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Reaction of *N*,*N*′-dimethylimidazolidine-2-selone (4) with TCNQ. Characterisation and X-ray crystal structure of the mixed-valence compound $4\cdot(\mathrm{TCNQ})_{1.167}$

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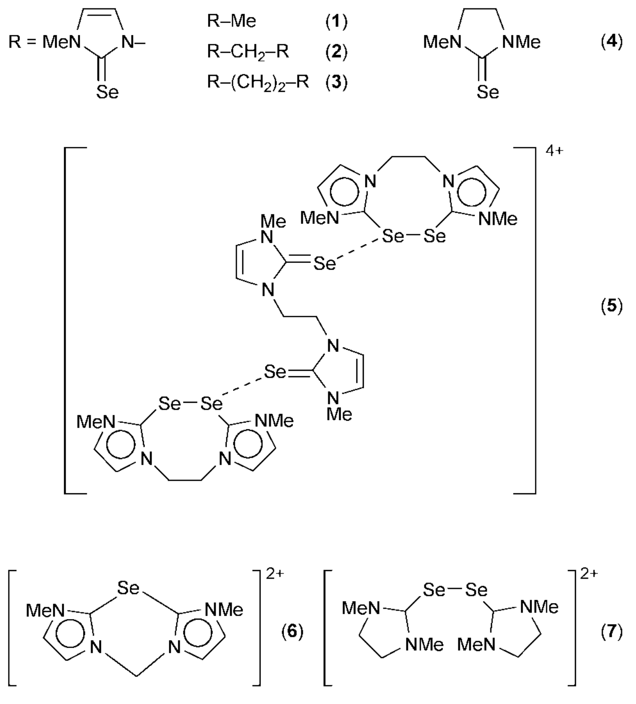
The reaction of *N*,*N*′-dimethylimidazolidine-2-selone (**4**) with TCNQ affords lustrous dark crystals with elemental analysis corresponding to the formula $\mathbf{4}\cdot(\mathrm{TCNQ})_{1.167}$. X-Ray crystal structure determination shows that this compound is formed by discrete $[\mathbf{4}_2]^{2+}$ dications, in which two oxidized imidazolidine molecules are bonded through an –Se–Se– bridge [2.5187(7) Å]. These dications interact on one side with a third disordered molecule of **4** (occupancy factor 0.5) *via* Se···Se soft interactions of 2.715(4) and 2.899(4) Å to give almost linear –Se–Se···Se– arrangements [Se(2)–Se(1)···Se(3), 177.64(6)° and Se(2)–Se(1)···Se(3a), 167.89(5)°]. The unit cell contains six imidazolidine molecules bearing a total of four positive charges, balanced by four negative charges distributed on seven TCNQ molecules, stacked in two dimers and a trimer. Structural data suggest that the negative charges are unevenly distributed on the TCNQ molecules. Single crystal infrared spectra also suggest the presence of at least three differently charged TCNQ's, and in addition indicate a room temperature optical gap of ~0.3 eV, placing this compound among wide bandgap semiconductors ($\sigma = 3.45 \times 10^{-3}$ S cm^{-1}). Cyclic voltammetry of **4** is discussed in comparison with those of previously studied imidazoline-2-selone derivatives (**1**–**3**), and shows that for this donor the achievement of a mixed valence compound with TCNQ is possible in MeCN.

Introduction

The discovery of superconductivity in organic charge transfer (CT) compounds[1] has increased interest in the synthesis of new electron donors, mainly based on S and Se containing molecules. We have contributed to this field of research by investigating a new class of electron donors based on imidazoline-2-selone derivatives (**1**–**3**) (see Scheme 1),[2–7] whose first oxidation potential is intermediate between those of TTF and BEDT-TTF.[4] **1**–**3** exhibit quite a surprising reactivity towards acceptors of different nature: for instance, the reaction of **1** and **3** with diiodine in CH_2Cl_2 yields hypervalent selenium compounds bearing the linear I–Se–I group, whereas **2** gives a normal CT adduct, characterised by the linear Se–I–I group.[6] Furthermore the reactions of **1**–**3** with TCNQ lead to mixed-valence compounds, which differ both in stack structure and charge distribution on the TCNQ units and in the nature of the products deriving from the oxidation of the donors. In particular, in the case of reaction of **3** with TCNQ, the mixed-valence $\mathbf{5}\cdot2[(\mathrm{TCNQ})_3^{2-}]$ salt is obtained, where the tetracation **5** consists of a neutral molecule of **3** bridging two dications bearing an intramolecular Se–Se bridge *via* intermolecular Se···Se soft interactions (see **5** in Scheme 1). The counterions are two triads of TCNQ molecules, each bearing two negative charges.[4] In the case of **2** as donor, the compound $\mathbf{6}\cdot[(\mathrm{TCNQ})_3^{2-}]$ is isolated: one TCNQ^{1-} and two $\mathrm{TCNQ}^{0.5-}$ units arranged in dimers are balanced by the cyclic dication $[C_9H_{12}N_4Se]^{2+}$ (**6**) which is formed by the elimination of one Se atom from the starting donor.[2,3] Although no single crystals suitable for X-ray diffraction studies were obtained by reaction of **1** with TCNQ, spectroscopic evidence suggests the formation of a mixed-valence oxidation compound having formula $[\mathbf{1}_3^{2+}][(\mathrm{TCNQ})_3^{2-}]$ and featuring Se–Se bridged dications



