

Charge Transfer Salts Obtained with Organic Donors (TTF, TMTTF, TMTSF, and BEDT-TTF)[†] and Tetracyanometallate Planar Dianions [M(CN)₄²⁻, M = Pt^{II}, Ni^{II}]

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The electrochemical preparations, X-ray crystal structures, d.c. conductivities and optical absorption of new charge transfer salts of general formula (D_x)²⁺C²⁻, where D indicates an organic donor and C a planar tetracyanometallate dianion, are presented.

The class of partially oxidized one-dimensional organic salts based on tetrathiafulvalene (TTF) and its derivatives,¹ and inorganic salts of tetracyanoplatinate,² Pt(CN)₄²⁻, have been two of the most extensively studied low-dimensional conducting and superconducting salts.^{1,2} The crystal structures of these two types of compounds contain linear segregated *mixed valence* stacks of planar organic radical cations or planar platinum complexes. We developed a program, aimed at investigating new charge transfer salts made of the two planar, organic and inorganic entities.

New conducting salts, (2)—(6), with different structures

and stoichiometries were obtained by anodic oxidation of the donor (2×10^{-3} M) under low constant current conditions (1 μ A) in the presence of tetra-alkylammonium³ salts of the dianion (10^{-2} M) as the supporting electrolyte. The salt (1) was obtained by slow diffusion of two 15 ml solutions of TTF (10^{-2} M) and (TBA)₂Pt(CN)₄ (TBA = tetrabutylammonium) (0.1 M) in acetonitrile with 3 ml of H₂O₂. These salts are presented in Table 1, together with the convenient crystal growth solvent, the conducting properties, and the unit cell dimensions. The stoichiometries were determined by X-ray structure analysis[‡] for (1), (2) and (3), since the groups of salts

[†] TTF = tetrathiafulvalene, TMTTF = tetramethyltetrathiafulvalene, TMTSF = tetramethyltetraselenafulvalene, BEDT-TTF or ET = bis(ethylenedithio)tetrathiafulvalene.

[‡] Complete X-ray structure analyses and physical properties are to be reported in subsequent full papers.

Table 1. Conductivity, unit cell parameters, and crystal growth solvent.

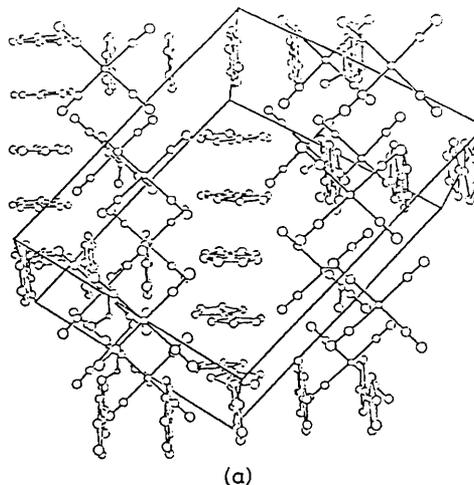
Salts ^a	σ^b	Solv. ^c	$a/\text{\AA}$	$b/\text{\AA}$	$c/\text{\AA}$	α°	β	γ	S.G., Z^c
(1) (P) ₂ (TTF) ₅ (ACN) ₂ ^d	I	ACN	11.697 ^e	15.005	17.020	78.33	75.54	72.98	$P\bar{1}$, 2
(2) (P)(TMTSF) ₃ ^d	0.25	DMF	7.957	10.817	12.834	85.85	86.58	76.17	$P\bar{1}$, 1
(3) (P)(ET) ₄ ^{d,f}	12	DMF	9.721	11.127	16.552	76.90	81.52	62.88	$P\bar{1}$, 1
(4) (N)(TMTTF) ₃	0.55	ACN	7.800	10.579	12.495	85.42	86.83	77.16	$P\bar{1}$, 1
(5) (N)(TMTSF) ₃	0.43	DMF	7.932	10.887	12.868	86.91	87.07	75.52	$P\bar{1}$, 1
(6) (N)(ET) ₄	2.04	DMF	9.699	11.140	16.430	77.18	82.13	63.01	$P\bar{1}$, 1

^a (P) = Pt(CN)₄, (N) = Ni(CN)₄. ^b Conductivity at 300 K in $\Omega^{-1} \text{cm}^{-1}$; I = insulator. ^c Solv. = solvent; DMF = dimethylformamide; ACN = acetonitrile; S.G. = space group; Z = number of formula units per unit cell. ^d X-Ray crystal structures were determined for these salts. ^e The estimated standard deviations on the last digit are 3–6. ^f This compound has also been reported recently but with a unit cell which is twice the one given here ($a = 11.002$, $b = 17.906$, $c = 16.625 \text{\AA}$, $\alpha = 77.28$, $\beta = 84.17$, $\gamma = 81.26^\circ$). See ref. 6.

