

A new monoclinic crystal phase of [Bu₄N][Ni(dmit)₂]

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The crystal structure of the title compound, tetrabutylammonium bis(2-thioxo-1,3-dithiole-4,5-dithiolato)nickelate(III), [N(C₄H₉)₄][Ni(C₃S₅)₂], is the fourth known phase of this polymorphous compound. It is monoclinic space group *P*2₁/*c*, with *a* = 20.040(2) Å, *b* = 13.1151(17) Å, *c* = 12.1093(15) Å, β = 105.456(15)°, and *V* = 3067.5(6) Å³ with *Z* = 4, for *D*_{calc} = 1.503 g cm⁻³. The [Ni(dmit)₂] anion packing arrangement consists of arrays of “side-on” touching anions and these arrays are connected *via* “head-to-tail” close S ··· S contacts.

KEY WORDS: Tetrabutylammonium; nickel; dmit; dithiolate complex; crystal structure; polymorphism.

Introduction

In the development of new molecular electrical conductors, the use of planar [M(dmit)₂]^{x-} anions with M = Ni, Pd, Pt and *x* = 2, 1, 0 < *x* < 1 has resulted in many interesting materials ranging from semiconductors to superconductors.¹ Often a tetraalkylammonium salt [R₄N][M(dmit)₂] is used as the starting compound. Replacing the ammonium cation with cations of various molecular and electronic structure and simultaneous oxidation by the cation or subsequent chemical or electrolytic oxidation of the anion to a fractionally oxidized state, results in a compound with a conductivity that depends on the formal fractional charge and the intermolecular contacts in the crystal structure.²

In literature some crystal structures have been published of fractionally oxidized semiconducting compounds like [Bu₄N]₂[Ni(dmit)₂]₇³ and [Bu₄N]₂[Ni(dmit)₂]₇ · 2CH₃CN.⁴ Two crystal phases of the [Bu₄N]₂[Ni(dmit)₂] compound with anion charge 2- have been found.^{5,6}

Three different crystal phases of the [Bu₄N][Ni(dmit)₂] are already known: two triclinic *P* $\bar{1}$ phases^{7,8} and a monoclinic *P*2₁/*c* phase.⁹ We now want to present another monoclinic phase of the [Bu₄N][Ni(dmit)₂].

Experimental

Synthesis

This new crystal phase has been obtained by recrystallization of [Bu₄N][Ni(dmit)₂] in a methanol/acetone mixture cooled at 277 K, in an attempt to replace the ammonium cation with a transition metal complex, like has been done previously with [Cu(bpy)₃]²⁺.¹⁰ The [Bu₄N][Ni(dmit)₂] was prepared using procedures described by Lindqvist *et al.*⁹

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Crystal structure determination and refinement of [Bu₄N][Ni(dmit)₂]

A crystal suitable for X-ray diffraction was cut from a larger block, glued to the tip of a glass fiber, and transferred into the cold nitrogen stream on a Nonius KappaCCD area detector system on rotating anode. Crystal data and details on data collection and refinement are given in Table 1.

Table 1. Crystal Data and Summary of Intensity Data Collection and Structure Refinement for [Bu₄N][Ni(dmit)₂]

Compound	C ₁₆ H ₃₆ N · C ₆ NiS ₁₀
CCDC deposit no.	CCDC-1003/6130
Colour/shape	Black/plate-shaped
Formula weight	693.91
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i> (No. 14)
Unit cell dimensions	<i>a</i> = 20.040(2) Å <i>b</i> = 13.1151(17) Å <i>c</i> = 12.1093(15) Å <i>β</i> = 105.456(15)°
<i>V</i> , Å ³	3067.5(6)
<i>Z</i>	4
<i>D</i> _{calc} , g cm ⁻³	1.503
<i>F</i> (000)	1452
<i>μ</i> _{calc} , cm ⁻¹	1.328
Max. crystal dimensions, mm	0.08 × 0.25 × 0.35
Diffractometer	Nonius KappaCCD
<i>T</i> , K	150
<i>θ</i> _{min} , <i>θ</i> _{max} , deg	1.6, 27.44
Wavelength (Mo Kα), Å	0.71073 (graphite monochromator)
Distance from crystal to detector, mm	40
X-ray exposure time, h	2.5
Data set (<i>hkl</i>)	−25 ≤ <i>h</i> ≤ 25, −16 ≤ <i>k</i> ≤ 16, −15 ≤ <i>l</i> ≤ 15
Total measured data	56731 (<i>R</i> _σ = 0.0324)
Total unique data	6978 (<i>R</i> _{int} = 0.0682)
MULABS transmission range	0.718–0.897
No. of parameters varied	311
<i>wR</i> 2 ^a	0.0680
<i>R</i> ^b	0.0268 [for 5681 <i>F</i> _o > 4σ(<i>F</i> _o)]
<i>S</i> ^c	1.006
<i>w</i> ^{-1d}	σ ² (<i>F</i> ²) + (0.0305 <i>P</i>) ² + 1.03 <i>P</i>
(Δ/σ) _{av} , (Δ/σ) _{max}	0.001, <0.001
Min. and max. residual density, e Å ⁻³	−0.75, 0.36

