

The New Synthetic Metals of $M(\text{dmise})_2$: $[\text{Me}_3\text{HN}][\text{Ni}(\text{dmise})_2]_2$ and $(\text{EDT-TTF})[\text{Ni}(\text{dmise})_2]$

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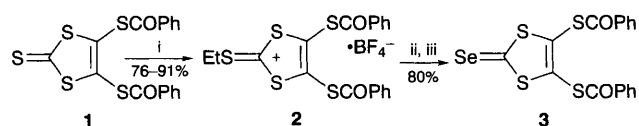
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Both of the newly synthesized $[\text{Me}_3\text{HN}][\text{Ni}(\text{dmise})_2]_2$ and $(\text{EDT-TTF})[\text{Ni}(\text{dmise})_2]$ exhibit metallic behaviour around room temperature at ambient pressure; tight-binding band calculation indicates that the former has a nearly three-dimensional Fermi surface owing to a strong intersheet interaction between their selone groups.

The ligands dmit (4,5-disulfanyl-1,3-dithiole-2-thione), dmise (4,5-disulfanyl-1,3-dithiole-2-selone) and analogues are currently attracting considerable interest as versatile building blocks of conducting materials.¹⁻⁶ In particular, dmise is a potentially useful ligand which extends a intermolecular interaction towards the third direction through the outstretched part of its π -conjugation system, *i.e.* the selone group.^{1,2} However, the solid state properties of metal-dmise systems have been reported only for two Me_4N^+ salts.^{1,2} Of particular interest among the unexplored metal-dmise systems are salts with small cations and charge transfer complexes with EDT-TTF (ethylenedithiotetrathiafulvalene), both of which have yielded superconductors in $\text{Ni}(\text{dmit})_2$ compounds.⁷ This communication concerns the synthesis and electrical properties of the two titled salts and some other related salts. We also make a brief reference to the crystal structure of $[\text{Me}_3\text{HN}][\text{Ni}(\text{dmise})_2]_2$. The synthetic route to the dmise ligand^{1,8} is straightforward but we somehow could not reproduce it well; we found particular difficulty in separating the desired selone from the unreacted thione compound. Therefore, we modified the synthetic procedure[†] (see Scheme 1), which facilitated the production of the pure complexes.[‡] The temperature dependence of the resistivity of $[\text{Me}_3\text{HN}][\text{Ni}(\text{dmise})_2]_2$ is shown in Fig. 1(a). It exhibits weakly metallic behaviour around room temperature with a conductivity (σ_{RT}) of 100 S cm^{-1} ; the resistivity gradually increases at low temperatures. The metallic region of the salt almost doubles for every 3 kbar increase in pressure, but the insulating phase is not completely suppressed even at 6 kbar. A similar electrochemical procedure using EDT-TTF and $[(\text{C}_4\text{H}_9)_4\text{N}][\text{Ni}(\text{dmise})_2]_2$ instead of $\text{Me}_3\text{HNClO}_4$ and $[(\text{C}_4\text{H}_9)_4\text{N}][\text{Ni}(\text{dmise})_2]_2$ gave black plateletlike crystals of $(\text{EDT-TTF})[\text{Ni}(\text{dmise})_2]$, which also exhibited metallic conductivity ($\sigma_{\text{RT}} = 100 \text{ S cm}^{-1}$) down to *ca.* 100 K and made a smooth transition into an insulator at low temperature [Fig. 1(b)]. These species have been found to be the second and third examples of molecular metals based on a $M(\text{dmise})_2$ complex, the first example being $\beta\text{-}[\text{Md}_4\text{N}][\text{Ni}(\text{dmise})_2]_2$.^{1,2} The crystal structure of the Me_3HN salt is shown in Fig. 2 (*crystal data*: triclinic, $P\bar{1}$, $a = 7.606(3)$, $b = 17.761(3)$, $c = 6.660(2) \text{ \AA}$, $\alpha = 100.27(2)$, $\beta = 114.93(2)$, $\gamma = 81.84(2)^\circ$, $V = 800.4(4) \text{ \AA}^3$, $Z = 1$, $R = 0.036$). The $\text{Ni}(\text{dmise})_2$ molecules stack along the a axis almost regularly; the interplanar distances are 3.464 and 3.557 Å . The cations are located near the inversion centre and they take either of the two statistically possible orientations (50%–50% disordered). Such a structural trend is quite different from $[\text{Me}_3\text{HN}][\text{Ni}(\text{dmit})_2]_2$,⁹ but is instead associated with a dmit-based superconductor $[\text{Me}_2(\text{C}_2\text{H}_5)_2\text{N}][\text{Pd}(\text{dmit})_2]_2$.¹⁰ There are short contacts between two selenium atoms ($< 4.0 \text{ \AA}$) in addition to many of those between sulfur atoms ($< 3.7 \text{ \AA}$) within each $\text{Ni}(\text{dmise})_2$ column as well as between the columns,

