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A new stable organic metal based on the BEDO-TTF donor and the doubly charged nitroprusside anion, $(BEDO\text{-}TTF)_4[Fe(CN)_5NO]$

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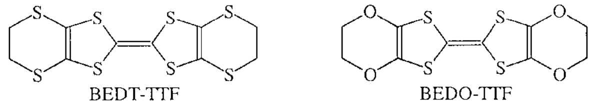
$(BEDO\text{-}TTF)_4[Fe(CN)_5NO]$ was synthesized by electrocrystallization using the nitroprussides $M_2[Fe(CN)_5NO]\cdot 2H_2O$ (M = K, Rb) as supporting electrolytes and TCE (1,1,2-trichloroethane) and DCE (1,2-dichloroethane) as solvents. The crystal structure of this new salt ($a = 4.0251(3)$, $b = 15.266(2)$, $c = 19.259(2)$ Å, $\alpha = 97.02(1)$, $\beta = 93.23(1)$, $\gamma = 96.04(1)°$, $V = 1165.1(2)$ Å^3, $Z = 3/4$, space group $P\bar{1}$) is characterized by the presence of β″-type radical cation layers and anion layers containing disordered nitroprusside anions. The stoichiometry was confirmed by a micro-Raman spectroscopic study and the band structure and Fermi surface of this new salt were studied by means of the extended Hückel tight binding method. $(BEDO\text{-}TTF)_4[Fe(CN)_5NO]$ is a two dimensional metal stable down to liquid helium temperatures.

Bis(ethylenedioxy)tetrathiafulvalene (BEDO-TTF)[1] is the oxygen substituted analogue of bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF).



Up to now many BEDO-TTF based radical cation salts with inorganic and organic anions have been synthesized and structurally characterized.[2–22] A large number of them are molecular metals including two superconductors $(BEDO\text{-}TTF)_3Cu_2(NCS)_3$[5] and $(BEDO\text{-}TTF)_2ReO_4\cdot H_2O$.[7,8] It is noteworthy that despite the similar size and shape of the BEDT-TTF and BEDO-TTF donors, the conducting layers of BEDO-TTF radical cation salts with a large variety of counterions generally have a different architecture from those of the corresponding BEDT-TTF salts. A comparison of the crystal structures of many of the presently known BEDO-TTF and BEDT-TTF organic metals leads to the following observations:

(1) Whereas for the BEDT-TTF salts several packing motifs of the radical cation layers (α, β, θ, κ, α″, β″ *etc.*) are found, most of the BEDO-TTF salts have the common β″ packing motif.† The only exceptions are three α″-salts $[(BEDO\text{-}TTF)_5(HCP)(PhCN)_{0.2}$,[16] $(BEDO\text{-}TTF)_6(HCDAH)$[25] and $(BEDO\text{-}TTF)_4Pt(CN)_4\cdot H_2O$[17]], one θ-salt $[(BEDO\text{-}TTF)_2Cl_{1.28}(H_3O)_{0.28}(H_2O)_{2.44}$[11–14]] and one κ-salt $[(BEDO\text{-}TTF)_2CF_3SO_3$[20]].

(2) In general, the crystals of the BEDO-TTF salts are not isostructural with those of the corresponding BEDT-TTF salts. There are only two examples for which the crystals are isostructural. However in these cases the physical properties are different: β″-$(BEDO\text{-}TTF)_2AuBr_2$ is a room temperature metal and exhibits a metal to insulator transition at 260 K[4] whereas β″-$(BEDT\text{-}TTF)_2AuBr_2$ is metallic down to 1.4 K;[26] κ-$(BEDO\text{-}TTF)_2CF_3SO_3$ is a room temperature metal exhibiting a metal to insulator transition at 150 K[23] whereas κ-$(BEDT\text{-}TTF)_2CF_3SO_3$ is an insulator.[27]

(3) Radical cation salts of BEDT-TTF and BEDO-TTF with the same anion have very often different compositions. Consider for instance the following pairs of salts: β-$(BEDT\text{-}TTF)_2ReO_4$[28] and β″-$(BEDO\text{-}TTF)_2ReO_4\cdot H_2O$,[7,8] α, β, θ, κ-$(BEDT\text{-}TTF)_2I_3$[29] and β″-$(BEDO\text{-}TTF)_{2.4}I_3$,[2] α″-$(BEDT\text{-}TTF)_2[CsHg(SCN)_4]$[30] and β″-$(BEDO\text{-}TTF)_5[CsHg(SCN)_4]_2$.[22]

Recently a series of electroconducting radical cation salts based on BEDT-TTF and some of its analogues with the photochromic nitroprusside anion ($[Fe(CN)_5NO]^{2-}$) have been synthesized.[31,32] The nitroprusside anion is interesting because it possesses an extremely long-living metastable excited state at low temperatures generated with laser light.[33–38] This electronic transition is probably accompanied by a change in the

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†Full information on the packing motifs for donor layers in organic metals can be found in the review papers by Mori.[23,24]

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geometry of the complex.[34] With this fact in mind, it was expected that the conducting properties of radical cation salts of this anion could be interesting to study. The X-ray study of the organic metals (BEDT-TTF)$_4$M[Fe(CN)$_5$NO]$_2$ (M = K, Rb) showed that the presence of the radical cation system in the crystals affects the geometry of the nitroprusside anion. Thus, the study of the photochromic properties of the radical cation salts with the nitroprusside anion is of special interest.

In this work we report on the synthesis of (BEDO-TTF)$_4$[Fe(CN)$_5$NO], a new radical cation salt of the nitroprusside anion. This salt has been characterized throughout single crystal X-ray structural and Raman spectra studies, conductivity measurements as well as electronic band structure calculations.

Experimental

Synthesis

Crystals of the BEDO-TTF salt with the nitroprusside anion were grown under anaerobic conditions on platinum wire electrodes ($d = 1$ mm) in H-shaped electrocrystallization cells under galvanostatic conditions ($I = 0.25$ µA cm^{-2}) using the nitroprussides (M$_2$[Fe(CN)$_5$NO] (M = Rb, K) or [(C$_6$H$_5$)$_4$P]$_2$[Fe(CN)$_5$NO]) as supporting electrolytes (Table 1). The electrocrystallization was performed at 25 °C. The composition of the salts was determined by X-ray structural and/or X-ray microprobe analyses.

Electrical resistivity measurements

The resistivity was measured by a standard four-probe dc method along the *a*-axis of the crystals. Contacts to the crystals were glued with a graphite paste using 10–20 µm diameter platinum wires.