Scheme 1

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interacting with a neutral molecule of **1**.[3] Also in this case, the two negative charges are not uniformly distributed on the TCNQ's, but one negative charge is localised on a TCNQ molecule while the other is localised on the remaining two TCNQ molecules, with stacks likely formed solely by $TCNQ^{0.5-}$ units. In all these products, the semiconducting properties (σ ranging from 10^{-2} to 6×10^{-4} S cm^{-1}) are most likely due to the TCNQ stacks.

The tendency of **1**–**3** to form closed-shell dications has been attributed to the stability of the positive imidazoline ring according to the $4n+2$ rule. However, aromaticity of the pentaatomic rings does not seem to be the determining factor in stabilising the positive charge, since compound **4**, which is lacking a C=C double bond in the ring, also shows an analogous tendency to form the dication **7** (Scheme 1): see for example either the products obtained by the reactions of **4** with IBr[5] and I_2[8] or the results described in the present paper, where the spectroscopic and X-ray crystal structure characterisations of the compound obtained by reaction of **4** with TCNQ are reported.

Experimental

N,*N*′-Dimethylimidazolidine-2-selone (**4**) was prepared according to the literature.[9] TCNQ and solvents were purchased from Aldrich and used as supplied. The use of TCNQ recrystallised from MeCN and vacuum sublimed gave the same results.

Synthesis of 4·(TCNQ)$_{1.167}$

A solution of TCNQ (0.11 g, 5.64×10^{-4} mol) in 20 cm^3 of acetonitrile (MeCN) was added to a solution of *N*,*N*′-dimethylimidazolidine-2-selone (0.05 g, 2.82×10^{-4} mol) in 20 cm^3 of MeCN. The resulting mixture was stirred for 2 h, then filtered and slowly concentrated to a small volume at room temperature. The obtained dark crystalline solid was washed with hexane and vacuum dried (0.07 g, 69.8% yield). Anal. Calc. for $C_{57}H_{44}N_{20}Se_3$: C, 54.95; H, 3.56; N, 22.48%. Found: C, 55.6; H, 3.6; N, 22.8%. Mp 180 °C with decomposition.

Cyclic voltammetry

Cyclic voltammetry experiments were recorded at a scan rate of 100 mV s^{-1}, using a conventional three-electrode cell, consisting of a combined working and counter platinum electrode and a standard Ag/AgCl (in KCl 3.5 M; 0.2223 V at 25 °C) reference electrode (the ΔE measured between a standard SCE electrode and the Ag/AgCl electrode used was 0.025 V at 25 °C). The experiments were performed at room temperature in anhydrous CH_2Cl_2 and MeCN. The solutions were about 1×10^{-3} mol dm^{-3} in the electroactive species (**1**–**4**, TCNQ) with Bu_4NBF_4 (0.1 mol dm^{-3}) as supporting electrolyte. A stream of argon was passed through the solution prior to the scan. Data were recorded on a computer controlled EG&G (Princeton Applied Research) potentiostat–galvanostat Model 273 EG&G, using Model 270 electrochemical analysis software.

FT-IR Spectra

Single crystal specular reflectance infrared (IR) spectra were obtained with a Bruker IFS66 FT-IR spectrometer, equipped with a Bruker A590 microscope, and KRS5 wire grid polarizer. The non absolute reflectivity data were converted to absorbance by standard Kramers–Kronig transformation.

Conductivity measurements

Conductivity measurements were made at room temperature on pellets (thickness 0.5 mm, diameter 12 mm) using the two-point probe method.

