Crystal Structures, Electrical Conductivity and Band-structure Calculations of Three New [cation][$Ni(C_3S_5)_2$]$_2$ Compounds†

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The mixed-valence radical salts [smdt][$Ni(C_3S_5)_2$]$_2$ **1**, [dmp][$Ni(C_3S_5)_2$]$_2$ **2** and [dmm][$Ni(C_3S_5)_2$]$_2$ **3** ($C_3S_5^{2-}$ = 1,3-dithiole-2-thione-4,5-dithiolate, smdt = *S*-methyl-1,3-dithianium, dmp = *N*,*N*-dimethylpyrrolidinium and dmm = *N*,*N*-dimethylmorpholinium) have been obtained by electrochemical oxidation of the corresponding [cation][$Ni(C_3S_5)_2$] complexes in acetonitrile. Single-crystal X-ray studies revealed that all three crystallise in essentially the same packing mode. Their structure consists of anionic diads stacked face-to-face along one direction. The stacks form layers of $Ni(C_3S_5)_2$ units which are separated by the cations. In the structure of **3** two types of $Ni(C_3S_5)_2$ layers exist, exhibiting different structural and electrical properties. The acceptor molecules neighbouring along the longest axis make an angle of 135 (**1**), 139 (**2**) and 152° (**3**) with each other, thereby forming a herringbone motif. In all three structures, short intermolecular S···S contacts can be found predominantly between $Ni(C_3S_5)_2$ units lying side-by-side to each other, but also within the stacks in **3**. At ambient pressure, all three $Ni(C_3S_5)_2$ compounds have room-temperature conductivities ranging between 1 and 70 S cm^{-1}. Their thermal behaviour is consistent with semiconductors having activation energies of about 0.14 eV. Band-structure calculations were carried out and found to be in agreement with the observed conductivities when some degree of electron correlation is taken into account. Calculation of molecular orbital overlaps indicated dimerisation of the anions, with a weak, essentially two-dimensional conduction pathway for salts **1** and **2**. In the crystal lattice of **3** one $Ni(C_3S_5)_2$ layer can be considered as conducting along the stacking direction, while in the second type of layer a two-dimensional conduction pathway appears to be present.

In 1984 the preparation of [ttf][$Ni(C_3S_5)_2$]$_2$ {ttf = tetrathiafulvalene [2-(1,3-dithiol-2-ylidene)-1,3-dithiole]; $C_3S_5^{2-}$ = 1,3-dithiole-2-thione-4,5-dithiolate (also called 4,5-dimercapto-1,3-dithiole-2-thionate, or 'dmit')} led to the discovery of the first formally inorganic molecular superconductor.[1] Recently, it was demonstrated by solid-state NMR techniques that in this salt the conduction pathway occurs *via* both the radical donor molecule ttf$^{\bullet+}$ and the anionic acceptor $Ni(C_3S_5)_2^{\bullet-}$ units.[2] Later, by reporting the high-pressure superconductivity of [NMe_4][$Ni(C_3S_5)_2$]$_2$, Kobayashi *et al.*[3] showed that an organic radical cation is not an absolute necessity to obtain a superconducting $M(C_3S_5)_2$ salt. In contrast to ttf$^{\bullet+}$, a spectator cation such as NMe_4^+ is not actively involved in the conductivity process, but influences the eventual packing mode of the $Ni(C_3S_5)_2$ molecules by its size and shape, and can therefore be considered as having a second-order effect on the compound's conductivity. This observation clearly increased the number of studies on new $M(C_3S_5)_2$ (M = Ni, Pd, Pt or Au) compounds in combination with small, closed-shell cations. Most cations used so far consist of the type tetraalkylammonium,[3-7] tetraalkylphosphanium,[4] alkali-metal ions[8-11] or even closed-shell dications.[12] Recently, the topic of dmit was reviewed.[13] Many $M(C_3S_5)_2$ salts show metallic behaviour down to a certain temperature, but since the superconductivity of α-[ttf][$Pd(C_3S_5)_2$]$_2$ and α′-[ttf][$Pd(C_3S_5)_2$]$_2$ was reported in 1989[13] no new superconductors based on $M(C_3S_5)_2$ have been discovered until very recently. It has now been proposed that β-[NMe_4][$Pd(C_3S_5)_2$]$_2$ becomes superconducting at 6.2 K under 6.5 kbar (6.5 × 10^8 Pa).[7b]

In this paper we present a new class of closed-shell cations, namely that containing small, saturated, cyclic cations. They have a size and shape which are not too different from those of the smaller tetraalkylammonium-type cations, and they also possess similar electronic properties. However, an advantage of using saturated, cyclic cations is that they can be varied almost without limit, and therefore they might be especially suited for the fine tuning of molecular interactions by choice of only marginally different components.[14]

The crystal structures, conductivity studies and tight-band structure calculations of three $Ni(C_3S_5)_2$ compounds containing various cyclic, saturated cations are reported. They are compared to each other and to [cation][$M(C_3S_5)_2$]$_2$ compounds known from the literature. A preliminary report of the

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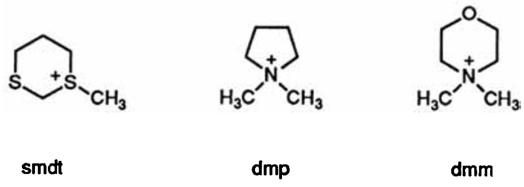
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.
Non S.I. unit employed: eV = 1.60 × 10^{-19} J.



Scheme 1

structures and conductivities of two of them, [smdt][$Ni(C_3S_5)_2]_2$ and [dmp][$Ni(C_3S_5)_2]_2$ (smdt = *S*-methyl-1,3-dithianium, dmp = *N*,*N*-dimethylpyrrolidinium), was presented at a conference.[15]

Experimental

Preparations.—*The* [cation]I *salts* (*cation = smdt, dmp, or dmm*). The smdt iodide was prepared from 1,3-dithiane and iodomethane according to Böhme and Krack.[16] The dmp and dmm iodides were prepared by adding a small excess of iodomethane to a solution of *N*-methylpyrrolidine or *N*-methylmorpholine, respectively, in acetone. This nucleophilic addition reaction is exothermic. Recrystallisation from methanol yields pure [cation]I.

The [cation][$Ni(C_3S_5)_2$] *complexes.* The 4,5-bis(benzoylthio)-1,3-dithiole-2-thione ligand and the salts $[cation]_2[Ni(C_3S_5)_2]$ and [cation][$Ni(C_3S_5)_2$] (with cation = smdt, dmp, or dmm) were prepared according to the general recipe of Steimecke *et al.*[17]

The [cation][$Ni(C_3S_5)_2]_2$ *complexes.* Crystals of [cation][$Ni(C_3S_5)_2]_2$ were grown by using the electrochemical oxidation method. An H-tube equipped with a fine-porosity frit was placed under an argon atmosphere and filled with a solution of [cation][$Ni(C_3S_5)_2$] (0.1 mmol) in dry acetonitrile (35 cm^3). No extra electrolyte was used. Two platinum-wire electrodes were placed in the dark olive-green solution and a constant current of approximately 1 μA was applied. After 2–10 d, black, lustrous platelets were isolated from the anode. They were washed with acetone and diethyl ether and dried. The stoichiometry of the compounds was concluded from the X-ray structure analysis.

Crystallography.—[smdt][$Ni(C_3S_5)_2]_2$ **1**. A black, platelet-shaped crystal was mounted on an Enraf–Nonius CAD-4 four-circle diffractometer and measured at room temperature using graphite-monochromated Cu-Kα radiation. Cell constants were determined from setting angles of 24 reflections. The 1698 independent reflections (of 3269 measured) for which $I > 2\sigma(I)$ were corrected for Lorentz and polarisation effects. The statistics of the normalised structure factors indicated a non-centrosymmetric space group. Three reference reflections monitored after every hour showed that after a total of 60 h of X-ray exposure no decomposition had occurred. All calculations were carried out on the Leiden University computer (IBM 3083) using programs written or modified by Mrs. E. W. M. Rutten-Keulemans and Dr. R. A. G. de Graaff. An absorption correction was applied using Monte-Carlo methods.[18] Scattering factors and corrections for anomalous dispersion were taken from ref. 19. Nickel atoms were located using a Patterson map. The structure was solved by automatic Fourier techniques, using the computer program AUTOFOUR.[20] Least-squares refinement on *F* of non-hydrogen atoms yielded their positional and anisotropic thermal parameters. Two hydrogen atoms were located from a Fourier difference map. The positions of the other hydrogen atoms were calculated, with C–H 1 Å. Hydrogen atoms were coupled to their neighbouring atoms in the refinement. Their isotropic thermal parameters were 6.2(1) $Å^2$. Relevant crystallographic data are listed in Table 1, final coordinates in Table 2.

