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Crystal structure and electrical conductivity of *N*-methylquinolinium bis(1,3-dithiole-2-thione-4,5-dithiolato)nickelate(III)

J. P. Cornelissen, E. J. Creyghton, R. A. G. de Graaff, J. G. Haasnoot* and J. Reedijk
Department of Chemistry, Gorlaeus Laboratories, Leiden University, P.O. Box 9502, 2300 RA Leiden (The Netherlands)

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Abstract

The crystal structure and electrical conductivity of [MeQ][Ni(dmit)$_2$] is reported (dmit = 1,3-dithia-2-thione-4,5-dithiolate and MeQ = *N*-methylquinolinium). The compound crystallises in the monoclinic space group $P2_1/n$, with $a = 17.55(1)$, $b = 10.893(7)$, $c = 23.11(2)$ Å, $\beta = 92.30(9)°$ and $Z = 4$ with the asymmetrical unit having formula $Ni_2C_{32}H_{20}N_2S_{20}$. The structure was solved by direct methods, Fourier and least-squares techniques. It consists of diads made up from two crystallographically independent Ni(dmit)$_2$ units, and two *N*-methylquinolinium cations lying next to the [Ni(dmit)$_2$]$_2$ diads. Both Ni(dmit)$_2$ units show considerable deviation from planarity, i.e. a distortion towards a V shape and a twist towards a more tetrahedral environment around the nickel atoms. The Ni(1)–S distances vary from 2.142(5)–2.167(5) Å, and the Ni(18)–S bond lengths are between 2.157(5)–2.2162(5) Å. The overall packing motive can be considered as being highly irregular. In the crystal lattice several short interdiad S...S contacts are present, the shortest one being 3.491(7) Å, building a two-dimensional network. In accordance with its structure and its stoichiometry, the compound behaves as a semiconductor with a relatively high room-temperature conductivity of 10^{-3} S cm^{-1}.

Introduction

Up to now, four compounds based on the M(dmit)$_2$ system (M = Ni, Pd, Pt; dmit = 1,3-dithiole-2-thione-4,5-dithiolate) which are able to exhibit superconductivity have been reported. Three of them originate from the combination of the open-shell cation TTF$^+$ (tetrathiafulvalene) with M(dmit)$_2$ [1–3]. In these three radical salts the electrical conductivity runs via both the donor and the acceptor units, as was recently confirmed by solid-state NMR measurements [4]. However, in the fourth superconductor, [Me$_4$N][Ni(dmit)$_2$]$_2$, a closed-shell cation is present in the lattice which is not able to be directly involved in the conduction process [5]. This means that it is possible to obtain superconductivity in a compound where only the acceptor stacks are responsible for the observed conductivity pathway.

Over the past decade, many M(dmit)$_2$ compounds have been synthesised with both types of cations (open-shell and closed-shell), some of them showing metallic properties over a certain temperature range [1–17]. Recently, we reported a new Ni(dmit)$_2$ salt featuring a type of cation which can be seen as an intermediate between both categories. In this compound of formula [tmiz][Ni(dmit)$_2$], with tmiz = 1,2,3-trimethylimidazolium, the cation, although formally possessing a non-fractional charge of 1+, still contains a delocalised π-system [18]. The compound crystallises in a non-segregated manner, displaying an extremely regular face-to-face stacking mode of the anions and the cations. It was believed that not only the S...S contacts found between the Ni(dmit)$_2$ units, but also the interaction between the electronic systems of both the cations and the anions might be responsible for its unusually high room-temperature conductivity.

To investigate whether this regular face-to-face stacking mode is a general feature for all Ni(dmit)$_2^-$ salts with planar, unsaturated cations, various other compounds of this class were synthesised. In the present paper the synthesis, structure and conductivity of [MeQ][Ni(dmit)$_2$] (MeQ = *N*-methylquinolinium) are reported.

