Inorg. Chem. **1992**, *31*, 2241–2248 **2241**

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Two Ni(dmit)$_2$ Compounds with a Divalent Closed-Shell Cation: Synthesis, Crystal Structure, and Electrical Conductivity of $[Me_3N(CH_2)_4NMe_3][Ni(dmit)_2]_5\cdot 2dmf$ and $[Me_3N(CH_2)_4NMe_3][Ni(dmit_2]_5\cdot 2CH_3CN$

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Received October 23, 1991

Electrochemical oxidation of a solution of $[Me_3N(CH_2)_4NMe_3][Ni(dmit)_2]_2$($[Me_3N(CH_2)_4NMe_3]^{2+} = C_{10}N_2H_{26}^{2+}$ = 2,2,7,7-tetramethyl-2,7-diazoniaoctane, dmit^{2-} = $C_3S_5^{2-}$ = 4,5-dimercapto-1,3-dithiole-2-thionato) yields either crystals with stoichiometry $[Me_3N(CH_2)_4NMe_3][Ni(dmit)_2]_5\cdot 2dmf$ (**1**), or crystals with formula $[Me_3N(CH_2)_4NMe_3][Ni(dmit)_2]_5\cdot 2CH_3CN$ (**2**), depending on the exact oxidation conditions. Single-crystal X-ray measurements were carried out for both compounds. Compound **1** crystallizes in triclinic space group $P\bar{1}$, with a = 11.020 (2) Å, b = 11.320 (3) Å, c = 19.900 (4) Å, α = 93.50 (2)°, β = 104.96 (2)°, γ = 110.01 (2)°, V = 2222.8 (9) Å^3, and Z = 1 for $Ni_5N_4C_{46}S_{50}H_{40}O_2$. Compound **2** crystallizes in triclinic space group $P1$, with a = 12.939 (3) Å, b = 20.379 (8) Å, c = 8.807 (2) Å, α = 102.07 (3)°, β = 103.17 (2)°, γ = 74.04 (2)°, V = 2147.1 (12) Å^3, and Z = 1 for $Ni_5N_4C_{44}S_{50}H_{32}$. Heavy-atom techniques were used and both structures were refined by least-squares methods to a residual R_w value of 0.0454 for 5461 reflections (**1**) and an R_w value of 0.037 for 3586 reflections (**2**). In both compounds several of the Ni(dmit)$_2$ units show considerable deviation from planarity. The packing motif of the acceptor molecules is essentially similar in **1** and **2**. Stacks of Ni(dmit)$_2$ monomers, dimers, and trimers form conduction sheets which are separated from each other by the dications and the solvent molecules. Short intermolecular S···S contacts build a two-dimensional network in the lattice of **1** and **2**. Conductivity measurements indicate a room temperature value of 0.1–1 S cm^{-1}. Both compounds behave as *semi*conductors with E_a = 0.2 eV, as evident from conductivity analyses made at lower temperature.

Introduction

The combination of the well-known M(dmit)$_2$ acceptor molecule (where dmit^{2-} = $C_3S_5^{2-}$ = 4,5-dimercapto-1,3-dithiole-2-thionato) with various closed-shell cations (or "spectator" cations) has so far resulted in one Ni(dmit)$_2$ salt which was able to show superconductivity: $[Me_4N][Ni(dmit)_2]_2$.[2] In this compound the stacking mode of the Ni(dmit)$_2$ units is very favorable for obtaining a maximum number of intermolecular S···S orbital overlaps, which are known to be responsible for the high conductivity.[3] Very recently, it has been claimed that also β-$[Me_4N][Pd(dmit)_2]_2$ goes into a superconducting state at 6.2 K under 6.5 kbar.[7]

Starting from these successful complexes, one can synthesize new compounds of the general formula $[cat]_x[M(L)_2]$ by either varying the cations or the anions. The latter means a change in the metal atom or in the ligand system. The former has been investigated preferentially over the past few years.[4–12]