X-Ray data collection and structure determination

Crystal data for 4·(TCNQ)$_{1.167}$. $C_{57}H_{44}N_{20}Se_3$, $M=1246.00$, triclinic, space group $P\bar{1}$ (No. 2), $a=8.1480(10)$, $b=15.388(2)$, $c=22.658(3)$ Å, $\alpha=96.086(9)$, $\beta=96.340(10)$, $\gamma=95.260(11)°$, $U=2792.2(6)$ Å^3, $D_c=1.482$ Mg m^{-3}, $T=293(2)$ K, $Z=2$, μ(Mo-Kα) $=2.035$ mm^{-1}, 10838 reflections measured, 9763 unique ($R_{int}=0.0113$). The intensity data were collected at room temperature on a CAD 4 Enraf-Nonius automatic diffractometer using graphite monochromated Mo-Kα radiation. Some selected bond distances and angles are given in Table 1. All data were corrected for Lorentz and polarization effects, and an empirical absorption correction, based on Ψ scans, was applied.[10] The reflections were processed by the direct methods program SIR92,[11] which provided a satisfactory set of starting parameters for many non-hydrogen atoms. After location of the missing non-hydrogen atoms by Fourier difference syntheses, the atomic positions were refined by the SHELXL-93 program package.[12] Non-hydrogen atoms were treated anisotropically, whereas 25 of the 54 hydrogen atoms were treated as fixed contributors in calculated positions with isotropic thermal parameters $B(H)=1.2\,B_{eq}$ (C, or N), the others were located in ΔF density maps and refined isotropi-

Table 1 Selected bond lengths (Å) and angles (°) for **4**·(TCNQ)$_{1.167}$

Se1–C1	1.911(4)	Se1–Se2	2.5187(7)
Se1–Se3	2.715(4)	Se3–Se3a	0.524(3)
Se3–C11	1.869(6)	Se3a–C11	1.823(6)
C1–N1	1.310(5)	C1–N2	1.312(5)
N1–C5	1.455(6)	N1–C2	1.469(6)
N2–C4	1.455(6)	N2–C3	1.465(6)
C2–C3	1.503(7)	Se2–C6	1.895(4)
C6–N3	1.312(5)	C6–N4	1.319(5)
N3–C9	1.456(6)	N3–C8	1.463(6)
N4–C10	1.449(7)	N4–C7	1.460(7)
C7–C8	1.518(8)	C16–C22	1.400(6)
C16–C17	1.425(6)	C16–C21	1.426(6)
C17–C18	1.345(6)	C18–C19	1.432(6)
C19–C25	1.391(6)	C19–C20	1.432(6)
C20–C21	1.344(6)	C22–C23	1.415(6)
C22–C24	1.423(7)	C23–N7	1.145(6)
C24–N8	1.134(6)	C25–C26	1.424(6)
C25–C27	1.428(6)	C26–N9	1.143(5)
C27–N10	1.141(5)	C28–C34	1.399(5)
C28–C33	1.427(5)	C28–C29	1.428(5)
C29–C30	1.342(5)	C30–C31	1.429(5)
C31–C37	1.388(5)	C31–C32	1.422(6)
C32–C33	1.350(6)	C34–C36	1.408(6)
C34–C35	1.422(6)	C35–N11	1.143(6)
C36–N12	1.145(6)	C37–C38	1.422(6)
C37–C39	1.423(6)	C38–N13	1.144(6)
C39–N14	1.140(6)	C40–C46	1.385(5)
C40–C41	1.432(5)	C40–C45	1.435(5)
C41–C42	1.340(5)	C42–C43	1.440(5)
C43–C49	1.383(5)	C43–C44	1.432(5)
C44–C45	1.340(6)	C46–C48	1.424(6)
C46–C47	1.427(6)	C47–N15	1.142(5)
C48–N16	1.135(6)	C49–C51	1.425(6)
C49–C50	1.434(6)	C5–N17	1.132(5)
C51–N18	1.142(5)	C52–C53	1.389(6)
C52–C56	1.421(6)	C52–C57	1.439(6)
C53–C55	1.430(7)	C53–C54	1.434(7)
C54–N19	1.134(6)	C55–N20	1.147(7)
C56–C57′	1.343(6)	C57–C56′	1.343(6)
N6a–C15a	1.426(19)	N6a–C13a	1.430(18)
N5a–C14a	1.397(16)	N5a–C12a	1.466(13)
C13a–C12a	1.534(19)		
C1–Se1–Se2	89.23(12)	C1–Se1–Se3	88.45(13)
Se2–Se1–Se3	177.64(6)	Se3a–Se3–C11	76.8(8)
Se3a–Se3–Se1	105.4(8)	C11–Se3–Se1	94.14(19)
Se3–Se3a–C11	86.9(8)		

[a] Symmetry transformations used to generate equivalent atoms: $' = -x, -y+1, -z+1$.

