

Structures of Tetramethylammonium Bis(2-thioxo-1,3-dithiole-4,5-dithiolato)niccolate(III) and Tetra-*n*-propylammonium Bis(2-thioxo-1,3-dithiole-4,5-dithiolato)niccolate(III)

BY J. H. VAN DIEMEN, L. R. GROENEVELD, A. LIND, R. A. G. DE GRAAFF, J. G. HAASNOOT AND J. REEDIJK*

Department of Chemistry, Gorlaeus Laboratories, Leiden University, PO Box 9502, 2300 RA Leiden, The Netherlands

(Received 16 March 1988; accepted 20 June 1988)

Abstract. $[\text{N}(\text{CH}_3)_4][\text{Ni}(\text{C}_3\text{S}_5)_2]$, $M_r = 525.52$, triclinic, $P\bar{1}$, $a = 10.017$ (9), $b = 15.481$ (7), $c = 18.485$ (8) Å, $\alpha = 110.31$ (4), $\beta = 95.14$ (4), $\gamma = 125.90$ (4)°, $V = 2008$ Å³, $Z = 4$, $D_x = 1.74$ g cm⁻³, $\lambda(\text{Mo K}\alpha) = 0.71073$ Å, $\mu = 19.65$ cm⁻¹, $F(000) = 1073$, $T = 295$ K, final $wR = 0.036$ for 2732 reflections [$I > 2\sigma(I)$]. The structure consists of an integrated network of anions and cations. The *non-planar* $[\text{Ni}(\text{C}_3\text{S}_5)_2]^-$ anions are stacked two by two; the pairs are rotated 90° with respect to one another. No significant intermolecular Ni–Ni or Ni–S distances have been found. Only intermolecular S–S contacts exist, shorter than the sum of the van der Waals radii of 3.70 Å. The minimum intermolecular S–S distance is 3.231 (4) Å. $[\text{N}(\text{C}_3\text{H}_7)_4][\text{Ni}(\text{C}_3\text{S}_5)_2]$, $M_r = 637.73$, monoclinic, $P2_1/c$, $a = 12.711$ (3), $b = 11.772$ (3), $c = 19.157$ (4) Å, $\beta = 105.24$ (2)°, $V = 2766$ Å³, $Z = 4$, $D_x = 1.53$ g cm⁻³, $\lambda(\text{Mo K}\alpha) = 0.71073$ Å, $\mu = 14.38$ cm⁻¹, $F(000) = 1282$, $T = 295$ K, final $wR = 0.045$ for 1731 reflections [$I > 2\sigma(I)$]. The structure can be described as an arrangement of *non-planar* $[\text{Ni}(\text{C}_3\text{S}_5)_2]^-$ anions as dimers, separated by $[\text{N}(\text{C}_3\text{H}_7)_4]^+$ cations. Two types of dimer can be distinguished. Only one type has a significant intermolecular S–S contact: 3.496 (1) Å.

Introduction. In the last two decades 1,1- and 1,2-dithiolenes have received considerable attention. One of the interesting features of these ligands is their ability to form stable complexes with (highly) oxidized metal ions. Transition-metal ions coordinated by the anionic ligand dmit (2-thioxo-1,3-dithiole-4,5-dithiolate) are known to yield compounds which are highly anisotropic (low-dimensional) metals or semiconductors (Kato, Mori, Kobayashi, Sasaki & Kobayashi, 1984). An isotropic superconductor with dmit has also been described (Bousseau, Valade, Legros, Cassoux, Garbaskas & Interrante, 1986). This compound consists of planar $[\text{Ni}(\text{dmit})_2]^{n-}$ anionic units ($n = 1, 2$) and open-shell cations, tetrathiafulvalene (TTF). Recently, another $[\text{Ni}(\text{dmit})_2]$ compound with superconducting

behaviour has been synthesized (Kim, Kobayashi, Sasaki, Kato & Kobayashi, 1987; Kobayashi, Kim, Sasaki, Kato, Kobayashi, Moriyama, Nishio, Kajita & Sasaki, 1987). The cationic part of this compound contains closed-shell cations: $[\text{N}(\text{CH}_3)_4]^+$.

