JOURNAL OF
Materials
CHEMISTRY

New semiconductors obtained by reaction of 4-imidazoline-2-selone† derivatives with TCNQ. Characterization and X-ray structure of $(C_9H_{12}N_4Se)^{2+}(TCNQ)_3^{2-}$

Francesco Bigoli,[a,b] Paola Deplano,[c] Francesco A. Devillanova,[c] Alberto Girlando,*[a] Vito Lippolis,[c] M.-Laura Mercuri,[c] M.-Angela Pellinghelli[a,b] and Emanuele F.Trogu[c]

[a]*Dip. Chimica Generale ed Inorganica, Chimica Analitica e Chimica Fisica, Parma University, 43100 Parma, Italy*

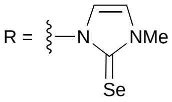
[b]*Centro di Studio Strutturistica Diffrattometrica del CNR viale delle Scienze 78, 43100 Parma, Italy*

[c]*Dip. Chimica e Tecnologie Inorganiche e Metallo-organiche, Cagliari University, 09124 Cagliari, Italy*

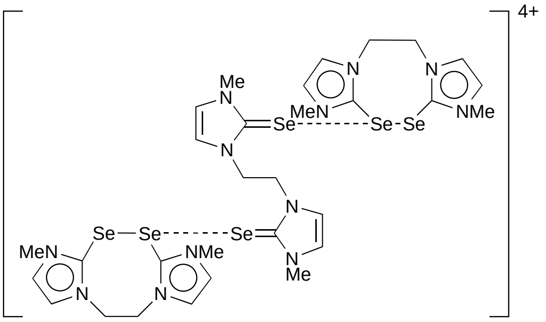
The charge transfer complexes **I**, **II** and **III** of three new electron donors, 1,1′-ethylenebis(3-methyl-4-imidazoline-2-selone) **1**, 1,1′-methylenebis(3-methyl-4-imidazoline-2-selone) **2** and 1,3-dimethyl-4-imidazoline-2-selone **3**, with TCNQ have been synthesized. We report the X-ray crystal structure of **II**, $(C_9H_{12}N_4Se)(TCNQ)_3$, which crystallizes in the triclinic system, space group *P*1, with one molecule per unit cell and $a = 7.563(7)$, $b = 10.371(6)$, $c = 13.575(5)$ Å, $\alpha = 95.00(2)$, $\beta = 95.54(2)$, $\gamma = 109.74(2)^\circ$. The comparison with the already described crystal structure of **I** and a detailed spectroscopic characterization of all three complexes, allows us to show that the change of the donor yields compounds characterized by quite different charge distributions and stack types. The semiconducting properties, ranging from $\sim 10^{-2}$ to 6×10^{-4} S cm^{-1}, are most likely due to the TCNQ stacks, where two negative charges are distributed among three TCNQ units. At room temperature, the charge is fully delocalized along the TCNQ stack of **I**, the semiconductor with the highest conductivity, whereas in **II** and **III** the charge is unevenly distributed among the TCNQ units. The donors show a strong tendency to form stable dications: in **I** and **III** they give rise to mixed-valence cations and a new dication with elimination of an Se atom is formed in **II**.

Among the various classes of electron donor molecules currently synthesized in the field of molecular metals, the derivatives of imidazoline-2-selone occupy a rather peculiar place. These molecules are good donors, having a first oxidation potential intermediate between those of TTF‡ and of BEDT–TTF,[1] but also exhibit a quite varied and interesting chemistry. Reaction with diiodine or interhalogens, for instance, yields several different types of compounds, such as insertion compounds, neutral adducts and dications.[2,3] We recently started investigating the charge transfer (CT) complexes of imidazoline-2-selone derivatives with π-electron acceptor molecules.

1 $R\text{-}(CH_2)_2\text{-}R$
2 $R\text{-}CH_2\text{-}R$
3 $R\text{-}CH_3$



The reaction of **1** with TCNQ produces a mixed-valence salt **I** formed by a tetracation (**4**) consisting of one centrosymmetrical molecule of the neutral ligand and two dications, mutually related by a symmetry center and bearing an Se—Se bridge.[1] The neutral ligand and the two dications are held together by an Se···Se donor–acceptor interaction between each Se atom of **1** and the adjacent Se of each dication. Two dinegative triads of TCNQ act as counterions. The TCNQ molecules are faced plane to plane in groups of three, closely resembling the trimerized stack structure of other TCNQ salts, like $Cs_2(TCNQ)_3$.[4] The similarity between the bond distances of the TCNQs in the triads suggested that the dinegative charge is not localized on the TCNQ units, but because of the lack of single crystal vibrational spectra no definite conclusion on the charge distribution could be reached.[1]



4

In the present paper we report the structural and spectroscopic characterization of the complex **II** obtained from R—(CH$_2$)—R (**2**) and TCNQ. Furthermore, we complete the characterization of **I** through its single crystal polarized infrared (IR) spectra from room temperature to 77 K. The comparison of the spectral data of **I** and **II** with those of the complex **III** obtained by reacting **3** with TCNQ also gives useful hints about the structure of the latter semiconductor. A preliminary comparison between the structure and spectroscopic properties of the three CT complexes obtained by reacting **1–3** with TCNQ is given in ref. 5.