X-Ray structure determination‡

Examination of numerous single crystals of the BEDO-TTF radical cation salt with the nitroprusside anion (Table 1) using the X-ray diffraction photo technique showed the existence of two types of single crystals: triclinic single crystals exhibiting sharp Bragg reflections and orthorhombic single crystals with very spreading diffuse reflections and the unit cell parameters: $a = 4.14(1)$, $b = 10.30(2)$, $c = 38.5(1)$ Å, $V = 1642$ Å^3. The X-ray structural analysis was only performed for the triclinic single crystals.

$C_{45}H_{32}FeN_6O_{17}S_{16}$, $M = 1497.6$, $P\bar{1}$, $a = 4.0251(3)$, $b = 15.266(2)$, $c = 19.259(2)$ Å, $\alpha = 97.02(1)$, $\beta = 93.23(1)$, $\gamma = 96.04(1)°$, $V = 1165.1(2)$ Å^3, μ (Mo-Kα) = 8.5 cm^{-1}, $Z = 3/4$. X-Ray experimental data (3143 reflections) were collected on an Enraf Nonius CAD-4F diffractometer [$T = 295$ K, Mo-Kα, $2\theta_{max} = 50°$] and averaged ($R_{av} = 1.2\%$) to yield 2735 non-zero independent reflections. The structure was solved by a direct method using the AREN programs[39] and was refined in the anisotropic–isotropic (for the anion atoms) approximation by using the SHELXL-97 package[40] to $R = 0.071$ for 302 parameters. The positions of the hydrogen atoms were determined geometrically and not refined.

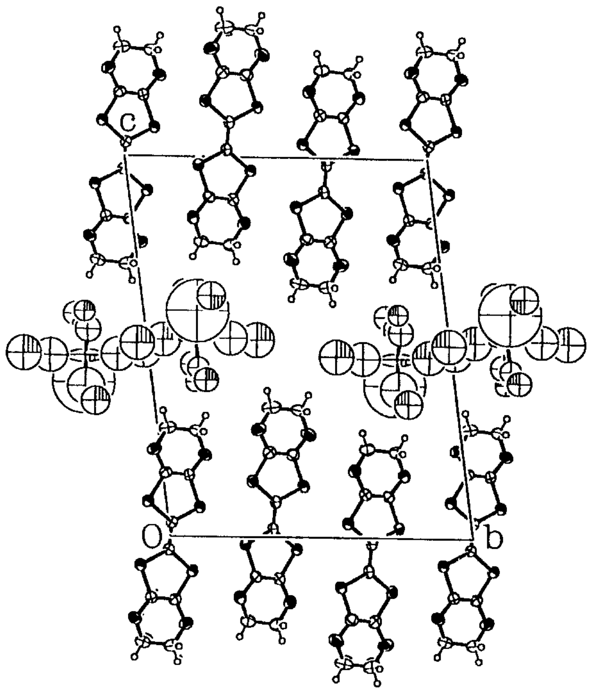

Fig. 1 Projection of the structure of (BEDO-TTF)$_4$[Fe(CN)$_5$NO] along the *a*-direction.

The position of the nitroprusside anion could not be exactly determined because of disorder in the anion layer. In fact, the cell parameter found ($a = 4.025$ Å) was too small to accommodate the nitroprusside anion. What happens is that on average there are three anions every four unit cells. Consequently, a four-times larger *a*-parameter (≈ 16.1 Å) could have been expected. However, disorder is too large to lead to a new long-range order. Indeed, no superlattices were detected even by rotation and Weissenberg methods. The structure described here is thus an average one. A similar situation was also reported earlier for several BEDO-TTF radical cation salts such as (BEDO-TTF)$_2$ClO$_4$,[4] (BEDO-TTF)$_{10}$[C(CN)$_3$]$_4$(H$_2$O)$_3$,[16] (BEDO-TTF)$_4$(SQA)(H$_2$O)$_6$,[16] (BEDO-TTF)$_5$(HCP)(PhCN)$_{0.2}$[16] and (BEDO-TTF)$_2$Br(H$_2$O)$_3$,[19] where the anions have not been exactly localized.

Raman spectra

The triclinic single crystals from different syntheses (Entries 1 and 2, Table 1) were used. Spectra were measured using a Renishaw Raman grating microscope spectrometer equipped with a He–Ne laser ($\lambda = 632.6$ nm) in 180° reflective geometry. The spectral resolution was 2 cm^{-1}. The laser power was attenuated down to 0.07 mW and focused into a 0.005 mm spot on the sample surface. The incident light was polarized along the [100] and [010] crystal axes and all polarization was collected for the scattered light. A slight difference between the two directions was observed in the absolute intensities of the peaks but not in the Raman shift frequencies. Two Raman-

Table 1 Conditions for the electrocrystallization of the (BEDO-TTF)$_4$NP (NP = [Fe(CN)$_5$NO]) salts

Entry	Salt	T/°C	Solvent[a,b]	Electrolyte	Time of crystallization	Symmetry of crystals
1	(BEDO-TTF)$_4$NP	25	DCE	Rb$_2$[NP]·2H$_2$O[c]	2 months	Triclinic
2	(BEDO-TTF)$_4$NP	25	TCE	K$_2$[NP]·2H$_2$O[c]	2 months	Triclinic
3	(BEDO-TTF)$_4$NP	25	DCE	(C$_6$H$_5$)$_4$P[NP]	1 month	Orthorhombic
4	(BEDO-TTF)$_4$NP	25	DCE	K$_2$[NP]·2H$_2$O[c]	1 month	Orthorhombic

[a]DCE: 1,2-dichloroethane, TCE: 1,1,2-trichloroethane. [b]Contains 5% EtOH. [c]18-crown-6-ether was added.

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‡CCDC reference number 1145/233. See http://www.rsc.org/suppdata/jm/b0/b003433i for crystallographic files in .cif format.

