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Single-Crystal Structure and Electrical Conductivity of 1,2,3-Trimethylimidazolium Bis(4,5-dimercapto-1,3-dithiole-2-thionato)nickelate(III)

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The electrochemical synthesis and characterization of a new member of the family of the [Cat]$[Ni(dmit)_2]$ coordination compounds (dmit = 4,5-dimercapto-1,3-dithiole-2-thionate), with Cat = 1,2,3-trimethylimidazolium, abbreviated as tmiz, is reported. [tmiz]$[Ni(dmit)_2]$ displays semiconducting behavior, with a room-temperature conductivity of 0.21 S/cm and an activation energy of 0.11 eV. A single-crystal structure determination (T = 300 K) of this complex was carried out. The crystals are triclinic, space group $P\bar{1}$, Z = 1, with a = 7.033 (2) Å, b = 7.918 (2) Å, c = 11.517 (3) Å, α = 106.43 (2)°, β = 70.79 (2)°, γ = 118.76 (2)°, and V = 524.89 Å^3. R_w = 0.0476 for 1402 independent significant reflections. The structure was solved by Patterson, Fourier, and least-squares techniques. The Ni atoms are located on centers of symmetry. The cation shows static disorder with the center of gravity on $(0,{}^1/_2,0)$, giving rise to inversion symmetry. The structure displays very regular, short, intermolecular S–S contacts responsible for the observed conductivity. Important interactions between two $Ni(dmit)_2^-$ units via the π-system of the cation are observed. The high conductivity contrasts with the very low conductivity of a compound of the same chemical composition, obtained by autoxidation.

Introduction

The class of coordination compounds based on the $M(dmit)_2$ unit (dmit = 4,5-dimercapto-1,3-dithiole-2-thionate) is a well-known source of highly conducting or even superconducting molecular solids.[1-3]

As the general formula of these compounds is $[Cat]_x[Ni(dmit)_2]$, where $0 < x < 2$, M = Ni, Pt, and Pd, and Cat is an often organic cation, many of the discoveries of new conducting materials belonging to the above-mentioned class were based on the variation of x and changing the cation. Up to now, all the cations of the closed-shell type used in these compounds were cations such as SR_3^+ and NR_4^+, R = alkyl.[1,4] In this paper the method used to extend the variety of cations to closed-shell cations containing a π-system, such as 1,2,3-trimethylimidazolium cation, hereafter abbreviated as tmiz, is described.

The delocalized π-system of the nearly planar cation may give rise to new, unknown interactions: planar cations may intercalate between sheets of $Ni(dmit)_2$ anions or form separate stacks. Apart from this structural influence, the planar cation can change the overall electronic structure, because of possible π-overlap of the molecular orbitals of the cation with those of the anion.

In the present paper synthesis, structure, and electrical conductivity of [tmiz]$[Ni(dmit)_2]$ are reported together with some preliminary results obtained by substitution of 1,2,3-trimethylimidazolium by 1,3-dimethylimidazolium cation.

Experimental Section

Synthesis of [tmiz]I. 1,2,3-Trimethylimidazolium iodide was prepared by dissolving 0.065 mol of commercially available 1,2-dimethylimidazole (Aldrich) without further purification in 45 mL of acetone. Then a solution of 0.07 mol of iodomethane (Jansen; no further purification) in 10 mL of acetone was added slowly with stirring. After 30 min the precipitate was filtered off and recrystallized from acetone (overall yield of 86%). Elemental analysis was in agreement with the molecular formula.

Synthesis of [tmiz][Ni(dmit)$_2$]. $[tmiz]_2[Ni(dmit)_2]$ was prepared according to the general recipe of Steimecke et al.[5] Electrooxidation of a saturated solution of this compound in acetonitrile yielded black platelets of composition [tmiz]$[Ni(dmit)_2]$.

Autoxidation of the unoxidized compound by air in acetic acid yielded a green, microcrystalline powder, which, according to elemental analysis, could also be characterized as [tmiz]$[Ni(dmit)_2]$.