Up until now, only monovalent closed-shell cations have been used, although Sakamoto et al.[13] and Nüsslein et al.[14] reported a series of Ni(dmit)$_2$ salts with divalent pyrazinium cations and doubly alkylated viologen systems, respectively. However, these dications should be classified as oxidants rather than closed-shell cations, as is proven by the charge transfer which occurs upon mixing solutions of $[Ni(dmit)_2]^-$ and of such dications. In this paper we report on two Ni(dmit)$_2$ complexes with the first truly "spectator" dication, namely $C_{10}N_2H_{26}^{2+}$ = 2,2,7,7-tetramethyl-2,7-diazoniaoctane (Figure 1). The choice to use this particular dication for making new Ni(dmit)$_2$ salts was based on the following idea:

In the crystal structure of $[Me_4N][Ni(dmit)_2]_2$ the slightly dimerized Ni(dmit)$_2$ units stack along two directions, [110] and [1$\bar{1}$0].[3] The tetramethylammonium cations are located in between stacks of Ni(dmit)$_2$ molecules. The separation between the nitrogen atoms along [110] is 7.65 Å. A dication best suited for mimicking the packing motif found in $[Me_4N][Ni(dmit)_2]_2$ would logically have to consist of two chemically separated tetramethylammonium-type monocations. By connecting two of these cations to each other, and at the same time keeping the nitrogens at a distance of approximately 7.65 Å, e.g. by means of a saturated carbon chain of the appropriate length, one would obtain a divalent cation with the positive charges isolated from one another by an electronically inert spacer. If such an alkylene bridge would be chosen as a spacer, a chain length between four and five carbons would bring the nitrogen atoms at a distance close to the desired value of 7.65 Å. Combination of this dication with Ni(dmit)$_2$ might yield a molecular lattice in which the packing of the anions would be similar to the one found in $[Me_4N][Ni(dmit)_2]_2$, with the positive centers placed at a regular distance close to 7.65 Å from each other. The result of this study is described below.

Experimental Section

Synthesis of 2,2,7,7-Tetramethyl-2,7-diazoniaoctane Dibromide. The synthesis was carried out at −20 °C. A solution of 0.5 mol of trimethylamine in 250 mL of ethanol was slowly added to a solution of 0.24 mol of 1,4-dibromobutane in 250 mL of ethanol. The desired white product precipitated upon standing at −20 °C overnight and was recrystallized from ethanol. The elementary analyses were in agreement with formula $C_{10}N_2H_{26}Br_2$.[15] Yield: 75%.

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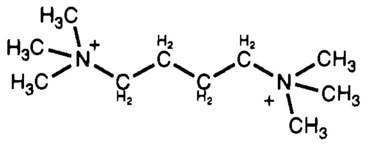

Figure 1. 2,2,7,7-Tetramethyl-2,7-diazoniaoctane dication.

Table I. Crystallographic Data for **1** and **2**

	1	**2**
empirical formula	$C_{46}H_{40}N_4Ni_5O_2S_{50}$	$C_{44}H_{32}N_4Ni_5S_{50}$
formula weight	2577.35	2513.21
space group	$P\bar{1}$ (No. 2)	$P1$ (No. 1)
a, Å	11.020 (2)	12.939 (3)
b, Å	11.320 (3)	20.379 (8)
c, Å	19.900 (4)	8.807 (2)
α, deg	93.50 (2)	102.07 (3)
β, deg	104.96 (2)	103.17 (2)
γ, deg	110.01 (2)	74.04 (2)
V, Å^3	2222.8 (9)	2147.3 (12)
Z	1	1
ρ(obs), g cm^{-3}	1.97	1.96
ρ(calc), g cm^{-3}	1.925	1.943
μ(Mo Kα), cm^{-1}	22.2	22.9
T, K	295	295
λ(Mo Kα), Å	0.710 69	0.710 69
R^a	0.0385	0.0367
$R_w{}^b$	0.0454	0.0370

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

Synthesis of $[Me_3N(CH_2)_4NMe_3][Ni(dmit)_2]_2$. The synthesis of $[Me_3N(CH_2)_4NMe_3][Ni(dmit)_2]_2$ is based on the large difference in solubility of the $[Bu_4N][Ni(dmit)_2]$ salt and the $[Me_3N(CH_2)_4NMe_3][Ni(dmit)_2]_2$ salt in acetonitrile, which enables a complete metathesis between the monovalent cations and the dications.