Table 2 Bond lengths d (Å) and angles ω (degrees) for the BEDO-TTF radical cations of $(BEDO\text{-}TTF)_4[Fe(CN)_5NO]$

Bond	d/Å	Angle	ω/°
S1–C1	1.733(7)	C1–S1–C2	94.5(3)
S1–C2	1.744(7)	C1–S2–C3	93.9(3)
S2–C1	1.748(6)	C2–O1–C4	109.8(5)
S2–C3	1.729(7)	C3–O2–C5	109.7(6)
O1–C2	1.345(8)	S1–C1–C1′	122.0(7)
O1–C4	1.441(9)	S2–C1–C1′	121.7(7)
O2–C3	1.356(8)	S1–C2–O1	117.3(5)
O2–C5	1.452(9)	S1–C2–C3	116.7(6)
C1–C1′	1.363(13)	O1–C2–C3	125.9(7)
C2–C3	1.349(10)	S2–C3–O2	117.4(5)
C4–C5	1.495(11)	S2–C2–C2	118.5(6)
S3–C6	1.736(7)	O2–C3–C2	124.2(7)
S3–C8	1.743(7)	O1–C4–C5	110.9(6)
S4–C6	1.730(6)	O2–C5–C4	111.4(6)
S4–C9	1.745(7)	C6–S3–C8	93.7(3)
S5–C7	1.751(7)	C6–S4–C9	94.1(3)
S5–C10	1.738(8)	C7–S5–C10	94.1(3)
S6–C7	1.737(7)	C7–S6–C11	94.6(3)
S6–C11	1.729(8)	C8–O3–C12	110.6(5)
O3–C8	1.363(8)	C9–O4–C13	110.3(5)
O3–C12	1.438(9)	C10–O5–C14	109.1(6)
O4–C9	1.355(8)	C11–O6–C15	111.1(6)
O4–C13	1.436(9)	S3–C6–S4	117.3(4)
O5–C10	1.358(9)	S3–C6–C7	121.4(5)
O5–C14	1.453(10)	S4–C6–C7	121.3(5)
O6–C11	1.352(9)	S5–C7–S6	116.2(4)
O6–C15	1.441(11)	S5–C7–C6	121.6(5)
C6–C7	1.375(10)	S6–C7–C6	122.2(5)
C8–C9	1.354(10)	S3–C8–O3	118.3(5)
C10–C11	1.359(10)	S3–C8–C9	117.9(5)
C12–C13	1.497(10)	O3–C8–C9	123.8(6)
C14–C15	1.467(12)	S4–C9–O4	118.3(5)
		S4–C9–C8	117.0(5)
		O4–C9–C8	124.7(6)
		S5–C10–O5	117.5(6)
		S5–C10–C11	117.5(6)
		O5–C10–C11	125.0(7)
		S6–C11–O6	118.5(6)
		S6–C11–C10	117.6(6)
		O6–C11–C10	123.9(7)
		O3–C12–C13	110.4(6)
		O4–C13–C12	111.0(6)
		O5–C14–C15	112.3(7)
		O6–C15–C14	111.4(7)

active C=C stretching vibrations of BEDO-TTF which correlate linearly with the charge were used for testing.[41]

Band structure calculations

The electronic structure of $(BEDO\text{-}TTF)_4[Fe(CN)_5NO]$ was studied by means of the extended Hückel tight binding method.[42] A modified Wolfsberg–Helmholtz formula[43] was used to calculate the non-diagonal H_{ij} matrix elements. Double-ζ orbitals[44] for C, O and S were used. The exponents and parameters used in the calculations were taken from previous work.[45]

Results and discussion

Fig. 1 shows the crystal structure of $(BEDO\text{-}TTF)_4[Fe(CN)_5NO]$ viewed along the a-axis. The structure is

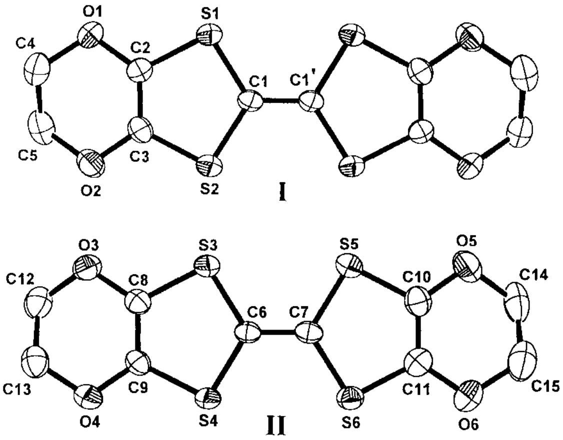

Fig. 2 Atom numbering for the BEDO-TTF radical cations I and II.

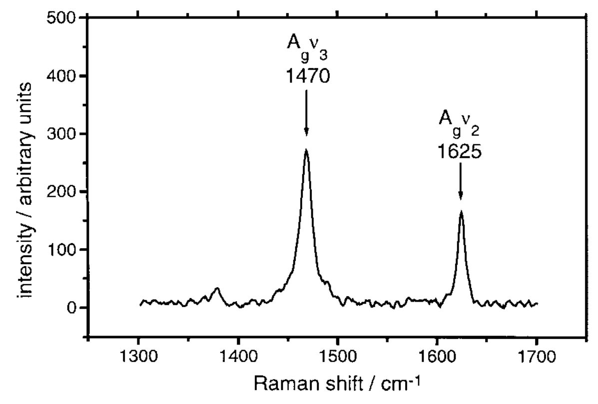

Fig. 3 Raman spectrum of the $(BEDO\text{-}TTF)_4[Fe(CN)_5NO]$ single crystals.

characterized by BEDO-TTF radical cation layers alternating with anion layers along the *c*-direction. The asymmetric unit cell contains two BEDO-TTF molecules, one of them (I) lies on a center of symmetry and the other one (II) in a general position. Both donor molecules have an eclipsed conformation of the outer ethylene groups as well as similar bond lengths and angles (Table 2, see Fig. 2 for atom labelling). The nature of the bond lengths and angle distribution probably corresponds to $(\text{BEDO-TTF})^{0.5+}$. It is noteworthy that the C=C double bonds C1–C1′ [1.363(11) Å] and C6–C7 [1.375(10) Å] are longer than the corresponding bond [1.342(9) Å] in the neutral $(\text{BEDO-TTF})^0$ molecule[4] but shorter than in the BEDO-TTF^{1+} radical cation [1.398 Å] of the $(\text{BEDO-TTF})I_3$ salt.[46] These bond lengths are close to those found in the 2 : 1 salts: $(\text{BEDO-TTF})_2ClO_4$,[4] $(\text{BEDO-TTF})_2ReO_4{\cdot}H_2O$,[8] $(\text{BEDO-TTF})_2Br{\cdot}3H_2O$,[19] $(\text{BEDO-TTF})_2CF_3SO_3$[10] and $(\text{BEDO-TTF})_2Cl_{1.28}(H_3O)_{0.28}(H_2O)_{2.44}$.[14]

A representative Raman spectrum is shown in Fig. 3. Two peaks are assigned to the stretching modes of the central (ν_3) and ring (ν_2) C=C bonds of BEDO-TTF. No difference between the spectra for the triclinic crystals from different syntheses (Entries 1 and 2, Table 1) was detected within experimental error. Recently we have found the following linear correlations between the formal charge of BEDO-TTF (ρ) and the experimental Raman shift frequencies ν_3 and ν_2:[41]

$$\rho = (1524.9 - \nu_3\ (\text{cm}^{-1}))/109.0, \quad \Delta\rho = \pm 0.05 \qquad (1)$$

$$\rho = (1660.8 - \nu_2\ (\text{cm}^{-1}))/74.1, \quad \Delta\rho = \pm 0.1 \qquad (2)$$

From the frequencies observed in this study we conclude that $\rho = 0.50 \pm 0.05$, which is an important additional confirmation of the $(\text{BEDO-TTF})_4[Fe(CN)_5NO]$ composition for the radical cation salt investigated.