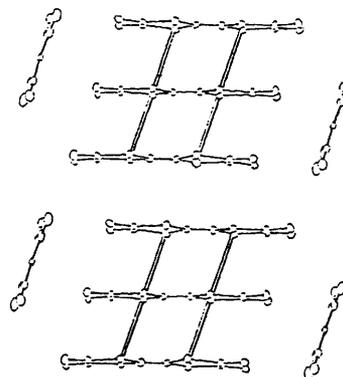
(2), (4) and (5), and (3) and (6) are isostructural (Table 1).

In compound (1)§ [Figure 1(a)], the unit cell contains two independent Pt(CN)₄(TTF)_{2.5} blocks; the TTF molecules of each block form centrosymmetrically-related isolated pentamers with eclipsed overlaps. Strong intrapentamer S...S interactions (3.32–3.61 Å) (corresponding van der Waals separation, 3.8 Å) are observed. The isolated Pt(CN)₄²⁻ dianions are separated by the disordered acetonitrile mol-

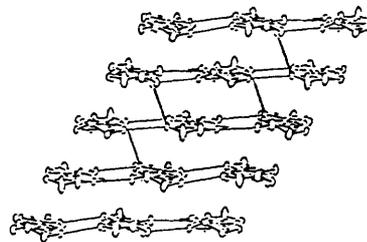
In compound (2)§ [Figure 1(b)], the TMTSF molecules form trimerised stacks with intra- and inter-trimer overlaps similar to those observed in the (TMTSF)₂X series.^{1b} The structural features of the two independent molecules are identical and suggest that these molecules have the same charges ($\rho + 2/3$), in agreement with the 3:1 stoichiometry and the semi-conducting character of this material. The



(a)



(b)



(c)

Figure 1. X-Ray crystal structures, (a) (TTF)₅[Pt(CN)₄]₂(ACN)₂: projection of the structure showing orthogonalized TTF pentamers. (b) (TMTSF)₃Pt(CN)₄: evidence of the stacking deformation, thin lines represent Se...Se intra-trimer contacts $\leq 3.8 \text{\AA}$. (c) (BEDT-TTF)₄Pt(CN)₄: sheet-like network stacking, thin lines represent the S...S inter-stack contacts $\leq 3.6 \text{\AA}$.

§ *Crystal data:* The cell dimensions, space groups, and Z are given in Table 1. For all the salts, the data were collected at 293 K on an Enraf-Nonius CAD4 diffractometer with monochromatized Mo-K α radiation ($\lambda = 0.71073 \text{\AA}$), using θ – 2θ scans.

For (1): C₂₂H₂₆N₁₀S₂₀Pt₂; $M = 1702.20$, $U = 2738.9 \text{\AA}^3$, $D_c = 2.064 \text{g cm}^{-3}$, $\mu = 59.34 \text{cm}^{-1}$, $F(000) = 1648$. Data were collected in the range $2 \leq 2\theta \leq 54^\circ$. 7267 Independent reflections were observed. Intensities were corrected for Lorentz and polarization effects. 4064 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; nonhydrogens anisotropic, disordered solvent molecule refined isotropically, hydrogen in idealized positions not refined. 638 Variables, weights $w = [\sigma^2(F_o) + (0.07F_o)^2]^{-1}$, $R = 0.044$, $R_w = 0.056$. Pt–C, 1.97(2), C–N, 1.16(3) Å (average).

For (2): C₃₄H₃₆N₄Se₁₂Pt; $M = 1643.30$, $U = 1077 \text{\AA}^3$, $D_c = 2.533 \text{g cm}^{-3}$, $\mu = 133.61 \text{cm}^{-1}$, $F(000) = 754$. Data were collected in the range $2 \leq 2\theta \leq 54^\circ$. 3769 Independent reflections were measured. Intensities were corrected for Lorentz and polarization effects. 2380 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; nonhydrogens anisotropic, hydrogens in idealized positions not refined. 233 Variables, weights $w = [\sigma^2(F_o) + (0.08F_o)^2]^{-1}$, $R = 0.034$, $R_w = 0.044$. Pt–C, 1.97(1), C–N, 1.17(1) Å (average).