It has been established that the stacking of the $[\text{M}(\text{dmit})_2]^{n-}$ ions can vary dramatically with a change of counterion (Kobayashi, Kim, Sasaki, Kato & Kobayashi, 1987), often resulting in totally different conducting properties. As part of a study to investigate the influence of the counterion in relation to the structure of $[\text{Ni}(\text{dmit})_2]^{n-}$ complexes, crystal structures are described of $[\text{N}(\text{CH}_3)_4][\text{Ni}(\text{dmit})_2]$ and $[\text{N}(\text{C}_3\text{H}_7)_4][\text{Ni}(\text{dmit})_2]$, both part of the series $(\text{NR}_4)[\text{Ni}(\text{dmit})_2]$ ($R = \text{CH}_3$, C_2H_5 , $n\text{-C}_3\text{H}_7$ and $n\text{-C}_4\text{H}_9$). Crystal structures of $(\text{NEt}_4)[\text{Ni}(\text{dmit})_2]$ and $(\text{NBu}_4)[\text{Ni}(\text{dmit})_2]$ have already been determined. The former is a one-dimensional zigzag chain with interchain distances > 3.8 Å (Groeneveld, Schuller, Kramer, Haasnoot & Reedijk, 1986; Kramer, Groeneveld, Joppe, Brom, de Jongh & Reedijk, 1987). The latter is, according to the atomic positions given by Lindqvist, Andersen, Sieler, Steimecke & Hoyer (1982), a network of intermolecular sulfur interactions along the x and y axes with no contacts in the z direction. The present structures of $(\text{NMe}_4)[\text{Ni}(\text{dmit})_2]$ and $(\text{NPr}_4)[\text{Ni}(\text{dmit})_2]$ differ significantly in the stacking of the $[\text{Ni}(\text{dmit})_2]^-$ anions from the two structures reported earlier.

Experimental. The dianionic starting products $(\text{NR}_4)_2[\text{Ni}(\text{dmit})_2]$ ($R = \text{CH}_3$ and C_3H_7) have been prepared according to the literature (Steimecke, Sieler, Kirmse & Hoyer, 1979; Valade, Legros, Bousseau, Cassoux, Garbaskas & Interrante, 1985). $[\text{N}(\text{CH}_3)_4]\text{Br}$ and $[\text{N}(\text{C}_3\text{H}_7)_4]\text{Br}$ have been used, instead of $[\text{N}(\text{C}_4\text{H}_9)_4]\text{Br}$. The $(\text{NR}_4)[\text{Ni}(\text{dmit})_2]$ coordination compounds can be prepared following two different pathways:

- (i) oxidation of $(\text{NR}_4)_2[\text{Ni}(\text{dmit})_2]$ with diiodine;
- (ii) autoxidation of $(\text{NR}_4)_2[\text{Ni}(\text{dmit})_2]$ using methods first described by Steimecke *et al.* (1979) for the synthesis of $(\text{NBu}_4)[\text{Ni}(\text{dmit})_2]$.

Crystals suitable for X-ray analysis were synthesized according to (i). 1 mmol of $(\text{NR}_4)_2[\text{Ni}(\text{dmit})_2]$

* To whom correspondence should be addressed.

was dissolved in 60 ml of acetone. To this solution, a solution of 0.5 mmol iodine and 200 mg NaI in 35 ml acetone was added at room temperature. The solution was evaporated to 30 or 40 ml. A black micro-crystalline precipitate was formed. Both compounds were recrystallized from acetone. Small crystals are green while larger crystals appear to be black and opaque. Black crystals were used for X-ray analysis. Experimental data for both compounds are shown in Table 1. Enraf-Nonius CAD-4 four-circle diffractometer with graphite-monochromatized Mo *K* α radiation. Cell constants were determined from setting angles of 24 reflections (θ between 10 and 12°). The intensities were determined from $\omega/2\theta$ scans and corrected for Lorentz and polarization effects. Absorption correction [for (NPr₄)[Ni(dmit)₂]] was applied using Monte-Carlo methods (de Graaff, 1973). Scattering factors and corrections for anomalous dispersion were taken from *International Tables for X-ray Crystallography* (1974). Nickel atoms were located using a Patterson map. Both structures were solved by automatic Fourier techniques, using the computer program *AUTOFOUR* (Kinneging & de Graaff, 1984). An extinction correction parameter of 8.71×10^{-4} was applied (for the propyl compound) according to Zachariasen (1967). Least-squares refinement on *F* of non-hydrogen-atom positional and anisotropic thermal parameters. Positions of hydrogen atoms were calculated except those on the terminal carbon atoms of the [N(C₃H₇)₄]⁺ cation. Refinement for the hydrogen positions of the methyl compound with Waser (1963) constraints. C—H = 0.95 Å for the methyl and 0.98 Å for the propyl compound. Isotropic temperature factors for the hydrogen atoms were 4.0 and 4.87 Å², respectively. Leiden University computer (IBM 3083); programs written or modified by Mrs E. W. Rutten-Keulemans and R. A. G. de Graaff.

