

Crystal structure and semiconductivity of tetraethylammonium bis(isotrithionedithiolato)nickelate(III)

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CRYSTAL STRUCTURE AND SEMICONDUCTIVITY OF TETRAETHYLAMMONIUM BIS(ISOTRITHIONEDITHIOLATO)NICKELATE(III).

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Abstract. The synthesis and crystal structure of $((C_2H_5)_4N)\{Ni(C_3S_5)_2\}$ is described. Space group $P2_1/n$ with $a=7.333(1)\text{\AA}$, $b=25.734(3)\text{\AA}$, $c=12.798(4)\text{\AA}$, $\beta=104.95(2)^\circ$ and $Z=4$. The structure consists of a one-dimensional zig-zag chain with alternating Ni-Ni distances of 4.163\AA and 4.243\AA , respectively. The temperature dependence of the conductivity shows an unusual behaviour. The relationship $\ln(\sigma) \propto T^{-1/2}$ is followed instead of the common semiconductor behaviour of $\ln(\sigma) \propto 1/T$. The unexpectedly high value of the conductivity is related to the size of the counter cation in the crystal lattice.

Considerable effort has been devoted to the preparation and study of conducting molecular solids and, in particular, the development of "molecular metals" and superconductors¹⁻³. The crystals of partially oxidized 1,2-dithiolene complexes have the conduction pathway based on the ligand-centered π -system (predominantly sulfur orbitals), while partially occupied $M-d_{z^2}$ electron energy band is responsible for the high conductivity of the inorganic one-dimensional metals containing tetracyanoplatinate and bis(oxalato)platinate anions⁴.

Transition metal ions coordinated by the organic ligand dmit (isotrithionedithiolato), provide a suitable acceptor molecule, which can be made to form highly anisotropic (low-dimensional) metals or semiconductors and also an isotropic superconductor³. In the literature examples of these systems are found exhibiting both 1- and 2-dimensional electronic behaviour⁵⁻⁶. We now report the synthesis of a semiconductor, with an unusual conducting behaviour, and the characterization by spectroscop-

pic and X-ray diffraction determination of the structure. The dianionic starting product $((C_2H_5)_4N)_2\{Ni(dmit)_2\}$, has been prepared following a synthetic method described in the literature^{5,7} using $(C_2H_5)_4NBr$ instead of $(C_4H_9)_4NBr$. Reaction of sodium or potassium with CS_2 yields the $dmit^{2-}$ anion, which is stabilized and isolated as the zinc salt. Subsequent reaction with benzoylchloride and sodium methoxide regenerates the $dmit^{2-}$ ligand; this is followed by the addition of the appropriate metal salt. The $(Et_4N)\{Ni(dmit)_2\}$ coordination compound has been prepared following different pathways: (i) oxidation of $(Et_4N)_2\{Ni(dmit)_2\}$ by iodine (I_2); (ii) auto-oxidation of $(Et_4N)_2\{Ni(dmit)_2\}$ using the methods, under identical experimental conditions, described first by Steimecke and co-workers⁷ for the synthesis of $(Bu_4N)\{Ni(dmit)_2\}$. The needle-shaped crystals, synthesized according to (i), were used for the chemical analysis, X-ray diffraction determination and the conductivity measurement. Elemental analy-

sis for $((C_2H_5)_4N)\{Ni(C_3S_5)_2\}$: calcd. Ni, 10.09; C, 28.91; H, 3.47; N, 2.41; S, 55.12; found Ni, 10.02; C, 28.57; H, 3.41; N, 2.19; S, 55.33. The downfield shifts of the C=C vibrations upon oxidation, (1434 cm^{-1} for Ni(II) and 1350 cm^{-1} for Ni(III)) is in agreement with those found in the literature for $((C_4H_9)_4N)_2\{Ni(dmit)_2\}$ ⁷.

The crystal structure of $(Et_4N)\{Ni(dmit)_2\}$ was determined to understand the unusual conductivity. Especially information about the stacking of the $\{Ni(dmit)_2\}^-$ -ions in this compound is important. The Ni(III) compound crystallizes in the space group $P2_1/n$ with parameters $a=7.333(1)\text{ \AA}$, $b=25.734(3)\text{ \AA}$, $c=12.798(4)\text{ \AA}$, $\beta=104.95(2)^\circ$, $Z=4$ and mol.wt.=581.6. The structure was solved from the Patterson function followed by the use of the program AUTOFOUR⁸ and least-squares refinement. Resulting final $R(R_w)$ values are 4.49(5.36) for 1474 significant reflections. The structure contains

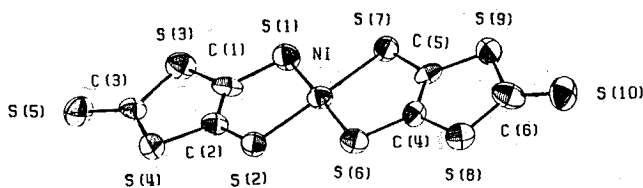


Figure 1. Ortep drawing of the $[Ni(III)(C_3S_5)_2]^-$ ion with atomic numbering

quasi-planar $\{Ni(dmit)_2\}^-$ -ions, face-to-face stacked along the a-axis with alternating Ni-Ni distances of 4.163 \AA and 4.243 \AA . The planes containing Ni, S1-S5, C1-C3 and Ni, S7-S10, C5-C6, respectively, have an inclination of 7.2° . The average value of the Ni-S bond distances is 2.157 \AA (Table 1), which clearly shows that the redox process within the nickeldithiolene complex has taken

Table 1. Bond lengths (\AA) and angles ($^\circ$) within the $\{Ni(C_3S_5)_2\}^-$ -ion, including cell parameter errors.