A solution of 2.6 mmol of 2,2,7,7-tetramethyl-2,7-diazoniaoctane dibromide in 50 mL of methanol was dropwise added to a solution of 5 mmol of $[Bu_4N][Ni(dmit)_2]$[16] in 500 mL of acetonitrile. Immediately, fine, black needles started to precipitate. The crystals were filtered, washed with methanol, and dried. The compound analyzed as $Ni_2C_{22}N_2H_{26}S_{20}$ and was used without further purification. Yield: 91%.

Synthesis of $[Me_3N(CH_2)_4NMe_3][Ni(dmit)_2]_5 \cdot 2dmf$ (1) and $[Me_3N(CH_2)_4NMe_3][Ni(dmit)_2]_5 \cdot 2CH_3CN$ (2). Method 1. A saturated solution of $[Me_3N(CH_2)_4NMe_3][Ni(dmit)_2]_2$ in a mixture of 25 mL of dry acetonitrile and 5 mL of dmf was poured into an H-tube equipped with a fine-porosity frit. No extra electrolyte was used. Two platinum wires (0.3 mm diameter) were put in the olive green solution and a constant current of approximately 1 μA was applied. Black, chunky crystals could be isolated from the anode after 4 days.

Method 2. The same procedure as described above was used for the synthesis of **2** but this time thicker electrodes (1 mm diameter) were put in the solution. Shiny, thick black plates were obtained after 5 days of electrooxidation.

X-ray Data Collection and Refinement

$[Me_3N(CH_2)_4NMe_3][Ni(dmit)_2]_5 \cdot 2dmf$ (1). A black, bar-shaped crystal of approximate dimensions 0.2 × 0.2 × 0.5 mm^3 was selected for the X-ray analysis and mounted on an Enraf-Nonius CAD-4 diffractometer. Crystal data and data collection parameters are presented in Table I. Data were collected at room temperature using graphite-monochromated Mo Kα (λ = 0.710 73 Å) radiation and have been corrected for Lorentz and polarization effects. Intensity data were collected by the $\omega/2\theta$ scan technique in the θ range 2–30°; h = −15 to 15, k = −15 to 15, l = 0–28. The transmission factors ranged from 75.71 to 112.58. Absorption correction (μ = 22.2 cm^{-1}) was applied using empirical methods (DIFABS).[17] Atomic scattering factors were taken from ref 18. The 5461 reflections with $I > 2.5\sigma(I)$ from a total of 12 901 were considered to be observed and used for the structure solution and refinement. The structure of **1** was solved according to the direct (SHELXS86)[19] method. Subsequent block-diagonal and full-matrix least-squares refinement and interpretation of difference Fourier maps using SHELX76[20] enabled all the non-hydrogen atoms to be located; they were refined anisotropically in space group $P\bar{1}$. The positions of the hydrogen atoms were fixed using the rigid group model. The hydrogens were refined isotropically with one overall temperature factor. R_{int} proved to be 0.0405. The final R value was 0.0385 and R_w = 0.0454 for $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ and $w = 1/(\sigma^2(F) + 0.000484F^2)$. Atomic fractional coordinates and thermal parameters for the non-hydrogen atoms are given in Table II.

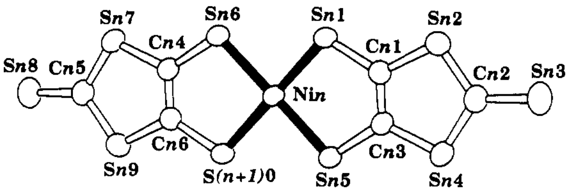

Figure 2. General labeling scheme for the $Ni(dmit)_2$ units in **1** ($1 \leq n \leq 3$) and **2** ($1 \leq n \leq 5$).

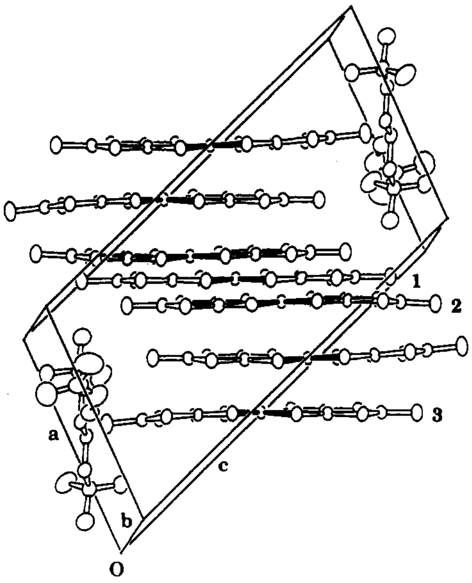

Figure 3. Unit-cell contents of structure **1** with the numbering of the crystallographically independent $Ni(dmit)_2$ molecules.