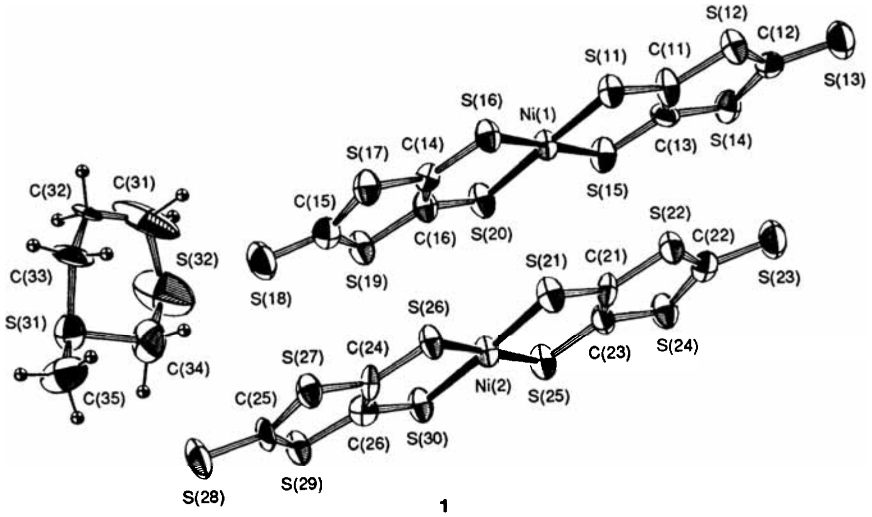
[dmp][$Ni(C_3S_5)_2]_2$ **2**. A black, platelet-shaped crystal was mounted on an Enraf-Nonius CAD-4 four-circle diffractometer. Cell constants were determined from setting angles of 23 reflections (θ between 39 and 43°). The intensities were collected at room temperature using graphite-monochromated Cu-Kα radiation. The statistics of the normalised structure factors indicated a centrosymmetric space group. Two reference reflections monitored after every hour showed that after a total of 60 h of X-ray exposure no decomposition had occurred. An absorption correction was applied and scattering factors and corrections for anomalous dispersion employed as above. The $Ni(C_3S_5)_2$ molecule was found by the direct-methods routine (SHELXS 86).[21] All subsequent Fourier syntheses and least-squares refinements were executed using XTAL 3.0.[22] The dmp cations appear to be highly disordered around the mirror plane at ($x,\frac{1}{4},z$) but seemed not to obey the symmetry of $P2_1/m$. For this reason the structure was refined in the asymmetric space group $P2_1$ while constraining the $Ni(C_3S_5)_2$ molecules to centrosymmetrically related positions. The molecular structure of the dmp cation could not be solved. In order to cope with the electron density of the cation, some atoms with population parameters between 0.2 and 0.6 and with locations near the expected position of the dmp cation were introduced (see Table 3). These atoms flattened the final Fourier difference map to a maximum and minimum residual peak of 0.6 and −0.6 e $Å^{-3}$, respectively. Relevant crystallographic data are listed in Table 1, final coordinates in Table 3.

[dmm][$Ni(C_3S_5)_2]_2$ **3**. A black, plate-like crystal was mounted in a Lindemann glass capillary. The lattice parameters at 295 K were determined by a least-squares fit to the setting angles of 25 independent reflections ($12.7 < \theta < 21.1°$) collected on an Enraf–Nonius CAD-4 four-circle diffractometer using Ni-filtered Cu-Kα radiation. The three reference reflections monitored after every hour indicated that after a total of 108.8 h of X-ray exposure no decomposition had occurred. The triclinic unit cell is Niggli reduced. Data reduction and application of Lorentz and polarisation correction were performed by using the local data reduction program HELENA. The program ABSORB[23] (Gaussian Integration) was used to apply absorption correction. The structure was solved by the direct-methods routine (SHELXS 86).[21] All subsequent least-squares refinements were executed using SHELX 76.[24] The refinement calculations were performed using the scattering factors for the respective neutral atoms, as tabulated by Cromer and Mann,[25] and were corrected for anomalous dispersion.[26] The hydrogen atoms of the carbons were included at calculated positions (C–H 1.08 Å) and their thermal parameters refined as two separate common-group factors. In the final full-matrix least-squares calculation all non-hydrogen atoms were modelled anisotropically. Relevant crystallographic data are listed in Table 1, final coordinates in Table 4. The geometric data were calculated using the program PLATON.[27]

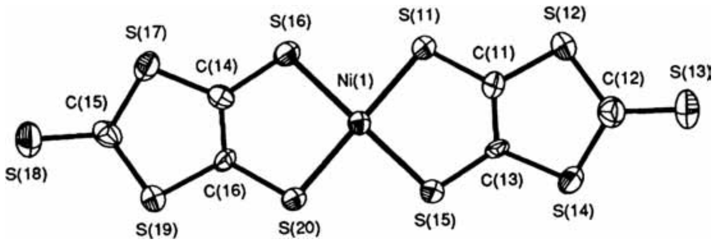
Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles for all three structures.

Results and Discussion

Description of the Crystal Structures of Compounds **1**–**3**.—Relevant bond lengths and angles are listed in Tables 5–7. The Ni–S bond distances vary from 2.145 to 2.179 Å, which is typical for $Ni(C_3S_5)_2$ molecules having a formal oxidation state of $\frac{1}{2}-$. The structures of [smdt][$Ni(C_3S_5)_2]_2$ **1** and [dmm][$Ni(C_3S_5)_2]_2$ **3** consist of two crystallographically independent $Ni(C_3S_5)_2$ units and one cation, as depicted in Fig. 1. In contrast the crystallographically independent unit in the structure of compound **2** contains only one $Ni(C_3S_5)_2$ molecule and half a *N*,*N*-dimethylpyrrolidinium cation. The latter is at $x,\frac{1}{4},z$ and is highly disordered. The $Ni(C_3S_5)_2$ molecules in **1**–**3** are essentially planar. In the monoclinic salts **1** and **2** the 2_1 operator of the space groups $P2_1$ and $P2_1/m$ is responsible for



1



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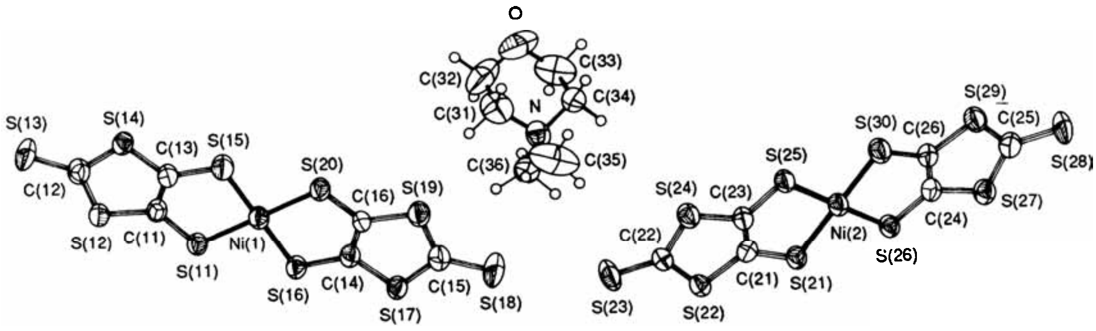

3

Fig. 1 The ORTEP[28] plots of the crystallographically independent units with atomic labelling schemes for compounds **1** (60% probability level), **2** (50% probability level, disordered cation is omitted) and **3** (50% probability level)

the fact that the acceptor units neighbouring along the *b* axis are arranged in a herringbone motif. The interstack angles are 135 (**1**), 139 (**2**) and 152° (**3**). A similar packing mode was previously found for the structures of β-$[NMe_2Et_2][Ni(C_3S_5)_2]_2$ and $[NMe_3Et][Ni(C_3S_5)_2]_2$,[4] as well as in several [cation][Pd$(C_3S_5)_2]_2$ salts.[7a]

Although at first impression the overall stacking mode seems essentially the same in compounds **1**–**3**, an important feature in the structure of **3** sets this salt apart from the other two. Due to the head-to-tail orientation of the two independent $Ni(C_3S_5)_2$ molecules with respect to each other (see Fig. 1) and its space group being $P\bar{1}$, stacks are formed, each containing solely *one* of the two crystallographically independent units. As a consequence, the lattice of **3** consists of two types of stacks, exhibiting different structural properties. Another compound in which the anions are known to crystallise in two non-equivalent stacks is α-$[NMe_4][Pd(C_3S_5)_2]_2$.[7a] In the structures of **1** and **2** all $Ni(C_3S_5)_2$ stacks are equivalent (see Fig. 2).

As is found in most other compounds of general formula $[cation][Ni(C_3S_5)_2]_2$,[4] a certain degree of dimerisation of the $Ni(C_3S_5)_2$ units, reflected by unequal interplanar spacings, is present in all three structures. Every two anions form a so-called 'diad'. This dimerisation is most pronounced in compound **2** and the $Ni(1)(C_3S_5)_2$ stacks in **3** (see Fig. 2). The various modes of overlap along the molecular stacks are shown in Figs. 3–5. It is obvious from Figs. 2 and 6 that the most significant intracolumnar overlap, resulting in the largest number of short (< 3.70 Å) S···S contacts, will be present in the $Ni(2)(C_3S_5)_2$ columns in structure **3**.

