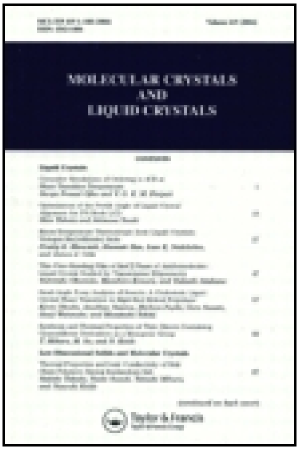

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ELECTRONIC, STRUCTURAL AND MAGNETIC PROPERTIES OF $(TTF)_6(NEt_4)[PMo_{12}O_{40}]$: A MIXED-VALENCE TTF SALT WITH A MAGNETIC POLYOXOMETALLATE

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Abstract. $(TTF)_6(NEt_4)[PMo_{12}O_{40}]$ has been characterised by EPR, IR and Resonance Raman Spectroscopy and by static magnetic susceptibility. From all these data the compound can be formulated as: $(Et_4N)^+(TTF^\circ)_2(TTF)_4{}^{3+}[PMo_{12}O_{40}]^{4-}$. The magnetic and the electrical properties are accounted for on this basis.

INTRODUCTION

The radical–ion salt $(TTF)_6(NEt_4)[PMo_{12}O_{40}]$ has been previously prepared by us[1,2] and by Ouahab *et al.*[3,4]. The crystal structure of $(TTF)_6(NEt_4)[PMo_{12}O_{40}]$ has been solved quite recently[4] and the compound was found to crystallize in the orthorhombic space group *Cmmm*. It consists of stacked TTF molecules along the **c** axis of the unit–cell surrounded by alternating inorganic anions and TTF molecules, the latter nearly perpendicular to those forming the stacks. If no $2\mathbf{k}_F$ distortion ($\mathbf{k}_F$ is the Fermi wavevector) or localization were present in the TTF chains, the compound would behave as a metal at room temperature. In fact, it is a semiconductor with a magnetic behavior typical of interacting localized spins.

In an attempt at (i) assessing the degree of charge of the TTF moieties and the charge of the anions and (ii) relating the observed physical properties to the crystal structure, we report and discuss the results of EPR, static magnetic susceptibility (SQUID magnetometry), visible and IR spectroscopic measurements of $(TTF)_6(NEt_4)[PMo_{12}O_{40}]$ and of the paramagnetic mixed–valence $(NBu_4)_4[PMo_{12}O_{40}]$ salt[5]. Resonance Raman scattering (RRS) data of the TTF derivative are also reported.

RESULTS

Optical properties

The powder electronic spectra of the compounds have been measured at

TABLE I Band positions observed in diffuse reflectance spectra[a].

$(NBu)_4[PMo_{12}O_{40}]$:	31,200	17,900 sh	12,500	8700 sh	7200[b]
$(TTF)_6(NEt)_4[PMo_{12}O_{40}]$:	30,000	24,800 sh	19,000	11,700	4200[b]

[a] Peak frequencies in cm^{-1}. [b] Very broad.

room temperature and the band positions are reported in Table I. The completely oxidised yellow $[PMo_{12}O_{40}]^{3-}$ anion shows the first absorption in the near UV, i.e. at about 31,000 cm^{-1}, which can be ascribed to the oxygen–to–metal charge transfer (CT) optical transition. The one–electron reduced $[PMo_{12}O_{40}]^{4-}$, green form, shows a very broad absorption band in the visible region at about 12,500 cm^{-1}, with an associated broad band at 7200 cm^{-1}. They have been assigned to Mo(V) $\rightarrow$ Mo(VI) intervalence absorptions[6], the first one involving edge–shared $[MoO_6]$ octahedra, the second involving corner–shared octahedra. The band at 17,900 cm^{-1} can be assigned as a *d–d* transition of the Mo(V) electronic configuration ($^2B_2 \rightarrow {}^2B_1$ in C_4 symmetry). No bands are observed below 5000 cm^{-1}. On the other hand, a very intense and broad absorption at lower energy is observed, with the maximum located at 4200 cm^{-1}, in the TTF derivative. The presence in the near infrared region of this large broad band, commonly labelled as A band[7], is an important feature of *mixed–valence organic CT compounds*. The other bands are located at 11,700, 19,000 and 24,800 cm^{-1} and have been observed and assigned previously in TTF single–valence and mixed–valence halide salts[7]. The lowest in energy, the so called B band, is a CT band between two adjacent TTF^+ cation radicals. It is quite difficult to identify in this region bands arising from the anion, nevertheless a shoulder is observed at about 7200 cm^{-1}.