which resembles $\beta\text{-}[\text{Me}_4\text{N}][\text{Ni}(\text{dmise})_2]_2$.^{1,2} But the most striking feature is that there are also found short contacts of $\text{Se}\cdots\text{Se}$ (3.486 and 3.801 Å) through the cation sheet, a feature which is also observed in $\alpha\text{-}[\text{Me}_4\text{N}][\text{Ni}(\text{dmise})_2]_2$ (3.277 Å).^{1,2} One of the $\text{Se}\cdots\text{Se}$ distances is even shorter than the shortest $\text{S}\cdots\text{S}$ contact (3.568 Å) in this salt. Tight-binding band calculation by extended Hückel methods indicated that $[\text{Me}_3\text{HN}][\text{Ni}(\text{dmise})_2]_2$ has even stronger intermolecular inter-



Scheme 1 Reagents and conditions: i, $\text{HC}(\text{OEt})_3$, $\text{Et}_2\text{O}\cdot\text{BF}_3$, CHCl_3 ; ii, iii, excess H_2Se ; iii, PhCOCl , MeOH , $-10 \text{ }^\circ\text{C}$

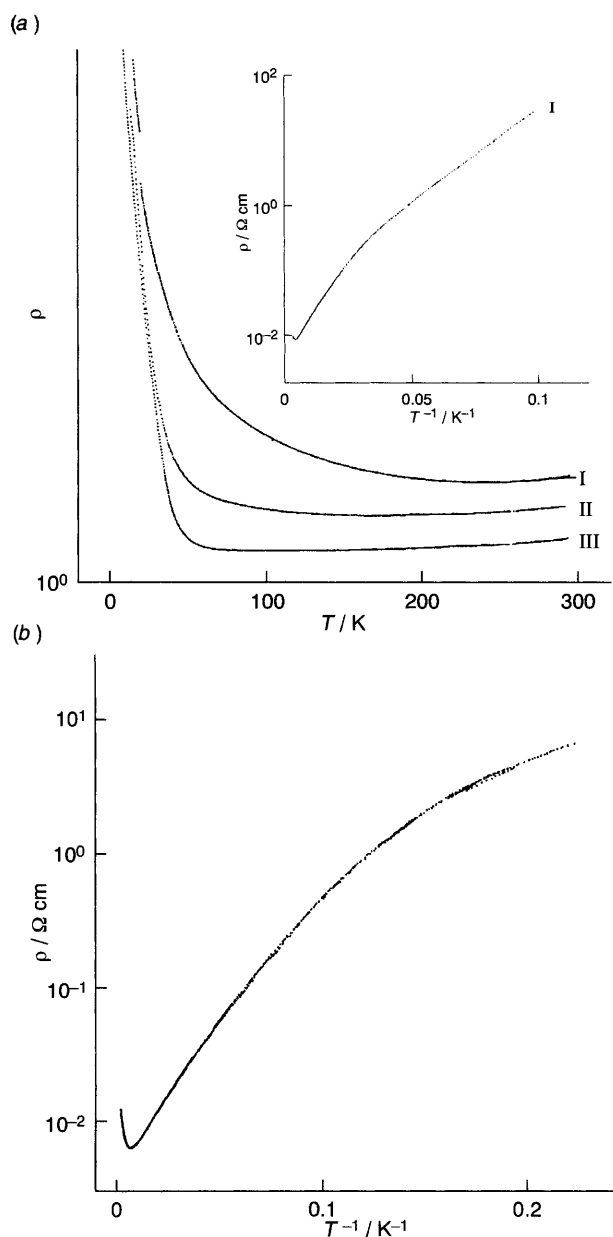


Fig. 1 Temperature dependencies of the electrical resistivity of: (a) $[\text{Me}_3\text{HN}][\text{Ni}(\text{dmise})_2]_2$ under I 1 bar, II 3 kbar and III 6 kbar; (b) $(\text{EDT-TTF})[\text{Ni}(\text{dmise})_2]$ at ambient pressure

actions along the long molecular axis than in the side-by-side direction, owing to a close selenium–selenium contact. This feature leads to a three-dimensional electronic structure (Fig. 3), indicating this complex to be a precursor of a three-dimensional molecular metal based exclusively on planar π -conjugated molecules. This situation possibly arises from both the small size of the anion ($[\text{Me}_3\text{HN}]^+$) and the spatially-extended terminal selenium atoms, which favour the packing motif that allows significant overlap of the selenium orbitals. The anisotropy of the resistivity of the single crystal of $[\text{Me}_3\text{HN}][\text{Ni}(\text{dmise})_2]_2$ by the Montgomery method has not yet been achieved because all the crystals obtained were too thin and fragile. On the other hand, the X-ray structural analysis of the EDT–TTF salt has not yet been completed satisfactorily because a crystal of high enough quality has not been available. Therefore a preliminary result is shown here. *Crystal data:* triclinic, $P\bar{1}$, $a = 23.43$, $b = 6.47$, $c = 4.23$ Å, $\alpha = 86.8$, $\beta = 90.2$, $\gamma = 95.1^\circ$, $V = 637.2$ Å³, $Z = 1$.