---

†4-Imidazoline = 2,3-dihydroimidazole.

‡List of abbreviations: BEDT–TTF = bis(ethylenedithio)tetrathiafulvalene; CT = charge transfer; IR = infrared; MEM = methylethylmorpholinium; TCNQ = 7,7,8,8-tetracyano-*p*-quinodimethane; TTF = tetrathiafulvalene.

Experimental

Materials

The electron donors **1**, **2** and **3** were prepared as previously described.[2] TCNQ, the solvents and the reagents were commercial products (Aldrich), used without further purification. Compounds **I**, **II** and **III** are the reaction products of TCNQ with **1**, **2** and **3**, respectively. The synthesis of **I** has already been described.[1] **II** and **III** were obtained by mixing CH_2Cl_2 solutions of **2** and **3** with a CH_3CN solution of TCNQ in 1 : 2 and 1 : 1 ratio, respectively. The mixed solutions were left to stand at room temperature, and after several days well-shaped crystals of **II** and lustrous dark-blue microcrystals of **III** were obtained in about 70% yield. *Elemental analysis*: **II**, Calc. for $C_{45}H_{24}N_{16}Se$: C 62.29, H 2.79, N 25.83; Found: C 62.38, H 2.62, N 25.42%. **III**, Calc. for $C_{17}H_{12}N_6Se$: C 53.79, H 3.16, N 22.15; Found: C 54.09, H 3.31, N 22.64%.

Spectroscopic measurements

Single crystal polarized infrared spectra were obtained with a Bruker IFS66 FT-IR spectrometer, equipped with a Bruker A590 microscope, and a KRS5 grid polarizer (Specac). Low temperature measurements under the IR microscope were performed by using a Linkam FTIR-600 liquid nitrogen cold stage. The FT-Raman spectra were recorded on a Bruker RFS100 FTR spectrometer, operating with an excitation frequency of 1064 nm (Nd:YAG laser). The power level of the laser source was 20–40 mW, and the powdered samples were dispersed in KBr and packed into a glass capillary for 180° scattering geometry. No sample decomposition was observed during the experiments.

Conductivity measurements

Conductivity measurements were made at room temperature on pellets (thickness 0.5 mm, diameter 12 mm) using the two-point probe method. $\sigma(\mathbf{I}) = 1.0 \times 10^{-2}$; $\sigma(\mathbf{II}) = 5.9 \times 10^{-4}$; $\sigma(\mathbf{III}) = 6.5 \times 10^{-3}$ S cm^{-1}.

X-Ray diffraction measurements

The diffraction measurements on the complex **II** were made on a Siemens AED diffractometer. The crystals to choose from were not of good quality; the one selected had dimensions of $0.05 \times 0.21 \times 0.36$ mm. Accurate unit cell parameters and the orientation matrix for data collection were obtained from least-squares refinements, using the setting angles of 29 reflections ($18° < \theta < 31°$). The check on the standard reflection showed no significant crystal decay under irradiation. Intensities were corrected for Lorentz and polarization effects. No correction for absorption was applied. The structure was solved and refined using the SHELX-76[6] and SHELX-86[7] computer programs. Only the non-hydrogen atoms of the dication were refined anisotropically. All hydrogen atoms were placed at their geometrical position (C—H: 0.96 Å) and refined by 'riding' on the corresponding atoms with unique isotropic thermal parameters [$U = 0.0969(86)$ Å^2]. In the last stages of refinement the best result was obtained using unit weights. Scattering factors and correction for anomalous dispersion effects were taken from ref. 8. Full crystallographic details, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, *J. Mater. Chem.*, 1998, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1145/84.

Results

Compounds **I**, **II** and **III**, obtained by reacting TCNQ with **1**, **2** and **3**, respectively, are molecular semiconductors with room temperature conductivities ranging from $\sim 10^{-2}$ to 6×10^{-4} S cm^{-1}. An almost complete characterization of **I**, including the crystal structure, has already been described,[1] as summarized in the introduction.

Table 1 Crystallographic data for compound **II**, $(C_9H_{12}N_4Se)(TCNQ)_3$

formula	$C_{45}H_{24}N_{16}Se$
M_w	867.75
crystal system	triclinic
space group	*P1*
a/Å	7.563(7)
b/Å	10.371(6)
c/Å	13.575(5)
α(°)	95.00(2)
β(°)	95.54(2)
γ(°)	109.74(2)
U/Å^3	989(1)
Z	1
D_c/Mg m^{-3}	1.457
radiation	Ni-filtered
wavelength	Cu-Kα(λ = 1.541838 Å)
T/K	295
μ/cm^{-1}	17.52
θ-range for intensity collection(°)	3–70
data collected	$\pm h, \pm k, l$
no. of measured reflections	3760
no. of reflections with $I > 2\sigma(I)$	2226
no. of refined parameters	317
min/max height in final Δρ map/eÅ^{-3}	−0.35/0.71
largest shift/e.s.d.	0.20
$R = \Sigma\lvert\Delta F\rvert/\Sigma\lvert F\rvert$	0.0596
$wR = \sqrt{\Sigma\, w(\Delta F)^2/\Sigma\, wF^2}$	0.0607

