A Novel Phase Transition in Conductive Molecular Crystals based on Metal Bis-diselenoalkene Complexes: $[TMTSF]_2[M\{Se_2C_2(CF_3)_2\}_2]$; M = Ni, Pt; TMTSF = tetramethyltetraselenafulvalene

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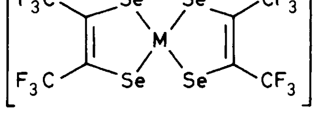
Single crystals of $[TMTSF]_2[M\{Se_2C_2(CF_3)_2\}_2]$ (TMTSF = tetramethyltetraselenafulvalene; M = Ni, Pt) have room-temperature conductivities of 20—65 Ω^{-1} cm^{-1} and upon cooling undergo an unprecedented phase transition in which the low temperature phase shows enhanced electrical conductivity: M = Ni, T_c = *ca.* 275 K; M = Pt, T_c = *ca.* 245 K.

Planar metal bis-dithioalkene complexes are attractive precursors for molecular metals because of their delocalized electronic structure and range of stable oxidation states.[1] Furthermore, close intermolecular contacts mediated by the chalcogen atoms of these complexes can produce conductive crystals that exhibit quasi-2- or 3-dimensional character,[2] as is found in the organic superconductors.[3] In principle, the selenium analogues of such complexes (metal bis-diselenoalkenes) would be better suited for the formation of extended, multi-dimensional molecular networks because of the increased Van der Waals radius and greater polarizability of selenium. However, relatively few metal bis-diselenoalkene complexes have been reported,[4,5] and only one family of conductive compounds has been briefly described.[5] We report here the synthesis and preliminary physical characterization of new molecular conductors that are based on metal bis-diselenoalkene complexes and that exhibit an unprecedented type of phase transition near room temperature.

Salts of the monoanions $[M\{Se_2C_2(CF_3)_2\}_2]^-$ (M = Ni, Pt) were prepared[6] by the reaction of bis(perfluoromethyl)ethylene diselenate[7] with low valent phosphine–metal complexes under conditions similar to those employed[8] for the preparation of the analogous sulphur species. Flexible black needles of formula $[TMTSF]_2[M\{Se_2C_2(CF_3)_2\}_2]$, [TMTSF = tetramethyltetraselenafulvalene; M = Ni, (**1**), M = Pt, (**2**)] were crystallized at a platinum wire anode by constant current (1—2 μA) electrolysis of a 1,1,2-trichloroethane solution containing TMTSF (4×10^{-3} M) and the corresponding monoanionic metal complex (2×10^{-3} M). The stoicheiometry of the products was determined by elemental analysis.



(**1**) M = Ni
(**2**) M = Pt

Four-probe D.C. conductivity studies show that (**1**) and (**2**) conduct well along the needle axis (σ_{RT} *ca.* 20 and 65 Ω^{-1} cm^{-1}, respectively) with weakly metallic temperature dependence near room temperature. Upon cooling single crystals of (**1**) through T_c *ca.* 275 K, an abrupt *increase* in conductivity is observed, followed by a broad plateau and activated behaviour below *ca.* 220 K (Figure 1). Slow warming back to room temperature reveals a pronounced hysteresis associated with the reverse transition (inset). The behaviour of the corresponding platinum compound (**2**) is qualitatively similar, except the transition upon cooling occurs at 245 K.

Polycrystalline samples of (**2**) have no detectable e.s.r. signal down to 77 K. At room temperature, similar samples of (**1**) show a single, broad ($\Delta H_{p\text{-}p}$ = 265 G : 1 G = 10^{-4} T) e.s.r. signal at g = 2.088. The temperature response of the peak-to-peak intensity of this signal (Figure 2) shows a break near T_c. This is unaccompanied by any detectable anomaly in the integrated intensity, and instead appears to result from a subtle change in lineshape at the transition. Temperature cycling (inset) confirms that the hysteresis seen in the conductivity data is an intrinsic property of these materials.

Preliminary results of X-ray diffraction studies indicate that the transition in conductivity correlates with a change in

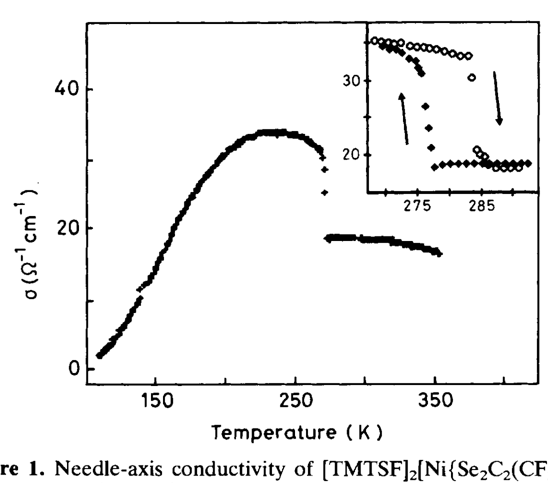


Figure 1. Needle-axis conductivity of $[TMTSF]_2[Ni\{Se_2C_2(CF_3)_2\}_2]$ single crystal (cooling). Inset shows hysteresis upon temperature cycling through phase transition.