Discussion. Positional parameters and equivalent isotropic thermal parameters for the non-hydrogen atoms are listed in Table 2. Bond distances and angles are given in Table 3. An *ORTEP* drawing (Johnson, 1965) of a [Ni(dmit)₂]⁻ anion, with the atomic labelling used in Tables 2 and 3, is given in Fig. 1. The two independent molecules of (NMe₄)[Ni(dmit)₂] (I) and the anion of (NPr₄)[Ni(dmit)₂] (II) have been given the same atomic numbering. Stereoviews of the stacking of the [Ni(dmit)₂]⁻ ions in both compounds are given in Figs. 2 and 3.*

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, distances and angles of the cations, and details of best weighted planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51170 (27 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Experimental data for (NMe₄)[Ni(dmit)₂] and (NPr₄)[Ni(dmit)₂]*

	(NMe ₄)[Ni(dmit) ₂]	(NPr ₄)[Ni(dmit) ₂]
Quadrants	$\pm h, \pm k, l$	$\pm h, k, \pm l$
θ range (°)	2–22	2–21
Standard reflections*	228, 228, 008	2, 0, 10, 139, 446
No. of reflections measured	5111	6294
No. of independent reflections	4919	3151
R_{int}	0.048	0.039
Significant reflections $ I > 2\sigma(I)$	2732	1731
h	–21 to 21	–12 to 12
k	–16 to 16	0 to 11
l	0 to 19	–19 to 19
Crystal size (mm)	0.32 × 0 × 22 × 0.18	0.29 × 0.20 × 0.12
Transmission-factor range	0.89–1.08	0.75–0.85
Max. shift/e.s.d. in final cycle	0.064	0.026
$\Delta\rho_{max}$ (e Å ⁻³)	0.30	0.40
$\Delta\rho_{min}$ (e Å ⁻³)	–0.29	–0.20
R	0.029	0.036
wR	0.036	0.045
Weighting scheme	$1/\sigma^2(F)$	$1/\sigma^2(F)$
$\sigma^2(F)$		σ_j^2 (counting statistics) + 0.014F ²

* Maximum intensity variation 6.65% for the methyl compound and 9.33% for the propyl compound.

In the [Ni(dmit)₂]⁻ anions of (I)(1), (I)(2) and (II) the Ni atoms do not deviate from the S₄ donor-atom plane by more than 0.011 (7) Å. The other sulfur atoms S3–S4–S5 and S8–S9–S10 are tilted out of the plane. Other properties of the [Ni(dmit)₂]⁻ anions of both (I) and (II) are given in Table 4. The average values of the Ni–S bond distances are 2.157 and 2.160 Å. These values are an indication that the redox process within the nickel dithiolene complex has taken place at the central nickel atom [for Ni^{II} the average value of the Ni–S bond distance is 2.21 Å (Lindqvist, Andersen, Sieler, Steimecke & Hoyer, 1982)].

