A New Two-dimensional Conducting Mixed Valence Compound derived from a Nickel Bisdithiolato-complex

Lydie Valade, Michèle Bousseau, Alain Gleizes, and Patrick Cassoux*

Laboratoire de Chimie de Coordination du CNRS, 205 route de Narbonne, 31400 Toulouse, France

The highly conducting electrocrystallized mixed valence $[Ni(dmit)_2](NBu_4)_{0.29}$ complex (H_2dmit = 4,5-dimercapto-1,3-dithiole-2-thione) shows an unusual two-dimensional structure as shown by *X*-ray diffraction methods and anisotropic conductivity measurements.

Most of the highly conducting molecular compounds, organic or inorganic, are one-dimensional systems.[1] However, the low temperature instability (Peierl's transition[2]) inherent in one-dimensional systems prevents the attainment of superconductivity, the ultimate goal. Superconducting non-stoicheiometric organic salts have recently been discovered[3]

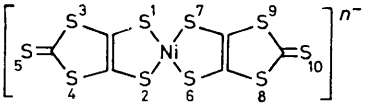

Figure 1. The $[Ni(dmit)_2]^{n-}$ species; $n = 1$, 0.29.

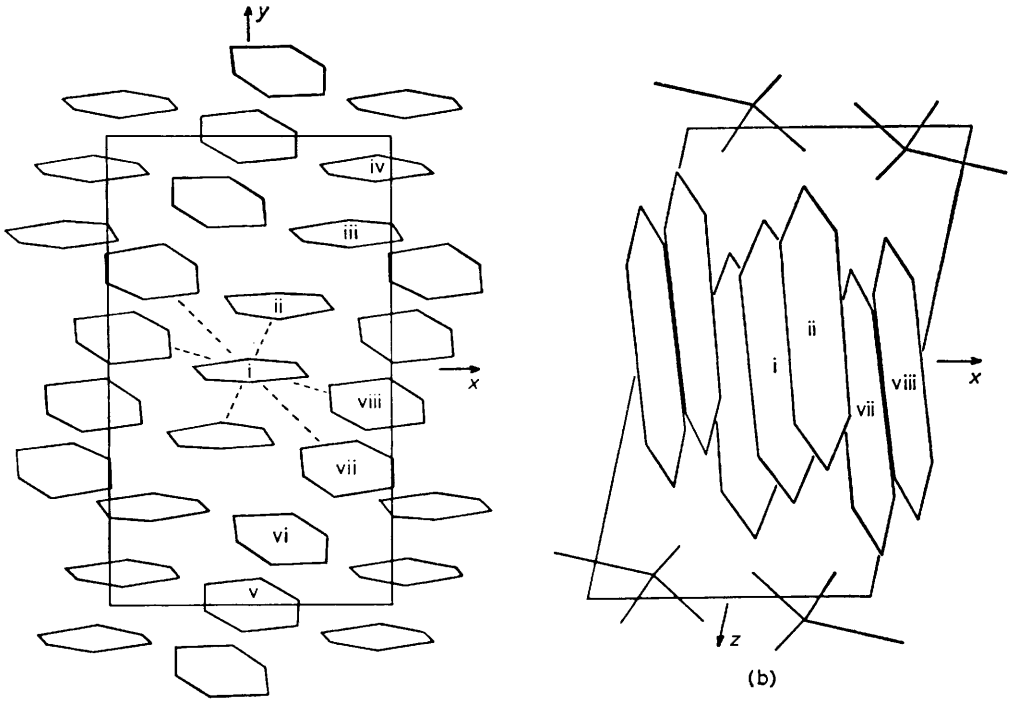

Figure 2. (a) View down the *c* axis of the packing of $Ni(dmit)_2$ units; units with roman numbers differing by 4 belong to the same stack (*e.g.* i and v, see text); intermolecular contacts are illustrated for unit i only by dashed lines. (b) View down the *b* axis illustrating the layered structure; the $Ni(dmit)_2$ units joined by dashed lines in Figure 2(a) are represented in Figure 2(b). For the sake of clarity, each $Ni(dmit)_2$ unit (see Figure 1) is represented by its contour and each (NBu_4) cation by lines joining the central N atom to the terminal C atoms.

in which interchain interactions (*i.e.* two-dimensionality) stabilize the metallic state. We report here the electrocrystallization, structure, and anisotropic conductivity of a new two-dimensional conducting mixed valence compound derived from a nickel bisdithiolato-complex.