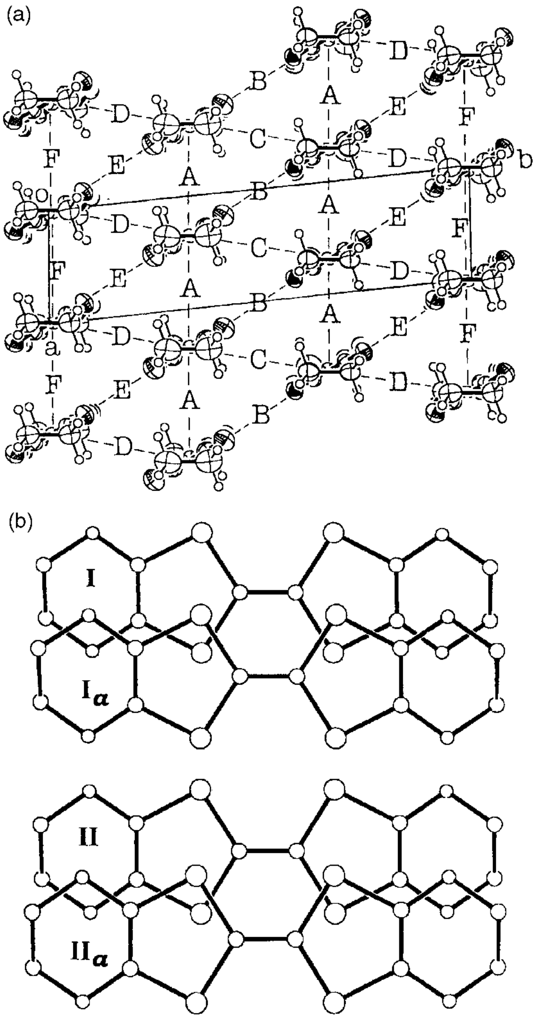

Fig. 4 a) Projection of the radical cation layer of $(\text{BEDO-TTF})_4[Fe(CN)_5NO]$ along the long molecular axis, and b) Overlap mode within the radical cation stacks. The six different types of donor···donor intermolecular interactions (see Table 3 for the associated short contacts) discussed in the text are shown in (a). Donors I (II) are those related through interactions F (A) along the *a*-direction.

The projection of the radical cation layer along the long molecular axis is shown in Fig. 4a. The cation packing in $(\text{BEDO-TTF})_4[Fe(CN)_5NO]$ is typical for most of the known BEDO-TTF-based organic metals. It is known as "I_3-type" according to Horiuchi *et al.*[16] because it was first found in BEDO-TTF salts for $(\text{BEDO-TTF})_{2.4}I_3$,[2] or β″-type according to the Mori structural classification of the salts of BEDT-TTF and analogues.[23,24] The radical cation layers contain two non-equivalent BEDO-TTF stacks parallel to the *a*-axis. The radical cations I and II are nearly parallel (dihedral angle I–II = 0.6(2)°). The stacking axis is tilted 60° (60.3°) with respect to the molecular plane I (II) and 91.1° (90.3°) with respect to the central C=C bond. This means that the stacks are only slipped along the transverse molecular axis (see Fig. 4b). The interplanar separations are 3.486 and 3.495 Å for I–I$_a$ and II–II$_a$, respectively. The donor stacks exhibit short intermolecular C–H···O and S···S distances (see interactions A and F in Table 3). There are also short interstack contacts along the [2$\bar{1}$0] (see interactions B and E in Table 3, dotted lines in Fig. 4a) and [110] directions (see interaction D in Table 3, dotted lines in Fig. 4a). Because of some disorder in the anion part, the specific interactions between the donors and the counterions could not be identified satisfactorily.

The conductivity measurements were carried out on single crystals along the stack direction (*i.e.*, the *a*-axis) and the σ_{RT} values obtained were 10–50 S cm^{-1}.[31] The temperature dependence of the dc resistivity along the *a*-axis exhibits metallic character down to 1.3 K (Fig. 5). The study of the photochromic properties of this salt is now in progress and will be reported elsewhere.

The calculated band structure for the BEDO-TTF layers of $(\text{BEDO-TTF})_4[Fe(CN)_5NO]$ in the region of the Fermi level is shown in Fig. 6a. Since there are three donors per repeat unit of the layer there are three bands mainly built from the HOMO of BEDO-TTF. The HOMOs of donors I and II are very similar in energy so that they strongly mix and lead to the quite dispersive bands of Fig. 6a. According to the stoichiometry, the BEDO-TTF donors have a +1/2 charge so that there are 4.5 electrons to fill these bands. Since the two higher bands overlap, both are partially filled. The important dispersion and partial occupation of these bands is in agreement with the metallic character of the salt.

In order to correlate the details of the crystal and electronic structure of this salt we have calculated the $\beta_{\text{HOMO–HOMO}}$ interaction energies[47] which are a useful measure of the nearest neighbor HOMO–HOMO interactions in the layer. The absolute values of these energies are reported in Table 3. It is worth noting that the BEDO-TTF layers can be seen as a series of parallel stacks of slipped donors along the *a*-direction, as a series of parallel chains of donors making lateral contacts along the [2$\bar{1}$0] direction, or as a series of parallel step-chains of donors along the [110] direction. The stacks of slipped donors are associated with interaction A or F, the chains along [2$\bar{1}$0] with interactions B or E, and the step-chains with interactions C and D. The interactions along the chains in the [2$\bar{1}$0] direction and along the step chains are comparable while those along the slipped stacks are smaller by a factor of two. However the later ones are far from negligible so that we must conclude that the BEDO-TTF layer is a strongly two-dimensional network of HOMO–HOMO interactions.

Table 3 Short S···S ($r \leqslant 3.70$ Å), S···O ($r \leqslant 3.35$ Å) and C–H···O (r (H···O)$\leqslant 2.72$ Å) distances as well as absolute values of the $\beta_{\mathrm{HOMO-HOMO}}$ interaction energies (eV) in the radical cation layer of (BEDO-TTF)$_4$[Fe(CN)$_5$NO].