Experimental

Materials

Synthesis of [MeQ]I

N-Methylquinolinium iodide was prepared by dissolving 0.065 mol of quinoline (Aldrich) in 45 ml

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*Author to whom correspondence should be addressed.

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of dry acetone. Then 0.07 mol of iodomethane (Janssen) was added slowly while stirring. After 30 min the white precipitate was filtered off and recrystallised from methanol/ether (overall yield 75%). Elemental analysis was in agreement with the molecular formula.

Synthesis of [MeQ][Ni(dmit)$_2$]

[MeQ][Ni(dmit)$_2$] was synthesised according to the general method of Steimecke *et al.* [19]. Single crystals of suitable size for X-ray diffraction and for conductivity measurements were grown in the following manner. One compartment of an H-tube equipped with a fine-porosity frit was filled with a saturated solution of [MeQ][Ni(dmit)$_2$] in dry acetonitrile. The second compartment was filled with a 0.01 M solution of [MeQ]ClO$_4$ in acetonitrile. After several days, in the first compartment black, sword shaped crystals could be isolated.

X-ray crystallography

A black, sword shaped crystal of approximate dimensions 0.2×0.1×0.5 mm was selected for the X-ray analysis and mounted on a CAD-4 diffractometer. Crystal data and data collection parameters are presented in Table 1. Unit-cell parameters were determined by least-squares methods applied to the setting angles of 25 reflections in the range −7 to −5° and 5 to 7° for θ. Data were collected at room temperature and have been corrected for Lorentz and polarisation effects.

TABLE 1. Experimental data for X-ray diffraction study on [MeQ][Ni(dmit)$_2$]

Formula	$Ni_2C_{32}H_{20}N_2S_{20}$
M_r	1191.12
Space group	$P2_1/n$
Crystal system	monoclinic
a (Å)	17.548(12)
b (Å)	10.893(7)
c (Å)	23.11(2)
β (°)	92.30(9)
Z	4
λ(Mo Kα) (Å)	0.71073
θ range (°)	2–22
No. unique reflections, ($I > 2\sigma(I)$)	1924
No. reflections measured	5749
R	0.049
R_w	0.050
Volume (Å^3)	4414(5)
D_c (g cm^{-3})	1.78
D_m (g cm^{-3})	1.78
μ (cm^{-1})	17.888
R_{int}	0.06
$F(000)$	1209.54
Scan type	$\omega/2\theta$

Structure solution and refinement

The structure was solved by direct methods (MULTAN78). First isotropic thermal parameters were used, followed by anisotropic parameters for all atoms of the anionic units. Hydrogen atoms were introduced in calculated positions and refined with fixed geometries with respect to their carrier atoms. The structure refined to an $R(R_w)$ value of 0.049 (0.050) with $R = [\Sigma(|F_o| - |F_c|)/\Sigma F_o]$ and $R_w = [\Sigma w(|F_o| - F_c|)^2/\Sigma w|F_o|^2]^{1/2}$. The final difference Fourier map showed no residual density. Scattering factors were taken from refs. 20 and 21. Atomic coordinates for the non-hydrogen atoms are given in Table 2. All calculations were carried out on the Leiden University IBM 3083 computer.

Results and discussion

Description of the X-ray structure

Table 3 lists all relevant bond distances and bond angles for the title compound. The asymmetrical unit with the labelling scheme is depicted in Fig. 1. Two crystallographically independent Ni(dmit)$_2$ units form a so-called 'diad' [22] with an angle of 1.6° between the mean planes through both molecules. In Fig. 1, the two *N*-methylquinolinium cations are lying behind the anionic units, more or less parallel to the Ni(dmit)$_2$ molecules generated by symmetry operation ($\frac{1}{2}-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$). Apart from the methyl group, the cations are essentially planar, making an angle of 4.7° with each other. The Ni(dmit)$_2$ units show a large deviation from planarity. For the unit around Ni(1), the mean planes through the dmit ligands are tilted over 5.24° towards a V shape, and the tetrahedral distortion around the Ni(1) atom amounts to 2.14°. For the second unit, around the Ni(18) atom, these deviations are even larger, 4.84 and 6.13°, respectively.