For (3): C₄₄H₃₂N₄S₃₂Pt; $M = 1837.91$, $U = 1550 \text{\AA}^3$, $D_c = 1.969 \text{g cm}^{-3}$, $\mu = 33.64 \text{cm}^{-1}$, $F(000) = 914$. Data were collected in the range $2 \leq 2\theta \leq 54^\circ$. 6069 Independent reflections were measured, 4199 absorption corrected data with $I \geq 6\sigma(I)$ were obtained. Intensities were corrected for Lorentz and polarization effects. The structure was solved by direct methods. Full matrix least squares refinement was used; nonhydrogen anisotropic, hydrogens in idealized positions not refined. 368 Variables, weights $w = [\sigma^2(F_o) + (0.07F_o)^2]^{-1}$, $R = 0.032$, $R_w = 0.045$. Pt–C, 1.983(6), C–N, 1.143(8) Å (average).

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.

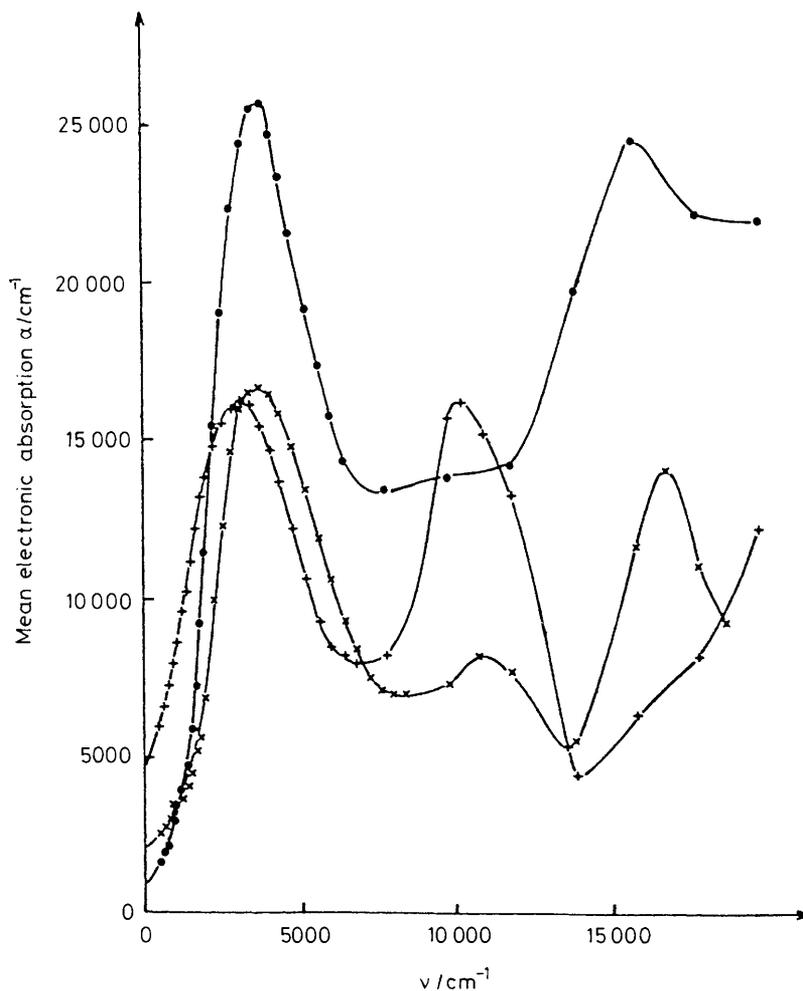


Figure 2. Room temperature mean electronic absorption ($\bar{\alpha}$) vs. energy. The electronic parameters (defined in the text) obtained from the fit of a Drude-Lorentz dielectric function are as follows (the vibrational bands which are present in the i.r. range have been suppressed for clarity).