The $Ni(C_3S_5)_2$ stacks form layers of acceptor molecules which are separated from each other by sheets of cations. The fact that there are two different acceptor stacks in salt **3** implies

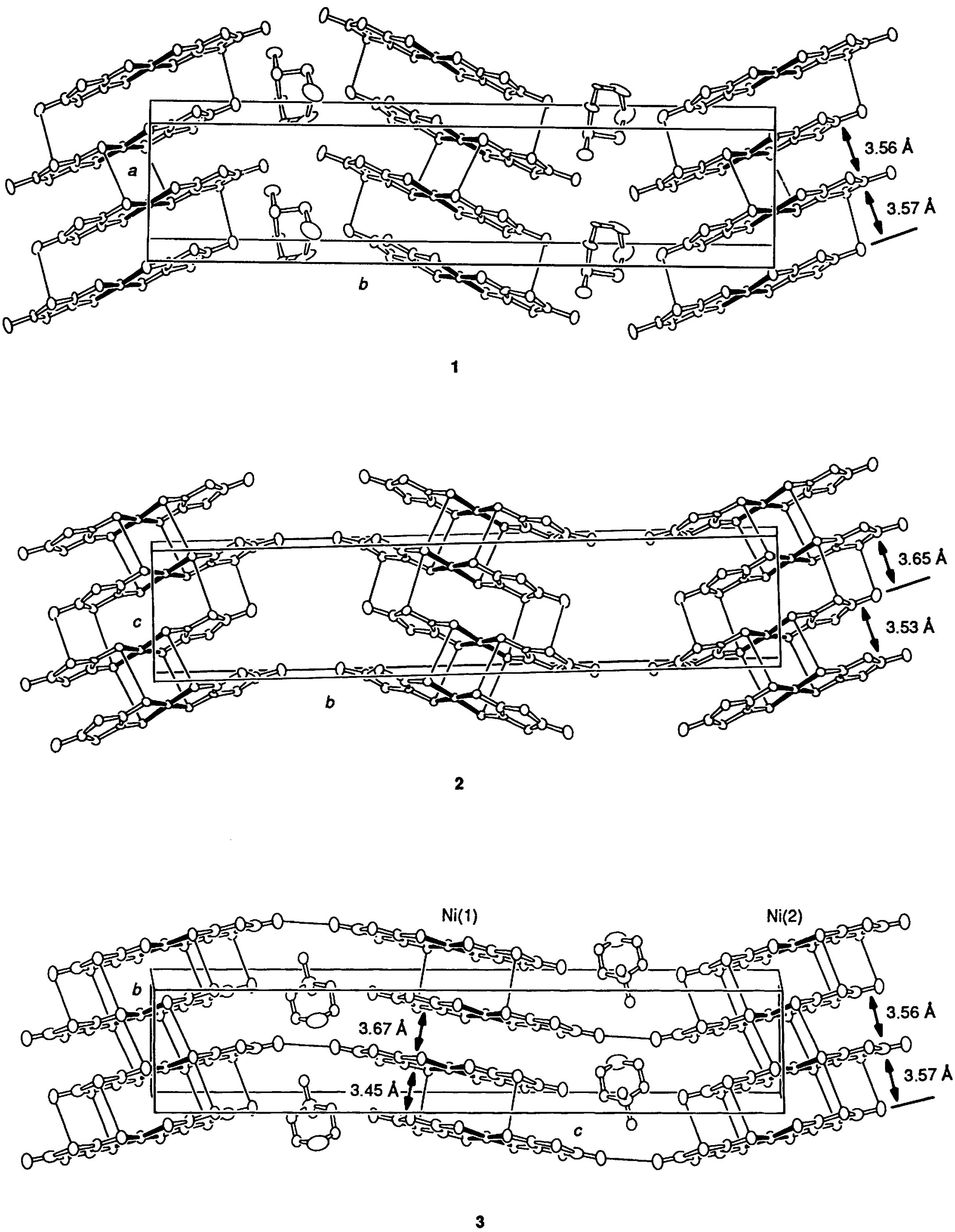

Fig. 2 Unit-cell contents of compounds **1**, **2** (disordered cations are omitted) and **3**. Thin black lines represent S···S contacts <3.70 Å

that two types of layers exist as well. As can be seen from Fig. 6, within a layer of acceptor molecules many S···S contacts shorter than 3.70 Å, the sum of the van der Waals radii, can be found between $Ni(C_3S_5)_2$ units laying side-by-side to each other. This is usually the direction in which the largest number of S···S interactions occur.[4,7a] Short contacts parallel to the long axis can only take place between sulfur atoms of the terminal thionyl groups, but nonetheless these interactions can play a role in the conductivity behaviour of such compounds, as they might add an extra dimension to the electrical conduction pathway.[29] It should be noted that in **1** the shortest S···S distances are found between the thionyl groups of the $Ni(C_3S_5)_2$ molecules and the sulfur atoms in the smdt cations. Tables 8–10 list all short S···S contacts occuring in compounds **1**–**3**, respectively.

Conductivity Measurements.—Temperature-dependent four-probe conductivity measurements were carried out using a

Table 1 Crystallographic data

Compound	**1**	**2**	**3**
Formula	$C_{17}H_{11}Ni_2S_{22}$	$C_{18}H_{14}NNi_2S_{20}$	$C_{18}H_{14}NNi_2OS_{20}$
M	1038.0	1002.9	1018.9
Space group	$P2_1$	$P2_1/m$	$P\bar{1}$
a/Å	8.015(5)	6.0488(3)	6.170(1)
b/Å	36.213(5)	36.763(2)	7.436(1)
c/Å	5.943(1)	7.7977(4)	37.901(2)
α/°	90	90	89.42(1)
β/°	102.65(3)	102.169(4)	87.87(1)
γ/°	90	90	78.22(1)
U/Å^3	1683(1)	1695.0(6)	1701.0(4)
Z	2	2	2
D_m/g cm^{-3}	2.01	2.00	2.00
D_c/g cm^{-3}	2.05	1.97	1.99
F(000)	1044.69	1001.9	1026
μ(Cu-Kα)/cm^{-1}	141.9	129.6	129.4
λ(Cu-Kα)/Å	1.541 78	1.541 78	1.541 80
Transmission factors	0.126–0.754	0.06–0.4	0.017–0.77
Crystal size/mm^3	0.25 × 0.25 × 0.05	0.3 × 0.4 × 0.01	0.82 × 0.46 × 0.02
Minimum ranges hkl	0–9, 0–44, −7 to 7	−7 to 7, 0–44, 0–9	−7 to 7, −9 to 0, −24 to 24
Scan type	ω–θ	ω–2θ	ω–2θ
Scan width/°	1.0 + tanθ	1.2 + 0.15 tanθ	0.53 + 0.15 tanθ
θ range/°	2–70	2.5–70	2–75
No. measured reflections	3498	3261	9062
No. unique reflections	1698[a]	2998[a]	5439[b]
No. parameters	402	344	382
Weighting scheme	$1/[\sigma^2(F_o) + 0.01\ F_o^2]$	$1/\sigma^2(F_o)$	$10.3/[\sigma^2(F_o) + 0.000\,293\ F_o^2]$
R[c]	0.039	0.047	0.077
R'[d]	0.035	0.045	0.107
Maximum, minimum electron density/e Å^{-3}	0.44, −0.45	0.6, −0.6	1.07, −0.90

[a] $I > 2\sigma(I)$. [b] $I > 2.5\sigma(I)$. [c] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [d] $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$.