$$^a wR2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}.$$

$$^b R = \sum ||F_o| - |F_c|| / \sum |F_o|.$$

$$^c S = [\sum [w(F_o^2 - F_c^2)^2] / (n - p)]^{1/2} \quad (p = \text{number of parameters}; n = \text{number of reflections}).$$

$$^d P = (\text{Max}(F_o^2, 0) + 2F_c^2) / 3.$$

Reduced-cell calculations did not indicate higher lattice symmetry.¹¹ Data were corrected for *Lp* effects and for absorption using a multiple scan algorithm (MULABS, incorporated in PLATON¹²). The structure was solved by automated direct methods (SHELXS86¹³). Refinement on *F*² was carried out by full-matrix least-squares techniques (SHELXL-97-2¹⁴); no observance criterion was applied during refinement. Hydrogen atoms were included in the refinement on calculated positions riding on their carrier atoms. The methyl groups were refined as rigid groups, allowing for rotations around the C–C bond. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined with a fixed isotropic displacement parameter related to the value of the equivalent isotropic displacement parameter of their carrier atoms by a fixed factor. Table 2 gives atomic coordinates and equivalent isotropic thermal parameters. Neutral atom scattering factors and anomalous dispersion corrections were taken from International Tables for Crystallography.¹⁵ Geometrical calculations and illustrations were performed with PLATON.¹²

Structure description

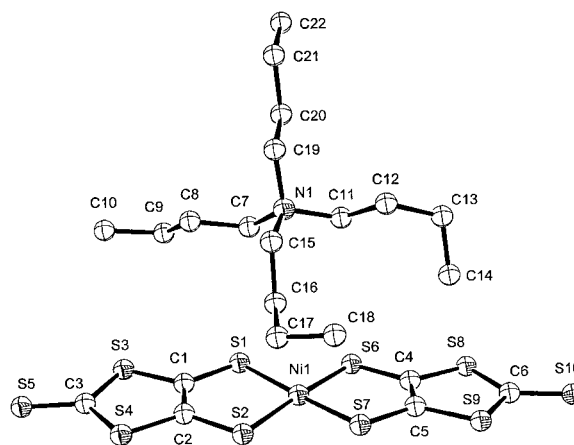
The crystallographically independent unit consists of one entire [Bu₄N]⁺ cation and one [Ni(dmit)₂][−] anion (Fig. 1).

The ammonium cation has two completely stretched out butyl chains and two butyl groups in which the terminal methyl units are in gauche position. This is reflected in the dihedral angles of −75.2(2)° and −62.15(19)° of the C(15)–C(18) and C(11)–C(14) butyl chains respectively, in comparison with 179.43(15)° and 177.88(14)° of the other C(7)–C(10) and C(19)–C(22) butyl chains.