$[Me_3N(CH_2)_4NMe_3][Ni(dmit)_2]_5 \cdot 2CH_3CN$ (2). A black, platelet-shaped crystal of approximate dimensions 0.3 × 0.4 × 0.1 mm^3 was selected for the X-ray analysis and mounted on an Enraf-Nonius CAD-4 diffractometer. Diffraction data were collected, using graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation and have been corrected for Lorentz and polarization effects. Relevant crystallographic data are summarized in Table I. Intensity data were collected by the $\omega/2\theta$ scan technique in the θ range 2–22°; h = −13 to 13, k = −21 to 21, l = 0–9. The transmission factors ranged from 100.00 to 62.60. Absorption correction (μ = 22.9 cm^{-1}) was applied by using empirical methods (DIFABS).[17] The 3586 independent reflections having $I > 2.5\sigma(I)$ from a total of 4974 reflections were considered to be observed and were used in the structure analysis. No equivalent reflections were measured. The structure was solved by using conventional direct methods (SHELXS86).[19] The atomic scattering factors were taken from literature.[18] All non-hydrogen atoms were located from successive difference Fourier maps. The sulfur and nickel atoms were refined with anisotropic temperature factors.

During the refinement process it was found that none of the nickel atoms could be placed at an inversion center, meaning that the structure had to be refined in the space group $P1$ rather than $P\bar{1}$. Nonetheless, a *pseudo*-inversion center seems to be present in the unit cell of **2**, as is indicated by the high number of matrix elements having a correlation greater than 0.5 with each other. Apparently, four out of five $Ni(dmit)_2$ units behave as if they are centrosymmetrically related, with only the fifth anion (namely $Ni(5)(dmit)_2$, see Figure 4) lowering the symmetry to space group $P1$. The positions of the hydrogen atoms were fixed using the rigid group model and were refined with one overall temperature factor. The function minimized was $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. The final values of discrepancy indices, R and R_w, were 0.0367 and

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Table II. Final Coordinates and Equivalent Isotropic Thermal Parameters of the Non-Hydrogen Atoms for $[Me_3N(CH_2)_4NMe_3][Ni(dmit)_2]_5 \cdot 2dmf$ (**1**)