Table 2 Final coordinates of the non-hydrogen atoms for $[smdt][Ni(C_3S_5)_2]_2$

Atom	x	y	z	Atom	x	y	z
Ni(1)	0.3105(4)	0	0.3514(4)	C(22)	−0.061(2)	−0.0939(4)	0.227(3)
S(11)	0.4632(6)	−0.0417(1)	0.5681(5)	S(23)	0.0044(6)	−0.1362(1)	0.1638(8)
C(11)	0.460(2)	−0.0766(4)	0.375(2)	S(24)	−0.1891(6)	−0.0679(1)	0.0196(7)
S(12)	0.5672(6)	−0.1184(1)	0.4523(7)	C(23)	−0.199(2)	−0.0299(4)	0.198(3)
C(12)	0.504(2)	−0.1394(4)	0.189(3)	S(25)	−0.3163(6)	0.0081(1)	0.1040(7)
S(13)	0.5620(6)	−0.1834(1)	0.1473(8)	S(26)	−0.2250(6)	0.0761(1)	0.7136(7)
S(14)	0.3853(6)	−0.1125(1)	−0.0209(7)	C(24)	−0.337(2)	0.1150(4)	0.619(2)
C(13)	0.375(2)	−0.0738(4)	0.147(2)	S(27)	−0.3465(6)	0.1529(1)	0.7979(7)
S(15)	0.2641(6)	−0.0350(1)	0.0500(7)	C(25)	−0.4710(2)	0.1813(4)	0.597(3)
S(16)	0.3545(6)	0.0351(1)	0.6511(7)	S(28)	−0.5295(7)	0.2227(1)	0.6531(8)
C(14)	0.239(2)	0.0730(4)	0.557(2)	S(29)	−0.5237(6)	0.1614(1)	0.3231(7)
S(17)	0.225(6)	0.1107(1)	0.7283(7)	C(26)	−0.423(2)	0.1199(4)	0.392(2)
C(15)	0.090(2)	0.1371(5)	0.525(3)	S(30)	−0.4214(6)	0.0845(1)	0.1977(7)
S(18)	0.0207(6)	0.1780(1)	0.5801(8)	S(31)	−0.1691(6)	0.2973(1)	0.2229(7)
S(19)	0.0337(6)	0.1159(1)	0.2543(7)	S(32)	−0.0803(9)	0.2386(2)	−0.051(1)
C(16)	0.148(2)	0.0754(4)	0.331(3)	C(31)	0.136(2)	0.2469(7)	0.134(3)
S(20)	0.1511(6)	0.0405(1)	0.1404(7)	C(32)	0.167(2)	0.2828(4)	0.217(3)
Ni(2)	−0.2695(4)	0.4259(8)	0.4065(3)	C(33)	0.051(2)	0.2930(6)	0.376(3)
S(21)	−0.1090(6)	0.0015(1)	0.6116(7)	C(34)	−0.207(2)	0.2494(5)	0.154(3)
C(21)	−0.109(2)	−0.0334(4)	0.422(2)	C(35)	−0.282(2)	0.3024(6)	0.448(3)
S(22)	0.0043(6)	−0.0742(1)	0.4916(7)				

Keithly model 225 current source and a model 616 electrometer. The four gold wires were attached to the single crystal with gold paint. At room temperature the electrical conductivity of salts **1** and **2** is between 1 and 10 S cm^{-1}, but the room-temperature conductivity for **3** is notably higher, *ca.* 70 S cm^{-1}. Upon cooling to 130 K all three compounds showed a semiconducting behaviour with values for E_a around 0.14 eV. During the conductivity measurements of compound **3** a peculiar phenomenon was observed. At *ca.* 200 K the crystal seemed to 'implode': an abrupt shattering of the complete crystal occurred. This happened for all four measured crystals of **3** at approximately the same temperature. Such crystal shattering at lower temperatures has been observed before in organic conductors, *e.g.* in κ-(bedtttf)$_2$Ag(CN)$_2$·H$_2$O [bedtttf = bis(ethylenedithio)tetrathiafulvalene], which apparently undergoes a destructive phase transition when cooled below 150 K.[30] Differential scanning calorimetry (DSC) experiments were carried out to check if a phase transition at 200 K occurs in **3**. The results obtained were reproducible and showed a small but significant increase in the heat flow, with a maximum at around 200 K. Again, after the measurements the crystals were shattered.

Band-energy Calculations. The intermolecular orbital overlaps between the LUMOs (lowest unoccupied molecular orbi-

Table 3 Final coordinates of the non-hydrogen atoms for [dmp][$Ni(C_3S_5)_2$]$_2$ **2**

Atom (*a*) Anion:	*x*	*y*	*z*	Atom (*b*) Cation:	*x*	*y*	*z*	Population
Ni(1)	0.529 9(1)	0.478 74(2)	0.211 4(1)	N(1)	0.211(2)	0.254 1(8)	0.539(2)	0.44
S(11)	0.831 8(2)	0.445 62(3)	0.257 2(2)	N(2)	0.250(2)	0.245 2(6)	0.439(2)	0.42
S(12)	0.910 0(2)	0.368 60(4)	0.148 6(2)	C(21)	0.362(8)	0.276(1)	0.315(6)	0.23
S(13)	0.756 8(4)	0.297 26(4)	−0.013 7(3)	C(22)	0.087(5)	0.226 3(8)	0.377(4)	0.48
S(14)	0.440 9(2)	0.359 32(4)	−0.021 (2)	C(23)	0.087(5)	0.280 1(8)	0.468(4)	0.60
S(15)	0.319 7(2)	0.435 95(3)	0.070 4(2)	C(24)	0.252(5)	0.269 6(9)	0.245(4)	0.32
S(16)	0.739 1(2)	0.520 02(3)	0.363 5(2)	C(25)	0.037(9)	0.277(1)	0.666(7)	0.20
S(17)	0.628 5(2)	0.595 39(4)	0.472 2(2)	C(26)	0.471(4)	0.256 0(9)	0.349(3)	0.48
S(18)	0.315 7(4)	0.657 22(4)	0.480 0(2)	C(27)	0.409(4)	0.242 2(7)	0.622(3)	0.46
S(19)	0.159 6(2)	0.588 89(4)	0.291 4(2)	C(28)	0.27(2)	0.296(3)	0.55(1)	0.44
S(20)	0.233 1(2)	0.512 96(3)	0.167 4(2)	C(29)	0.247(4)	0.258 7(8)	0.758(3)	0.49
C(11)	0.734 7(8)	0.405 8(1)	0.155 5(6)	C(30)	0.157(8)	0.295(1)	0.448(6)	0.38
C(12)	0.704(1)	0.339 8(1)	0.034 5(7)	C(31)	−0.003(8)	0.258(2)	0.632(6)	0.48
C(13)	0.511 1(8)	0.401 8(1)	0.072 9(6)	C(32)	0.136(6)	0.238(1)	0.704(5)	0.32
C(14)	0.554 1(8)	0.554 5(1)	0.364 8(6)	C(33)	0.168(6)	0.216(1)	0.673(5)	0.27
C(15)	0.368(1)	0.615 8(1)	0.416 4(7)	C(34)	0.11(1)	0.280(2)	0.514(9)	0.38
C(16)	0.329 9(8)	0.551 5(1)	0.277 9(6)	C(35)	0.474(4)	0.254(1)	0.547(3)	0.57
				C(36)	0.165(7)	0.212(1)	0.369(6)	0.31
				C(37)	0.335(5)	0.259(1)	0.285(4)	0.54

Table 4 Final coordinates of the non-hydrogen atoms for [dmm][$Ni(C_3S_5)_2$]$_2$ **3**

Atom	*x*	*y*	*z*
Ni(1)	0.438 6(2)	0.228 4(2)	0.471 16(3)
S(11)	0.733 0(3)	0.165 7(3)	0.501 08(5)
S(12)	0.815 4(3)	0.230 6(3)	0.577 18(5)
S(13)	0.675 7(5)	0.363 6(4)	0.649 47(6)
S(14)	0.354 2(3)	0.392 2(3)	0.592 09(5)
S(15)	0.235 9(3)	0.342 8(3)	0.516 44(5)
S(16)	0.648 3(3)	0.117 3(3)	0.426 47(5)
S(17)	0.544 2(3)	0.075 1(3)	0.350 22(5)
S(18)	0.239 4(5)	0.091 8(4)	0.290 94(6)
S(19)	0.078 8(3)	0.220 2(3)	0.363 33(5)
S(20)	0.144 7(3)	0.289 9(3)	0.440 41(5)
C(11)	0.644(1)	0.244(1)	0.541 19(2)
C(12)	0.615(2)	0.331(1)	0.609 0(2)
C(13)	0.424(1)	0.320(1)	0.548 4(2)
C(14)	0.469(1)	0.141(1)	0.393 2(2)
C(15)	0.282(1)	0.128(1)	0.333 1(2)
C(16)	0.244(1)	0.216(1)	0.400 0(2)
Ni(2)	0.475 2(2)	0.220 0(2)	0.019 86(3)
S(21)	0.674 2(3)	0.099 7(3)	0.063 56(5)
S(22)	0.541 8(3)	0.037 4(3)	0.139 72(5)
S(23)	0.221 8(4)	0.065 9(4)	0.200 72(6)
S(24)	0.081 9(3)	0.190 6(3)	0.128 68(5)
S(25)	0.171 2(3)	0.268 3(3)	0.051 59(5)
S(26)	0.776 5(3)	0.175 2(4)	−0.012 20(5)
S(27)	0.864 9(4)	0.268 2(4)	−0.088 15(5)
S(28)	0.727 3(5)	0.415 8(4)	−0.158 52(6)
S(29)	0.403 7(4)	0.430 9(3)	−0.097 78(5)
S(30)	0.277 5(3)	0.353 3(3)	−0.022 59(5)
C(21)	0.477(1)	0.110(1)	0.096 6(2)
C(22)	0.279(1)	0.096(1)	0.159 2(2)
C(23)	0.258(1)	0.187(1)	0.091 6(2)
C(24)	0.691(1)	0.267(1)	−0.051 3(2)
C(25)	0.670(2)	0.375(1)	−0.116 7(2)
C(26)	0.466(1)	0.349(1)	−0.055 5(2)
O	0.929(1)	0.761(1)	0.257 3(3)
N	0.657(1)	0.495(1)	0.248(2)
C(31)	0.786(2)	0.504(2)	0.280 1(4)
C(32)	0.819(2)	0.697(3)	0.286 2(5)
C(33)	0.799(2)	0.769(2)	0.228 1(4)
C(34)	0.766(2)	0.587(2)	0.217 9(3)
C(35)	0.660(2)	0.302(2)	0.239 7(5)
C(36)	0.418(1)	0.592(2)	0.253 8(3)