Interaction[a]	S···S/Å	S···O/Å	C – H···O/Å	$\beta_{\mathrm{HOMO-HOMO}}$
A	3.620, 3.644	–	2.635 (×2), 2.706 (×2)	0.0873
B	3.392 (×2), 3.428	3.245 (×2)	–	0.2129
C	–	–	–	0.1704
D	3.685, 3.690	–	–	0.1855
E	3.391, 3.414, 3.443	3.203, 3.280	–	0.2151
F	3.621 (×2)	–	2.661, 2.662, 2.671, 2.696	0.0971

[a] See Fig. 4a for labeling.

That the interactions along the step-chains are among the stronger of the layer is also the case for most BEDT-TTF radical cation salts with this type of packing (note that two S···S contacts of 3.700 and one of 3.717 Å are associated with interaction C although they are not reported in Table 3 because they are slightly longer that the usual metric criterion of $r \leqslant 3.70$ Å to designate the short S···S contacts). What may be more surprising is that the interactions along the [2$\bar{1}$0] direction which are lateral contacts and hence lead to π-type interactions between the HOMOs, as opposed to the mainly σ-type interactions along the step-chains, are so strong. In the analogous BEDT-TTF layers these interactions are smaller by a factor of approximately two.[32,47,48] The reason lies in the very short S···S contacts which override the intrinsic weakness of the π-type interactions with respect to the σ-type ones. These very short contacts are a consequence of the smaller size of the oxygen atoms with respect to the sulfur ones which allows for closer lateral contacts between the two almost coplanar donors. This is an important difference with the BEDT-TTF salts with similar packing which of course influences the nature of the Fermi surface. As shown in Table 3, interactions B and E are also associated with short S···O contacts for the same reason. However, these contacts do not play a role in the enhancement of the HOMO–HOMO interactions for these lateral contacts because, the HOMO of BEDO-TTF has a very small contribution from the p orbitals of the oxygen sites. This is in contrast with the situation in the BEDT-TTF salts where although the outer sulfur p orbitals contribute to the BEDT-TTF HOMO with a lesser weight than the inner ones (approximately a third), this contribution is not negligible at all. Consequently, the short contacts involving the oxygens of BEDO-TTF can be neglected in rationalizing the strength of the HOMO–HOMO interactions and thus, the dispersion of the HOMO bands. Finally, note that the interactions along the step-chains are twice larger than those along the slipped stacks. Both types of interactions are mostly of σ-type but, whereas in the latter the two donors are slipped along the short molecular axis, two adjacent donors of the step-chain are slipped along both the short and long molecular axes. This leads to only two S···S contacts per interaction along the slipped stacks but three (as well as some S···C contacts) along the step-chains and thus, to the larger $\beta_{\mathrm{HOMO-HOMO}}$ interaction energies.

The important result of Table 3 is that the two different interactions associated with a given mode of interaction (*i.e.*, slipped stacks, chains with lateral contacts and step-chains) are almost the same. In addition, the $\beta_{\mathrm{HOMO-HOMO}}$ interaction energies calculated for the prototypic BEDO-TTF layer of (BEDO-TTF)$_{2.4}$I$_3$, with a repeat unit of just one donor, are also very similar (0.1044 for the slipped stacks, 0.2204 for the chains with lateral contacts and 0.1843 for the step-chains). This means that, on the basis of the HOMO–HOMO interactions, and despite some structural differences (*i.e.*, some relative slidings between adjacent pairs of donors though keeping the general architecture of the I$_3$-type network) the two salts are

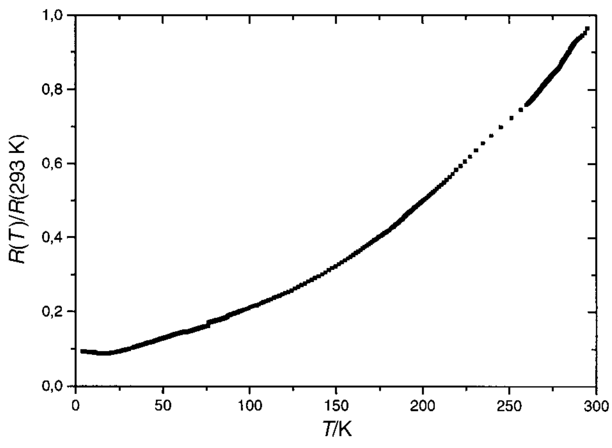

Fig. 5 Temperature dependence of dc resistivity for the (BEDO-TTF)$_4$[Fe(CN)$_5$NO] single crystals.

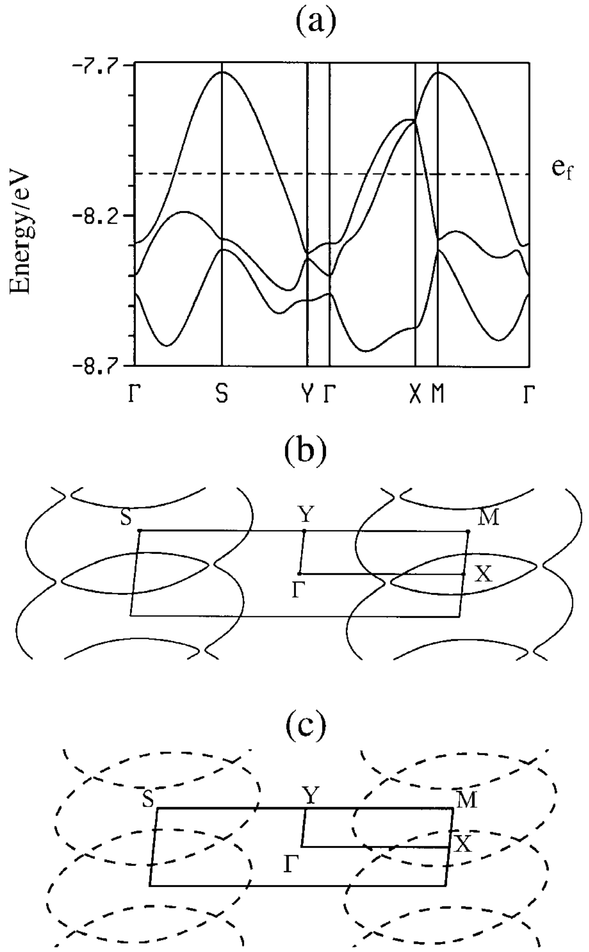

Fig. 6 a) Calculated dispersion relations for the HOMO bands of the donor layers of (BEDO-TTF)$_4$[Fe(CN)$_5$NO], b) calculated Fermi surface, and c) idealized Fermi surface represented as a series of superposing ellipses. This Fermi surface is very similar to that which will be obtained after folding the Fermi surface for a β″-layer with a single BEDT-TTF$^{+1/2}$ as repeat unit.

practically identical. Consequently, the Fermi surface calculated for $(BEDO\text{-}TTF)_4[Fe(CN)_5NO]$ (see Fig. 6b) must be strongly related to that for $(BEDO\text{-}TTF)_{2.4}I_3$ assuming the same oxidation state for the donor.