atom	x	y	z	U_{eq},[a] Å^2
Ni(1)	1	$^1/_2$	$^1/_2$	0.0297 (2)
S(11)	0.91510 (10)	0.59820 (10)	0.42330 (10)	0.0361 (4)
S(12)	0.69960 (10)	0.50190 (10)	0.28300 (10)	0.0412 (4)
S(13)	0.50570 (10)	0.2963 (2)	0.16560 (10)	0.0570 (5)
S(14)	0.67170 (10)	0.23910 (10)	0.29270 (10)	0.0430 (4)
S(15)	0.87890 (10)	0.31630 (10)	0.43630 (10)	0.0367 (4)
C(11)	0.8031 (4)	0.4787 (4)	0.3582 (2)	0.0320 (12)
C(12)	0.6200 (5)	0.3437 (5)	0.2431 (2)	0.0407 (14)
C(13)	0.7881 (4)	0.3524 (4)	0.3638 (2)	0.0335 (12)
Ni(2)	0.24070 (10)	0.11630 (10)	0.52740 (10)	0.0294 (2)
S(21)	0.32230 (10)	0.01600 (10)	0.60430 (10)	0.0358 (4)
S(22)	0.53780 (10)	0.11150 (10)	0.74560 (10)	0.0377 (4)
S(23)	0.74910 (10)	0.31600 (10)	0.85770 (10)	0.0591 (5)
S(24)	0.57200 (10)	0.37450 (10)	0.73530 (10)	0.0416 (4)
S(25)	0.35950 (10)	0.30020 (10)	0.59270 (10)	0.0360 (4)
S(26)	0.12130 (10)	−0.06770 (10)	0.46290 (10)	0.0370 (4)
S(27)	−0.08470 (10)	−0.14510 (10)	0.31870 (10)	0.0412 (4)
S(28)	−0.24800 (10)	−0.0905 (2)	0.18970 (10)	0.0588 (5)
S(29)	−0.04950 (10)	0.11750 (10)	0.30560 (10)	0.0406 (4)
S(30)	0.15940 (10)	0.21510 (10)	0.44890 (10)	0.0367 (4)
C(21)	0.4349 (4)	0.1361 (4)	0.6699 (2)	0.0317 (12)
C(22)	0.6244 (4)	0.2697 (4)	0.7831 (2)	0.0387 (14)
C(23)	0.4520 (4)	0.2617 (4)	0.6651 (2)	0.0334 (12)
C(24)	0.0315 (4)	−0.0313 (4)	0.3894 (2)	0.0342 (12)
C(25)	−0.1328 (5)	−0.0412 (5)	0.2671 (2)	0.0393 (14)
C(26)	0.0500 (4)	0.0939 (4)	0.3829 (2)	0.0342 (12)
Ni(3)	0.50490 (10)	0.26090 (10)	0.4396 (10)	0.0297 (2)
S(31)	0.42120 (10)	0.36430 (10)	0.36500 (10)	0.0369 (4)
S(32)	0.21760 (10)	0.27570 (10)	0.21980 (10)	0.0403 (4)
S(33)	0.0426 (2)	0.08090 (10)	0.09350 (10)	0.0628 (5)
S(34)	0.19020 (10)	0.01300 (10)	0.22350 (10)	0.0435 (4)
S(35)	0.38700 (10)	0.07850 (10)	0.37130 (10)	0.0362 (4)
S(36)	0.62930 (10)	0.44500 (10)	0.50230 (10)	0.0358 (3)
S(37)	0.84160 (10)	0.52500 (10)	0.64400 (10)	0.0384 (3)
S(38)	1.00870 (10)	0.4743 (2)	0.77200 (10)	0.0608 (5)
S(39)	0.80490 (10)	0.26270 (10)	0.65950 (10)	0.0407 (4)
S(40)	0.58870 (10)	0.16300 (10)	0.51800 (10)	0.0365 (4)
C(31)	0.3138 (4)	0.2461 (4)	0.2966 (2)	0.0318 (12)
C(32)	0.1449 (4)	0.1205 (4)	0.1745 (2)	0.0387 (14)
C(33)	0.2993 (4)	0.1208 (4)	0.2987 (2)	0.0333 (12)
C(34)	0.7212 (4)	0.4100 (4)	0.5753 (2)	0.0310 (12)
C(35)	0.8905 (4)	0.4221 (5)	0.6956 (2)	0.0380 (14)
C(36)	0.7025 (4)	0.2850 (4)	0.5819 (2)	0.0301 (12)
N(1)	0.7911 (4)	0.6116 (4)	0.0385 (2)	0.0446 (12)
C(41)	0.8631 (5)	0.5189 (5)	0.0373 (3)	0.0436 (17)
C(42)	0.9675 (5)	0.5547 (4)	−0.0028 (3)	0.0436 (16)
C(43)	0.6981 (6)	0.5672 (6)	0.0833 (3)	0.0634 (19)
C(44)	0.7062 (6)	0.6084 (6)	−0.0339 (3)	0.0712 (19)
C(45)	0.8904 (6)	0.7426 (5)	0.0717 (3)	0.073 (2)
O(1)	0.3209 (7)	0.9628 (7)	0.0412 (4)	0.179 (3)
N(2)	0.4475 (6)	0.8136 (7)	0.0377 (4)	0.109 (2)
C(46)	0.3571 (5)	0.8668 (5)	0.0044 (3)	0.0468 (17)
C(47)	0.2829 (8)	0.8175 (7)	−0.0718 (4)	0.101 (3)
C(48)	0.4760 (5)	0.7348 (5)	0.0123 (3)	0.0463 (17)

[a] U_{eq} = $^1/_3$ of the trace of the orthogonalized U.

0.0372, respectively, with $w = 1/(\sigma^2(F) + 0.000318F^2)$. Refined positional parameters for the non-hydrogen atoms are presented in Table III.