Table 2 Anodic peak (E_{pa}) and cathodic peak (E_{pc}) determined by cyclic voltammetry in CH_2Cl_2 and MeCN (value in parentheses) for **1**–**4** (1×10^{-3} mol l^{-1}). Half-wave reduction potentials of TCNQ (1×10^{-3} mol l^{-1}) measured in CH_2Cl_2 and MeCN (value in parentheses). Pt electrodes; scan rate: 100 mV s^{-1}; Bu_4NBF_4 supporting electrolyte (0.1 mol dm^{-3})

	E_{pa} (**1**)	E_{pa} (**2**)	E_{pc}
1[ab]	+0.57	+0.75	+0.08
	(+0.41)	(+0.55)	(+0.13)
2[a]	+0.60	+0.73	+0.24
	(+0.43)	(+0.79)	(+0.15)
3[a]	+0.50	+0.66	+0.04
	(+0.43)	—[c]	(+0.06)
4[d]	+0.92	+1.38	+0.07
	(+0.46)	(+0.75)	(+0.09)
	$E_{1/2}$ (**1**)	$E_{1/2}$ (**2**)	
TCNQ[d]	+0.17	−0.49	
	(+0.16)	(−0.40)	

[a] Potentials measured in CH_2Cl_2 are referenced to SCE (saturated calomel electrode),[7] whereas potentials measured in MeCN are referenced to Ag/AgCl (in KCl 3.5 M; 0.2223 V, −0.025 V *vs.* a standard SCE electrode at 25 °C). [b] Scan rate was 50 mV s^{-1} for measurements in MeCN. [c] The second oxidation potential is hidden under the first oxidation wave. [d] In both solvents, potentials are referred to Ag/AgCl.

cally. The final R [$I > 2\sigma(I)$] and R' (all data) indices were 0.0442 and 0.1274.

CCDC reference number 1145/212. See http://www.rsc.org/suppdata/jm/a9/a908136d/ for crystallographic files in .cif format.

Drawings were performed with the ORTEP[13] plotting program. Major calculations were carried out on an Alpha 3000/800S computer.

Results and discussion

Among the various criteria that must be fulfilled for the design of organic metals there is that of an incomplete charge transfer between the electron donor and the acceptor.[14,15] In this respect, it has been pointed out that the difference between the donor's oxidation potential and the acceptor's reduction potential should be in the range −0.05 to 0.32 V.[14] Thus, before discussing the characterisation of the title compound **4**·$(TCNQ)_{1.167}$ it is useful to examine in some detail the redox properties of its constituents. We have carried out cyclic voltammetries of **4** and TCNQ either in the solvent (MeCN) used for the synthesis of the complex or in CH_2Cl_2 for comparison with the data reported for **1**–**3**.[7] The results are summarised in Table 2. The cyclic voltammogram of **4** in CH_2Cl_2 scanned in the anodic direction and reversed at +1.8 and –1.8 V to the starting potential (0.0 V; see Fig. 1) shows two irreversible oxidations at +0.92 and +1.38 V, and one irreversible reduction at +0.07 V *versus* Ag/AgCl (see Experimental section). As observed for **1**–**3** in CH_2Cl_2,[7] when the scan is performed in the cathodic direction, the reduction peak does not appear. This peak could therefore be attributed to the reduction of the oxidation products. However, the anodic peaks observed for **1**–**3** in CH_2Cl_2 are at lower potentials (0.50–0.75 V range, see Table 2),[7] demonstrating that **4** is less easily oxidizable than **1**–**3** in this solvent. In the case of **1**–**3** the two oxidation peaks were tentatively attributed to a two-step process involving the initial oxidation of one molecule which then interacts with an unoxidized selenium atom of a second imidazoline moiety to give a radical species containing an Se–Se bond with a bond order of 0.5. The electron in the antibonding molecular orbital of this radical intermediate is removed in the second oxidation step to give a final dication bearing an Se–Se linkage.[7] The same could be valid for **4**, where oxidation products are formed at higher potentials due to the lack of the C=C double bond in the pentaatomic ring. However, the reduction of the allegedly formed dication occurs for **4** in CH_2Cl_2 at a potential very close to those observed for **1** and **3**.[7]