Table I. Crystallographic Parameters for [tmiz]$[Ni(dmit)_2]$

chem formula	$C_{12}H_{11}N_2NiS_{10}$	V	524.89 Å^3
a	7.033 (2) Å	Z	1
b	7.918 (2) Å	fw	562.58
c	11.517 (3) Å	space group	$P\bar{1}$ (No. 2)
α	106.4 (2)°	T	300 K
β	70.79 (2)°	radiation, λ	Mo Kα, 0.71073 Å
γ	118.76 (2)°	μ	18.87 cm^{-1}

Table II. Atomic Fractional Coordinates and Isotropic Thermal Parameters for Non-Hydrogen Atoms in [tmiz]$[Ni(dmit)_2]$ (Standard Deviations in Parentheses)[a]

	x/a	y/b	z/c	B_{iso}, Å^2
		Anion		
Ni	0	0	0	2.85 (2)
S(1)	0.1200 (2)	0.1163 (2)	0.1695 (1)	3.70 (3)
S(2)	−0.3087 (2)	0.0263 (2)	0.0891 (1)	3.60 (3)
S(3)	−0.0975 (3)	0.2481 (2)	0.4311 (1)	4.05 (3)
S(4)	−0.4874 (2)	0.1716 (2)	0.3551 (1)	4.15 (3)
S(5)	−0.4616 (2)	0.3285 (2)	0.6188 (1)	5.74 (5)
C(1)	−0.0971 (7)	0.1544 (6)	0.2745 (4)	3.1 (1)
C(2)	−0.2850 (7)	0.1190 (6)	0.2406 (4)	3.0 (1)
C(3)	−0.3553 (8)	0.2538 (7)	0.4766 (4)	3.8 (1)
		Cation		
N(k1)	−0.030 (1)	0.551 (1)	0.092 (1)	3.9 (3)
N(k2)	−0.067 (1)	0.423 (1)	−0.106 (1)	4.3 (3)
C(k1)	0.056 (1)	0.494 (1)	−0.025 (1)	3.3 (3)
C(k2)	−0.251 (1)	0.455 (1)	−0.035 (1)	5.2 (4)
C(k3)	−0.046 (1)	0.489 (1)	0.085 (1)	6.5 (5)
C(k4)	0.690 (2)	0.638 (4)	0.200 (1)	4.0 (4)
C(k5)	0.284 (1)	0.502 (2)	−0.056 (1)	5.0 (4)
C(k6)	−0.015 (2)	0.358 (4)	−0.240 (1)	4.6 (4)

[a] $B_{iso} = (8/3)\pi^2 Tr(U)$.

Single-Crystal X-ray Analysis. A single crystal with approximate dimensions 0.1 × 0.1 × 0.01 mm^3 was mounted on a CAD-4 diffractometer, and X-ray intensities (Mo Kα, T = 300 K) were collected. Intensities were not corrected for absorption or extinction effects (μ = 18.9 cm^{-1}). Atomic scattering factors were taken from ref 6. The structure was solved from the Ni positions obtained from a Patterson synthesis map; automatic Fourier methods using the program AUTOFOUR[7] and difference Fourier maps were used to locate the disordered cation. Positions of hydrogen atoms were located from difference Fourier maps except for the hydrogen atoms of the C(k4) and C(k6) methyl groups (see Figure 2), which were calculated. Full-matrix least-squares refinement in space group $P\bar{1}$ (177 variables, anisotropic thermal param-

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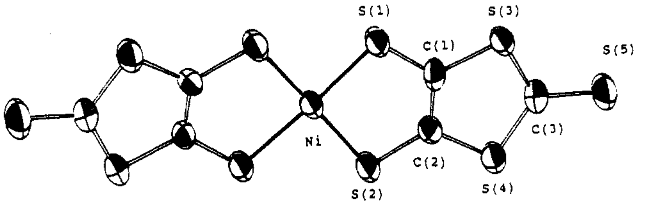

Figure 1. Ni(dmit)$_2$ unit and atomic labeling system.

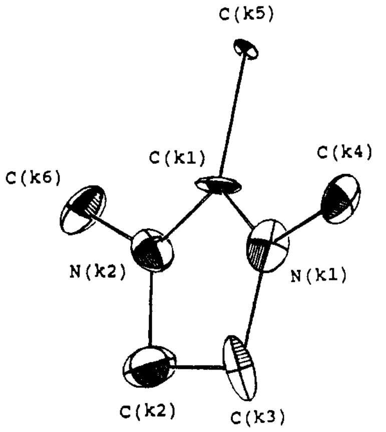

Figure 2. Cation and atomic labeling system.