As expected from the numerical values of the three different interaction energies, the Fermi surface for $(BEDO\text{-}TTF)_{2.4}I_3$ [16] is the typical one for a two-dimensional metal. It is a closed loop with elliptical shape centered at the (b*/2, 0) point of the two-dimensional Brillouin zone (b is the repeat vector along the slipped stacks of this salt).[16] We have verified that this shape is kept for reasonable changes of the BEDO-TTF oxidation state. The repeat unit for the donor layers of $(BEDO\text{-}TTF)_4[Fe(CN)_5NO]$ now contains three donors along the step-chains direction (*i.e.*, $(a+b)$, a being the direction along which the slipped stacks run). Thus the repeat unit is three times larger than that of the parent layers of $(BEDO\text{-}TTF)_{2.4}I_3$ and, consequently, the Brillouin zone should be three times smaller. This means that the Fermi surface for the donor layers of $(BEDO\text{-}TTF)_4[Fe(CN)_5NO]$ must be the appropriately folded version of the ellipse-shape Fermi surface of $(BEDO\text{-}TTF)_{2.4}I_3$ (assuming a $+1/2$ charge for the donors). The expected Fermi surface on the basis of this reasoning would look like that shown in Fig. 6c, which is a slightly idealized version of the real Fermi surface (see Fig. 6b) where the weakly avoided crossings have been neglected. Because of the folding, the ellipses centered at the borderline of the Brillouin zone parallel to the b*-direction, overlap and, in the real Fermi surface (Fig. 6b), because of weakly avoided crossings, there is a formally closed portion centered at X and a pair of very wavy lines parallel to the b*-direction. This Fermi surface has no nesting at all and thus it is not expected that $(BEDO\text{-}TTF)_4[Fe(CN)_5NO]$ can exhibit either charge or spin density wave type instabilities leading to the total or partial suppression of the metallic state. In principle, it is predicted that at least one Shubnikov–deHaas (SdH) frequency should be observable in magnetoresistance experiments. In view of the very weakly avoided crossings, even at low magnetic fields a second frequency corresponding to the full ellipse could also be observable through magnetic breakdown. Since there are 1.5 holes in the two partially filled bands (assuming the stoichiometry proposed here) this frequency should very closely correspond to a cross section area of three-quarters of the Brillouin zone. So far it has not been possible to observe SdH oscillations for this salt, presumably because of the anion disorder.

The very weakly avoided crossings make immediately apparent the parentage with the Fermi surface of $(BEDO\text{-}TTF)_{2.4}I_3$. However this is so because of the simultaneous occurrence of two facts. First, the two donors I and II, and thus their HOMOs, are very similar. Second, the two different HOMO–HOMO intermolecular interactions of each type (*i.e.*, A and F, B and E,…) are also very similar. However this is not necessarily the case for any BEDO-TTF β″-type lattice. The shape of the anion can force stronger differences which can lead to stronger avoided crossings making the relationship with the ellipse-like shape less apparent. Also, the shape of the anion can lead to unit cells with different number of molecules and thus different types of folding can be needed to generate the appropriate Fermi surface from the parent I_3-type one. Since most frequently the ellipses will overlap, quite different shapes for the real Fermi surfaces can be obtained after taking into account the avoided crossings. Let us note that even two salts which are structurally and electronically as similar as $(BEDO\text{-}TTF)_4[Fe(CN)_5NO]$ and $(BEDO\text{-}TTF)_{2.4}I_3$ can lead to differences in their Fermi surfaces that, if it were not for disorder related problems, could have been observed in magnetoresistance experiments. The analogies and differences between the Fermi surfaces of different β″-type BEDO-TTF salts certainly would be very interesting to study. A general theoretical study of the possible Fermi surface shapes for β″-type BEDO-TTF salts will be discussed elsewhere.[49]

Conclusion

The crystal and electronic structures as well as the Raman spectra of the new radical cation salt $(BEDO\text{-}TTF)_4[Fe(CN)_5NO]$ have been studied. The present work makes clear that despite using the same electrocrystallization conditions, the nature of the donor has a strong influence on the composition and stoichiometry of the nitroprusside anion salts.[31] The singly charged inorganic cations (M) of the $M_2[Fe(CN)_5NO]\cdot 2H_2O$ electrolytes enter into the composition of the BEDT-TTF salts while the BEDO-TTF salts do not incorporate these cations. Essentially, the $(BEDT\text{-}TTF)_4M[Fe(CN)_5NO]_2$ (M = Na, K, Rb, NH_4, Tl, Cs) salts contain triply charged anions (stoichiometry $4:3^-$) and the $(BEDO\text{-}TTF)_4[Fe(CN)_5NO]$ salt contains a doubly charged anion (stoichiometry $4:2^-$). $(BEDO\text{-}TTF)_4[Fe(CN)_5NO]$ is a two-dimensional organic metal stable to very low temperatures although it is not superconducting above 1.3 K. It does not exhibit SdH oscillations in a magnetic field. The lack of superconductivity and SdH oscillations are probably related to the disorder of the anions.

$(BEDO\text{-}TTF)_4[Fe(CN)_5NO]$ is a new member of the family of BEDO-TTF-based radical cation salts with the so-called I_3- or β″-type donor layers.[23,24] Many BEDO-TTF salts with inorganic and organic anions so far structurally analyzed posses this very special donor molecular packing pattern. The origin of this phenomenon can be attributed to the existence of short (and strong) C–H···O intermolecular hydrogen bonding contacts,[4,50] to the BEDO-TTF low ionization potential and the ability of its self-aggregation.[9,51] However it is noteworthy that in spite of the similarity of the β″-type donor molecule packing motifs the salts exhibit different electroconducting properties.