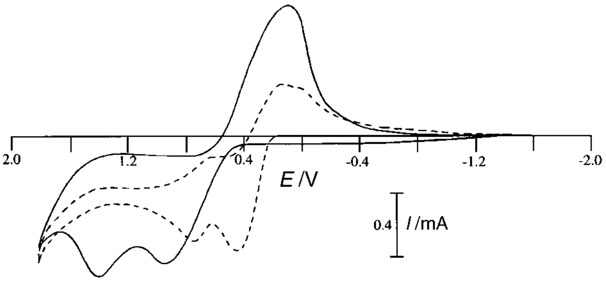

Fig. 1 Cyclic voltammogram of **4** in CH_2Cl_2 (full line) and MeCN (dashed line) scanned in the anodic direction starting from 0.0 V. Scan rate 100 mV s^{-1}, supporting electrolyte 0.1 mol dm^{-3} Bu_4NBF_4.

When MeCN is used as solvent, the two oxidation processes in the cyclic voltammograms of **1**–**4** shift considerably at lower potentials with the values observed for **4** being much closer to those observed for **1**–**3**. This seems to agree with a better stabilization of the dication formed in MeCN than in CH_2Cl_2. On the other hand the reduction process is only slightly affected by the change of solvent for all the compounds **1**–**4** (see Fig. 1 and Table 2). Considering the difference $E_{pa}(1)-E_{1/2}(1)$ between the first oxidation potential of the donors **1**–**4** and the half-wave reduction potential of TCNQ, it is clear that **1**–**4** meet the criteria ($-0.05 < E_{pa}(1)-E_{1/2}(1) < 0.32$) for the achievement of a mixed valence compound with TCNQ[14] in MeCN only, whereas **3** is somewhat at the borderline also in CH_2Cl_2 (see Table 2). However, one has to keep in mind that the degree of charge transfer is determined by the competition between the cost of ionizing the donor–acceptor couple, as expressed by the above difference, and the gain in Madelung energy for the formation of an ionic solid.[15] Since, as we shall show below, we have always observed the formation of dications as oxidation products of **1**–**4** from the reaction with TCNQ, the gain in Madelung energy is greater than that occurring in the commonly studied cases of 1 : 1 salts with monocations and monoanions. Therefore we expect also **4**·$(TCNQ)_{1.167}$ obtained from MeCN solutions to exhibit partial charge transfer or mixed valence character.

The characterisation of **4**·$(TCNQ)_{1.167}$ has been carried out by single-crystal X-ray diffraction and vibrational spectroscopy. The asymmetric unit consists of three *N*,*N'*-dimethylimidazolidine-2-selone (**4**) molecules, a half TCNQ molecule situated on the inversion centre [TCNQ(4) in Fig. 2] and three

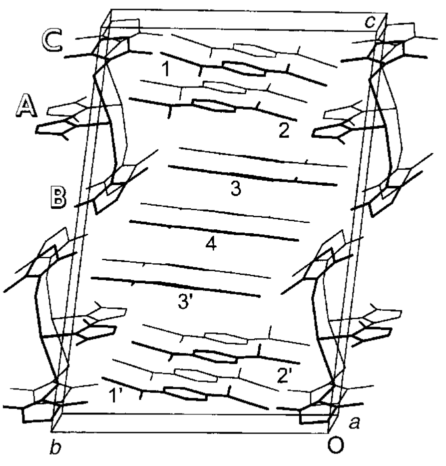

Fig. 2 Unit cell content of the **4**·$(TCNQ)_{1.167}$ compound. A, B and C identify the planes containing the molecules of **4**.

whole molecules [TCNQ(1), TCNQ(2) and TCNQ(3) of Fig. 2] in general positions. Consequently, the unit cell contains six **4** molecules and seven TCNQ molecules, and the compound may be formulated as **4**$_6$(TCNQ)$_7$.