The tendency to adopt a V shape is found to be rather common in the literature for Pd(dmit)$_2$ and Pt(dmit)$_2$ compounds [1, 13]. However, in these structures the anions form diads through a relatively strong metal–metal interaction. This would bring the dmit ligands of both units too close together, resulting in the observed non-planarity. Such a metal–metal bond is clearly not present in [MeQ][Ni(dmit)$_2$], therefore in this case the large distortion must originate from steric effects. A more or less similar deviation from planarity was found in [Bu$_4$N]-[Ni(dmit)$_2$] [23], [Et$_4$N][Ni(dmit)$_2$] [24], and especially [Ph$_4$As][Ni(dmid)$_2$] [25] (dmid = 1,3-dithiole-2-one-4,5-dithiolate).

Figures 2 (front view) and 3 (top view, without cations) show the contents of two unit cells. As seen

TABLE 2. Fractional atomic coordinates ($\times 10^4$ for non-metal atoms, $\times 10^5$ for Ni atoms) and isotropic thermal parameters (with e.s.d.s in parentheses) for the non-hydrogen atoms in the compound [MeQ][Ni(dmit)$_2$]

Atom	*x/a*	*y/b*	*z/c*	B_{iso}
Ni1	35473(11)	3475(18)	37391(9)	362(6)
S10	2631(2)	99(5)	3091(2)	411(14)
S17	2774(3)	527(5)	4428(2)	455(14)
S12	905(2)	9(5)	3214(2)	436(14)
S15	1047(3)	430(5)	4444(2)	473(15)
S14	−491(3)	69(5)	3893(3)	58(2)
S2	4344(2)	167(5)	3054(2)	455(15)
S9	4444(3)	666(5)	4388(2)	502(15)
S4	6063(3)	606(5)	3064(2)	50(2)
S7	6143(3)	987(5)	4294(2)	512(15)
S6	7563(3)	1143(5)	3646(3)	67(2)
C13	444(10)	146(16)	3850(7)	42(5)
C11	1850(8)	180(15)	3500(7)	36(5)
C16	1886(9)	368(16)	4102(7)	38(5)
C3	5192(10)	509(16)	3419(7)	46(6)
C8	5244(9)	697(14)	3981(7)	38(5)
C5	6644(9)	934(17)	3670(8)	48(6)
Ni18	44603(11)	39314(18)	37347(9)	350(6)
S21	1866(2)	3435(5)	3143(2)	433(14)
S23	421(3)	3536(5)	3763(2)	57(2)
S19	3577(2)	3617(5)	3074(2)	456(15)
S24	1926(2)	3857(5)	4373(2)	435(14)
S27	5255(2)	3885(5)	3045(2)	443(14)
S26	3651(2)	4103(5)	4412(2)	417(14)
S34	5348(2)	4163(5)	4399(2)	412(14)
S29	6966(3)	4238(5)	3064(2)	49(2)
S32	7063(2)	4491(5)	4304(2)	476(15)
S31	8488(3)	4581(5)	3658(3)	67(2)
C22	1360(9)	3596(14)	3751(7)	38(5)
C20	2770(9)	3640(15)	3456(6)	37(5)
C25	2813(9)	3853(16)	4041(6)	37(5)
C28	6131(9)	4140(15)	3413(7)	33(5)
C33	6137(9)	4257(14)	4020(7)	38(5)
C30	7570(9)	4457(15)	3673(7)	41(5)
Nk1	4587(13)	1845(21)	1134(10)	109(6)
Ck2	492(1)	198(2)	63(1)	92(7)
Ck3	451(1)	222(2)	13(1)	93(7)
Ck4	379(2)	238(3)	6(1)	119(8)
Ck4A	341(1)	222(2)	59(1)	84(6)
Ck5	265(1)	229(2)	59(1)	88(6)
Ck6	2275(13)	2133(21)	1085(10)	77(6)
Ck7	2646(13)	1848(21)	1611(10)	80(6)
Ck8	3418(11)	1803(18)	1625(8)	59(4)
Ck8A	3787(11)	1946(18)	1110(8)	58(4)
Ck9	493(2)	169(3)	168(1)	117(8)
N2k1	9253(13)	2205(21)	2036(10)	106(6)
C2k2	9915(13)	2129(19)	1787(9)	70(5)
C2k3	9955(14)	2310(22)	1170(9)	80(6)
C2k4	938(2)	251(3)	76(1)	119(8)
C2k4A	8638(11)	2608(19)	1087(9)	61(4)
C2k5	800(1)	281(2)	76(1)	78(6)
C2k6	7354(13)	2918(20)	995(10)	75(5)
C2k7	7247(13)	2780(21)	1610(9)	76(6)
C2k8	7880(11)	2517(20)	1950(10)	67(5)
C2k8A	8552(10)	2441(18)	1681(8)	52(4)
C2k9	919(2)	207(3)	259(1)	115(8)