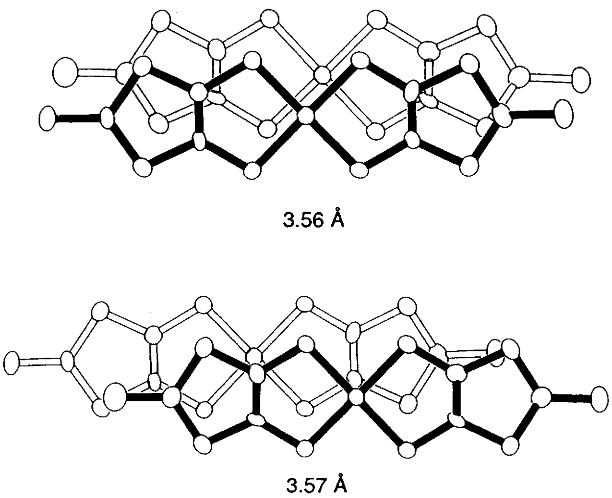

Fig. 3 Modes of intermolecular overlapping of $Ni(C_3S_5)_2$ molecules in compound **1**

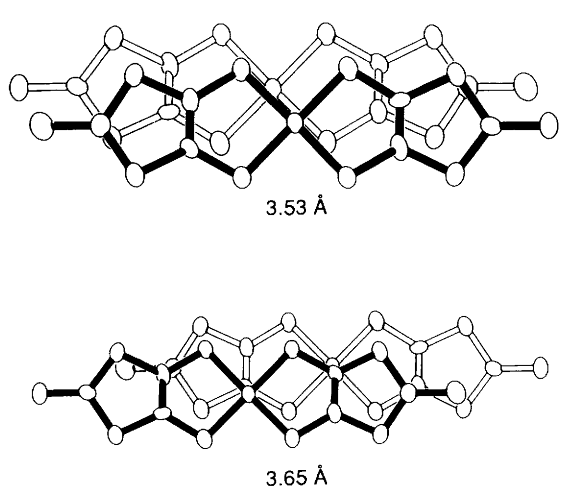

Fig. 4 Modes of intermolecular overlapping of $Ni(C_3S_5)_2$ molecules in compound **2**

Table 5 Selected bond distances (Å) and angles (°) for [smdt][Ni$(C_3S_5)_2$]$_2$ **1**

Ni(1)–S(11)	2.179(5)	S(14)–C(13)	1.73(2)	Ni(2)–S(21)	2.159(5)	S(24)–C(23)	1.75(1)
Ni(1)–S(15)	2.158(4)	C(13)–S(15)	1.70(2)	Ni(2)–S(25)	2.154(5)	C(23)–S(25)	1.69(2)
Ni(1)–S(16)	2.153(4)	S(16)–C(14)	1.68(1)	Ni(2)–S(26)	2.154(4)	S(26)–C(24)	1.70(2)
Ni(1)–S(20)	2.157(5)	C(14)–S(17)	1.73(1)	Ni(2)–S(30)	2.158(5)	C(24)–S(27)	1.75(1)
S(11)–C(11)	1.71(1)	C(14)–C(16)	1.38(2)	S(21)–C(21)	1.70(1)	C(24)–C(26)	1.38(2)
C(11)–S(12)	1.75(2)	S(17)–C(15)	1.72(2)	C(21)–S(22)	1.74(2)	S(27)–C(25)	1.72(2)
C(11)–C(13)	1.38(2)	C(15)–S(18)	1.64(2)	C(21)–C(23)	1.37(2)	C(25)–S(28)	1.63(2)
S(12)–C(12)	1.71(2)	C(15)–S(19)	1.75(2)	S(22)–C(22)	1.70(1)	C(25)–S(29)	1.75(1)
C(12)–S(13)	1.69(2)	S(19)–C(16)	1.74(2)	C(22)–S(23)	1.69(2)	S(29)–C(26)	1.71(2)
C(12)–S(14)	1.70(2)	C(16)–S(20)	1.70(1)	C(22)–S(24)	1.70(2)	C(26)–S(30)	1.73(1)
S(11)–Ni(1)–S(15)	93.2(2)	S(21)–Ni(2)–S(25)	92.6(2)	C(11)–C(13)–S(15)	120(1)	C(21)–C(23)–S(25)	122(1)
S(11)–Ni(1)–S(16)	87.2(2)	S(21)–Ni(2)–S(26)	86.6(2)	S(14)–C(13)–S(15)	124.1(9)	S(24)–C(23)–S(25)	122.4(9)
S(11)–Ni(1)–S(20)	177.9(2)	S(21)–Ni(2)–S(30)	177.8(2)	Ni(1)–S(15)–C(13)	102.8(5)	Ni(2)–S(25)–C(23)	102.3(5)
S(15)–Ni(1)–S(16)	179.5(2)	S(25)–Ni(2)–S(26)	178.6(2)	Ni(1)–S(16)–C(14)	103.1(5)	Ni(2)–S(26)–C(24)	102.0(5)
S(15)–Ni(1)–S(20)	86.8(2)	S(25)–Ni(2)–S(30)	87.4(2)	S(16)–C(14)–S(17)	123.8(8)	S(26)–C(24)–S(27)	122.6(9)
S(16)–Ni(1)–S(20)	92.8(2)	S(26)–Ni(2)–S(30)	93.4(2)	S(16)–C(14)–C(16)	121(1)	S(26)–C(24)–C(26)	123(1)
Ni(1)–S(11)–C(11)	101.1(5)	Ni(2)–S(21)–C(21)	103.0(5)	S(17)–C(14)–C(16)	116(1)	S(27)–C(24)–C(26)	114(1)
S(11)–C(11)–S(12)	121.9(8)	S(21)–C(21)–S(22)	123.5(9)	C(14)–S(17)–C(15)	98.1(7)	C(24)–S(27)–C(25)	98.1(7)
S(11)–C(11)–C(13)	122(1)	S(21)–C(21)–C(23)	120(1)	S(17)–C(15)–S(18)	123(1)	S(27)–C(25)–S(28)	123.9(9)
S(12)–C(11)–C(13)	116(1)	S(22)–C(21)–C(23)	117(1)	S(17)–C(15)–S(19)	113(1)	S(27)–C(25)–S(29)	112.8(9)
C(11)–S(12)–C(12)	96.5(7)	C(21)–S(22)–C(22)	95.5(8)	S(18)–C(15)–S(19)	123(1)	S(28)–C(25)–S(29)	123(1)
S(12)–C(12)–S(13)	121.1(9)	S(22)–C(22)–S(23)	123(1)	C(15)–S(19)–C(16)	96.6(8)	C(25)–S(29)–C(26)	97.7(7)
S(12)–C(12)–S(14)	115(1)	S(22)–C(22)–S(24)	117(1)	C(14)–C(16)–S(19)	116(1)	C(24)–C(26)–S(29)	117(1)
S(13)–C(12)–S(14)	124.0(9)	S(23)–C(22)–S(24)	120.4(9)	C(14)–C(16)–S(20)	121(1)	C(24)–C(26)–S(30)	119(1)
C(12)–S(14)–C(13)	97.4(8)	C(22)–S(24)–C(23)	95.5(7)	S(19)–C(16)–S(20)	122.6(9)	S(29)–C(26)–S(30)	124.3(9)
C(11)–C(13)–S(14)	116(1)	C(21)–C(23)–S(24)	115(1)	Ni(1)–S(20)–C(16)	102.3(6)	Ni(2)–S(30)–C(26)	102.9(5)

Table 6 Selected bond distances (Å) and angles (°) for [dmp]-[Ni$(C_3S_5)_2$]$_2$ **2**