Crystal structure of II

Compound **II** crystallizes in the triclinic system, space group *P*1, *Z* = 1, and can be formulated as $(C_9H_{12}N_4Se)(TCNQ)_3$. A summary of the crystallographic data is reported in Table 1. The structure (Fig. 1) consists of homologous layers of alternating $(C_9H_{12}N_4Se)^{2+}$ dications and $(TCNQ)_3^{2-}$ anions, roughly parallel to the *ab* plane, the cations and anions lying roughly parallel to the *bc* and *ac* planes, respectively.

Compound **II** differs from **I** in both the cation and the anion structure. In **I**, a mixed-valence cation is present, with dications characterized by an Se—Se bridge and the formation of an

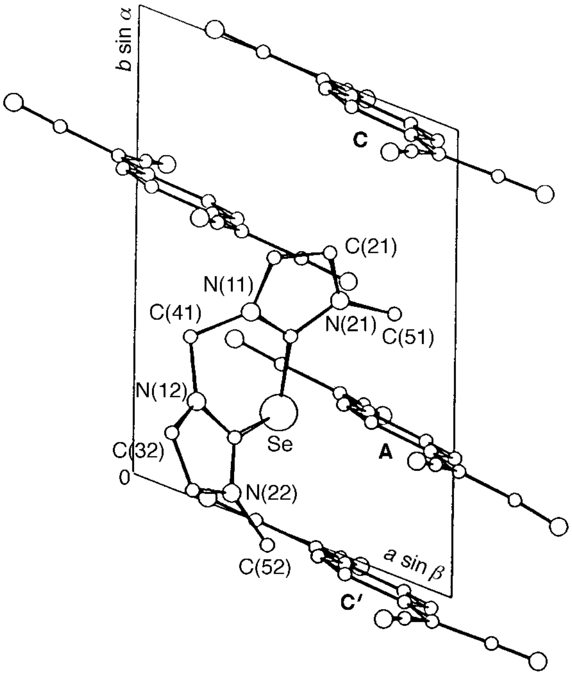


Fig. 1 Projection of the structure of **II** along [001]

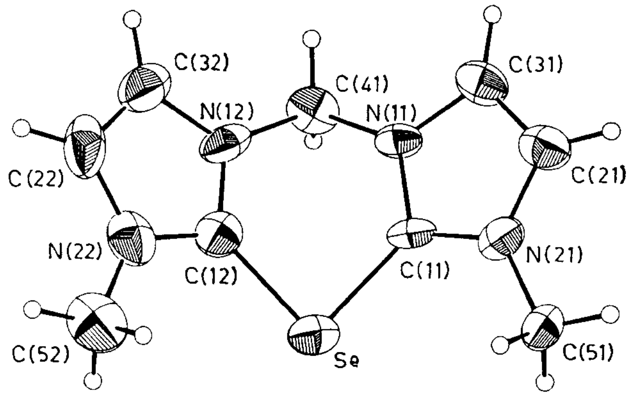


Fig. 2 Perspective view of $(C_9H_{12}N_4Se)^{2+}$ cation in **II**, showing the atomic numbering scheme. The thermal ellipsoids are drawn at the 30% probability level.

eight-membered central ring (see structural formula **4** in the introduction). In **II**, the donor **2** gives rise to a dication with elimination of one Se atom, and the formation of a six-membered ring. The molecular structure and atomic labelling scheme of the dication are shown in Fig. 2; the bond lengths and angles are given in Table 2. The central ring of $(C_9H_{12}N_4Se)^{2+}$ has a boat conformation, with θ and ϕ^9 equal to 86.6(9)° and −6.1(9)°, respectively, whereas the dihedral angle between the two planar imidazoline rings is of 50.2(5)°. The dication structural data are in agreement with those observed in the diiodine neutral adducts of **2**,[2] and of its sulfur anologue,[10] and in the insertion derivatives of **2** with chlorine.[11] The TCNQ stacks of the complex **I** are formed by triads in a zig-zag arrangement. In **II**, on the other hand, the TCNQ stack is better described as being made up of TCNQ dimers (**A** and **C′** in Fig. 1), separated by a third TCNQ (**B**), shifted in the *a* direction. The dihedral angles between the mean-weighted planes of the non-exactly planar TCNQ molecules are in the range 1.5(2)–3.9(2)°.

We have not been able to obtain single crystals of **III** suitable for X-ray analysis, so that all the information on the complex **III** formed by reacting **3** with TCNQ relies on the spectroscopic measurements reported in the following section.

Spectroscopic studies

Vibrational spectroscopy is an invaluable tool for a detailed characterization of organic semiconductors,[12] particularly when it is associated with X-ray structure determination or when it is used in the analysis of an homologous series of compounds, as in the present case. We have recorded the powder Raman spectra and the single crystal polarized IR spectra of **I**, **II** and **III**, and the interpretation of the data will be reported in that order. Tables 3 and 4 report the frequencies observed in the Raman and IR spectra (polarization perpendicular to the stack) for the three compounds.