	C.T. band parameters/cm ⁻¹		
	ω_{CT}	Γ	ω_p
(+) [BEDTTTF] ₄ [Ni(CN) ₄]	~1800	3750	7060
(●) [TMTSF] ₃ [Ni(CN) ₄]	2750	2870	8060
(X) [TMTTF] ₃ [Ni(CN) ₄]	3000	4100	7180

stacking mode is irregular; indeed, the intra-trimer Se ··· Se contacts (3.66–3.78 Å) [Figure 1(b)], are shorter than those commonly observed in the 2 : 1 series,⁴ while the inter-trimer Se ··· Se contacts are longer than the corresponding 4 Å van der Waals distances. TMTTF and TMTSF give isostructural salts with both Pt(CN)₄ and Ni(CN)₄. Additionally, a (TMTTF)₂Ni(CN)₄ phase has been obtained under different experimental conditions.⁵

In compound (3)§ the ET molecules form tetramerized slipped stacks⁶ [Figure 1(c)]. The intra-stack S ··· S contacts are greater than the corresponding 3.8 Å van der Waals separations, while inter-stack S ··· S contacts smaller than 3.8 Å are observed. This stacking mode is generally observed in other ET salts.^{1d} The salts (3) and (6) are rare examples of 4 : 1 stoichiometries with dianions in the ET series. The change of the charge on the anion results in salts where the sheet-like network packing and the formal charge of +0.5 on each ET molecule are similar to those often observed in the ET salts with monoanion.^{1d}

The common structural features of these salts are: (i) the bond lengths within the planar Pt(CN)₄ units agree well with

those observed, *e.g.*, in K₂Pt(CN)₄·3H₂O⁷ [average Pt–C, 1.989(2) and C–N, 1.159(2) Å]; (ii) in the Pt(CN)₄ units the Pt atoms are fully oxidized, as indicated by the facts that they are not stacked and that the Ni(CN)₄ dianions, which are too inefficient to give a partially oxidized linear chain,² give isostructural salts (see Table 1); (iii) the Pt(CN)₄ dianions form with the organic radical cation a dihedral angle of about 70°.

In a preliminary investigation, we measure the d.c. electrical conductivity at room temperature (Table 1), using a standard four probe method, and the visible and i.r. electronic absorption spectra, on dispersed KBr pellets using the standard procedure.⁸ Because of the isomorphism between the two series of Pt and Ni salts, we have chosen to present the electronic absorption bands, at room temperature, of the Ni series¶ (Figure 2). The main characteristic, observed for every compound, is the presence of an intense charge transfer (CT)

¶ The spectroscopic data for the Pt salts have been measured and are essentially identical to those of the Ni salts. These results will be reported elsewhere.

band around 3000 cm^{-1} ('A' peak), which is the sign of a mixed valence system; this result confirms that these compounds are low-dimensional CT conductors, as evidenced by d.c. conductivity experiments. Using a Drude-Lorentz model which is representative of the interband transitions in a 1-D extended Hubbard model where the electronic correlations are large,⁹ we have fitted the low energy CT band. For a Lorentz oscillator, we define the following parameters: ω_{CT} , characteristic of the resonance frequency, Γ , the full-width-at-half-maximum, and ω_{p} , the plasma frequency (Figure 2, insert). We have observed two different types of behaviour for these compounds. On the one hand, in the ET salts, besides the low energy CT band, there is a second intense band around 10000 cm^{-1} ('B' peak) which is characteristic of a double charge site, as already detected in other ET salts; e.g., the same behaviour has been observed in $\beta\text{-(ET)}_2\text{ICl}_2$;¹⁰ this comparison indicates that this compound could reveal an interesting low temperature electronic state. On the other hand, we have observed for the isomorphous TMTTF and TMTSF salts, a qualitative behaviour reminiscent of the corresponding classical 2:1 salts.⁹ In particular, we detect a very weak B-type band which indicates that the probability of doubly occupied sites in these compounds is low. Nevertheless, these show trimerized stacks with a mean degree of ionicity $\rho = 2/3$. This structural situation is basically different for the physical properties,¹¹ in particular concerning the vibrational characteristics. Indeed, we have already detected vibronic modes in the i.r. range⁸ which are characteristic of an irregular stacking.

More detailed investigations on electronic and magnetic properties, are needed in order to understand the physical properties of this new series of organomineral salts. Moreover, in order to obtain new materials where mixed valence states could coexist both in organic and inorganic systems, we now attempt to answer the question: is it possible to stabilize together the two partially oxidized chains of organic and inorganic entities (especially in the case of the tetracyano-

platinate dianions) in the same solid, as in organic charge transfer salts like TTF-TCNQ (TCNQ = tetracyanoquinodimethane)?

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