Ni(1)–S(11)	2.161(1)	S(15)–C(13)	1.706(5)
Ni(1)–S(15)	2.170(1)	S(16)–C(14)	1.691(5)
Ni(1)–S(16)	2.163(1)	S(17)–C(14)	1.735(5)
Ni(1)–S(20)	2.160(1)	S(17)–C(15)	1.718(6)
S(11)–C(11)	1.709(5)	S(18)–C(15)	1.651(5)
S(12)–C(11)	1.738(5)	S(19)–C(15)	1.732(5)
S(12)–C(12)	1.733(6)	S(19)–C(16)	1.734(5)
S(13)–C(12)	1.655(6)	S(20)–C(16)	1.697(5)
S(14)–C(12)	1.714(6)	C(11)–C(13)	1.378(6)
S(14)–C(13)	1.739(5)	C(14)–C(16)	1.387(6)
S(11)–Ni(1)–S(15)	93.44(5)	S(12)–C(11)–C(13)	116.5(4)
S(11)–Ni(1)–S(16)	85.89(5)	S(12)–C(12)–S(13)	122.7(4)
S(11)–Ni(1)–S(20)	178.64(6)	S(12)–C(12)–S(14)	113.7(3)
S(15)–Ni(1)–S(16)	177.24(7)	S(13)–C(12)–S(14)	123.5(3)
S(15)–Ni(1)–S(20)	87.89(5)	S(14)–C(13)–S(15)	123.5(3)
S(16)–Ni(1)–S(20)	92.80(5)	S(14)–C(13)–C(11)	115.0(4)
Ni(1)–S(11)–C(11)	102.1(2)	S(15)–C(13)–C(11)	121.5(4)
C(11)–S(12)–C(12)	96.8(3)	S(16)–C(14)–S(17)	123.2(3)
C(12)–S(14)–C(13)	98.0(2)	S(16)–C(14)–C(16)	121.2(4)
Ni(1)–S(15)–C(13)	101.8(2)	S(17)–C(14)–C(16)	115.5(4)
Ni(1)–S(16)–C(14)	102.6(2)	S(17)–C(15)–S(18)	123.4(3)
C(14)–S(17)–C(15)	97.3(2)	S(17)–C(15)–S(19)	114.3(3)
C(15)–S(19)–C(16)	96.7(2)	S(18)–C(15)–S(19)	122.3(3)
Ni(1)–S(20)–C(16)	102.7(2)	S(19)–C(16)–S(20)	123.1(3)
S(11)–C(11)–S(12)	122.4(3)	S(19)–C(16)–C(14)	116.1(3)
S(11)–C(11)–C(13)	121.1(4)	S(20)–C(16)–C(14)	120.7(4)

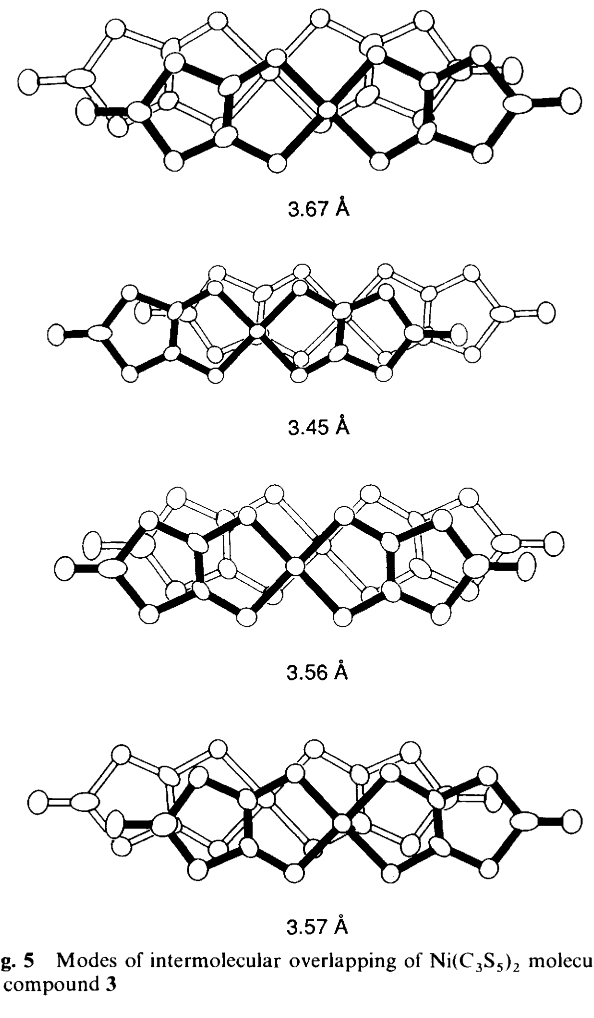

Fig. 5 Modes of intermolecular overlapping of Ni$(C_3S_5)_2$ molecules in compound **3**

tals) of neighbouring Ni$(C_3S_5)_2$ units were calculated using the scheme described in ref. 31. For the calculation of the molecular orbitals the extended-Hückel program ICON 8[32] was used, with semiempirical parameters taken from refs. 33 and 34.

In Fig. 7 the letters A, B, p, q, r, s represent the various intermolecular orbital overlaps. Table 11 lists the values of these overlaps for all three structures. In compounds **1** and **2**, the intradimer overlaps A (corresponding to the overlap mode with spacing 3.56 Å for **1** and spacing 3.53 Å for **2**, see Figs. 3 and 4) are the largest, *i.e.* of the order of 0.02. The second largest overlaps take place *via* the interdimer contacts between the stacks, and are denoted as q. These values are roughly a factor of 10 smaller than the intradimer interactions, and are of the

Table 7 Selected bond distances (Å) and angles (°) for $[dmm][Ni(C_3S_5)_2]_2$ **3**

Ni(1)–S(11)	2.145(2)	Ni(2)–S(21)	2.173(2)	S(15)–C(13)	1.690(8)	S(25)–C(23)	1.693(8)
Ni(1)–S(15)	2.161(2)	Ni(2)–S(25)	2.159(2)	S(16)–C(14)	1.693(7)	S(26)–C(24)	1.682(8)
Ni(1)–S(16)	2.157(2)	Ni(2)–S(26)	2.152(2)	S(17)–C(14)	1.724(7)	S(27)–C(24)	1.732(8)
Ni(1)–S(20)	2.159(2)	Ni(2)–S(30)	2.163(2)	S(17)–C(15)	1.732(9)	S(27)–C(25)	1.712(9)
S(11)–C(11)	1.689(8)	S(21)–C(21)	1.707(8)	S(18)–C(15)	1.663(8)	S(28)–C(25)	1.650(8)
S(12)–C(11)	1.726(8)	S(22)–C(21)	1.750(7)	S(19)–C(15)	1.707(9)	S(29)–C(25)	1.74(1)
S(12)–C(12)	1.754(9)	S(22)–C(22)	1.731(8)	S(19)–C(16)	1.749(8)	S(29)–C(26)	1.739(8)
S(13)–C(12)	1.624(8)	S(23)–C(22)	1.623(8)	S(20)–C(16)	1.684(7)	S(30)–C(26)	1.668(8)
S(14)–C(12)	1.725(9)	S(24)–C(22)	1.746(8)	C(11)–C(13)	1.38(1)	C(21)–C(23)	1.37(1)
S(14)–C(13)	1.756(8)	S(24)–C(23)	1.742(8)	C(14)–C(16)	1.40(1)	C(24)–C(26)	1.41(1)
S(11)–Ni(1)–S(15)	92.76(9)	S(21)–Ni(2)–S(25)	93.24(9)	S(17)–C(15)–S(19)	113.7(4)	S(24)–C(23)–S(25)	123.5(5)
S(11)–Ni(1)–S(16)	85.99(9)	S(21)–Ni(2)–S(26)	87.43(9)	S(18)–C(15)–S(19)	124.3(5)	S(24)–C(23)–C(21)	115.4(6)
S(11)–Ni(1)–S(20)	179.2(1)	S(21)–Ni(2)–S(30)	177.1(1)	S(19)–C(16)–S(20)	123.8(5)	S(25)–C(23)–C(21)	121.1(6)
S(15)–Ni(1)–S(16)	178.4(1)	S(25)–Ni(2)–S(26)	179.2(1)	S(19)–C(16)–C(14)	114.2(5)	S(26)–C(24)–S(27)	123.7(5)
S(15)–Ni(1)–S(20)	88.02(9)	S(25)–Ni(2)–S(30)	86.27(9)	S(20)–C(16)–C(14)	122.0(6)	S(26)–C(24)–C(26)	120.2(6)
S(16)–Ni(1)–S(20)	93.24(8)	S(26)–Ni(2)–S(30)	93.04(9)	C(14)–S(17)–C(15)	97.6(4)	S(27)–C(24)–C(26)	116.1(6)
Ni(1)–S(11)–C(11)	103.3(3)	Ni(2)–S(26)–C(24)	102.8(3)	C(15)–S(19)–C(16)	98.3(4)	S(27)–C(25)–S(28)	123.4(6)
C(11)–S(12)–C(12)	97.8(4)	Ni(2)–S(30)–C(26)	102.3(3)	Ni(1)–S(20)–C(16)	102.1(3)	S(27)–C(25)–S(29)	113.7(4)
C(12)–S(14)–C(13)	98.2(4)	Ni(2)–S(21)–C(21)	101.3(3)	S(11)–C(11)–S(12)	123.4(5)	S(28)–C(25)–S(29)	122.9(5)
Ni(1)–S(15)–C(13)	102.0(3)	Ni(2)–S(25)–C(23)	102.4(3)	S(11)–C(11)–C(13)	120.0(6)	S(29)–C(26)–S(30)	123.9(5)
Ni(1)–S(16)–C(14)	102.8(3)	S(21)–C(21)–C(23)	121.9(6)	S(12)–C(11)–C(13)	116.6(6)	S(29)–C(26)–C(24)	114.4(6)
S(15)–C(13)–C(11)	122.0(6)	S(21)–C(21)–S(22)	122.3(5)	S(12)–C(12)–S(13)	122.3(6)	S(30)–C(26)–C(24)	121.6(6)
S(16)–C(14)–S(17)	124.0(5)	S(22)–C(21)–C(23)	115.7(6)	S(12)–C(12)–S(14)	112.4(4)	C(21)–S(22)–C(22)	98.5(4)
S(16)–C(14)–C(16)	119.8(5)	S(22)–C(22)–S(23)	124.2(5)	S(13)–C(12)–S(14)	125.3(5)	C(22)–S(24)–C(23)	98.6(4)
S(17)–C(14)–C(16)	116.1(5)	S(22)–C(22)–S(24)	111.7(4)	S(14)–C(13)–S(15)	123.0(5)	C(24)–S(27)–C(25)	97.9(4)
S(17)–C(15)–S(18)	121.9(5)	S(23)–C(22)–S(24)	124.1(5)	S(14)–C(13)–C(11)	115.0(6)	C(25)–S(29)–C(26)	97.9(4)

