

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

Toshio Naito,^a Akane Sato,^a Kouichi Kawano,^a Akiko Tateno,^a Hayao Kobayashi^{*a} and Akiko Kobayashi^b

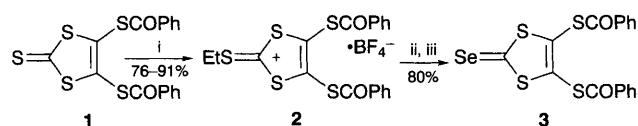
^a Department of Chemistry, Faculty of Science, Toho University, Miyama 2-2-1, Funabashi, Chiba 274, Japan

^b Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo 7-3-1, Bunkyo-ku, Tokyo 113, Japan

Both of the newly synthesized $[\text{Me}_3\text{HN}][\text{Ni}(\text{dmise})_2]_2$ and (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-disulfany-1,3-dithiole-2-thione), dmise (4,5-disulfany-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 $[(\text{C}_4\text{H}_9)_4\text{N}][\text{Ni}(\text{dmise})_2]^\dagger$ gave black plateletlike crystals of (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 β - $[\text{Md}_4\text{N}][\text{Ni}(\text{dmise})_2]_2$.^{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 $\text{\AA}$. 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 β - $[\text{Me}_4\text{N}][\text{Ni}(\text{dmise})_2]_2$.^{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 $\text{\AA}$) through the cation sheet, a feature which is also observed in α - $[\text{Me}_4\text{N}][\text{Ni}(\text{dmise})_2]_2$ (3.277 $\text{\AA}$).^{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 $\text{\AA}$) 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, excess H_2Se ; iii, PhCOCl , MeOH , -10°C

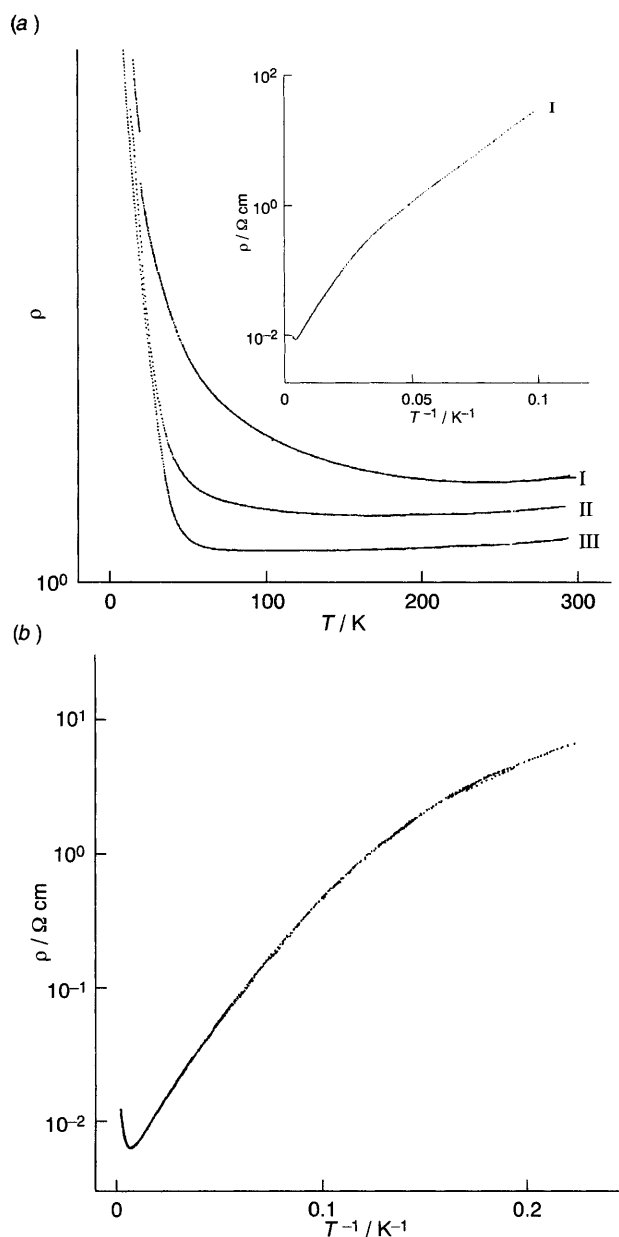


Fig. 1 Temperature dependencies of the electrical resistivity of: (a) $[\text{Me}_3\text{HN}][\text{Ni}(\text{dmise})_2]_2$ under I 1 bar, II 3 kbar and III 6 kbar; (b) (EDT-TTF) $[\text{Ni}(\text{dmise})_2]$ at ambient pressure

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 $\text{Me}_x(\text{C}_2\text{H}_5)_{4-x}\text{N}$

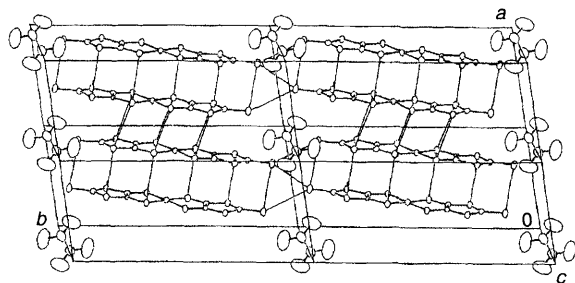


Fig. 2 Crystal structure of $[\text{Me}_3\text{HN}][\text{Ni}(\text{dmise})_2]_2$. The Me_3HN cation is disordered and both of the two possible orientations are depicted. Thin lines indicate intermolecular short contacts between chalcogen atoms ($\text{S}\cdots\text{S} < 3.70$ Å, $\text{Se}\cdots\text{Se}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

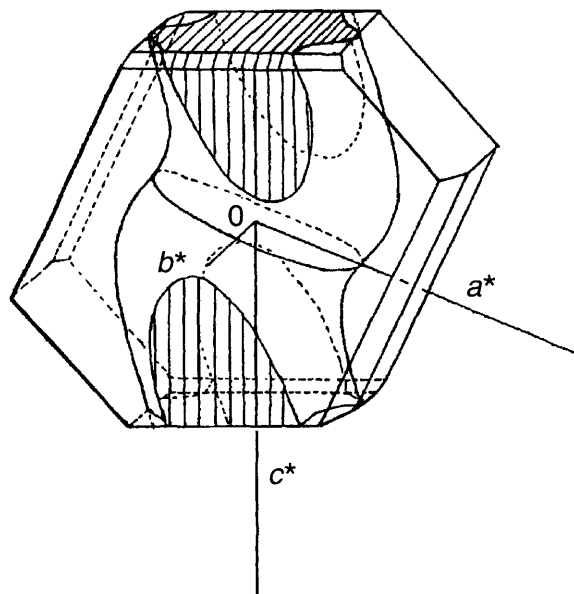


Fig. 3 Schematic view of the Fermi surface of $[\text{Me}_3\text{HN}][\text{Ni}(\text{dmise})_2]_2$

($x = 0$ –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.

The authors are grateful to TOYOTA Physical and Chemical Research Institute for financial support. We thank the Ministry of Education, Science and Culture of Japan for a Grant-in-Aid for Scientific Research.

Received, 15th November 1994; Com. 4/06978A

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 ¹³ 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.