(NMe₄)[Ni(dmit)₂] (I). Intermolecular contacts (Table 5) between [Ni(dmit)₂]⁻ ions are formed by S–S contacts shorter than the van der Waals diameter of sulfur (3.70 Å). No important Ni–S contacts exist between the anions: the shortest distance is 3.98 Å, which is significantly larger than the sum of the van der Waals radii (3.48 Å). Fig. 2 shows the packing of the [Ni(dmit)₂]⁻ ions. In contrast with (NEt₄)[Ni(dmit)₂] (Groeneveld, Schuller, Kramer, Haasnoot & Reedijk, 1986) the present structure does not consist of independent chains of anions and cations. The anions are stacked, side by side, in pairs with the central Ni atoms at a relatively large distance from one another. The neighbouring pairs are rotated 90°. Cations are positioned between the anion pairs which results in a tight network of anions and cations. The overall packing in this structure can be best described by two segregated stacks of anions, which are rotated 90° and slipped into each other. Each individual stack consists of a chain of two 'side by side' stacked anions. The pairs of the two segregated stacks are stacked 'face to face'.

(NPr₄)[Ni(dmit)₂] (II). Compared to (I) the propyl compound (II) has only two significant intermolecular S–S contacts, 3.496 and 3.701 Å (Table 5). In particular, the S4–S10 contact may give orbital

Table 2. Fractional atomic coordinates [$\times 10^5$ for Ni(1), Ni(2) and $\times 10^4$ for the other atoms] and isotropic thermal parametersTable 3. Bond lengths (Å) and angles (°) within the [Ni(C₃S₅)₂]⁻ ion; *e.s.d.*'s include allowance for cell-parameter errors