TABLE 3. Selected bond distances (Å) and angles (°) of [MeQ][Ni(dmit)$_2$]

Ni1–S2	2.162(5)	Ni18–S27	2.160(5)
Ni1–S9	2.156(5)	Ni18–S34	2.157(5)
Ni1–S10	2.167(5)	Ni18–S19	2.158(5)
Ni1–S17	2.142(5)	Ni18–S26	2.162(5)
C16–S17	1.71(2)	C25–S26	1.69(1)
C16–S15	1.70(2)	C25–S24	1.76(2)
C16–C11	1.40(2)	C25–C20	1.37(2)
C11–S10	1.70(2)	C20–S19	1.70(2)
C11–S12	1.77(2)	C20–S21	1.73(2)
C13–S12	1.71(2)	C22–S21	1.70(2)
C13–S15	1.73(2)	C22–S24	1.74(2)
C13–S14	1.65(2)	C22–S23	1.65(2)
C8–S9	1.72(2)	C33–S34	1.67(2)
C8–S7	1.74(2)	C33–S32	1.75(2)
C8–C3	1.31(2)	C33–C28	1.41(2)
C3–S2	1.72(2)	C28–S27	1.75(2)
C3–S4	1.77(2)	C28–S29	1.70(2)
C5–S7	1.72(2)	C30–S32	1.74(2)
C5–S4	1.74(2)	C30–S29	1.74(2)
C5–S6	1.63(2)	C30–S31	1.62(2)
S10–Ni1–S17	92.9(2)	S19–Ni18–S27	86.6(2)
S10–Ni1–S2	88.0(2)	S19–Ni18–S26	93.0(2)
S10–Ni1–S9	177.8(2)	S19–Ni18–S34	177.6(2)
S17–Ni1–S2	179.0(2)	S27–Ni18–S26	176.2(2)
S17–Ni1–S9	86.2(2)	S27–Ni18–S34	93.4(2)
S2–Ni1–S9	92.8(2)	S26–Ni18–S34	87.2(2)

from Fig. 2, the Ni(dmit)$_2$ diads and the cations form non-segregated stacks with the diads sandwiched between layers of *N*-methylquinolinium cations. Within a stack, the anions and the cations generated by symmetry operation ($\frac{1}{2}-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$) are oriented more or less parallel to each other. The distance of the plane through the unit around Ni(1) to the plane through the cation lying between two diads is 3.47 Å, and that between the cation and the unit around Ni(18) is 3.64 Å, which means that the cations do have some π-stacking interaction with the acceptor molecules. However, the large intra-diad separation (*vide infra*) prevents these contacts to be continuous through the lattice in the direction of the *b* axis. The stacks neighbouring along the *c* axis run alternatingly parallel and non-parallel with respect to each other. This packing motive results in a kind of 'Ni(dmit)$_2$ wave' along the *c* axis.