Many BEDO-TTF-based organic metals with this type of radical cation layers have been prepared and characterized but only two of them $(BEDO\text{-}TTF)_3Cu(NCS)_3$[5] and $(BEDO\text{-}TTF)_2ReO_4\cdot H_2O$[7,8] have been found to be superconductors. The radical cation salts $(BEDO\text{-}TTF)_{2.4}I_3$,[2,19] $(BEDO\text{-}TTF)_2Cl(H_2O)_3$§,[15] $(BEDO\text{-}TTF)_{10}[C(CN)_3]_4(H_2O)_3$,[16] $(BEDO\text{-}TTF)_4(SQA)(H_2O)_6$[16] and $(BEDO\text{-}TTF)_2Br(H_2O)_3$[19] are stable metals down to 1.3–4.0 K. But the radical cation salts $(BEDO\text{-}TTF)_2AuBr_2$,[4] $(BEDO\text{-}TTF)_2ClO_4$[5] $(BEDO\text{-}TTF)_5[CsHg(SCN)_4]_2$[22] and $(BEDO\text{-}TTF)_4[C_4N_6]H_2O$[20] exhibit a M–I transition at 260, 200, 85 and 8 K, respectively. Our analysis of the electronic structure of the $(BEDO\text{-}TTF)_4[Fe(CN)_5NO]$ salt suggests that the Fermi surface of all these systems must be strongly related. However, the shape and chemical nature of the counter ions, which can vary the size of the unit cell as well as lead to changes in the values of the transfer integrals, can lead to subtle but significant differences in the band structure and Fermi surface of this type of BEDO-TTF salts despite their common origin.

Finally, it is important to remember that we have been able to determine the (BEDO-TTF) sublattice in the crystal structure of $(BEDO\text{-}TTF)_4[Fe(CN)_5NO]$ and we could not observe any superlattice. Note, that for a related chemical system, namely BEDO-TTF + $Rb_2[Fe(CN)_5NO]\cdot 2H_2O$–TCE + 5% EtOH, we obtained single crystals with a superlattice ($a = 4.15\times 4$, $b = 21.00$, $c = 39.0\times 2$ Å) and some diffuse

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§There are two crystal modifications of hydrated BEDO-TTF chloride. Both are stable organic metals down to 1.3 K but have different types of conducting layers and different counterion networks.[15] One of them[11–13] was earlier classified as "Cl"-type[16] (or θ-type[24]). But now that the β″-type has also been found for $(BEDO\text{-}TTF)_2Cl(H_2O)_3$, the Cl-type descriptor does not look quite appropriate.

lines. According to microprobe X-ray analysis this salt incorporates into its composition TCE solvent molecules.

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References

1 T. Suzuki, H. Yamochi, G. Srdanov, K. Hincelman and F. Wudl, *J. Am. Chem. Soc.*, 1989, **111**, 3108.

2 F. Wudl, H. Yamochi, T. Suzuki, H. Isotalo, C. Fite, H. Kasmai, K. Liou, G. Srdanov, P. Coppens, K. Maly and A. Frost-Jensen, *J. Am. Chem. Soc.*, 1990, **112**, 2461.

3 F. Wudl, H. Yamochi, T. Suzuki, H. Isotalo, C. Fite, K. Liou, H. Kasmai and G. Srdanov in *The Physics and Chemistry of Organic Superconductors*, ed. G. Saito and S. Kagoshima, Springer-Verlag, Berlin, 1990, p. 358.

4 M. A. Beno, H. H. Wang, K. D. Carlson, A. M. Kini, G. M. Frankenbach, J. R. Ferraro, N. Larson, C. D. McCabe, J. Thompson, C. Purnama, M. Vashon, J. M. Williams, D. Jung and M.-H. Whangbo, *Mol. Cryst. Liq. Cryst.*, 1990, **181**, 145.

5 M. A. Beno, H. H. Wang, A. M. Kini, K. D. Carlson, U. Geiser, W. K. Kwok, J. E. Thompson, J. M. Williams, J. Ren and M.-H. Whangbo, *Inorg. Chem.*, 1990, **29**, 1599.

6 H. Yamochi, T. Nakamura, G. Saito, T. Kikuchi, S. Sato, K. Nozawa, M. Kinoshita, T. Sugano and F. Wudl, *Synth. Met.*, 1991, **42**, 1741.

7 S. Kahlich, D. Schweitzer, I. Heinen, S. E. Lan, B. Nuber, H. J. Keller, K. Winzer and H. W. Helberg, *Solid State Commun.*, 1991, **8**, 191.

8 L. I. Buravov, A. G. Khomenko, N. D. Kushch, V. N. Laukhin, A. I. Schegolev, E. B. Yagubskii, L. P. Rozenberg and R. P. Shibaeva, *J. Phys. I*, 1992, **2**, 529.

9 H. Yamochi, S. Horiuchi, G. Saito, M. Kusunoki, K. Sakaguchi, T. Kikuchi and S. Sato, *Synth. Met.*, 1993, **55-57**, 2096.

10 M. Fettouhi, L. Ouahab, D. Serhani, J.-M. Fabre, L. Ducasse, J. Amiell, R. Canet and P. Delhaes, *J. Mater. Chem.*, 1993, **3**, 1101.

11 D. Schweitzer, S. Kahlich, I. Heinen, S. E. Lan, B. Nuber, H. J. Keller, K. Winzer and H. W. Helberg, *Synth. Met.*, 1993, **56**, 2827.

12 T. Mori, K. Oshima, H. Okuno, K. Kato, H. Mori and S. Tanaka, *Phys. Rev.*, 1995, **B51**, 11110.

13 E. I. Zhilyaeva, S. A. Torunova, R. N. Lyubovskaya, S. V. Konovalikhin, O. A. Dyachenko, R. B. Lyubovskii and S. I. Pesotskii, *Synth. Met.*, 1996, **83**, 7.

14 R. P. Shibaeva, S. S. Khasanov, B. Zh. Narymbetov, L. V. Zorina, L. P. Rozenberg, A. V. Bazhenov, N. D. Kushch, E. B. Yagubskii, C. Rovira and E. Canadell, *J. Mater. Chem.*, 1998, **8**, 1151.

15 R. P. Shibaeva, S. S. Khasanov, B. Zh. Narymbetov, L. V. Zorina, A. V. Bazhenov, N. D. Kushch, E. B. Yagubskii and E. Canadell, *Synth. Met.*, 1999, **102**, 1650.

16 S. Horiuchi, H. Yamochi, G. Saito, K. Sakaguchi and M. Kusunoki, *J. Am. Chem. Soc.*, 1996, **118**, 8604.

17 E. I. Zhilyaeva, R. N. Lyubovskaya, S. A. Torunova, S. V. Konovalikhin, O. A. Dyachenko and R. B. Lyubovskii, *Synth. Met.*, 1996, **80**, 91.