The donor (EDT–TTF) and acceptor $[\text{Ni}(\text{dmise})_2]$ molecules make segregated columns, running in parallel with each other along the (001) direction. They both stack regularly with repeating separations of 3.75 Å for the EDT–TTF and 3.50 Å for the $\text{Ni}(\text{dmise})_2$ column. Their molecular planes have tilts from the stacking direction, as is often the case; the dihedral angle between the least-squares planes of the donor and acceptor molecules is 124° . The general trend mentioned above is quite different from either α -, β -(EDT–TTF) $[\text{Ni}(\text{dmit})_2]$ ¹¹ or (EDT–TTF)₂ $[\text{Pd}(\text{dmit})_2]_2$ ¹². By a similar synthetic method we obtained single crystals (thin plates or needles) of $\text{Me}_x(\text{C}_2\text{H}_5)_{4-x}\text{N}$

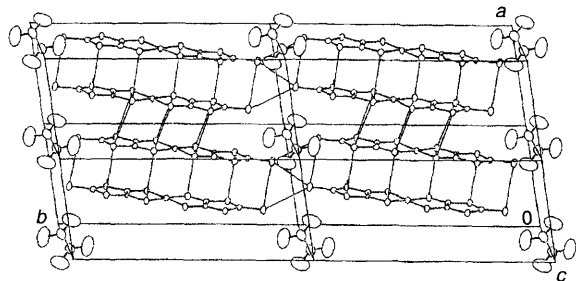


Fig. 2 Crystal structure of $[\text{Me}_3\text{HN}][\text{Ni}(\text{dmise})_2]_2$. The Me_3HN cation is disordered and both of the two possible orientations are depicted. Thin lines indicate intermolecular short contacts between chalcogen atoms ($\text{S}\cdots\text{S} < 3.70$ Å, $\text{Se}\cdots\text{Se} < 4.00$ Å).

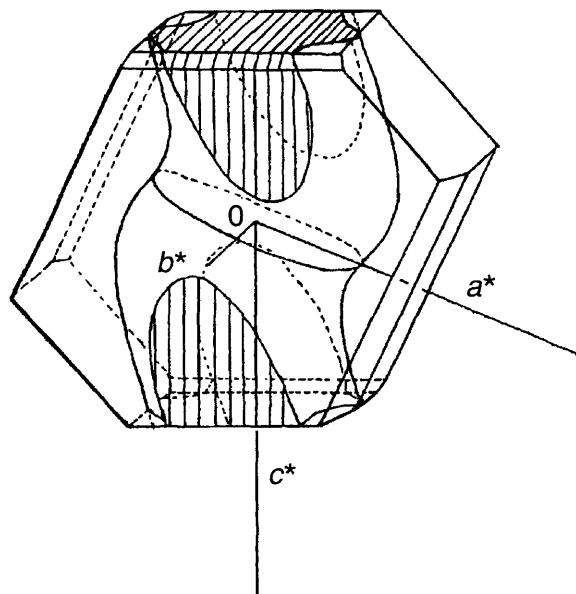


Fig. 3 Schematic view of the Fermi surface of $[\text{Me}_3\text{HN}][\text{Ni}(\text{dmise})_2]_2$

($x = 0$ –4) salts of $\text{Ni}(\text{dmise})_2$ and Me_4N salts of $\text{Pd}(\text{dmise})_2$; all of the Ni analogues are semiconductors with $\sigma_{\text{RT}} = 10^{-1}$ – 1 S cm^{-1} and activation energy $E_a = 0.12$ – 0.15 eV, while the Pd analogue, which is also a semiconductor, has $\sigma_{\text{RT}} = 10^{-1}$ S cm^{-1} and $E_a = 0.05$ eV. The X-ray structural analysis of these salts and the EDT–TTF salt, as well as synthesis of related salts are now in progress and will be reported in due course.