Table III. Intramolecular Distances and Angles of Anion (Standard Deviations in Parentheses)

	Distances (Å)		
Ni–S(1)	2.166 (1)	Ni–S(2)	2.159 (1)
S(1)–C(1)	1.705 (4)	S(2)–C(2)	1.721 (1)
S(3)–C(1)	1.745 (4)	S(3)–C(3)	1.733 (5)
S(4)–C(2)	1.721 (1)	S(4)–C(3)	1.733 (5)
S(5)–C(3)	1.632 (5)	C(1)–C(2)	1.378 (4)
	Angles (deg)		
S(1)–Ni–S(2)	93.10 (4)	Ni–S(1)–C(1)	102.2 (1)
Ni–S(2)–C(2)	102.81 (5)	S(1)–C(1)–S(3)	123.4 (2)
C(1)–S(3)–C(3)	123.00 (5)	C(1)–S(3)–C(3)	98.0 (2)
C(2)–S(4)–C(3)	97.6 (2)	S(3)–C(3)–S(4)	112.8 (2)
S(3)–C(3)–S(5)	123.4 (3)	S(4)–C(3)–S(5)	123.8 (3)

eters for all non-hydrogen atoms) converged to $R = 0.0374$ and $R_w = 0.0476$ for 1402 independent significant reflections. During the first refinement stages constraints with low weights according to the method of Waser[8] for all distances and several angles of the cation were necessary, because of static disorder. Refinement of the structure in space group $P1$ did not lead to a better model. Crystallographic parameters and atomic fractional coordinates and thermal parameters for non-hydrogen atoms are given in Table I and II, respectively.

Results and Discussion

A. Description of the Structure of [tmiz][Ni(dmit)$_2$]. A projection of the anionic unit is shown in Figure 1, together with the atomic labeling system used. An overview of some relevant intramolecular distances and angles is given in Table III. The observed bond lengths are all of magnitudes similar to those observed for other compounds of general formula [Cat][Ni(dmit)$_2$], though the mean Ni–S distance (2.163 Å) is somewhat larger than in most other compounds. For comparison, the Ni–S distances observed for Cat = NR$_4$, R = Me, Et, Pr, and Bu, are 2.158,[9] 2.157,[10], 2.160,[9] and 2.156[11] Å. This is probably indicative of a more negatively charged anion. The Ni(dmit)$_2^-$ unit is almost completely planar, as is shown by a calculation of the distances of the atoms to a plane through Ni, S(1), and S(2). Only the outer sulfur atom S(5) and the ring atom S(3) have a significant deviation from this plane (0.070 Å compared to 0.082 Å). In Figure 2 the atomic labeling system used for the cation on $(0,{}^1/_2,0)$ is depicted. Only one of the two positions occupied by the cation in the crystal structure is shown for reasons of clarity. These two modes of occupation are of equal weight, confirming the space group used in the refinement. No satellite reflections were observed, ruling out the possibility of a supercell with the cation ordered.

Table IV. Selected Bond Lengths and Angles of the tmiz Ion[a]

	Distances (Å)		
C(k1)–N(k1)	1.327 (1)	C(k1)–N(k2)	1.320 (2)
C(k1)–C(k5)	1.487 (1)	N(k1)–C(k3)	1.382 (1)
N(k1)–C(k4)	1.459 (1)	C(k2)–C(k3)	1.339 (1)
N(k2)–C(k2)	1.384 (2)	N(k2)–C(k6)	1.460 (2)
	Angles (deg)		
C(k1)–N(k1)–C(k3)	100.6 (2)	N(k1)–C(k3)–C(k2)	108.3 (2)
C(k3)–C(k2)–N(k2)	108.4 (2)	C(k2)–N(k2)–C(k1)	100.7 (2)
N(k2)–C(k1)–N(k1)	117.8 (2)	C(k1)–N(k1)–C(k4)	129.9 (2)
N(k1)–C(k1)–C(k5)	119.0 (3)	C(k1)–N(k2)–C(k6)	130.4 (3)

[a] Distances and angles were refined with Waser constraints; a maximum deviation of 10% from the constrained value was allowed.