The [Ni(dmit)₂] anion has Ni–S distances (Table 3) in the range of 2.1590(5)–2.1717(5) Å with an average of 2.1658(3) Å, which is within the range of Ni–S distances of 2.132–2.182 Å and slightly higher than the average

Table 2. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters of [Bu₄N][Ni(dmit)₂]

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Ni(1)	0.239238(10)	0.25322(2)	0.47550(2)	0.0183(1)
S(1)	0.33664(2)	0.21413(4)	0.59741(3)	0.0242(1)
S(2)	0.28949(2)	0.33337(3)	0.36414(3)	0.0232(1)
S(3)	0.48538(2)	0.26505(4)	0.59862(4)	0.0279(1)
S(4)	0.44107(2)	0.37548(4)	0.38482(4)	0.0278(1)
S(5)	0.59176(2)	0.35605(4)	0.49733(4)	0.0377(2)
S(6)	0.18852(2)	0.16228(3)	0.57823(3)	0.0232(1)
S(7)	0.14211(2)	0.30164(3)	0.35946(4)	0.0248(1)
S(8)	0.03657(2)	0.11796(3)	0.55223(4)	0.0276(1)
S(9)	-0.00639(2)	0.24782(3)	0.35266(4)	0.0275(1)
S(10)	-0.11374(2)	0.13818(4)	0.43513(5)	0.0414(2)
C(1)	0.39590(8)	0.27156(13)	0.53749(14)	0.0218(5)
C(2)	0.37531(8)	0.32368(12)	0.43726(14)	0.0218(5)
C(3)	0.51016(9)	0.33336(14)	0.49343(15)	0.0264(5)
C(4)	0.10271(8)	0.17779(12)	0.50780(14)	0.0216(5)
C(5)	0.08281(8)	0.23896(12)	0.41389(14)	0.0210(5)
C(6)	-0.03197(8)	0.16708(14)	0.44679(15)	0.0280(5)
N(1)	0.25808(6)	0.53593(10)	0.76891(10)	0.0171(4)
C(7)	0.31513(8)	0.45651(12)	0.79046(13)	0.0193(5)
C(8)	0.38764(8)	0.49760(13)	0.80205(14)	0.0245(5)
C(9)	0.43982(8)	0.41249(13)	0.83913(15)	0.0276(5)
C(10)	0.51385(9)	0.44570(15)	0.84875(17)	0.0359(6)
C(11)	0.19072(8)	0.47895(12)	0.76132(13)	0.0190(5)
C(12)	0.12574(8)	0.54473(13)	0.73557(15)	0.0261(5)
C(13)	0.06110(8)	0.47965(13)	0.72455(15)	0.0265(5)
C(14)	0.04822(10)	0.40338(16)	0.62681(17)	0.0381(6)
C(15)	0.25454(8)	0.59376(12)	0.65830(12)	0.0189(4)
C(16)	0.24608(9)	0.52608(13)	0.55355(13)	0.0263(5)
C(17)	0.22383(9)	0.58581(14)	0.44134(14)	0.0265(5)
C(18)	0.14863(10)	0.61712(17)	0.40896(17)	0.0443(7)
C(19)	0.27165(8)	0.61368(11)	0.86550(12)	0.0184(4)
C(20)	0.28212(9)	0.56787(13)	0.98404(13)	0.0238(5)
C(21)	0.29185(8)	0.65027(13)	1.07534(13)	0.0228(5)
C(22)	0.30161(10)	0.60424(15)	1.19390(14)	0.0340(6)

**Fig. 1.** Displacement ellipsoid drawing at a 50% probability level of the crystallographically independent units of this new crystal phase of [Bu₄N][Ni(dmit)₂], one [Bu₄N]⁺ cation, and [Ni(dmit)₂]⁻ anion; hydrogen atoms are omitted for clarity.**Table 3.** Selected Geometric Parameters (Å, deg) of this New Crystal Phase of [Bu₄N][Ni(dmit)₂]

Bond length (Å)	
Ni1—S1	2.1717(5)
Ni1—S2	2.1590(5)
Ni1—S6	2.1626(5)
Ni1—S7	2.1700(6)
S1—C1	1.7215(17)
S2—C2	1.7165(17)
S3—C1	1.7502(17)
S4—C2	1.7457(17)
S3—C3	1.7346(19)
S4—C3	1.7267(19)
S5—C3	1.6504(19)
S6—C4	1.7159(17)
S7—C5	1.7146(17)
S8—C4	1.7442(17)
S9—C5	1.7471(17)
S8—C6	1.7312(18)
S9—C6	1.7305(18)
S10—C6	1.6509(18)
C1—C2	1.358(2)
C4—C5	1.362(2)
N1—C7	1.517(2)
N1—C11	1.524(20)
N1—C15	1.5244(19)
N1—C19	1.5206(19)
Bond angle (deg)	
S1—Ni1—S7	179.28(2)
S1—Ni1—S2	93.16(2)
S1—Ni1—S6	87.36(2)
S2—Ni1—S6	175.37(2)
S2—Ni1—S7	86.57(2)
S6—Ni1—S7	93.21(2)