The infrared spectra of $(TTF)_6(NEt_4)[PMo_{12}O_{40}]$ recorded at room tempearture and at $T = 14$ K are shown in Figure 1. Vibrational absorption bands are superimposed on the tail of the lowest electronic energy band. Typical vibrations of $[PMo_{12}O_{40}]^{4-}$ can be identified[8] at 1055, 949, 859, 789, 383 cm^{-1}. As far as the TTF molecule is concerned, there are basically two effects which can complicate the assignment in organic conductors though, once understood, they can provide useful information[9]. The first one is related to the interaction between the totally symmetric a_g modes and the radical π–electrons, the so called vibronic effect. The second one is the observed frequency shift of the normal modes that depends on the average charge occupation, ρ, of the molecule. Between 700 and 600 cm^{-1} there are two bands at 668 and 615 cm^{-1}, which can tentatively be assigned to the b_{3u}, ν_{34} mode arising from $TTF^{(\rho+)}$ and TTF°, respectively[10]. The frequency of this mode (ω_{34}) is the most sensitive to the degree of charge ρ among those of the normally IR active *ungerade* modes[10]. According to the linear relation

$$\rho = \frac{\omega_{34}(TTF^{\rho+}) - \omega_{34}(TTF^{\circ})}{\omega_{34}(TTF^{+}) - \omega_{34}(TTF^{\circ})} = \frac{1}{65}[\omega_{34}(TTF^{\rho+}) - \omega_{34}(TTF^{\circ})]$$

we find $\rho = +0.80$. To confirm this information, RRS spectra of a powder sample dispersed in KBr were recorded. The $a_g\nu_3$ mode is the most sensitive and well tested probe of the effective fractional charge on TTF molecules in organic molecular conductors[9,10]. The observed 1449 cm^{-1} frequency value (Figure 2)

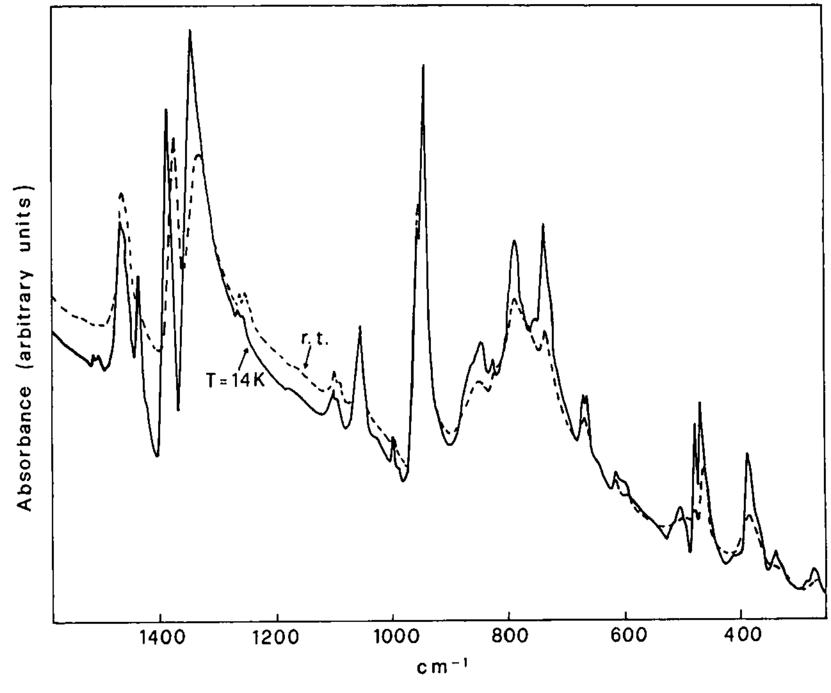

FIGURE 1 Infrared absorption spectrum of $(TTF)_6(NEt_4)[PMo_{12}O_{40}]$ at room temperature (dashed line) and 14 K (full line).