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Footnotes

† *Ligand synthesis:* bis(benzoyl)-protected dmit **1** was stirred in refluxing chloroform for three hours with $[(\text{C}_2\text{H}_5\text{O})_2\text{CH}]^+\text{BF}_4^-$, which was prepared *in situ* from triethyl orthoformate and boron trifluoride diethyl ether complex to yield the corresponding 2-ethylthio-1,3-dithiolium salt **2** in 76–91% yield. The dithiolium salt **2** was treated with a large excess of gaseous H_2Se in methanol at -10°C for 3.5 h, then at room temp. for 30 min. The reddish-orange needles were precipitated after addition of excess benzoyl chloride. This compound could be recrystallized from cold chloroform–methanol but silica gel column chromatography (CH_2Cl_2 –hexane 1 : 1) was more effective for the separation from the starting material (thione **1**). Thus obtained bis(benzoyl)-protected dmise **3** was transformed into $[(\text{C}_4\text{H}_9)_4\text{N}][\text{Ni}(\text{dmise})_2]$ by an analogous procedure described by Steimecke *et al.*¹⁴ Conventional electrochemical crystallization (0.42 mmol dm^{-3} of $[\text{Me}_3\text{HN}][\text{Ni}(\text{dmise})_2]$ in acetonitrile with $\text{Me}_3\text{HNCIO}_4$ (34 mmol dm^{-3}) under galvanostatic conditions (0.2 μA) produced black elongated platelets of $[\text{Me}_3\text{HN}][\text{Ni}(\text{dmise})_2]_2$.

‡ All compounds gave satisfactory spectral and/or elemental analyses.

References

- J. P. Cornelissen, B. Pomarède, A. L. Spek, D. Reefman, J. G. Haasnoot and J. Reedijk, *Inorg. Chem.*, 1993, **32**, 3720.
- J. P. Cornelissen, D. Reefman, J. G. Haasnoot, A. L. Spek and J. Reedijk, *Recl. Trav. Chim. Pays-Bas*, 1991, **110**, 345.
- C. Faulmann, J.-P. Legros, P. Cassoux, J. P. Cornelissen, L. Brossard, M. Inokuchi, H. Tajima and M. Tokumoto, *J. Chem. Soc., Dalton Trans.*, 1994, 249.
- R.-M. Olk, R. Kirmse, E. Hoyer, C. Faulmann and P. Cassoux, *Z. Anorg. Allg. Chem.*, 1994, **620**, 90.
- R.-M. Olk, B. Olk, J. Rohloff, J. Reinhold, J. Sieler, K. Trübenbach, R. Kirmse and E. Hoyer, *Z. Anorg. Allg. Chem.*, 1992, **609**, 103.
- R.-M. Olk, C. Semmelmann, R. Kirmse, K. Köhler, E. Hoyer and B. Olk, *Z. Anorg. Allg. Chem.*, 1990, **581**, 59 and references cited therein.
- A. Kobayashi, H. Kim, Y. Sasaki, R. Kato, H. Kobayashi, S. Moriyama, Y. Nishio, K. Kajita and W. Sasaki, *Chem. Lett.*, 1987, 1819; A. Kobayashi, H. Kim, Y. Sasaki, S. Moriyama, Y. Nishio, K. Kajita, W. Sasaki, R. Kato and H. Kobayashi, *Synth. Met.*, 1988, **27**, B339; H. Tajima, M. Inokuchi, A. Kobayashi, T. Ohta, R. Kato, H. Kobayashi and H. Kuroda, *Chem. Lett.*, 1993, 1235.
- V. Y. Khodorkovskii, J. Kreicberga, K. A. Balodis and O. Y. Neiland, *Izv. Akad. Nauk Latv. SSR, Ser. Khim.*, 1988, 120.
- J.-P. Legros, L. Valade, B. Garreau, B. Pomarède, P. Cassoux, L. Brossard, S. Dubois, A. Audouard and J.-P. Ulmet, *Synth. Met.*, 1993, **55**–**57**, 2146; B. Pomarède, B. Garreau, I. Malfant, L. Valade, P. Cassoux, J.-P. Legros, A. Audouard, L. Brossard, J.-P. Ulmet, M.-L. Doublet and E. Canadell, *Inorg. Chem.*, 1994, **33**, 3401 and references cited therein.
- H. Kobayashi, K. Bun, T. Naito, R. Kato and A. Kobayashi, *Chem. Lett.*, 1992, 1909.
- R. Kato, H. Kobayashi, A. Kobayashi, T. Naito, M. Tamura, H. Tajima and H. Kuroda, *Chem. Lett.*, 1989, 1839.
- B. Garreau, B. Pomarède, C. Faulmann, J.-M. Fabre, P. Cassoux and J.-P. Legros, *C. R. Acad. Sci., Ser. 2*, 1991, **313**, 509.
- D. L. Klayman and T. Scott-Griffin, *J. Am. Chem. Soc.*, 1973, **95**, 177; A. Moradpour, V. Peyrussan, I. Johansen and K. Bechgaard, *J. Org. Chem.*, 1983, **48**, 388.
- G. Steimecke, H. J. Sieler, R. Kirmse and E. Hoyer, *Phosphorus Sulfur*, 1979, **7**, 49.