$$[Ni(dmit)_2](NBu_4)_x$$

(**1**) $x = 1$
(**2**) $x = 0.29$

Chemical oxidation of $[Ni(dmit)_2](NBu_4)$ (**1**) (H_2dmit = 4,5-dimercapto-1,3-dithiole-2-thione) (Figure 1) with bromine gave badly characterized conducting powders.[4] We have now obtained single crystals of the well defined mixed valence species $[Ni(dmit)_2](NBu_4)_{0.29}$ (**2**) by galvanostatic electrocrystallization of a solution (10^{-3} M) of (**1**) in acetonitrile on a platinum electrode, with $(NBu_4)BF_4$ (0.1 M) as the supporting electrolyte, at a current of 1 μA and a stabilized temperature of 10 °C. The formula of (**2**) was determined by elemental analysis, electron microprobe analysis on the single crystals, mass spectra, and *X*-ray crystal structure analysis. The conductivity of these crystals, measured along the needle axis (axis *a*; see below) by a conventional four-probe technique, is *ca.* 10 Ω^{-1} cm^{-1} at 300 K. It should be noted that this value is not much higher than the conductivity of the powder obtained by chemical oxidation (*ca.* 1 Ω^{-1} cm^{-1}); the measurements were made on compressed pellets.[4] This result suggested the possibility of an unexpected anisotropy in the conducting behaviour of this compound. Moreover, temperature-dependent measurements show a peculiar thermally-activated conductivity; the activation energy determined in the 300—158 K range [E_a (300—158 K) = 0.17 eV] is, surprisingly, higher than the value determined at lower temperature [E_a (158—77 K) = 0.05 eV] and a smooth transition is observed between these two conductive modes at *ca.* 158 K.

A single crystal was mounted on an Enraf–Nonius CAD-4 computer-controlled four-circle *X*-ray diffractometer (Mo-K_α radiation) and the crystal structure elucidated.† There are 14 $[Ni(dmit)_2]$ and 4 (NBu_4) species per unit cell. The quasi-planar $[Ni(dmit)_2]$ molecules are stacked parallel to the *b* axis (Figure 2). Within a unit cell the two $[Ni(dmit)_2]$ molecules of a stack are related by a transformation which can be described as a translation of the nickel atoms close to $\vec{b}/2$ (*ca.* 11.95 Å) and a rotation of the mean plane by *ca.* 33° around the S(5)–S(10) axis. S–S Intermolecular contacts shorter than or nearly equal to the van der Waals distance (3.66 Å) are observed between molecules of different stacks; the shortest S–S distance is 3.47(2) Å. It should be noted that these interactions are of two kinds. The first one, an approximately π type, involves partially overlapping molecules and develops in the stacking direction; the second one, an approximately σ type, occurs in strips roughly perpendicular to the stacking axis. Thus the stacks are aggregated into thick layers parallel to (001) and form two-dimensional networks separated by layers of (NBu_4) cations.

† *Crystal data:* $(C_6S_{10}Ni)(C_{16}H_{36}N)_{0.29}$, triclinic, space group $P\bar{1}$ $a = 13.604$, $b = 22.965$, $c = 24.270$ Å, $\alpha = 108.16$, $\beta = 103.09$, $\gamma = 89.67°$, $D_m = 1.75$, $D_c = 1.73$ g cm^{-3}, $U = 7000$ Å^3, $Z = 14$, present R value 0.11 for 3851 reflections. The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

The two-dimensional structure of this compound was confirmed by a determination of the anisotropy of the conductivities using the Montgomery method.[5] The single crystals used for these measurements (*ca.* 0.30 × 0.30 × 0.08 mm^3) were oriented on the automatic *X*-ray diffractometer. The ratio of the conductivity values along the *a* and *b* axes is *ca.* 2 (equation 1).

$$\sigma_a \gtrsim \sigma_b \gg \sigma_c \quad (1)$$

It is noteworthy that the conductivity σ_a along the layers of the [Ni(dmit)$_2$] species is higher than the conductivity σ_b along the stacking axis. This emphasises the major rôle of the S–S intermolecular contacts which, as seen previously, could give rise to strong interactions along both *a* and *b* axes. The lowest conductivity, along the *c* axis (*ca.* $10^{-3}\ \Omega^{-1}\ cm^{-1}$), is consistent with the existence of a barrier formed by the layers of (NBu_4) cations parallel to (001).

In conclusion, [Ni(dmit)$_2$](NBu_4)$_{0.29}$ is the first example of a conducting metal complex in which two-dimensionality is a key feature.

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