$B(\text{iso}) = \frac{8}{3}\pi^2 \text{trace}(U)$				$B(\text{iso})(\text{Å}^2)$
x	y	z		
[N(CH₃)₄][Ni(C₃S₅)₂]				
Ni(1)	42482 (10)	19031 (7)	61719 (5)	3.14 (3)
S1(1)	6303 (2)	2732 (1)	7327 (1)	4.23 (6)
S2(1)	2256 (2)	395 (2)	6336 (1)	4.28 (6)
S3(1)	6280 (2)	1872 (1)	8572 (1)	3.79 (6)
S4(1)	2525 (2)	-263 (2)	7673 (1)	4.28 (6)
S5(1)	4565 (2)	134 (2)	9202 (1)	5.11 (7)
S6(1)	2258 (2)	1049 (1)	4982 (1)	3.85 (6)
S7(1)	6221 (2)	3488 (2)	6075 (1)	4.36 (6)
S8(1)	2291 (2)	2036 (2)	3811 (1)	4.01 (6)
S9(1)	5975 (2)	4228 (2)	4789 (1)	4.51 (7)
S10(1)	4056 (3)	3927 (2)	3285 (1)	5.62 (8)
C1(1)	5223 (8)	1710 (6)	7678 (4)	3.3 (2)
C2(1)	3439 (8)	678 (5)	7242 (4)	3.1 (2)
C3(1)	4460 (8)	555 (5)	8515 (4)	3.6 (2)
C4(1)	3330 (8)	2158 (6)	4686 (4)	3.2 (2)
C5(1)	5051 (8)	3202 (5)	5158 (4)	3.2 (2)
C6(1)	4091 (8)	3411 (6)	3930 (4)	3.9 (2)
Ni(2)	101175 (11)	9628 (8)	85174 (6)	3.70 (3)
S1(2)	12416 (2)	2615 (2)	8591 (1)	5.07 (7)
S2(2)	11686 (2)	1106 (2)	9510 (1)	4.27 (7)
S3(2)	16297 (2)	4436 (2)	9762 (1)	5.20 (7)
S4(2)	15642 (2)	3075 (2)	10615 (1)	4.72 (7)
S5(2)	19337 (2)	5393 (2)	11162 (1)	6.14 (8)
S6(2)	7818 (2)	-608 (2)	8521 (1)	4.71 (7)
S7(2)	8534 (2)	745 (2)	7481 (1)	4.65 (7)
S8(2)	3922 (2)	-2425 (2)	7393 (1)	4.91 (7)
S9(2)	4553 (2)	-1219 (2)	6420 (1)	4.93 (7)
S10(2)	859 (3)	-3498 (2)	5960 (2)	7.46 (9)
C1(2)	14095 (8)	3090 (5)	9396 (4)	3.9 (2)
C2(2)	13786 (8)	2450 (5)	9800 (4)	3.6 (2)
C3(2)	17195 (9)	4355 (6)	10559 (4)	4.6 (3)
C4(2)	6137 (8)	-1118 (6)	7706 (4)	3.8 (2)
C5(2)	6425 (8)	-540 (5)	7253 (4)	3.6 (2)
C6(2)	3010 (9)	-2426 (6)	6562 (4)	4.8 (3)
N1	558 (7)	3077 (5)	1247 (3)	4.0 (2)
C(11)	-436 (10)	2777 (7)	425 (4)	6.0 (3)
C(12)	-102 (10)	3436 (7)	1878 (5)	6.9 (4)
C(13)	246 (9)	1985 (6)	1183 (4)	5.5 (3)
C(14)	2487 (9)	4113 (7)	1531 (5)	6.2 (3)
N2	465 (8)	3081 (5)	6235 (4)	4.5 (2)
C(21)	830 (11)	4236 (7)	6575 (5)	8.2 (4)
C(22)	1536 (12)	3097 (8)	6860 (5)	8.1 (4)
C(23)*	-1484 (11)	2025 (7)	5973 (6)	8.9 (5)
C(24)	931 (10)	2868 (7)	5491 (5)	6.9 (4)
[N(C₃H₇)₄][Ni(C₃S₅)₂]				
Ni	782 (1)	-98 (1)	1260 (1)	3.57 (3)
S1	717 (2)	-1584 (2)	1916 (1)	4.13 (7)
S2	2464 (2)	-381 (2)	1276 (1)	4.17 (7)
S3	2459 (2)	-3339 (2)	2571 (1)	4.22 (7)
S4	4061 (2)	-2194 (2)	2009 (1)	4.38 (7)
S5	4719 (2)	-4257 (2)	2911 (2)	5.93 (9)
S6	817 (2)	1288 (2)	528 (1)	4.49 (8)
S7	-861 (2)	288 (2)	1303 (1)	4.95 (8)
S8	-916 (2)	2971 (2)	-201 (1)	4.86 (8)
S9	-2468 (2)	2062 (2)	499 (1)	5.45 (9)
S10	-3116 (2)	3996 (2)	-526 (1)	6.04 (9)
C1	2014 (6)	-2119 (7)	2066 (4)	3.4 (3)
C2	2760 (6)	-1598 (7)	1791 (4)	3.4 (2)
C3	3794 (6)	-3320 (7)	2511 (4)	3.9 (3)
C4	-460 (7)	1836 (7)	391 (4)	3.6 (3)
C5	-1184 (7)	1401 (7)	719 (4)	3.8 (3)
C6	-2234 (7)	3069 (7)	-101 (4)	4.6 (3)
N	2699 (5)	1617 (5)	3554 (3)	3.2 (2)
C11	2990 (6)	2085 (7)	2880 (4)	3.9 (3)
C12	2287 (7)	3016 (8)	2436 (5)	5.9 (3)
C13	2738 (8)	3410 (8)	1818 (5)	5.3 (3)
C21	3561 (6)	740 (7)	3909 (4)	3.8 (3)
C22	3617 (8)	-367 (7)	3521 (5)	5.1 (3)
C23	4581 (7)	-1077 (7)	3931 (5)	4.8 (3)
C31	1562 (6)	1079 (7)	3310 (4)	3.9 (3)
C32	1138 (7)	530 (8)	3909 (5)	5.1 (3)
C33	51 (7)	-41 (8)	3590 (5)	5.3 (3)
C41	2697 (6)	2561 (7)	4091 (4)	4.0 (3)
C42	3719 (7)	3279 (8)	4329 (5)	5.6 (3)
C43*	3695 (9)	3979 (9)	5002 (6)	7.4 (4)

* Atoms showing high thermal anisotropy.