Results and Discussion

Description of the X-ray Structures of 1 and 2. Tables IV and V list all relevant bond distances and bond angles for compounds **1** and **2**. One Ni(dmit)$_2$ molecule with the general labeling scheme used for all the crystallographically independent anions of both compounds is shown in Figure 2.

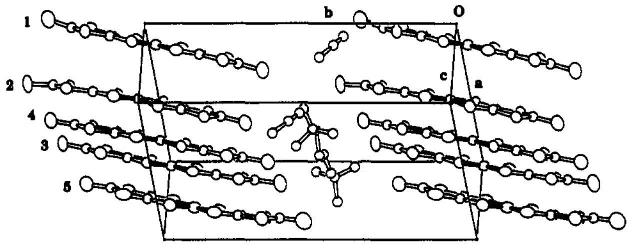

Figure 4. Unit-cell contents of structure **2** with the numbering of the crystallographically independent Ni(dmit)$_2$ molecules.

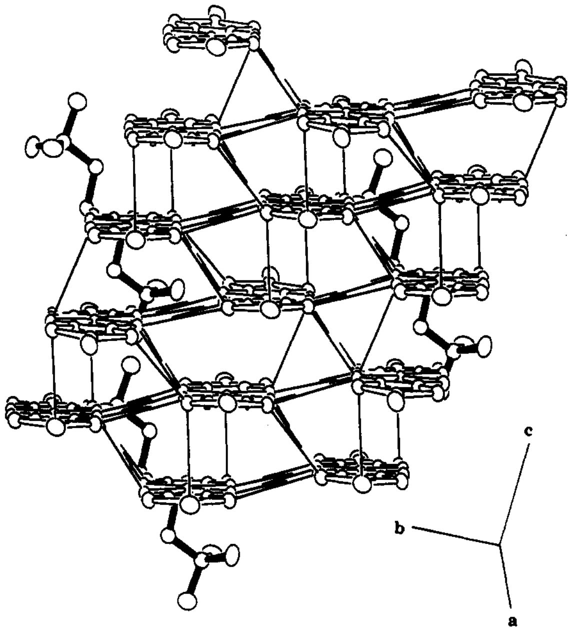

Figure 5. Layer of Ni(dmit)$_2$ molecules in **1**. For clarity solvent molecules have been omitted. Single black lines represent short S···S contacts.

In Figure 3 and 4 the unit-cell contents of the structures of **1** and **2** are depicted. Several of the Ni(dmit)$_2$ units show a more or less considerable deviation from planarity. The normally square-planar NiS$_4$ coordination geometry is twisted to a more tetrahedral configuration, and the thionyl groups in some of the dmit ligands show significant puckering. In compound **1**, S23 possesses the largest out-of-plane distortion (0.064 (13) Å with respect to the mean plane through S21, C21, S22, C22, S23, S24, C23, S25). The largest tetrahedral twist occurs between the dmit ligands around Ni3, namely 6.42 (10)°. For compound **2**, these values are 0.07 (2) Å (out-of-plane distance for S28 with respect to the mean plane through S26, C24, S27, C25, S28, S29, C26, S30) and 7.1 (2)° (angle between the dmit groups around Ni5).

The tendency to adopt a V-shaped distortion has been found to be quite common in the literature for Pd(dmit)$_2$ and Pt(dmit)$_2$ compounds.[7,21] However, in these structures the anions form dimers through relatively strong metal–metal interaction. Such a metal–metal bond is clearly not present in **1** and **2**; therefore in these cases the large distortion must originate from steric or electronic effects. Other salts in which the acceptor molecules show a more or less similar deviation from planarity are $[Bu_4N][Ni(dmit)_2]$,[22] $[Et_4N][Ni(dmit)_2]$,[23] $[Ph_4As][Ni(dmid)_2]$[24] (dmid^{2-} = $C_3S_4O^{2-}$ = 1,3-dithiole-2-one-4,5-dithiolate), and $[MeQ][Ni(dmit)_2]$.[25] Two recently prepared Ni(dmit)$_2$ compounds are $[HNMe_3]_2[Ni(dmit)_2]_5 \cdot 2CH_3CN$[26] and its isostructural $[H_3NMe]_2[Ni(dmit)_2]_5 \cdot 2CH_3CN$ which have a stoichiometry identical to the title compounds.[27] Not only does the lattice of