In the crystal, three independent *N*,*N*′-dimethylimidazolidine-2-selone (**4**) molecules are bound together to give an almost linear –Se–Se···Se– moiety [Se(2)–Se(1)–Se(3) 177.64(6)°] (see Fig. 3). One of the **4** molecules bearing the Se(3) atom is affected by disorder, which can be described essentially as a ~180° rotation of the molecule around the axis passing through the C(11) atom and the C(12)–C(13) bond (the two positions have been refined with occupancy factor 0.50 : 0.50) and a slight swinging in the plane centred on C(11) [Se(2)–Se(1)–Se(3a) 167.89(5)°]. The planes containing the three units of **4** (identified as A, B and C in Fig. 2 and 3) form angles ranging from 13° to 33°. The angles C–Se–Se are in the 88.32(13)–96.82(13)° range. The –Se–Se···Se– arrangement resembles that found in the tris(selenourea) cation $[\mathrm{SeC(NH_2)_2}]_3{}^{2+}$ [Se–Se bond distances, in the three reported structures, range between 2.597(2) and 2.717(2) Å][16] and that of the dication 1,11-(methanoselenomethano)-5*H*,7*H*-dibenzo[*b*,*g*][1,5]diselenocine [Se–Se bond distances 2.556(2) and 2.645(2) Å; Se–Se–Se angle 170.21(6)°].[17] Nevertheless, in the present structure, the –Se–Se···Se– arrangement [Se(1)–Se(2) 2.5187(7) Å; Se(1)–Se(3) and Se(1)–Se(3a) 2.715(4) and 2.899(4) Å respectively] is more asymmetric than in the other two cases, the shortest Se–Se distance corresponding to a bond order of 0.58.[18] The Se(1)–Se(2) bond distance is longer than that reported for the 1,5-diselenoniabicyclo[3.3.0]octane dication {$[\mathrm{C_6H_{12}Se_2}]^{2+}$, 2.382(2) Å},[19] than those found in a series of dications bearing the –Se–Se– bridge [including some cases in which the Se–Se framework strongly interacts with the $\mathrm{Cl^-}$ and $\mathrm{Br^-}$ anions; Se–Se ranging from 2.409(2) to 2.440(2) Å; bond order ranging from 0.83 to 0.75],[5] and than that reported for the mixed-valence compound **5**·2[$(\mathrm{TCNQ})_3{}^{2-}$] [Se–Se bond distance 2.451(2) Å], where a central neutral molecule of **3** interacts through its two selenium atoms with two cyclic dications (see Scheme 1).[4] Therefore, on the basis of structural features, the oxidation product of **4** in **4**·(TCNQ)$_{1.167}$ seems to be intermediate between the cases of $[\mathrm{SeC(NH_2)_2}]_3{}^{2+}$ [16] (or 1,11-(methanoselenomethano)-5*H*,7*H*-dibenzo[*b*,*g*][1,5] diselenocine)[17] and those of previously reported dications.[4,5,20] The dication in **4**·(TCNQ)$_{1.167}$ could be considered either as a dication bearing the –Se–Se– bridge and acting as acceptor towards the selenium atom of a third donor molecule, or more simply as a tris(*N*,*N*′-dimethylimidazolidine-2-selone) [(**4**)$_3$]$^{2+}$ dication, characterised by a very asymmetric –Se–Se···Se– arrangement.

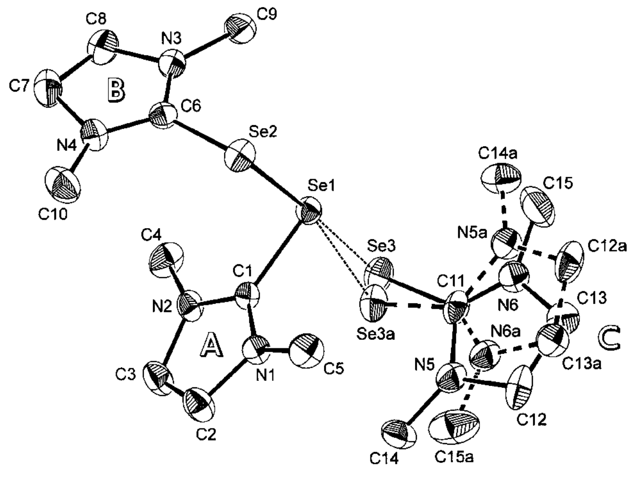

Fig. 3 Tris(*N*,*N*′-dimethylimidazolidine-2-selone) [(**4**)$_3{}^{2+}$] dication showing the atom labelling scheme. Thermal ellipsoids at 30% probability. Hydrogen atoms have been omitted for clarity. A, B and C identify the planes containing the molecules of **4** (see Fig. 2).