[N(CH₃)₄][Ni(C₃S₅)₂]			
Molecule 1	Molecule 2		
Ni-S1	2.158 (3)	2.157 (3)	
Ni-S2	2.159 (2)	2.162 (2)	
Ni-S6	2.159 (3)	2.160 (3)	
Ni-S7	2.153 (2)	2.163 (2)	
S1-C1	1.709 (6)	1.710 (6)	
S2-C2	1.711 (6)	1.712 (6)	
S3-C1	1.732 (6)	1.740 (6)	
S3-C3	1.718 (6)	1.736 (7)	
S4-C2	1.722 (6)	1.743 (6)	
S4-C3	1.731 (6)	1.707 (7)	
S5-C3	1.637 (6)	1.647 (7)	
S6-C4	1.731 (6)	1.700 (6)	
S7-C5	1.719 (6)	1.711 (6)	
S8-C4	1.730 (6)	1.744 (6)	
S8-C6	1.713 (7)	1.713 (7)	
S9-C5	1.728 (6)	1.744 (6)	
S9-C6	1.718 (6)	1.725 (7)	
S10-C6	1.657 (6)	1.653 (7)	
C1-C2	1.377 (8)	1.353 (8)	
C4-C5	1.352 (8)	1.357 (8)	
S1-Ni-S2	92.6 (1)	93.2 (1)	
S1-Ni-S7	86.3 (1)	87.7 (1)	
S2-Ni-S6	88.3 (1)	86.1 (1)	
S6-Ni-S7	93.0 (1)	93.3 (1)	
N1-S1-C1	102.9 (2)	101.9 (2)	
Ni-S2-C2	103.1 (2)	102.0 (2)	
C1-S3-C3	97.3 (3)	97.6 (3)	
C2-S4-C3	97.4 (3)	98.0 (3)	
Ni-S6-C4	102.5 (2)	101.6 (2)	
Ni-S7-C5	102.4 (2)	101.9 (2)	
C4-S8-C6	96.9 (3)	97.7 (3)	
C5-S9-C6	97.1 (3)	97.2 (3)	
S1-C1-S3	123.2 (4)	122.5 (4)	
S1-C1-C2	121.0 (5)	121.9 (5)	
S3-C1-C2	115.9 (5)	115.6 (5)	
S2-C2-S4	123.7 (3)	123.1 (4)	
S2-C2-C1	120.4 (5)	121.0 (5)	
S4-C2-C1	115.9 (4)	115.9 (5)	
S3-C3-S4	113.5 (3)	112.8 (4)	
S3-C3-S5	122.7 (4)	122.4 (4)	
S4-C3-S5	123.8 (4)	124.8 (4)	
S6-C4-S8	123.3 (4)	122.1 (4)	
S6-C4-C5	120.3 (5)	122.4 (5)	
S8-C4-C5	116.4 (5)	115.5 (5)	
S7-C5-S9	122.6 (4)	123.2 (4)	
S7-C5-C4	121.6 (5)	120.8 (5)	
S9-C5-C4	115.8 (4)	116.0 (5)	
S8-C6-S9	113.8 (4)	113.5 (4)	
S8-C6-S10	124.0 (4)	122.4 (4)	
S9-C6-S10	122.2 (4)	124.1 (4)	
[N(C₃H₇)₄][Ni(C₃S₅)₂]			
Ni-S1	2.168 (3)	S1-Ni-S2	93.19 (9)
Ni-S2	2.156 (2)	S1-Ni-S7	87.87 (9)
Ni-S6	2.159 (3)	S2-Ni-S6	86.39 (9)
Ni-S7	2.160 (3)	S6-Ni-S7	92.9 (1)
S1-C1	1.717 (8)	Ni-S1-C1	102.2 (3)
S2-C2	1.724 (8)	Ni-S2-C2	101.7 (3)
S3-C1	1.741 (8)	C1-S3-C3	97.7 (4)
S3-C3	1.731 (8)	C2-S4-C3	97.4 (4)
S4-C2	1.744 (8)	Ni-S6-C4	101.8 (3)
S4-C3	1.724 (9)	Ni-S7-C5	101.9 (3)
S5-C3	1.646 (8)	C4-S8-C6	98.3 (4)
S6-C4	1.701 (8)	C5-S9-C6	98.8 (4)
S7-C5	1.700 (8)	S1-C1-S3	123.6 (5)
S8-C4	1.750 (9)	S1-C1-C2	120.7 (7)
S8-C6	1.739 (9)	S3-C1-C2	115.7 (6)
S9-C5	1.756 (8)	S2-C2-S4	121.4 (5)
S9-C6	1.730 (9)	S2-C2-C1	122.1 (6)
S10-C6	1.622 (9)	S4-C2-C1	116.4 (6)
C1-C2	1.35 (1)	S3-C3-S4	112.8 (5)
C4-C5	1.35 (1)	S3-C3-S5	123.6 (5)
		S4-C3-S5	123.6 (5)
		S6-C4-S8	122.0 (5)
		S6-C4-C5	121.7 (7)
		S8-C4-C5	116.3 (7)
		S7-C5-S9	123.3 (5)
		S7-C5-C4	121.6 (7)
		S9-C5-C4	115.2 (7)
		S8-C6-S9	111.5 (5)
		S8-C6-S10	123.2 (6)
		S9-C6-S10	125.3 (5)