Partial vibrational data for **I** have already been published, but no definite conclusion could be reached about the charge distribution on the TCNQ sites.[1] The single crystal IR spectra up to 2500 cm^{-1} are reported in Fig. 3. The spectrum polarized parallel to the stack is similar to that of the powders,[1] being dominated by the electronic CT transition (maximum around 5000 cm^{-1}, not shown in Fig. 3) along the TCNQ stack. Superimposed on it the vibronic bands typical of the TCNQ molecule[13] are clearly identified. These bands correspond to the totally symmetric (a_g) modes of TCNQ, the intramolecular modes which, modulating the on-site energies, are coupled to the CT electron and borrow IR intensity from the CT transition.[12] As for the powder spectra, these bands are normal absorptions below *ca.* 1000 cm^{-1}, but above this frequency they appear as indentations in the continuum single-electron transition. This well known phenomenon[14] allowed us to

Table 3 Raman spectra of the compounds **I**, **II** and **III**[a]

I $\tilde{\nu}$/cm^{-1}	**II** $\tilde{\nu}$/cm^{-1}	**III** $\tilde{\nu}$/cm^{-1}	tentative assignment[b]
227 w	229 w	226 m	
308 w			
332 m	331 m	328 m	T, $a_g\nu_9$
		433 w	
490 w			
567 w			
609 w	605 m	600 m	T, $a_g\nu_8$
705 w	708 w	706 w	
967 m	970 w,br	962 m	T, $a_g\nu_6$
1156 m			D
1196 s	1195 s	1195 s	T, $a_g\nu_5$
1374 m,br			
	1388 m	1384 w	T, $a_g\nu_4$
1413 s	1417 s	1417 s	T, $a_g\nu_4$
	1451 m	1443 m	D?
1603 s	1601 s	1601 s	T, $a_g\nu_3$
2202 m	2205 m,br	2205 m,br	T, $a_g\nu_2$

[a] Qualitative relative intensities indicated by: s, strong; m, medium; w, weak; br, broad; sh, shoulder. [b] D: donor; T: TCNQ. For the numbering of the normal modes see ref. 13.

Table 2 Selected bond distances (Å) and angles (°) for the dication in complex **II** (e.s.d. in parentheses)

	bond length/A°		Angle(°)
Se—C(11)	1.908(13)	C(21)—N(21)—C(51)	127.1(12)
Se—C(12)	1.865(13)	C(11)—N(21)—C(51)	124.6(11)
N(11)—C(11)	1.319(17)	C(11)—N(21)—C(21)	108.2(11)
N(11)—C(31)	1.402(16)	C(12)—N(12)—C(32)	109.7(11)
N(11)—C(41)	1.440(14)	C(41)—N(12)—C(32)	127.3(12)
N(21)—C(11)	1.348(14)	C(41)—N(12)—C(12)	122.6(12)
N(21)—C(21)	1.353(21)	C(22)—N(22)—C(52)	126.3(15)
N(21)—C(51)	1.468(18)	C(12)—N(22)—C(52)	125.3(13)
N(12)—C(41)	1.468(21)	C(12)—N(22)—C(22)	108.2(12)
N(12)—C(12)	1.345(20)	N(11)—C(11)—N(21)	107.5(11)
N(12)—C(32)	1.366(20)	Se—C(11)—N(21)	128.0(9)
N(22)—C(12)	1.351(20)	Se—C(11)—N(11)	124.1(9)
N(22)—C(22)	1.387(23)	N(21)—C(21)—C(31)	110.1(13)
N(22)—C(52)	1.446(27)	N(11)—C(31)—C(21)	103.5(12)
C(21)—C(31)	1.358(21)	N(11)—C(41)—N(12)	108.7(11)
C(22)—C(32)	1.353(31)	N(12)—C(12)—N(22)	107.4(13)
C(11)—Se—C(12)	88.4(5)	Se—C(12)—N(22)	128.7(10)
C(31)—N(11)—C(41)	126.6(11)	Se—C(12)—N(12)	123.8(9)
C(11)—N(11)—C(41)	122.5(11)	N(22)—C(22)—C(32)	107.5(16)
C(11)—N(11)—C(31)	110.7(10)	N(12)—C(32)—C(22)	107.1(15)

Table 4 Infrared spectra, polarized perpendicularly to the stack, of the compounds **I**, **II** and **III**[a]