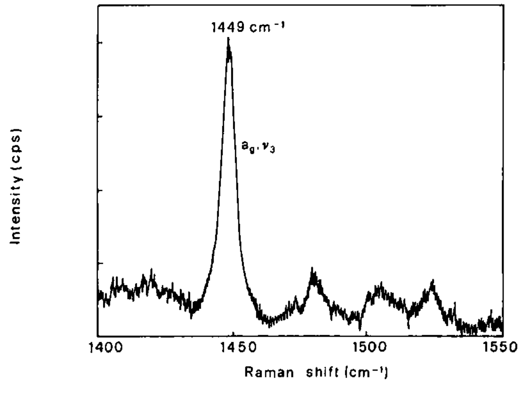

FIGURE 2 Resonance Raman spectrum of $(TTF)_6(NEt_4)[PMo_{12}O_{40}]$ powders dispersed in KBr at 12 K. Exciting wavelength $\lambda_o = 530.9$ nm.

corresponds to an average degree of charge $\rho = +0.7 \pm 0.1$ based on a linear interpolation procedure similar to that used for the ν_{34} mode.

If we assume that the anion is charged (4–) (see the magnetic properties below) and take into account the estimated value of ρ, the charge distribution in the studied compound should be

$$(NEt_4)^+(TTF)_4^{3+}(TTF^\circ)_2[PMo_{12}O_{40}]^{4-}$$

It is then natural to identify the two neutral molecules with those arranged outside the TTF chains with their long axes parallel to the chain axis.

In segregated stack structures, the vibronic effects can give information on the presence of structural distortions of the organic chains (dimerizations, tetramerizations, etc.)[9]. The bands at 1378, 1335, and at 461 cm^{-1} are strong and broad and can be assigned to the IR inactive a_g modes made active by the vibronic effect[9,10]. The observation of these vibronically induced absorptions at room temperature is a signature of the presence of a distorted chain structure.

The investigation of the temperature dependence of these absorptions provides further insights into the structural properties. Figures 1 and 3 show that, on cooling, the spectrum shows the appearance of bands at 1432 and 495 cm^{-1} and a marked increase of the intensity of those at 1378 and 476 cm^{-1} relative to the main peaks at 1335 and 466 cm^{-1}. The growth of satellite absorptions of the main vibronic bands below 230 K (see Figure 3) indicates the occurrence of a structural change that most likely involves a variation in the period or, at least, an increase in the amplitude of the distortion of the TTF chains. The appearance of similar satellite absorptions has been previously observed[11] for radical–ion salts of TMTSF, TCNQ and DCNQI in correspondence with the formation of a tetrameric distortion of the organic stacks. It is therefore tempting to attribute the observed infrared vibronic features to a similar tetrameric distortion of the TTF stacks also in the present case. The three charges could then be distributed over the four molecules in a tetrameric unit according to the scheme:

$$\ldots(D^+D^+)(D^{\frac{1}{2}+}D^{\frac{1}{2}+})(D^+D^+)(D^{\frac{1}{2}+}D^{\frac{1}{2}+})\ldots$$

In other words, the charges along the TTF chains are modulated in such a way that fully charged $(TTF^+)_2$ dimers alternate with $(TTF)_2^+$ dimers in which two molecules share a single positive charge. Such a charge localization could be stabilised, if not induced, by the interaction with the large inorganic clusters bearing a (4–) charge. Of course the tendency to delocalize the electronic charges implied in the charge transfer interaction should partially smooth out the charge localization described in the above scheme.

Electrical and magnetic properties

The room temperature d.c. electrical conductivity of single–crystals of $(TTF)_6(NEt_4)[PMo_{12}O_{40}]$ has been measured to be $\sigma = 1.7 \times 10^{-2}$ S cm^{-1}. This value is suggestive of semiconducting properties although the temperature dependence of the conductivity was not measured.