18 S. Horiuchi, H. Yamochi, G. Saito and K. Matsumoto, *Synth. Met.*, 1997, **86**, 1809.

19 S. Horiuchi, H. Yamochi, G. Saito, J. K. Jeszka, A. Tracz, A. Spoczynska and J. Ulanski, *Mol. Cryst. Liq. Cryst.*, 1997, **296**, 365.

20 B. H. Ward, G. E. Granroth, J. B. Walden, K. A. Abboud, M. W. Meisel, P. G. Rasmussen and D. R. Talham, *J. Mater. Chem.*, 1998, **8**, 1373.

21 E. I. Zhilyaeva, R. N. Lyubovskaya, S. V. Konovalikhin, O. A. Dyachenko and R. B. Lyubovskii, *Synth. Met.*, 1998, **94**, 35.

22 E. I. Zhilyaeva, O. A. Bogdanova, R. N. Lyubovskaya, R. B. Lyubovskii, K. A. Lyssenko and M. Yu. Antipin, *Synth. Met.*, 1999, **99**, 169.

23 T. Mori, *Bull. Chem. Soc. Jpn.*, 1998, **71**, 2509.

24 T. Mori, H. Mori and S. Tanaka, *Bull. Chem. Soc. Jpn.*, 1999, **72**, 179.

25 H. Yamochi, K. Tsutsumi, T. Kawasaki and G. Saito, *Mater. Res. Soc. Symp. Proc.*, 1998, **488**, 641.

26 M. Kurmoo, D. R. Talham, P. Day, I. D. Parker, R. H. Friend, A. M. Stringer and J. A. K. Howard, *Solid. State Commun.*, 1987, **61**, 459.

27 M. Fettouhi, L. Ouahab, C. Gomez-Garcia, L. Ducasse and P. Delhaes, *Synth. Met.*, 1995, **70**, 1131.

28 S. S. P. Parkin, E. M. Engler, R. R. Schumaker, R. Lagier, V. Y. Lee, J. Voiron, K. Carneiro, J. C. Scott and R. L. Greene, *J. Phys.*, 1983, **44**, C3–791.

29 J. M. Williams, J. R. Ferraro, R. J. Thorn, K. D. Carlson, U. Geiser, H. H. Wang, A. M. Kini and M.-H. Whangbo, *Organic Superconductors (Including Fullerenes). Synthesis, Structure, Properties, and Theory*, Prentice Hall, Englewood Cliffs, NJ, 1992.

30 H. Mori, S. Tanaka, T. Mori, Y. Maruyama, H. Inokuchi and G. Saito, *Solid State Commun.*, 1991, **78**, 49.

31 L. Kushch, L. Buravov, V. Tkacheva, E. Yagubskii, L. Zorina, S. Khasanov and R. Shibaeva, *Synth. Met.*, 1999, **102**, 1646.

32 M. Gener, E. Canadell, S. S. Khasanov, L. V. Zorina, R. P. Shibaeva, L. A. Kushch and E. B. Yagubskii, *Solid State Commun.*, 1999, **111**, 329.

33 M. R. Pressprich, M. A. White, V. Vekhter and P. Coppens, *J. Am. Chem. Soc.*, 1994, **116**, 5233.

34 M. D. Carducci, M. R. Pressprich and P. Coppens, *J. Am. Chem. Soc.*, 1997, **119**, 2669.

35 H. Zöllner, W. Krasser and T. Woike, *Chem. Phys. Lett.*, 1989, **161**, 497.

36 H. Zöllner, T. Woike, W. Krasser and S. Haussühl, *Z. Kristallogr.*, 1989, **188**, 139.

37 T. Woike, W. Krasser, P. Bechthold and S. Haussühl, *Phys. Rev. Lett.*, 1984, **53**, 1767.

38 T. Woike and S. Haussühl, *Solid State Commun.*, 1993, **86**, 333.

39 V. I. Andrianov, AREN-88. System of Programs for Solving and Refinement of Crystal Structures, Institute of Crystallography AN SSSR, Moscow, 1988.

40 G. M. Sheldrick SHELXL-93, Program for the Refinement of Crystal Structure, Göttingen University, Germany, 1993.

41 O. Drozdova, H. Yamochi, K. Yakushi, M. Uruichi, S. Horiuchi and G. Saito, *J. Am. Chem. Soc.*, 2000, **122**, 4436.

42 M.-H. Whangbo and R. Hoffmann, *J. Am. Chem. Soc.*, 1978, **100**, 6093.

43 J. Ammeter, H.-B. Bürgi, J. Thibeault and R. Hoffmann, *J. Am. Chem. Soc.*, 1978, **100**, 3686.

44 (*a*) M.-H. Whangbo, J. M. Williams, P. C. W. Leung, M. A. Beno, T. J. Emge, H. H. Wang, K. D. Carlson and G. W. Crabtree, *J. Am. Chem. Soc.*, 1985, **107**, 5815; (*b*) E. Clementi and C. Roetti, *At. Nucl. Data Tables*, 1974, **14**, 177.

45 S. S. Khasanov, B. Zh. Narymbetov, L. V. Zorina, L. P. Rosenberg, R. P. Shibaeva, N. D. Kushch, E. B. Yagubskii, R. Rousseau and E. Canadell, *Eur. Phys. J. B*, 1998, **1**, 419.

46 S. Horiuchi, H. Yamochi, G. Saito and K. Matsumoto, *Mol. Cryst. Liq. Cryst.*, 1996, **284**, 357.

47 M.-H. Whangbo, J. M. Williams, P. C. W. Leung, M. A. Beno, T. J. Emge and H.-H. Wang, *Inorg. Chem.*, 1985, **24**, 3500. These interaction energies (β) should not be confused with the conventional transfer integrals (t) although they have the same physical meaning. The β values are usually larger than the t ones mainly because overlap is included in extended Hückel calculations..

48 L. F. Veiros and E. Canadell, *J. Phys. I*, 1994, **4**, 939.

49 M. Gener, R. Rousseau and E. Canadell, unpublished work.

50 M.-H. Whangbo, D. Jung, J. Ren, M. Evain, J. J. Novoa, F. Mota, S. Alvarez, J. M. Williams, M. A. Beno, A. M. Kini, H. H. Wang and J. R. Ferraro, in *The Physics and Chemistry of Organic Superconductors*, ed. G. Saito and S. Kagoshima, Springer-Verlag, Berlin, Heidelberg, 1990, p. 262.

51 H. Yamochi, S. Horiuchi and G. Saito, *Phosphorus, Sulfur, Silicon*, 1992, **67**, 305.