Ni-S1	2.151(4)	Ni-S1-C1	102.0(4)
Ni-S2	2.158(4)	Ni-S2-C2	101.6(4)
Ni-S6	2.159(4)	Ni-S6-C4	100.6(5)
Ni-S7	2.163(4)	Ni-S7-C5	102.4(5)
S1-C1	1.74(1)	S1-C1-C2	120(1)
S2-C2	1.69(1)	S1-C1-S3	122.4(7)
S3-C1	1.73(1)	C2-C1-S3	118(1)
S3-C3	1.77(1)	S2-C2-S4	121.9(7)
S4-C2	1.76(1)	S2-C2-C1	123(1)
S4-C3	1.72(1)	C1-C2-S4	115(1)
S5-C3	1.61(1)	C1-S3-C3	97.7(6)
S6-C4	1.73(1)	C2-S4-C3	99.2(6)

S7-C5	1.71(1)	S3-C3-S4	110.9(7)
S8-C4	1.76(1)	S3-C3-S5	123.2(7)
S8-C6	1.73(1)	S4-C3-S5	125.9(8)
S9-C5	1.73(1)	S6-C4-C5	123.1(9)
S9-C6	1.75(1)	S6-C4-S8	120.5(7)
S10-C6	1.64(1)	C5-C4-S8	116.4(9)
C1-C2	1.34(1)	S7-C5-S9	124.7(7)
C4-C5	1.36(1)	S7-C5-C4	120(1)
S1-Ni-S2	93.3(1)	C4-C5-S9	115.2(9)
S1-Ni-S7	87.1(1)	C4-S8-C6	97.9(6)
S2-Ni-S6	86.0(1)	C5-S9-C6	99.2(6)
S6-Ni-S7	93.8(2)	S8-C6-S9	111.1(7)
		S8-C6-S10	124.6(8)
		S9-C6-S10	123.9(8)

place at the central nickel atom (for Ni(II) the average value of the Ni-S bond distances is 2.21 \AA). Short intermolecular contacts between the $\{Ni(dmit)_2\}^-$ -ions within the chain are expected to give a considerable overlap of the valence orbital and could therefore give rise the observed conductivity behaviour (Table 2, Figure 2). It appears that in this compound the chains are well separated since the smallest interchain S-S contact is of the order of 3.8 \AA , which is larger than the corresponding Van der Waals radius (3.70 \AA). The face-to-face distances along the a-axis are approximately 3.5 and 3.7 \AA . These distances are comparable with the face-to-face distances found in the compound $(Et_4N)_{0.5}\{Ni(dmit)_2\}$ which are respectively 3.437 and 3.759 \AA ⁶. Calculations of the intermolecular overlap integrals (S) of $(Et_4N)_{0.5}\{Ni(dmit)_2\}$, indicated that the overlap integrals along the face-to-face stacking are much larger than the inter-stack overlap integrals which is consistent with the highest value of σ along that direction.

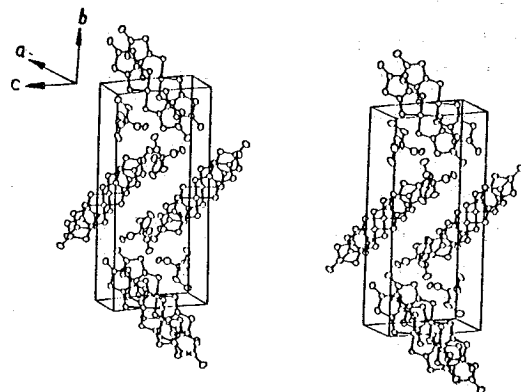


Figure 2. Stereoscopic drawing of the unit cell of $(Et_4N)[Ni(dmit)_2]$ with stacking along the a-axis.

Table 2. Some relevant distances within the chain in Å

Ni(1) - Ni(2)	4.163	
Ni(1) - Ni(3)	4.243	
S8(1) - S4(2)	3.660	symmetry
S4(1) - S8(2)	3.660	operations
Ni(1) - S2(3)	3.506	(1) x,y,z
S2(1) - Ni(3)	3.506	(2) 1-x,-y,1-z
S5(1) - S8(3)	3.711	(3) -x,-y,1-z
S8(1) - S5(3)	3.711	

The room temperature conductivity, two-probe technique, of the Ni(III) is $4 \times 10^{-5} (\Omega \text{cm})^{-1}$ (for $((\text{C}_4\text{Hg})_4\text{N})_1[\text{Ni}(\text{dmit})_2] \sigma \approx 3 \times 10^{-8}$) and in preliminary experiments we find that $\sigma_{\parallel} : \sigma_{\perp}$ exceeds 100. The "activation" energy is 0.25 eV¹⁰ when analyzed as $\ln \sigma \propto T^{-1}$ over a small temperature range around room temperature. However, the temperature dependence of the conductivity differs markedly from the usual semiconductor behaviour.

The $\ln(\sigma) \propto T^{-1/2}$ law holds over seven decades in the conductivity. Such a behaviour in one-dimensional compounds can be attributed to a potential disorder induced on the conducting chain by randomness in the donor system¹¹. The room temperature X-ray study and crystal structure indicate that both donors and acceptors form a regular array without any static disorder. Therefore, the application of the above theory seems inadequate¹⁰. More details about the conductivity measurement and the explanation of the data can be found in the literature¹⁰.

Further work in this area is directed to explanation of the conducting behaviour of this compound versus the structure and the synthesis of related coordination compounds with different metals and/or cations. This research is sponsored by the Leiden Materials Science Centre (Werkgroep Fundamenteel Materialenonderzoek).

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