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Table III. Relevant Bond Distances (Å) and Angles (deg) for $[Me_3N(CH_2)_4NMe_3][Ni(dmit)_2]_5 \cdot 2dmf$ (**1**)

Ni(1)–S(11)	2.1500 (16)	Ni(2)–S(30)	2.1611 (18)	S(29)–C(26)	1.738 (4)	S(32)–C(32)	1.735 (4)
Ni(1)–S(15)	2.1489 (15)	S(21)–C(21)	1.698 (4)	S(30)–C(26)	1.700 (4)	S(33)–C(32)	1.643 (4)
S(11)–C(11)	1.688 (4)	S(22)–C(21)	1.737 (4)	C(21)–C(23)	1.382 (6)	S(34)–C(32)	1.729 (4)
S(12)–C(11)	1.727 (4)	S(22)–C(22)	1.725 (4)	C(24)–C(26)	1.380 (6)	S(34)–C(33)	1.737 (4)
S(12)–C(12)	1.732 (5)	S(23)–C(22)	1.651 (4)	C(31)–C(33)	1.376 (6)	S(35)–C(33)	1.712 (4)
S(13)–C(12)	1.639 (5)	S(24)–C(22)	1.723 (5)	C(34)–C(36)	1.378 (6)	S(36)–C(34)	1.697 (4)
S(14)–C(12)	1.736 (5)	S(24)–C(23)	1.733 (4)	Ni(3)–S(31)	2.1607 (18)	S(37)–C(34)	1.729 (4)
S(14)–C(13)	1.734 (4)	S(25)–C(23)	1.711 (4)	Ni(3)–S(35)	2.1699 (18)	S(37)–C(35)	1.730 (5)
S(15)–C(13)	1.690 (4)	S(26)–C(24)	1.701 (4)	Ni(3)–S(36)	2.1502 (18)	S(38)–C(35)	1.643 (5)
C(11)–C(13)	1.397 (6)	S(27)–C(24)	1.732 (4)	Ni(3)–S(40)	2.1640 (18)	S(39)–C(35)	1.729 (5)
Ni(2)–S(21)	2.1541 (18)	S(27)–C(25)	1.735 (5)	S(31)–C(31)	1.705 (4)	S(39)–C(36)	1.751 (4)
Ni(2)–S(25)	2.1593 (18)	S(28)–C(25)	1.642 (5)	S(32)–C(31)	1.744 (4)	S(40)–C(36)	1.695 (4)
Ni(2)–S(26)	2.1548 (18)	S(29)–C(25)	1.731 (5)				