Table 8 Intermolecular S···S contacts <3.70 Å in $[smdt][Ni(C_3S_5)_2]_2$ **1**. Symmetry operation applied on second atom

S(11)···S(14$^{\mathrm{I}}$)	3.686(6)	S(17)···S(20$^{\mathrm{I}}$)	3.660(6)
S(11)···S(15$^{\mathrm{I}}$)	3.579(6)	S(17)···S(30$^{\mathrm{II}}$)	3.653(6)
S(11)···S(24$^{\mathrm{II}}$)	3.548(6)	S(18)···S(27)	3.582(7)
S(13)···S(31$^{\mathrm{III}}$)	3.494(7)	S(18)···S(32$^{\mathrm{I}}$)	3.324(7)
S(13)···S(28$^{\mathrm{IV}}$)	3.630(5)	S(20)···S(21$^{\mathrm{V}}$)	3.653(4)
S(14)···S(23)	3.568(7)	S(21)···S(24$^{\mathrm{I}}$)	3.647(6)
S(15)···S(16$^{\mathrm{V}}$)	3.651(5)	S(21)···S(25$^{\mathrm{I}}$)	3.676(5)
S(15)···S(25$^{\mathrm{VI}}$)	3.656(7)	S(25)···S(26$^{\mathrm{V}}$)	3.567(5)
S(16)···S(20$^{\mathrm{I}}$)	3.638(6)	S(26)···S(30$^{\mathrm{I}}$)	3.582(6)
S(16)···S(26$^{\mathrm{VI}}$)	3.626(6)	S(27)···S(30$^{\mathrm{I}}$)	3.574(6)
S(16)···S(25$^{\mathrm{II}}$)	3.472(4)	S(28)···S(32$^{\mathrm{I}}$)	3.688(9)

Symmetry operations: I $x, y, z + 1$; II $x + 1, y, z + 1$; III $-x, y - \frac{1}{2}, -z$; IV $-x, y - \frac{1}{2}, 1 - z$; V, $x, y, z - 1$; VI $x + 1, y, z$.

Table 9 Intermolecular S···S contacts <3.70 Å in $[dmp][Ni(C_3S_5)_2]_2$ **2**. Symmetry operation applied on second atom

S(11)···S(15$^{\mathrm{VI}}$)	3.573(2)	S(13)···S(13$^{\mathrm{VIII}}$)	3.475(2)
S(11)···S(20$^{\mathrm{VI}}$)	3.637(2)	S(16)···S(20$^{\mathrm{VI}}$)	3.642(2)
S(11)···S(20$^{\mathrm{VII}}$)	3.590(2)	S(17)···S(15$^{\mathrm{IX}}$)	3.698(2)
S(12)···S(15$^{\mathrm{VI}}$)	3.644(2)	S(20)···S(20$^{\mathrm{XI}}$)	3.546(2)
S(12)···S(18$^{\mathrm{VII}}$)	3.580(2)		

Symmetry operations (see also Table 8): VII $-x + 1, -y + 1, -z$; VIII x, $-y + \frac{1}{2}, z$; IX, $-x + 1, -y + 1, -z + 1$; XI $-x, -y + 1, -z$.

Table 10 Intermolecular S···S contacts <3.70 Å in $[dmm][Ni(C_3S_5)_2]_2$ **3**. Symmetry operation applied on second atom

S(11)···S(15$^{\mathrm{VI}}$)	3.677(3)	S(21)···S(27$^{\mathrm{XIV}}$)	3.662(3)
S(11)···S(20$^{\mathrm{VI}}$)	3.616(3)	S(21)···S(29$^{\mathrm{XV}}$)	3.668(3)
S(11)···S(11$^{\mathrm{XII}}$)	3.688(3)	S(21)···S(30$^{\mathrm{XVI}}$)	3.675(3)
S(12)···S(15$^{\mathrm{VI}}$)	3.623(3)	S(24)···S(28$^{\mathrm{VII}}$)	3.578(4)
S(12)···S(20$^{\mathrm{IX}}$)	3.676(3)	S(25)···S(26$^{\mathrm{XVII}}$)	3.663(3)
S(15)···S(15$^{\mathrm{XIII}}$)	3.595(3)	S(25)···S(26$^{\mathrm{XV}}$)	3.583(4)
S(15)···S(20$^{\mathrm{XIII}}$)	3.583(3)	S(25)···S(27$^{\mathrm{VII}}$)	3.689(4)
S(16)···S(20$^{\mathrm{VI}}$)	3.612(3)	S(26)···S(30$^{\mathrm{VI}}$)	3.610(3)
S(18)···S(23)	3.434(3)	S(26)···S(26$^{\mathrm{XIV}}$)	3.529(4)
S(21)···S(25$^{\mathrm{VI}}$)	3.555(3)		

Symmetry operations (see also Tables 8 and 9): XII $-x + 2, -y, -z + 1$; XIII $-x, -y + 1, -z + 1$; XIV $-x + 2, -y, -z$; XV $-x + 1, -y, z$; XVI $-x + 1, y, -z$; XVII $x - 1, y, z$.

Table 11 Intermolecular orbital overlap (× 10^3) of the LUMOs of $Ni(C_3S_5)_2$ in compounds **1–3** [**3a** for $Ni(1)(C_3S_5)_2$ layer, **3b** for $Ni(2)(C_3S_5)_2$ layer]

Lattice	A	B	p	q	r	s
1	16	1.4	2.5	2.5	<0.1	0.3
2	24	0.3	3	3	<0.1	<0.1
3a	0.1	<0.1	2.2	2.2	<0.1	2.2
3b	16	8	0.6	0.6	<0.1	0.7

same order of magnitude as the interdimer overlap in the stacks (B). The salts **1** and **2** should therefore be regarded as essentially 'zero-dimensional' (since there is no significant continuous overlap in the stacking direction), and only weakly two-dimensional conductors. These data compare quite well with the orbital overlaps obtained for $[NMe_3Et][Ni(C_3S_5)_2]_2$ and β-$[NMe_2Et_2][Ni(C_3S_5)_2]_2$, two salts which are isostructural with **1** and **2**.[4]

A band-structure calculation ignoring electron-correlation effects indicates compounds **1** and **2** to be metallic or semi-metallic. However, Coulomb repulsion can be very important for the actual conductivity behaviour of such compounds.[31] Inclusion of a small Coulomb repulsion would split the conduction band, resulting in an energy gap.

The electronic structure of salt **3** differs from that of **1** and **2** due to its different structural features. In the stacks consisting of $Ni(2)(C_3S_5)_2$ molecules the intradimer orbital overlap A (corresponding to the overlap mode with spacing 3.56 Å, see Fig. 5) has a value of approximately 0.016, which is comparable to those in compounds **1** and **2**. However, in the $Ni(2)(C_3S_5)_2$ columns the interdimer overlap B is quite large, too, having a value of 0.008. The transfer integrals between the stacks are more than 10 times smaller. Thus, the layers of $Ni(2)(C_3S_5)_2$ molecules can be considered as conducting almost exclusively along the stacking direction. This is in contrast with the layers