I $\tilde{\nu}$/cm^{-1}	**II** $\tilde{\nu}$/cm^{-1}	**III** $\tilde{\nu}$/cm^{-1}	tentative assignment[b]
626 w			
646 s			
675 m			$2D^{2+}$
707 w			D
		734 m	$2D^{2+}$
751 m	747 m	744 m	D
	759 w		
800 w	805 m		
830 m			
1033 w		1023 w	$2D^{2+}$
	1079 w		
	1097 w	1092 m	D
1122 m	1115 w		
1147 w	1134 w	1132 m	D
1176 m	1170 m		
	1209 s	1203 s	T, $b_{2u}\nu_{36}$
	1230 m	1222 s	D
1251 w			
	1333 m	1334 s	D, $2D^{2+}$
1375 s	1349 m	1372 w	D?
		1405 w	
1442 w	1453 w	1430 m	D
	1480 w	1492 s	$2D^{2+}$
	1503 w	1505 sh	T, $b_{1u}\nu_{20}$
1517 s	1524 s	1519 sh	T, $b_{1u}\nu_{20}$
1566 s	1569 ms	1560 m	D, $2D^{2+}$
	1633 m	1629 w	
	2162 s	2158 s	T, $b_{2u}\nu_{33}$
	2175 s	2176 s	T, $b_{1u}\nu_{19}$
2191 s	2189 s		T, $b_{2u}\nu_{33}$
	2194 s		T, $b_{2u}\nu_{33}$
2198 s	2198 s	2198 s	T, $b_{1u}\nu_{19}$
	2203 s	2207 sh	T, $b_{1u}\nu_{19}$

[a] Qualitative relative intensities indicated by: s, strong; m, medium; w, weak; br, broad; sh, shoulder. [b] D: donor; T: TCNQ. For the numbering of the normal modes see ref. 13.

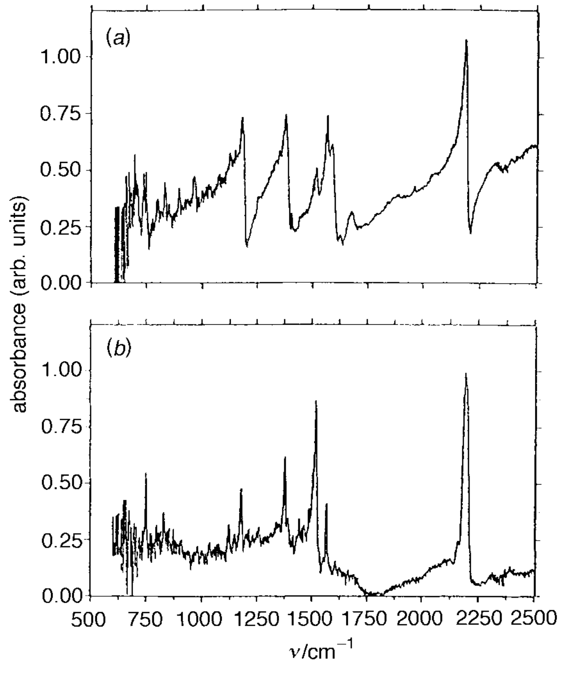


Fig. 3 Polarized IR spectra of **I**: (*a*) electric vector parallel to the stack axis; (*b*) electric vector perpendicular to the stack axis

estimate the room temperature optical gap of **I** at *ca.* 1000 cm^{-1} (~0.12 eV).[1]

In the previous work,[1] the frequency of the Raman active TCNQ $a_g\nu_4$ mode, observed for **I** at 1413 cm^{-1} (Table 3), suggested a uniform charge distribution (ρ) among the trimeric TCNQ units. However, in trimerized stacks the a_g frequencies may be perturbed by electron–phonon coupling.[15] A safe and accurate estimate of ρ must then rely on the frequencies of the normally IR active *ungerade* modes. The IR spectra of **I** polarized perpendicularly to the stack (Fig. 3 and Table 4) yield a straightforward assignment of the main in-plane (b_{1u} and b_{2u}) vibrations of TCNQ. The C≡N stretching frequencies around 2200 cm^{-1} have often been used to determine the average charge on the TCNQ units.[16] The spectra of **I** show two C≡N stretching bands, one of b_{1u} and the other of b_{2u} symmetry, again indicating uniform charge distribution. However, since several authors have reported deviations from the expected linear dependence of the C≡N frequencies from ρ,[17–19] we prefer to use the CC stretching mode $b_{1u}\nu_{20}$.[17] Its frequency occurs at 1517 cm^{-1} (Table 4), indicating an average charge of 0.6_8. We can now safely conclude that in **I** the $2e^-$ charge is uniformly distributed among the three TCNQ units in the trimerized stack. This finding explains well the remarkable conductivity of **I**: about two orders of magnitude higher than that of $Cs_2(TCNQ)_3$.[20]

We have also obtained single crystal polarized IR spectra at low temperature, to detect the presence of phase transitions in the complex **I**. Fig. 4 compares the C≡N stretching region (perpendicular polarization) at 300 and 77 K. It is seen immediately that the room temperature doublet becomes a complex structure at liquid nitrogen temperature, with at least five maxima clearly identified. Indeed, at temperatures below 250 K the charge is no longer uniformly distributed on the TCNQ sites, as revealed by the structure of the C≡N stretching region. The change appears to occur rather smoothly with temperature variation, so it is hardly possible to speak of a phase transition, nor can we determine precisely the difference in charge among the TCNQ sites, which remains rather small. The intensity of the vibronic bands in the parallelel IR spectrum does not change significantly, indicating that the stack structure is affected very little by the localization of the charge.

