , monoclinic,  $P2_1/c$ ,  $a = 11.589(4)$ ,  $b = 19.385(5)$ ,  $c = 13.681(3)$  Å,  $\beta = 99.53(2)^\circ$ ,  $U = 3030.9$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 3.175$  g cm<sup>-3</sup>,  $\mu = 187.94$  cm<sup>-1</sup>,  $F(000) = 2600$ ,  $\lambda(Mo-K\alpha) = 0.71073$  Å. Enraf-Nonius CAD4 diffractometer. Data were collected in the range  $2 \leq 2\theta \leq 50^\circ$  with the  $\theta$ - $2\theta$  scan mode. 5045 Independent reflections were observed. Intensities were corrected for Lorentz and polarization effects. 2294 Absorption corrected data with  $I \geq 3\sigma(I)$  were obtained. The structure was solved by direct methods. Full matrix least squares anisotropic refinement was done for all non-hydrogens, except one oxygen atom of the anion, two carbon atoms of the TMTSF molecules, and the disordered solvent molecule, which were refined isotropically; hydrogen in idealized positions were not refined; 310 variables, weights  $w = [\sigma^2(F_o) + (0.07F_o)^2]^{-1}$ ,  $R = 0.049$ ,  $R_w = 0.063$ .

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

(3.07–3.09 Å) (van der Waals distance, 3.4 Å) and Se<sub>TMTSF</sub> ··· O<sub>anion</sub> (3.17–3.30 Å) (van der Waals distance, 3.5 Å) contacts are observed for (1) and (3) respectively, indicating strong anion–cation interactions. In each salt the structural features of the independent TTF or TMTSF molecules are identical and suggest that they have the same mean charge ( $\rho + 2/3$ ). This result is consistent with the 3:1 stoichiometry and the semiconducting behaviour of these salts. The d.c. electrical conductivities measured at room temperature using a standard four probe method are  $\sigma_{300\text{ K}} = 1.4 \times 10^{-3}$ ,  $0.5 \times 10^{-3}$ , and  $3 \times 10^{-3} \Omega^{-1} \text{ cm}^{-1}$  for (1), (2), and (3) respectively.

In preliminary work, the visible and i.r. electronic absorption spectra of the three compounds on dispersed KBr pellets were examined<sup>11</sup> using the standard procedure.<sup>12</sup> The main characteristic observed for each compound is the presence of an intense charge transfer (CT) band around  $6000 \text{ cm}^{-1}$  [compounds (1) and (2)] and  $3000 \text{ cm}^{-1}$  [compound (3)], which is the sign of a mixed valence system: this result confirms that these compounds are low-dimensional CT conductors, as shown by the d.c. conductivity experiments. Moreover,  $a_g$  vibronic modes characteristic of an irregular stacking have been detected.<sup>11</sup>

In order to understand the physical properties of these new charge transfer salts, studies of their optical, electronic, and magnetic properties are in progress and will be reported elsewhere. Beside this, the investigations of other ODIA salts by successive substitutions<sup>13</sup> of the metals within the anions are in progress. These substitutions, giving isostructural Lindquist anions<sup>13</sup> of formula  $[M'_n M_{6-n} O_{19}]^{(n+2)-}$  ( $M' = \text{Nb}$ ;  $n = 1, 2, 3, 4$ ), constitute an approach for the introduction of a mixed valence state in the inorganic system.

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