Ni—S distance of 2.160(6) Å found for other [cation][Ni(dmit)₂] compounds with anion charge 1⁻ in the CSD database.¹⁶ The anion has a 6.15(2)° tetrahedral distortion between the least-square planes of each Ni(dmit) part.

The angle between the least-square planes of the [Ni(dmit)₂] anions with symmetry code [*x*, *y*, *z*] and [*-x*, $\frac{1}{2} + y$, $\frac{1}{2} - z$] is 70.63(4)°. Two kinds of intermolecular close S...S contacts (Table 4) between the [Ni(dmit)₂] anions are present (distance < 2*r*_{van der Waals} = 3.70 Å). There are “side-on” S...S contacts between arrays of anions ([*x*, *y*, *z*], [*x*, $\frac{1}{2} - y$, $\frac{1}{2} + z$] arrays and

Table 4. Intermolecular S...S Contacts (Å) Shorter Than 3.70 Å of This New Crystal Phase of [Bu₄N][Ni(dmit)₂]^a

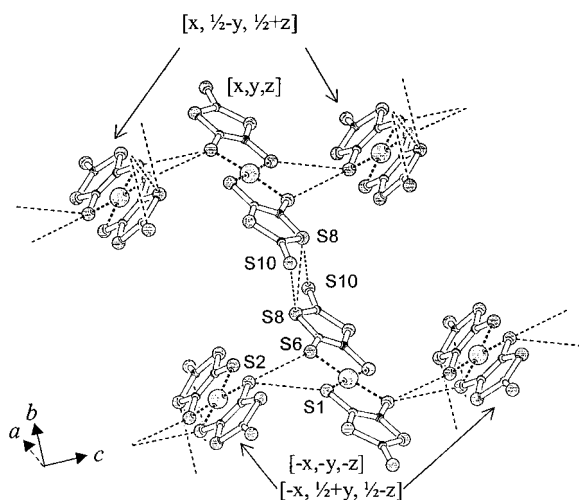
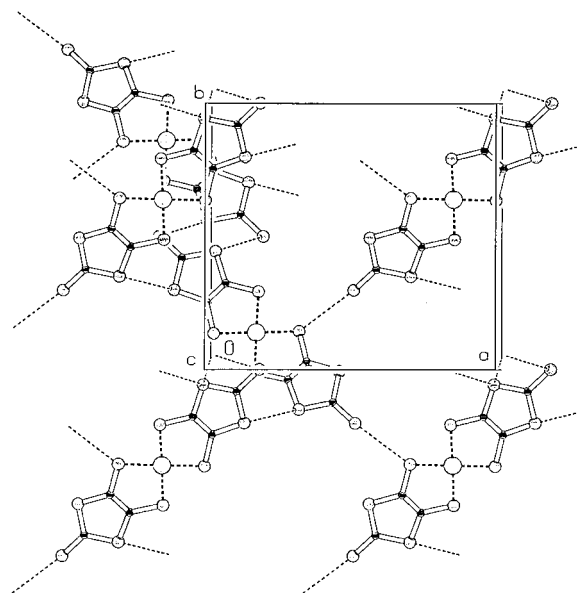
S1...S2 ⁱ	3.6524(7)
S2...S6 ⁱ	3.5143(7)
S8...S8 ⁱⁱ	3.5119(7)
S8...S10 ⁱⁱ	3.6843(7)

^aSymmetry code: ⁱ $[x, \frac{1}{2} - y, \frac{1}{2} + z]$; ⁱⁱ $[-x, -y, -z]$.

$[-x, \frac{1}{2} + y, \frac{1}{2} - z]$, $[-x, -y, -z]$ arrays) propagating in the [001] direction. Also ‘head-to-tail’ contacts are present, which propagate in the [010] direction, at alternating anion pairs $([x, y, z], [-x, -y, -z])$ and then $[-x, \frac{1}{2} + y, \frac{1}{2} - z]$, $[x, \frac{1}{2} - y, \frac{1}{2} + z]$, connecting the arrays that stretch out in the [001] direction (Figs. 2 and 3).