Table 6. *The (NR₄)[Ni(dmit)₂] compounds*

	R = CH ₃	R = C ₂ H ₅	R = n-C ₃ H ₇	R = n-C ₄ H ₉
Space group	P1	P2 ₁ /n	P2 ₁ /c	P2 ₁ /c
Side/side (a) or face/face (b)	a + b	b	b	a
Ni-S distance (Å)	2.158	2.157	2.160	2.156
Variations in S-S contacts (Å)	3.23-3.71	3.51-3.71	3.50-3.70	3.40-3.61
σ(S cm ⁻¹)	5 × 10 ⁻⁶	4 × 10 ⁻⁵	6 × 10 ⁻⁸	5 × 10 ⁻⁹

orbital overlap can be formed by the S5-S5 contacts (3.231 Å, Table 5) and probably the S9-S10 contacts (3.691 Å). The second pathway is a zigzag interaction between both molecules (Table 5) with contacts mainly along the x axis. These pathways may explain the relatively high single-crystal conductivity at room temperature found for this compound (5 × 10⁻⁶ S cm⁻¹), compared to the related (NBu₄)[Ni(dmit)₂] (5 × 10⁻⁹ S cm⁻¹) (Groeneveld, Schuller, Kramer, Haasnoot & Reedijk, 1986). The single-crystal conductivity of (NPr₄)[Ni(dmit)₂], 6 × 10⁻⁸ S cm⁻¹, is of the same order of magnitude as the conductivity of (NBu₄)[Ni(dmit)₂]. The 'isolated character' of the anionic part of (NPr₄)[Ni(dmit)₂] and (NBu₄)[Ni(dmit)₂] may cause the relatively low conductivity.

In Table 6 the main differences between the (NR₄)[Ni(dmit)₂] compounds (R = CH₃, C₂H₅, n-C₃H₇, and n-C₄H₉) are summarized.

We would like to express our gratitude to Mr G. J. Kramer for performing the conductivity measurements and to Mr S. Gorter for data collection. This research is

sponsored by the Leiden Materials Science Centre (Werkgroep Fundamenteel Materialenonderzoek).

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Structure of catena-Poly[bis(ethylenediamine)nickel(II)-μ-cyano-dicyanonickel(II)-μ-cyano]

BY JURAJ ČERNÁK, JOZEF CHOMIČ AND DANICA BALOGHOVÁ

Department of Inorganic Chemistry, University of P. J. Šafárik, Moyzesova 11, 041 54 Košice, Czechoslovakia

AND MICHAL DUNAJ-JURČO

Department of Inorganic Chemistry, Slovak Technical University, Radlinského 9, 812 35 Bratislava, Czechoslovakia

(Received 24 November 1987; accepted 22 June 1988)

Abstract. Ni(en)₂Ni(CN)₄, *M_r* = 341.67, monoclinic, *P*2₁/*n*, *a* = 7.104 (3), *b* = 10.671 (3), *c* = 9.940 (2) Å, β = 114.68 (2)°, *V* = 684.7 (4) Å³, *Z* = 2, *D_m* = 1.68 (1), *D_x* = 1.66 Mg m⁻³, λ(Mo *K*α) = 0.71069 Å, μ = 2.70 mm⁻¹, *F*(000) = 352, *T* = 295 K, *R* = 0.0487

for 1137 unique reflections. The structure is built up of infinite electroneutral [-Ni(en)₂-NC-Ni(CN)₂-CN-]_∞ chains parallel to the *c* axis. The Ni(1) atom is square-planar coordinated by four cyano groups. The *trans*-coordinated cyano groups form bridges to two