Table V. Intermolecular Contacts between Anions (Å) (Standard Deviations in Parentheses)[a]

S(3)–S(3′)	3.592 (2)	C(3)–C(3‴)	3.636 (8)
S(2)–S(2″)	3.700 (2)	S(5)–C(2‴)	3.691 (2)

[a] Symmetry operations involved: prime, $-x$, $1 - y$, $1 - z$; double prime, $-1 - x$, $-y$, $-z$; triple prime, $-1 - x$, $-y$, $1 - z$.

Table VI. Short Distances between the tmiz$^+$ and Ni(dmit)$_2^-$ Units (Å) (Standard Deviations in Parentheses)[a]

C(k3)–S(2)	3.49 (1)	C(k1)–S(2)	3.66 (1)
C(k1)–S(2′)	3.52 (1)	C(k3)–S(5″)	3.66 (1)
N(k1)–S(2)	3.64 (1)	C(k2)–S(2‴)	3.61 (1)

[a] Symmetry operations involved: prime, $-x$, $1 - y$, $-z$; double prime, $-1 - x$, $1 - y$, $1 - z$; triple prime, $-1 - x$, $-y$, $-z$.

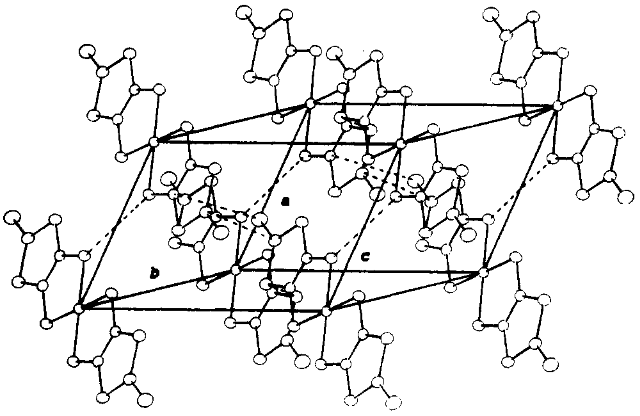

Figure 3. Overview of the unit cell, showing all important contacts between anionic units.

Table IV contains relevant bond distances and angles. As can be seen from the bond lengths C(k1)–N(k1) and C(k1)–N(k2), the positive charge is delocalized on the two nitrogen atoms, as expected. This is also reflected in the observation of equal bond lengths N(k1)–C(k4) and N(k2)–C(k6). A least-squares-plane calculation through the ring system of the cation indicates that the molecule is essentially planar, with the methyl groups lying also in the plane.

Figure 3 depicts a view of the unit cell, omitting all cations for clarity. Several important features of the structure emerge from this drawing. First of all, a number of contacts between different anionic units exists, all of them giving rise to possible overlap of the molecular orbitals. In Table V these intermolecular contacts have been tabulated.

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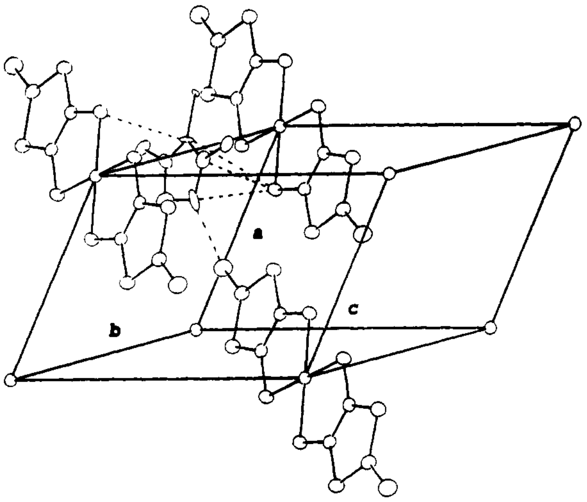

Figure 4. Contacts between the cation and the anion.

Secondly, the symmetry of the space group $P\bar{1}$ forces these contacts to be regular in space, so there is no dimerization of the Ni(dmit)$_2^-$ units, though some very short intermolecular contacts occur.

Figure 4 shows the position of the tmiz$^+$ unit in the unit cell; the static disorder in the position of the cation is not shown. There are also some short distances between the tmiz$^+$ ion and the anionic unit (Table VI); furthermore, the angle between the least-squares planes through the cation and the anion is only 5.2°, which shows that both molecules are nearly parallel to one another.