The crystal structure and conductivity show that **II** is a

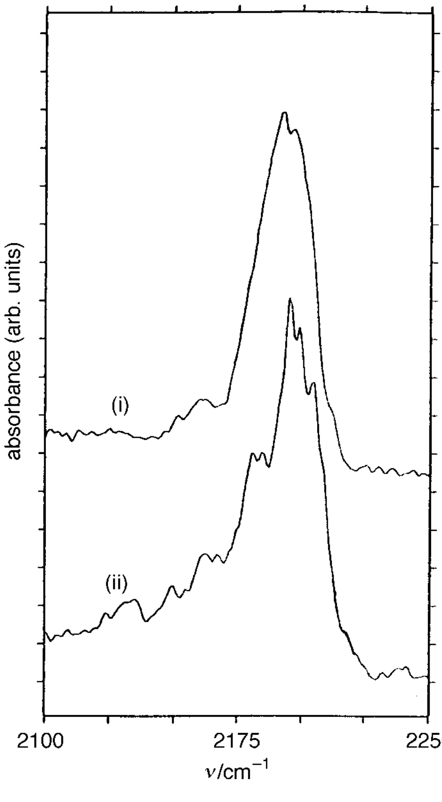


Fig. 4 Polarized IR spectra of **I** in the C≡N stretching region, at (i) room (300 K) and (ii) liquid nitrogen (77 K) temperature. Only the polarization perpendicular to the stack axis is shown.

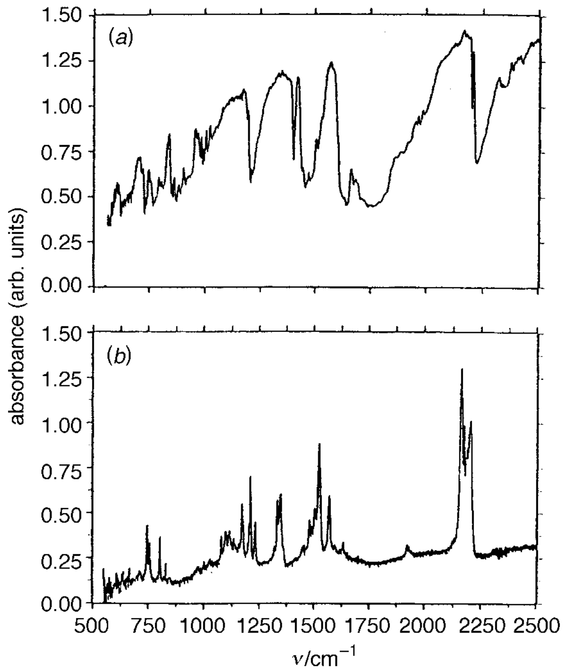


Fig. 5 Polarized IR spectra of **II**: (*a*) electric vector parallel to the stack axis; (*b*) electric vector perpendicular to the stack axis

quite different complex from **I**. The spectroscopic measurements offer further clues about the origin of the difference. Fig. 5 reports the IR absorption spectra polarized parallel and perpendicular to the stack axis. The spectra polarized parallel to the stack show the CT electronic absorption with a maximum beyond 5000 cm^{-1}, over which the vibronic transitions due to the TCNQ a_g modes are superimposed. The optical gap can again be estimated from the frequency above which the vibronic bands appear as indentations ($\sim$1000 cm^{-1} or $\sim$0.12 eV). However, it should be noted that, at variance with what is observed in **I**, the structure of the indentations is rather complex. Apart from other difficult to analyze features, a doublet structure is clearly resolved, with a narrow component immediately below the main transition. This fact suggests that in **II** the 2e$^-$ charge is not uniformly distributed on the TCNQ sites,[21] as the following analysis will confirm.

As shown by the X-ray data, the donors give rise to a new type of dication, whose vibrational frequencies are of course unknown. Therefore, it is difficult in some cases to disentangle the frequencies due to TCNQ from those of the dication. In the Raman spectrum (Table 3) we observe three bands (1451, 1417 and 1388 cm^{-1}) in the spectral region of the TCNQ $a_g\nu_4$ mode (see above).[13] The first one would indicate the presence of neutral TCNQ, but since other Raman or IR bands attributable to this species are not seen, we prefer to attribute this band to the donor. If the other two bands are assigned to TCNQ, they indicate the presence of at least two differently charged TCNQs, one with intermediate charge and one fully charged. The IR spectra polarized perpendicularly to the stack (Fig. 5 and Table 4) confirm that in **II** the charge is unevenly distributed on the TCNQ sites. The C≡N spectral region shows six bands, instead of the two expected for uniform charge distribution, suggesting the presence of three differently charged TCNQs, one with $\rho\sim1$ and the other two both with a charge close to 0.5. The assessment of the precise estimate of ρ cannot rely on the C≡N stretching frequencies, however,[17–19] and we can reasonably assign only two bands in the C–C stretching region, at 1503 and 1524 cm^{-1}. If they are both assigned to the TCNQ $b_{1u}\nu_{20}$ mode, they would indicate a charge of $\rho\sim1$ and of $\rho\sim0.5$, respectively, consistent with what can be qualitatively deduced from the analysis of the C≡N stretching region.