The TCNQ molecules stack in columns along the crystallographic *c* axis (see Fig. 4) to form dimers [TCNQ(1) and TCNQ(2) in Fig. 3] and trimers [TCNQ(3) , TCNQ(4) and TCNQ(3′) in Fig. 3]. The average distances between atoms and mean planes of TCNQ(1) and TCNQ(2) molecules are 3.275(6) Å with 2.951(6) and 3.710(6) Å as minimum and maximum distances. The average distances between atoms and mean planes of TCNQ(3) and TCNQ(4) molecules are 4.005(6) Å with 3.948(6) and 4.108(6) Å as minimum and maximum distances. The seven TCNQ molecules in the unit cell should carry four negative charges.

One method used to estimate the average charge associated with each TCNQ molecule(s) is to look at the C–C bond lengths. A well established procedure is based on ratios or differences of C–C bond lengths derived from a wide crystallographic database of TCNQ salts and complexes.[21] However, in the present case the errors in the determination of the bond lengths are too large to give confidence to the estimated ionicities. In applying the method we have found a total charge of 3.3 instead of 4 electrons localised on the seven TCNQ molecules within the unit cell and therefore we limit ourselves to the qualitative results, which suggest that the negative charges are unevenly distributed both within the TCNQ dimer and trimer.

Further information about the charge transfer and the average charge on TCNQ molecules can be obtained through vibrational spectroscopy,[22] but again the ρ estimation turns out to be difficult and rather approximate. Indeed, we predict perturbing effects due to electron–molecular vibration (e–mv) interaction,[22] in addition to the difficulty of disentangling the TCNQ bands from those of the complex counter-ion. In particular, the indications from the Raman spectra may be deceptive, since in the presence of trimerized structures and mixed-valence, the Raman frequencies are perturbed by e–mv interaction.[23] Therefore, we only report the IR spectra here: in this case the use of microreflectance techniques[24] has allowed to obtain polarized data from single crystals, so that the e–mv induced bands can be easily distinguished from the normally active, unperturbed bands.[22]

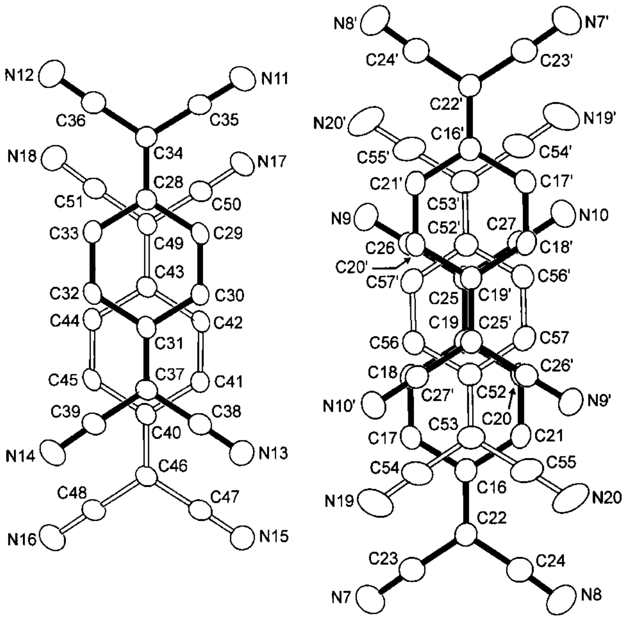

Fig. 4 TCNQ molecular stacking in the unit cell 1,2 and 3,4,3′ from left to right (see Fig. 2), along the crystallographic *c* axis. Within the trimer, the TCNQ(4) molecule lies on a crystallographic inversion centre and TCNQ(3) and TCNQ(3′) are symmetry related [see Table 1 for the definition of the symmetry operator (′)].

Fig. 5a and 5b report the IR spectra of **4**·$(TCNQ)_{1.167}$ from 650 to 5000 cm^{-1}, polarized respectively parallel and perpendicular to the crystallographic *c* axis. In the spectrum polarized along *c*, that is, along the TCNQ stack, one easily identifies the broad absorption around 4200 cm^{-1} as CT transition(s) between TCNQ's. In the vibrational region, the spectrum is characterised by a series of strong absorptions, due to the TCNQ total-symmetric vibrations, borrowing intensity from the nearby CT transition (e–mv induced bands).[22] All these bands appear as normal absorptions, and not as indentations over the continuum CT transition, as found in several TCNQ semiconductors.[25] Accordingly, the room temperature optical gap is estimated at over 2400 cm^{-1} ($\sim$0.3 eV), much higher than for other TCNQ complexes with imidazoline-2-selone derivatives.[2–4] Furthermore, the e–mv induced bands show the multiplet structure typical of non-uniform charge distribution on the TCNQ sites.[26] The above analysis suggests strong charge localisation, placing **4**·$(TCNQ)_{1.167}$ among wide band-gap semiconductors. Pressed-pellet conductivity of **4**·$(TCNQ)_{1.167}$, 3.45×10^{-3} S cm^{-1} at room temperature, is similar to the conductivity values measured for the CT compounds obtained between **1**–**3** and TCNQ.[2–4]