The magnetic properties observed for $(TTF)_6(NEt_4)[PMo_{12}O_{40}]$ are rather intriguing. The EPR spectra on powder samples have been recorded at room

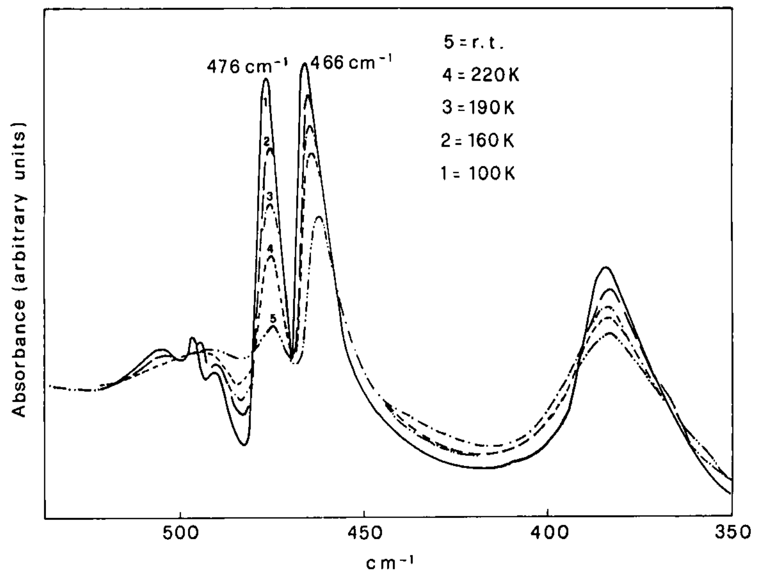

FIGURE 3 Temperature dependence of the infrared absorptions of $(TTF)_6(NEt_4)[PMo_{12}O_{40}]$ in the spectral region 350 – 550 cm^{-1}.

and at liquid nitrogen temperature. In unraveling the contributions of the inorganic clusters and of the organic donor stacks to the magnetic properties, the measurements of the EPR and magnetic susceptibility of $(NBu_4)_4[PMo_{12}O_{40}]$ has been very instrumental. The tetrabutylammonium salt is EPR silent at room temperature and shows a single-line signal ($g = 1.9444$) with no hyperfine structure at $T = 100$ K. The linewidth H is 50 G. There is agreement with what has been observed in a previous work on a frozen solution of this compound[5]. The magnetic susceptibility of $(NBu_4)_4[PMo_{12}O_{40}]$ has been measured at 100 G in the 6 – 300 K temperature range. The measured susceptibility has been corrected for the diamagnetic contribution of all the atoms. The observed molar paramagnetic susceptibility, χ_M, can be described by the relation: $\chi_M = \chi_{TIP} + C/T$, where χ_{TIP} is the temperature independent paramagnetism and C/T is a Curie-type contribution. This relation was used to fit the experimental data and the parameter values were found to be: $\chi_{TIP} = 7.78 \times 10^{-4}$ emu / mole and $C = 0.3402$ emu K / mol. The Curie contribution is associated to the presence of one electron spin per inorganic cluster localised on one of the molybdenum atoms at low temperatures.

$(TTF)_6(NEt_4)[PMo_{12}O_{40}]$ is also EPR silent at 300 K. On lowering the temperature to 100 K, a single-line ($g = 1.9482$, $H = 150$ G) with no hyperfine structure is observed. The plot of the magnetic susceptibility of $(TTF)_6(NEt_4)[PMo_{12}O_{40}]$ vs. temperature is reported in Figure 4(a). The measured susceptibility was corrected for the diamagnetic contribution of all the