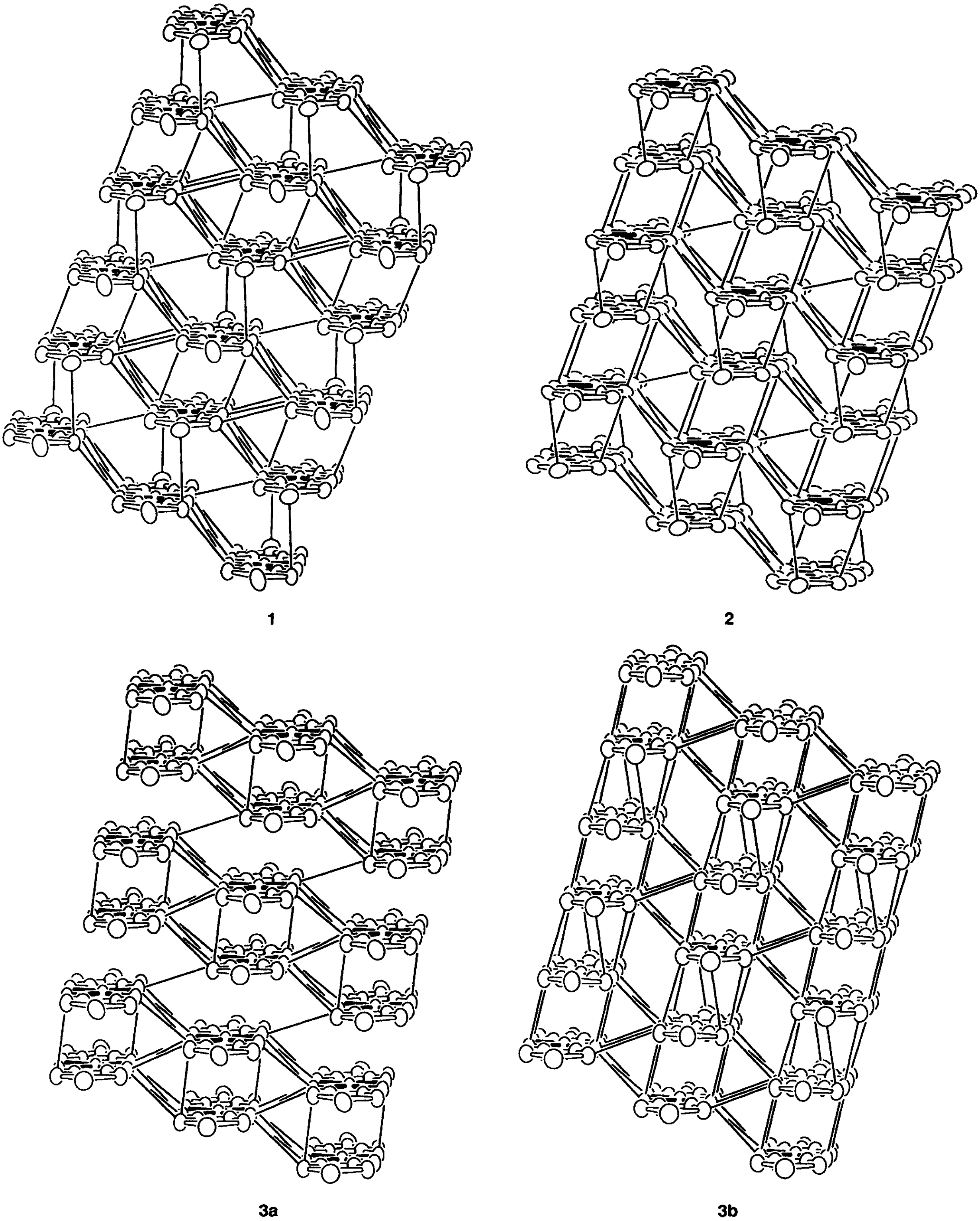

Fig. 6 The layer of acceptor molecules in compounds **1**–**3** [**3a**, Ni(1)$(C_3S_5)_2$ layer; **3b**, Ni(2)$(C_3S_5)_2$ layer]. Thin black lines indicate S···S contacts < 3.70 Å

built up from Ni(1)$(C_3S_5)_2$ units. Within one stack there is almost no intermolecular overlap. The largest intrastacking overlap A is about 0.0001, and is found between the Ni(1)$(C_3S_5)_2$ molecules having a separation of 3.45 Å. The orbital overlaps between the stacks are a factor of 20 *larger*, and have an identical value in two directions (p, q and s). As a result, the Ni(1)$(C_3S_5)_2$ units form a two-dimensional conducting layer. This observation is rather unexpected since from electronic structure studies on related [cation][Ni$(C_3S_5)_2$]$_2$ systems it was found that the transverse interactions are generally much less than the interactions along the column.[35] It should be noted, however, that the absolute values for the orbital overlaps in the Ni(1)$(C_3S_5)_2$ layer (see Table 11) differ little from those reported for other [cation][Ni$(C_3S_5)_2$]$_2$ compounds.[3,4,7] An explanation for the absence of any significant interaction in the direction of the Ni(1)$(C_3S_5)_2$ stacks is probably the unfavourable mode of overlap between the acceptor units (see Fig. 5).[36]

The relatively numerous S···S contacts in salt **3** will be

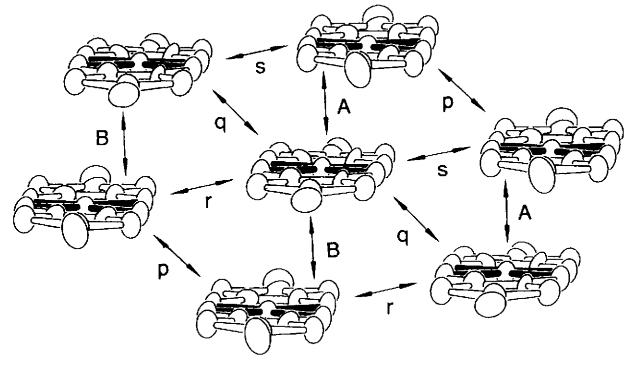

Fig. 7 General scheme of the intermolecular orbital overlaps of the LUMOs of the acceptor molecules in compounds **1**–**3**

responsible for the higher room-temperature conductivity of this compound. Again, band-structure calculations without electron correlations would predict a metallic behaviour for **3**. Including an electron–electron repulsion term leads to the experimentally observed energy gap.

When comparing the very similar structures of [smdt][$Ni(C_3S_5)_2]_2$, [dmp][$Ni(C_3S_5)_2]_2$ and [dmm][$Ni(C_3S_5)_2]_2$ one might come to the conclusion that this type of cyclic, saturated cations would always induce a herringbone type of lattice. Since changing the cation from *N*,*N*-dimethylpyrrolidinium to *N*,*N*-dimethylmorpholinium to *S*-methyl-1,3-dithianium does not affect the overall stacking mode of the anions very drastically, it would seem that more subtle variations of these cyclic cations should leave the herringbone motif intact. However, recent results and publications show this assumption to be untrue. The use of the cation *N*,*N*-dimethylpiperidinium (dmpip), which differs only marginally from *N*,*N*-dimethylmorpholinium, yields a mixed-valence salt with formula [cation][$Ni(C_3S_5)_2]_2$ which possesses a completely different packing mode of the anions.[37] In [dmpip][$Ni(C_3S_5)_2]_2$ the acceptor molecules stack in a 'spanning overlap' fashion, and the compound is therefore isostructural with α-[NMe_2Et_2][$Ni(C_3S_5)_2]_2$.[4] Both these salts remain two-dimensional metallic conductors down to low temperature. Furthermore, a preliminary crystal structure determination[36] of the corresponding *S*-methyltetrahydrothiophenium salt, which we prepared very recently, does not feature the typical herringbone motif: $C_{17}H_{11}Ni_2S_{21}$, triclinic, space group $P\bar{1}$, $Z = 2$, $a = 7.79$, $b = 11.96$, $c = 18.35$ Å, $\alpha = 80.77$, $\beta = 88.23$, $\gamma = 77.28°$, $U = 1646$ Å^3.

From the results presented in this paper as well as those known from the literature it appears that a herringbone type of lattice is not very promising for obtaining a metallic conductor at ambient pressure. Tight-binding calculations have shown that, from an electronic point of view, all of these compounds possess a large degree of dimerisation. Moreover, due to the unfavourable b_{2g} symmetry of the LUMO,[35] the transverse interdimer interactions are too weak to make up for the Coulomb repulsion which accounts for the presence of a band gap. It should be recalled, however, that the conductivity measurements on these crystals have so far only been performed at atmospheric pressure. Higher pressures are known to decrease the destructive effect of dimerisation and can even transform a compound which shows only semiconducting behaviour at ambient pressure into a superconductor.[7]

The fact that until now all known $Ni(C_3S_5)_2$ salts with cyclic, saturated cations are isostructural to those featuring small tetraalkylammonium-type cations demonstrates that such cyclic cations have a size and shape which are at least comparable to those of a cation like NMe_4^+. Therefore, in theory, they have the potential to form new molecular metals, and even superconductors, in combination with $M(C_3S_5)_2$ or its derivatives. However, the bottleneck of the design of new synthetic metals ('lattice engineering') based on such acceptor molecules obviously remains the, as yet, unpredictable nature of the crystal structure due to the extremely subtle molecular interactions taking place.[38] More than in the organic donor-based salts, *e.g.* the superconducting (bedttf)$_2$X series,[39] it is almost impossible to tell what effect a minor variation in one of the building blocks will have on the anionic lattice. Apart from that, multiple phases often exist and can even be obtained from the same batch,[4,13] which indicates that their crystal lattice energies must be very similar.

Nonetheless, it is clear that the only way to gain a better insight into the factors which determine the crystal structures of inorganic molecular conductors is a thorough, systematic variation of the components. In the case of the [cation][$Ni(C_3S_5)_2]_2$ salts this would mean the introduction of a series of subtly and methodically altered cations. Considering the vast number of possible modifications, the class of cyclic, saturated cations seems best suited for this strategy.

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