In the light of the above data, and of the X-ray analysis, we suggest that the TCNQ offset of the stack (**B** in Fig. 2) bears a unit negative charge, whereas the other electron is slightly unevenly distributed among the **A** and **C** TCNQ units, as in the dimerized stack structure of MEM(TCNQ)$_2$.[22] As far as we know, the present stack structure and charge distribution have not been encountered so far in TCNQ stacks. The charge localization of **II** as opposed to the charge delocalization of **I** may well explain the large difference in room temperature conductivities (5.9×10^{-4} *vs.* 1.0×10^{-2} S cm^{-1}) between the two compounds.

We have not been able to obtain single crystals of **III** suitable for X-ray analysis, so that all the information on the complex formed by reacting **3** with TCNQ relies on the spectroscopic measurements. Fig. 6 shows the IR spectra polarized parallel and perpendicular to the stack axis, whereas Tables 3 and 4 report the Raman and IR frequencies. The IR spectrum polarized parallel to the stack shows an electronic transition centered around 4000 cm^{-1}, lower than for **I** or **II**, but without trace of vibronic absorptions. Therefore the stack along which the CT transition occurs, most probably the TCNQ stack, is a regular one, *i.e.* a stack with constant distance between the molecular units.[12] In such a case one would expect a uniform charge distribution, but the Raman spectrum in the TCNQ $a_g\nu_4$ mode spectral region is rather similar to that of **II** (Table 3), where the charge is localized. Analogous information comes from the IR spectrum polarized perpendicular to the stack. The spectrum (Fig. 6 and Table 4) shows four bands in the C≡N stretching region, indicating two differently charged TCNQ units, one with charge $\sim$1 and the other between 0.4 and 0.5. Careful analysis of the $b_{1u}\nu_{20}$ spectral region, partially obscured by the presence of a strong absorption due to the donor at 1492 cm^{-1} (see below) confirms the presence of both TCNQ$^-$ and TCNQ$^{-0.5}$ units.

The comparison of the IR spectrum of **III** (Table 4) with those of the neutral donor **3** and of the dication formed by the latter by reaction with Br$_2$[11] indicates the presence of a mixed-valence counterion. Since analytical results indicate that **III** contains TCNQ and **3** in a 1 : 1 molar ratio, we suggest that the complex is composed of a mixed-valence dication formed by the dimerized donor with an Se–Se bridge and a neutral molecule of **3**, and by a triad of TCNQs bearing two negative

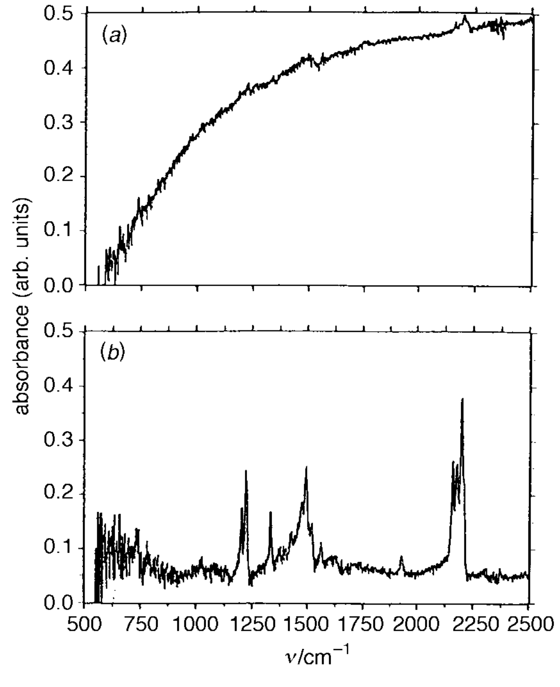


Fig. 6 Polarized IR spectra of **III**: (*a*) electric vector parallel to the stack axis; (*b*) electric vector perpendicular to the stack axis

charges. At this point we can advance two hypotheses about the structure of the TCNQ stack. The first is that the stack somehow resembles that of **II**, with two $TCNQ^{-0.5}$ and one $TCNQ^{-1}$ units forming a repetitive trimeric pattern. In the second hypothesis the TCNQ bearing unit negative charge instead does not belong to the stack, which is made up solely from $TCNQ^{0.5-}$ units. We have performed single crystal low temperature IR measurements to verify whether complex **III** undergoes a Peierls transition. In such a case, the frequency and shape of the vibronic bands would help us to decide between the two hypotheses. However, we have not detected phase transitions down to liquid nitrogen temperature. With the lack of further data, and considering that the conductivity and the electronic spectrum of **III** differ from those of **II**, we prefer the second of the two above-mentioned hypotheses, *i.e.* a TCNQ stack formed solely by $TCNQ^{0.5-}$ units. The fact that we have not observed the Peierls transition, together with the problems encountered in obtaining the X-ray structure of **III**, suggest the presence of structural disorder in the compound.