The S...S interactions between the molecules occur predominantly along the *c* and *a* axes (Figs. 2 and 3), thereby forming a two-dimensional network. Table 4 lists all intermolecular S...S contacts shorter than 3.70 Å, the sum of the van der Waals radii. Surprisingly, there are no significant intra-diad interactions. The shortest intra-diad Ni...S distance is found between Ni(18) and S(9), namely 3.865(6) Å, but is still far too long to warrant even *semi*-coordination. Also, no significant intra-diad S...S contacts

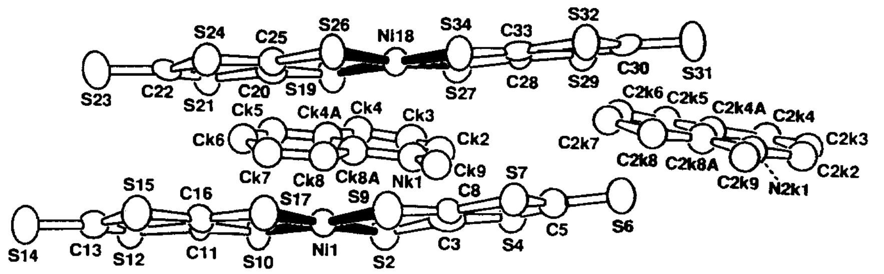

Fig. 1. Crystallographically independent unit in [MeQ][Ni(dmit)$_2$] with atomic labelling scheme. Hydrogen atoms are omitted for clarity.

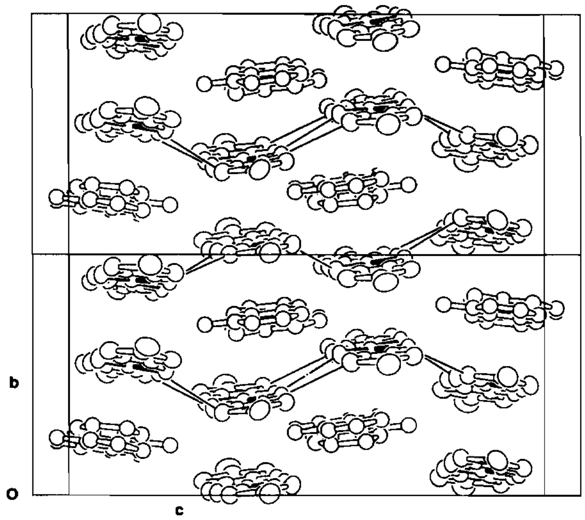

Fig. 2. Two unit cells depicted along the *a* axis. Intermolecular contacts shorter than 3.70 Å are represented by single black lines.

are present, the shortest one occurring between S(7) and S(34) at 3.742(7) Å. This large intra-diad separation should be compared to the one found in [Me$_4$P][Ni(dmit)$_2$]$_2$ [7], in which the dimerisation effect is far stronger and results in an intradimer spacing of 3.32–3.33 Å. A compound in which the acceptor molecules are actually held together by an apical coordination bond is (Bu$_4$N)$_1$Ni(dsit)$_2$ (with dsit = 1,3-dithiole-2-thione-4,5-diselenolate) [26]. In this structure an intradimer Ni–Se bond of 2.49 Å results in tightly bonded dimeric units and in that sense they are comparable to the (BEDT-TTF)$_2$ dimers in the κ-phase (BEDT-TTF)$_2$X salts [27]. In conclusion, these comparisons indicate that the [Ni(dmit)$_2$]$_2$ diads in [MeQ][Ni(dmit)$_2$] consist of only very loosely connected Ni(dmit)$_2$ units.