The structure reported here is isomorphous with the structures of the compounds [Bu₄N][C₆NiS₁₀]_{0.4}(C₆NiSe₁₀)_{0.6}¹⁷ (CSD TOHXIX) and [Bu₄N][Ni(C₃Se₅)₂]¹⁸ (CSD JEVDAP). Furthermore, the unit cell and anion arrangement of the structure of [Bu₄N][Pt(dmit)₂]¹⁹ (CSD FUFVOR10) with space group *C2/c* are very similar to those of the present structure.

Detailed comparison of the present structure with the other known structures of [Bu₄N][Ni(dmit)₂] in the literature has been possible with

**Fig. 2.** Close S...S contacts between [Ni(dmit)₂] anions in this new crystal phase of [Bu₄N₄][Ni(dmit)₂]; [Bu₄N] cations are omitted for clarity.**Fig. 3.** [Ni(dmit)₂] anion packing arrangement with close S...S contacts indicated by dotted lines in the Lindqvist phase⁹ of [Bu₄N][Ni(dmit)₂]; [Bu₄N] cations are omitted for clarity.

only two of the three published phases. The structure described by Sjölin *et al.*⁷ is not available in the Cambridge Structural Database.

Lindqvist's monoclinic *P2₁/c* structure⁹ has an [Ni(dmit)₂] anion packing arrangement that consists of anions with their longitudinal axes rotated at an approximately right angle. Each anion has intermolecular ‘head-to-side’ close S...S contacts with five other anions with S...S distances in a range of 3.402–3.611 Å. The packing is greatly different from the phase presented here (Fig. 3).

The triclinic *P1̄* phase described by Mentzafos *et al.*⁸ has an anion packing that consists of arrays of ‘side-on’ touching [Ni(dmit)₂] anions with close S...S contacts of 3.618 and 3.695 Å that propagate in the [100] direction between anions with alternating symmetry codes $[x, y, z]$ and $[-x, -y, -z]$, the least-square planes of which make an angle of 77.20°. Between the $[-x, -y, -z]$ anions from neighboring arrays ‘head-to-tail’ close S...S contacts of 3.5854 Å are present that propagate in the [010] direction

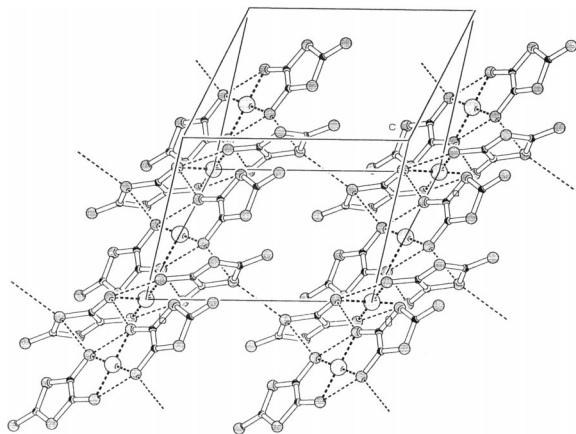


Fig. 4. [Ni(dmit)₂] anion packing arrangement with close S...S contacts indicated by dotted lines in the Mentzafos phase⁸ of [Bu₄N][Ni(dmit)₂]; [Bu₄N] cations are omitted for clarity.

(Fig. 4). The crystal structure presented here resembles most closely the [Bu₄N][Ni(dmit)₂] phase published by Mentzafos *et al.*⁸

Note. Statistical data on Ni—S distances taken from 26 references of compounds with monovalent [Ni(dmit)₂][−] anions with the following CSD codes: BARBEB, DEPNUH, HANLUD, HANMAK, HOGTUS, ITTNBU01, ITTNBU02, JEC DIE, JITGUO, KIQJEZ, LALSAS, MAMNAP, MAMNET, NIPWIS, NUSQEX, NUSQEX01, NUSQOH, NUSQOH01, PAQMID, SAXQUD, SOSPUL, SOSPUL, TESWAP, TESWET, VUYPAG, VUYPEK CSD release date: October 2000.

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