Conclusions

The donors **1**, **2** and **3**, based on the same imidazoline-2-selone group, react with TCNQ to produce new molecular semiconductors (**I**, **II** and **III**) showing conductivities ranging from $\sim 10^{-2}$ to 6×10^{-4} S cm^{-1} at room temperature. Structural and spectroscopic results show that **I**, **II** and **III** complexes are quite different. In **I** and **III** the donor gives rise to mixed-valence cations, whereas a new dication with elimination of an Se atom is formed in **II**. In any case the donors confirm the tendency to form closed-shell dications. The imidazoline ring loses one electron in agreement with the $4n+2$ rule, but then two rings associate through Se bridges. The charge transfer and conductivity are essentially associated with the TCNQ stacks. In all three complexes, two negative charges are distributed among three TCNQ units. Yet, the TCNQ stack structure and charge distribution is different, the most interesting case being that of **I**, the complex with highest conductivity. At 300 K the charge is fully delocalized along the trimerized TCNQ stack, and becomes localized below 250 K.

We wish to thank Dr C. Bellitto (Istituto di Chimica dei Materiali, CNR, Rome) for the conductivity measurements. This work has been supported by the Ministry of University and of Scientific and Technological Research (MURST) and by the National Research Council (CNR) under the Coordinate Project No. 96/215.

References

1 F. Bigoli, P. Deplano, F. A. Devillanova, A. Girlando, V. Lippolis, M.-L. Mercuri, M.-A. Pellinghelli and E. F. Trogu, *Inorg. Chem.*, 1996, **35**, 5403.

2 F. Bigoli, M.-A. Pellinghelli, P. Deplano, F. A. Devillanova, V. Lippolis, M.-L. Mercuri and E. F. Trogu, *Gazz. Chim. Ital.*, 1994, **124**, 445.

3 F. Bigoli, F. Demartin, P. Deplano, F. A. Devillanova, F. Isaia, V. Lippolis, M.-L. Mercuri, M.-A. Pellinghelli and E. F. Trogu, *Inorg. Chem.*, 1996, **35**, 3194; F. Bigoli, P. Deplano, F. A. Devillanova, V. Lippolis, M.-L. Mercuri, M.-A. Pellinghelli and E. F. Trogu, *Chem. Ber.*, in press.

4 C. J. Fritchie and P. Arthur, *Acta Crystallogr.*, 1966, **21**, 139.

5 F. Bigoli, P. Deplano, F. A. Devillanova, A. Girlando, V. Lippolis, M.-L. Mercuri, A. Pelagatti, M.-A. Pellinghelli and E. F. Trogu, *Synth. Met.*, 1997, **86**, 1853.

6 G. M. Sheldrick, *SHELX-76: Programs for Crystal Structure Determination*, University of Cambridge, UK, 1976.

7 G. M. Sheldrick, *SHELX-86: Program for the Solution of Crystal Structures*, Universität Göttingen, Germany, 1986.

8 *International Tables for X-ray Crystallography*, The Kynoch Press, Birmingham, 1974, vol. IV.

9 D. Cremer and J. A. Pople, *J. Am. Chem. Soc.*, 1975, **97**, 1354.

10 F. Bigoli, P. Deplano, F. A. Devillanova, M.-L. Mercuri, M.-A. Pellinghelli, A. Sabatini, E. F. Trogu and A. Vacca, *J. Chem. Soc., Dalton Trans.*, 1996, 3583.

11 F. Bigoli and P. Deplano, *et al.*, in preparation.

12 C. Pecile, A. Painelli and A. Girlando, *Mol. Cryst. Liq. Cryst.*, 1989, **171**, 69.

13 R. Bozio, I. Zanon, A. Girlando and C. Pecile, *J. Chem. Soc., Faraday Trans. 2*, 1978, **74**, 235.

14 M. J. Rice, L. Pietronero and P. Bruesch, *Solid State Commun.*, 1977, **21**, 757.

15 A. Painelli, C. Pecile and A. Girlando, *Mol. Cryst. Liq. Cryst.*, 1986, **134**, 1.

16 J. S. Chappell, A. N. Bloch, W. A. Bryden, M. Maxfield, T. O. Poehler and D. O. Cowan, *J. Am. Chem. Soc.*, 1981, **103**, 2442.

17 A. Girlando, A. Painelli and C. Pecile, *Mol. Cryst. Liq. Cryst.*, 1984, **112**, 325.

18 M. Meneghetti and C. Pecile, *J. Chem. Phys.*, 1986, **84**, 4149.

19 K. A. Hutchison, G. Srdanov, R. Menon, J.-C. P. Gabriel, B. Knight and F. Wudl, *J. Am. Chem. Soc.*, 1996, **118**, 13081.

20 K. D. Cummings, D. Tanner and J. Miller, *Phys. Rev.*, 1981, **B24**, 4142.

21 R. Swietlik, *Synth. Met.*, 1995, **74**, 115.

22 M. J. Rice, V. M. Yartsev and C. S. Jacobsen, *Phys. Rev.*, 1980, **B21**, 3437.

Paper 7/07223F; *Received* 6*th October*, 1997