Conductivity measurements

Electrical conductivity was measured on single crystals by using the two-probe contact method. Gold wires were glued to the crystal surface by gold paint. The compound behaves as a semiconductor, exhibiting a room-temperature conductivity of 10^{-3} S cm^{-1}.

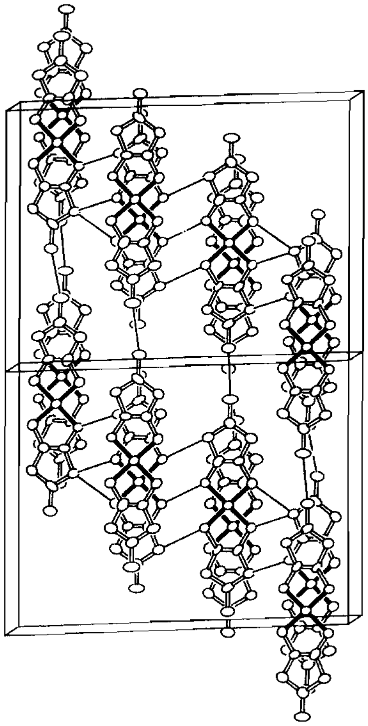

Fig. 3. Two unit cells depicted along the *b* axis. The cations are omitted for clarity. Intermolecular contacts shorter than 3.70 Å are represented by single black lines.

TABLE 4. Intermolecular S...S contacts (Å) shorter than 3.70 Å. Symmetry operation applied on second atom

S21–S10	3.521(7)	$\frac{1}{2}-x$	$-\frac{1}{2}+y$	$\frac{1}{2}-z$
S19–S12	3.491(7)	$\frac{1}{2}-x$	$-\frac{1}{2}+y$	$\frac{1}{2}-z$
S26–S32	3.610(7)	$1-x$	$1-y$	$1-z$
S34–S34	3.578(9)	$1-x$	$1-y$	$1-z$
S9–S9	3.67(1)	$1-x$	$-y$	$1-z$
S14–S6	3.631(7)	$-1+x$	y	z
S23–S31	3.574(7)	$-1+x$	y	z
S12–S27	3.690(6)	$\frac{1}{2}-x$	$-\frac{1}{2}+y$	$\frac{1}{2}-z$

This value is higher than normally found for a $Ni(dmit)_2$ compound possessing a formal charge of 1− [23, 24, 28], but can be explained by taking into account the numerous molecular interactions among the dmit ligands, as shown in the crystal structure, giving rise to a two-dimensional electrical conduction pathway.

Conclusions

The observed conductivity of $[MeQ][Ni(dmit)_2]$ is in agreement with its stoichiometry and with the data obtained from its crystal structure.

When the structures of $[MeQ][Ni(dmit)_2]$ and $[tmiz][Ni(dmit)_2]$ are compared, it is clear that they are completely different. Whereas in $[tmiz][Ni(dmit)_2]$ the planar tmiz cations induce a regular, face-to-face packing motive, combination of $Ni(dmit)_2$ with a cation like *N*-methylquinolinium, which is even more planar than tmiz, apparently alters the picture completely. The acceptor molecules form pairs which stack along the *b* axis with slabs of cations inbetween them. The methyl groups are pointing towards the $[Ni(dmit)_2]_2$ diads and the resulting steric hindrance is likely to be responsible for the observed non-planarity of the anions.

The origin for this large difference in stacking mode between $[tmiz][Ni(dmit)_2]$ and the title compound is as yet unclear, but it illustrates the fact that a planar, closed-shell cation does not implement one exclusive stacking mode of the acceptor molecules. Further investigations are needed to gain a better perception as to what extent the molecular packing is determined by the electronic and steric properties of the cations.

Supplementary material

Atomic coordinates for the hydrogen atoms, thermal parameters of the anions, a list of all bond distances and angles, and a list of calculated and observed structure factors are available from the authors on request.

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