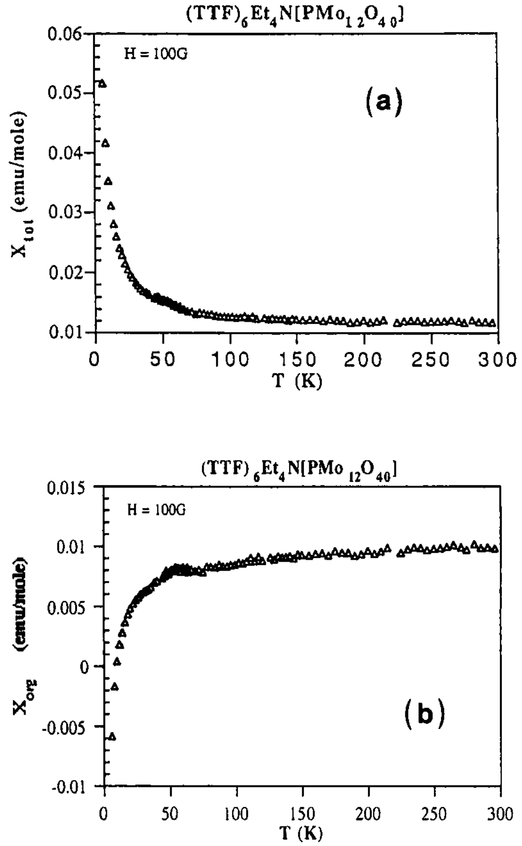

FIGURE 4 (a): Total paramagnetic susceptibility of $(TTF)_6(NEt_4)[PMo_{12}O_{40}]$ vs. temperature. (b): Estimated TTF chain contribution.

atoms. At low temperature the susceptibility appears to be Curie-like. Above 100 K it is almost temperature independent but with values markedly higher than those measured for the $(NBu_4)_4[PMo_{12}O_{40}]$ salt.

A simple attempt at extracting from the total susceptibility (χ_{tot}) the contribution of the TTF chains was accomplished by subtracting both the temperature independent paramagnetism and the Curie susceptibility estimated for the tetrabutilammonium salt. The temperature dependent TTF chain susceptibility (χ_{org}) estimated in this way is shown in Figure 4(b). In the high temperature range ($210 < T < 300$ K) the organic susceptibility could be explained either in terms of an activated behaviour with a very small magnetic gap of 23 meV or in terms of an Heisenberg chain susceptibility. The steeper decrease of χ_{org} at lower temperatures suggests an increase of the magnetic gap amplitude possibly associated to the structural change already indicated by the temperature dependent infrared results.

DISCUSSION

Combining infrared, Raman and ESR results we have provided evidence that in the title compound the inorganic anions are in the reduced $[PMo_{12}O_{40}]^{4-}$ paramagnetic state and that three positive charges are shared by four molecules in the organic chains whereas the TTF molecules lying parallel to the chains are essentially neutral. We have also obtained spectroscopic evidence that the TTF chains are distorted in a tetrameric fashion and that such distortion evolves with lowering the temperature towards either a larger amplitude tetramerization or a distortion of different periodicity, possibly the formation of octameric units. A plausible origin for such an increase of periodicity lies with the fact that the room temperature crystal structure contains a disordered anion sublattice that may undergo an ordering transition in analogy with what happens in several other organic conductors[13].

Contrary to previous suggestions[4], the TTF chains contribute to the magnetic properties of $(TTF)_6(NEt_4)[PMo_{12}O_{40}]$ as one should expect if three electrons are present per formula unit. Experimental support to this view is provided by the comparison with the magnetic properties measured for the paramagnetic $(NBu_4)_4[PMo_{12}O_{40}]$ salt. The observation of a single line in the ESR spectrum of the title compounds may indicate that the spins on the organic and inorganic subsytems are interacting. The possible occurrence of a structural transition at low temperature leading to an octameric structure of the TTF chains with antiferromagnetically coupled spins deserves further structural and magnetic studies.

The comparatively low electrical conductivity measured at room temperature is suggestive of semiconducting properties. This is in contrast with the expectation that, with five electrons left on four TTF molecules, the four tight binding bands should be filled up to half the third band yielding a metallic band structure. The observed semiconducting behaviour is likely attributable to an electron localization caused by the combined effect of the presence of strong electron correlations and of the interaction with localized charges and spins on the inorganic anions.

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