As far as the determination of the charge distribution on the TCNQ sites is concerned, the IR spectra polarized perpendicularly to the stack axis (Fig. 5b) confirm the mixed valence character already suggested by the X-ray crystal structure. A strong absorption due to the counter ion, centred around 1580 cm^{-1}, partially obscures the spectral region of the b_{1u} ν_{20} C–C stretching mode, whose frequency was used to estimate ρ in other complexes of TCNQ with selone derivatives.[3] Therefore, we can only rely on the frequencies of the b_{1u} and b_{2u} C–N stretching modes, expected between 2230 and 2150 cm^{-1}.[27] In the above spectral region, we find four bands at 2203, 2197, 2180 and 2158 cm^{-1}. At first sight, from these frequencies one might deduce the presence of only two differently charged species, as each gives rise to two absorptions. However, the possible presence of overlaps is to be considered: for instance, the shoulder at 2203 cm^{-1} gives $\rho \sim 0.5$ electrons if attributed to the b_{1u} ν_{19} mode, and $\rho \sim 0.3$ electrons if attributed to the b_{2u} ν_{33} mode. Considering the overlaps and all possible choices in the assignments, we find that in this region the observed spectrum is compatible with the presence of three differently charged TCNQ's, with $\rho \sim 0.3$, 0.5 and 0.7 electrons. The band at 2158 cm^{-1}, attributable to the b_{2u} ν_{33} mode, would actually indicate $\rho \sim 0.9$ electrons, but it should be kept in mind that in any case the indications from the CN stretching frequencies are to be taken cautiously.[28] Consequently, the negative charge seems to be unevenly distributed on the TCNQ molecules, but unfortunately it is not possible at the moment to say the amount of charge located on the dimer and trimer units.

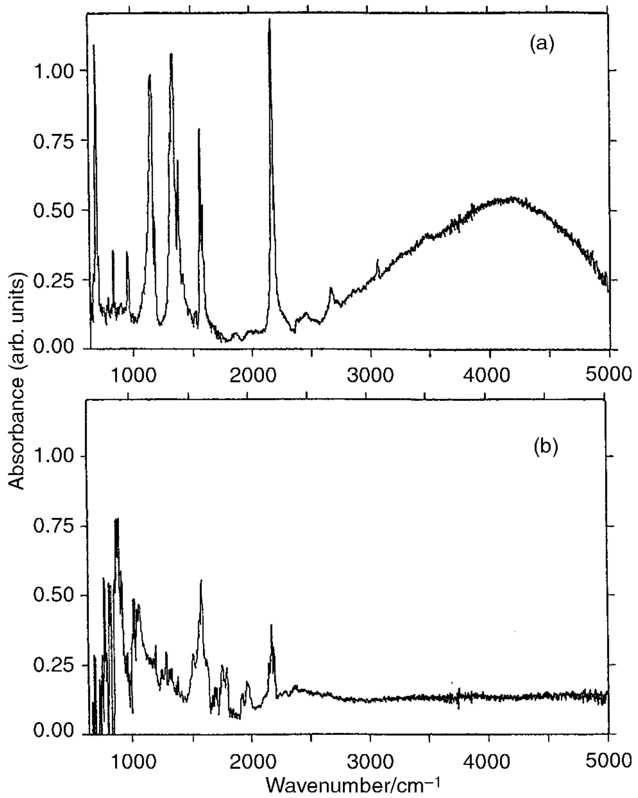

Fig. 5 Kramers–Kronig transformed spectra obtained from the polarized reflectance spectra of **4**·$(TCNQ)_{1.167}$. The resulting ordinate is absorbance in arbitrary units. (a): electric vector parallel to the *c* crystallographic axis; (b): electric vector perpendicular to *c*.

In conclusion, the present study confirms the strong tendency towards the formation of dications as oxidation products in the new family of donors based on imidazoline-2-selone. In the present like in the other complexes with TCNQ, the conductivity is presumably due to the anion stack only. The dications formed by the donors probably induce charge localisation on the TCNQ units along the stacks, yielding in all cases semiconducting behaviour.

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