Clearly, these short distances, combined with the nearly parallel orientation of the two molecular units, will result in considerable overlap of the electronic systems of both ions.

B. Electrical Conductivity. In the temperature range 80–300 K the dc conductivity of [tmiz][Ni(dmit)$_2$] in the plane of the crystals is expressed by the relation expected for a semiconductor:

$$\sigma = \sigma_0 e^{-E_a/kT}$$

where σ_0 is the infinite-temperature conductivity and E_a an activation energy. A least-squares fit of the experimental data to this formula gave as best parameter values $\sigma_0 = 4.1$ S/cm and $E_a = 0.11$ eV. The room-temperature conductivity is 0.21 S/cm.

This room-temperature conductivity is very high when compared to that of other compounds of the general formula [Cat][Ni(dmit)$_2$]. For Cat = NR$_4$, R = Me, Et, Pr, and Bu, the conductivities are all in the range 5×10^{-9} to 4×10^{-5} S/cm.[9-11] A possible explanation for this high conductivity and low activation energy is apparently the highly regular character of the contacts between different anionic units; within the experimental error no Peierls distortion is observed. This may be due to the well-known fact of a Peierls distortion in a one-dimensional chain being prohibited by extensions in more dimensions.[12] Indeed, though the strongest interaction is observed in one direction via the 3.59-Å S–S contacts, Table V shows that there are also short contacts between Ni(dmit)$_2^-$ units in other directions.

The role of the cation in the conduction mechanism is not clear. The planar character of the cation stimulates face-to-face stacking of all molecules, enabling the formation of S–S contacts. In order to obtain some insight in the role of the methyl groups of the cation, the 1,2,3-trimethylimidazolium cation was replaced by 1,3-dimethylimidazolium cation. Black crystals were obtained of the same shape, with a similar room-temperature conductivity of 0.23 S/cm and an activation energy of 0.11 eV. Apparently, no drastic changes occur on the replacement.

With regards to the influence of the electronic system, it seems reasonable to assume a fairly strong interaction between anionic and cationic molecules. Band-structure calculations will be performed to gain information on this aspect.[13]

The results on the conducting properties of this sample are in contrast with results of conductivity measurements on an isomeric compound, prepared by autoxidation. The conductivity of this green, microcrystaline compound is about 6×10^{-5} S/cm. This difference in conductivity is probably caused by differences in the crystal structures, not permitting regular molecular overlap. This is for example found in the compound [Et$_4$N][Ni(dmit)$_2$], where the anionic units are dimerized.[14] Unfortunately, no single crystals of this isomer have been obtained so far. The difference in crystal structure with respect to the electrooxidized compound, however, has been confirmed by powder diffraction analysis.

The difference in electrical conductivity is also reflected in the optical spectra of both compounds; while the black compound has no sharp defined peaks in its IR spectrum and an extremely broad absorption in the near-IR–vis region, the green one has all the absorptions that are characteristic of the singly oxidized Ni(dmit)$_2^-$ species in both IR and near-IR–vis spectra.[5] Furthermore, whereas the black compound has a very broad absorption of low intensity in its EPR spectrum ($g = 2$), the green isomer has a relatively small peak with high intensity ($g = 2.1$).

Concluding Remarks

[tmiz][Ni(dmit)$_2$] is the first compound known so far of the family [Cat][Ni(dmit)$_2$] showing a highly regular ordered assembly of Ni(dmit)$_2^-$ units. This property is reflected in a very high room-temperature conductivity of 0.21 S/cm.

A possible explanation for this feature is given in terms of short intermolecular contacts between Ni(dmit)$_2^-$ units in different directions, creating a quasi-three-dimensional network and an as yet unknown interaction via the electronic system of the cation.

Finally, a different modification of [tmiz][Ni(dmit)$_2$] can be obtained by autoxidation, which does show the characteristic features of all other known compounds of the previously mentioned family, i.e. low conductivity and a green color. This illustrates the phase selectivity of the electrocrystallization technique.

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Supplementary Material Available: Tables of crystallographic details, anisotropic thermal parameters, hydrogen positions and thermal parameters, bond distances and angles involving hydrogen atoms, and equations of least-squares planes and deviations (5 pages); a table of calculated and observed structure factors (6 pages). Ordering information is given on any current masthead page.

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