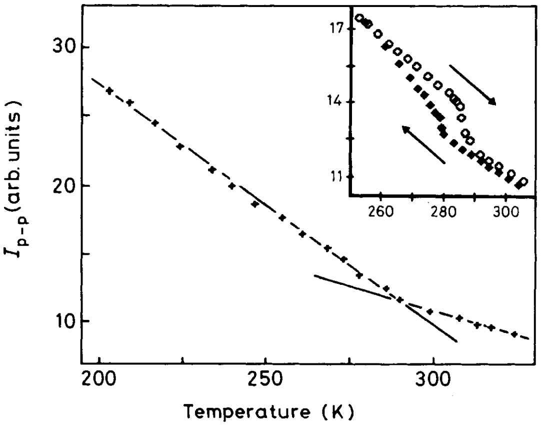


Figure 2. Temperature dependence of peak-to-peak e.s.r. intensity for polycrystalline $[TMTSF]_2[Ni\{Se_2C_2(CF_3)_2\}_2]$. Inset shows that the change in slope is accompanied by a small change in value, and displays the hysteresis upon temperature cycling.

structure.[9] By analogy to studies on the related, non-conducting metal dithioalkene salts of the type $[TTF][M\{S_2C_2(CF_3)_2\}_2]$ (TTF = tetrathiafulvalene; M = Cu, Au, Pt),[10] the change may be a first-order phase transition involving the ordering of rotationally disordered $-CF_3$ substituents.

To our knowledge, compounds (**1**) and (**2**) provide the first example of a structural transition in which the low temperature state is more conductive than the high temperature state. Indeed, the superconducting state provides the only other case of a transition to a low temperature state of higher conductivity.

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References

1 L. Alcacer and H. Novais, in 'Extended Linear Chain Compounds,' Vol. 3, ed. J. S. Miller, Plenum Press, New York, 1983, pp. 319—351.

2 A. Kobayashi, Y. Sasaki, H. Kobayashi, A. E. Underhill, and M. M. Ahmad, *J. Chem. Soc., Chem. Commun.*, 1982, 390; R. Kato, T. Mori, A. Kobayashi, Y. Sasaki, and H. Kobayashi, *Chem. Lett.*, 1984, 1; M. Bousseau, L. Valade, M.-F. Bruniquel, P. Cassoux, M. Garbauskas, L. Interrante, and J. Kasper, *Nouv. J. Chim.*, 1984, 3; L. Valade, J.-P. Legros, M. Bousseau, P. Cassoux, M. Garbauskas, and L. V. Interrante, *J. Chem. Soc., Dalton Trans.*, 1985, 783; R. Kato, H. Kobayashi, A. Kobayashi, and Y. Sasaki, *Chem. Lett.*, 1985, 131; H. Kobayashi, R. Kato, A. Kobayashi, and Y. Sasaki, *ibid.*, 1985, 191; H. Kobayashi, R. Kato, A. Kobayashi, and Y. Sasaki, *ibid.*, 1985, 535.

3 G. Saito, T. Enoki, K. Toriumi, and H. Inokuchi, *Solid State Commun.*, 1982, **42**, 557; J. M. Williams, M. A. Beno, J. C. Sullivan, L. M. Banovetz, J. M. Braan, G. S. Blackman, C. P. Carlson, D. L. Greer, and D. M. Loesing, *J. Am. Chem. Soc.*, 1983, **105**, 643.

4 A. Davison and E. T. Shawl, *Inorg. Chem.*, 1970, **9**, 1820; D. J. Sandman, J. C. Stark, L. A. Acampora, L. A. Samuelson, and G. W. Allen, *Mol. Cryst. Liq. Cryst.*, 1984, **107**, 1; F. Wudl, E. T. Zellers, and S. D. Cox, *Inorg. Chem.*, 1985, **24**, 2864.

5 G. C. Papavassiliou, *Mol. Cryst. Liq. Cryst.*, 1982, **86**, 159; *Z. Naturforsch. Teil B*, 1982, **37**, 825.

6 W. B. Heuer and B. M. Hoffman, manuscript in preparation.

7 A. Davison and E. T. Shawl, *Chem. Commun.*, 1967, 670.

8 A. Davison, D. V. Howe, and E. T. Shawl, *Inorg. Chem.*, 1967, **6**, 458.

9 W. B. Heuer, J. A. Ibers, and B. M. Hoffman, work in progress.

10 J. A. Ibers, L. J. Pace, J. Martinsen, and B. M. Hoffman, *Struct. Bonding (Berlin)*, 1982, **50**, 1, and refs. therein.