S(11)–Ni(1)–S(15)	92.80 (6)	S(21)–Ni(2)–S(25)	93.12 (6)	S(27)–C(24)–C(26)	116.1 (3)	C(35)–S(39)–C(36)	96.8 (2)
S(11)–Ni(1)–S(15b)	87.20 (6)	S(21)–Ni(2)–S(26)	86.66 (7)	S(27)–C(25)–S(28)	122.6 (3)	S(31)–C(31)–S(32)	122.6 (3)
Ni(1)–S(11)–C(11)	103.18 (15)	S(21)–Ni(2)–S(30)	179.05 (8)	S(27)–C(25)–S(29)	113.6 (2)	S(31)–C(31)–C(33)	121.5 (3)
Ni(1)–S(15)–C(13)	102.94 (15)	S(25)–Ni(2)–S(26)	179.52 (9)	S(28)–C(25)–S(29)	123.8 (3)	S(32)–C(31)–C(33)	116.0 (3)
S(11)–C(11)–S(12)	123.6 (3)	S(25)–Ni(2)–S(30)	87.53 (7)	S(29)–C(26)–S(30)	123.1 (3)	S(32)–C(32)–S(33)	122.9 (3)
S(11)–C(11)–C(13)	120.3 (3)	S(21)–C(21)–S(22)	123.3 (3)	S(29)–C(26)–C(24)	115.9 (3)	S(32)–C(32)–S(34)	113.2 (2)
C(11)–S(12)–C(12)	97.2 (2)	S(21)–C(21)–S(23)	121.1 (3)	S(30)–C(26)–C(24)	121.0 (3)	S(33)–C(32)–S(34)	123.9 (3)
C(12)–S(14)–C(13)	97.0 (2)	C(21)–S(22)–C(22)	96.9 (2)	S(31)–Ni(3)–S(35)	92.98 (6)	S(34)–C(33)–S(35)	123.6 (3)
S(12)–C(11)–C(13)	116.1 (3)	C(22)–S(24)–C(23)	96.9 (2)	S(31)–Ni(3)–S(36)	85.64 (7)	S(34)–C(33)–C(31)	115.6 (3)
S(12)–C(12)–S(13)	123.2 (3)	S(22)–C(21)–C(23)	115.6 (3)	S(31)–Ni(3)–S(40)	177.50 (8)	S(35)–C(33)–C(31)	120.7 (3)
S(12)–C(12)–S(14)	114.0 (2)	S(22)–C(22)–S(23)	122.5 (3)	S(35)–Ni(3)–S(36)	176.16 (8)	S(36)–C(34)–S(37)	123.2 (3)
S(13)–C(12)–S(14)	122.8 (3)	S(22)–C(22)–S(24)	114.4 (2)	S(35)–Ni(3)–S(40)	89.03 (7)	S(36)–C(34)–C(36)	120.2 (3)
S(14)–C(13)–S(15)	123.6 (3)	S(23)–C(22)–S(24)	123.2 (3)	S(36)–Ni(3)–S(40)	92.45 (6)	S(37)–C(34)–C(36)	116.6 (3)
S(14)–C(13)–C(11)	115.7 (3)	S(24)–C(23)–S(25)	123.1 (3)	Ni(3)–S(31)–C(31)	102.49 (16)	S(37)–C(35)–S(38)	121.9 (3)
S(15)–C(13)–C(11)	120.8 (3)	S(24)–C(23)–C(21)	116.2 (3)	Ni(3)–S(35)–C(33)	102.35 (15)	S(37)–C(35)–S(39)	114.2 (2)
Ni(2)–S(21)–C(21)	102.69 (16)	S(25)–C(23)–C(21)	120.7 (3)	Ni(3)–S(36)–C(34)	103.38 (16)	S(38)–C(35)–S(39)	124.0 (3)
Ni(2)–S(25)–C(23)	102.37 (15)	C(24)–S(27)–C(25)	97.2 (2)	Ni(3)–S(40)–C(36)	102.55 (16)	S(39)–C(36)–S(40)	123.2 (3)
Ni(2)–S(26)–C(24)	102.98 (15)	C(25)–S(29)–C(26)	79.2 (2)	C(31)–S(32)–C(32)	97.3 (2)	S(39)–C(36)–C(34)	115.4 (3)
Ni(2)–S(30)–C(26)	102.69 (16)	S(26)–C(24)–S(27)	123.3 (3)	C(32)–S(34)–C(33)	97.8 (2)	S(40)–C(36)–C(34)	121.4 (3)
S(26)–Ni(2)–S(30)	92.70 (6)	S(26)–C(24)–S(26)	120.6 (3)	C(34)–S(37)–C(35)	97.0 (2)		

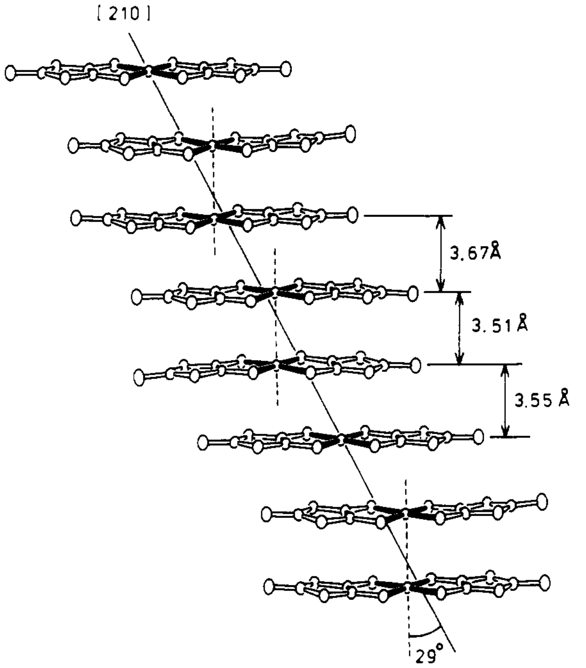

Figure 6. Stacking mode in **1**.

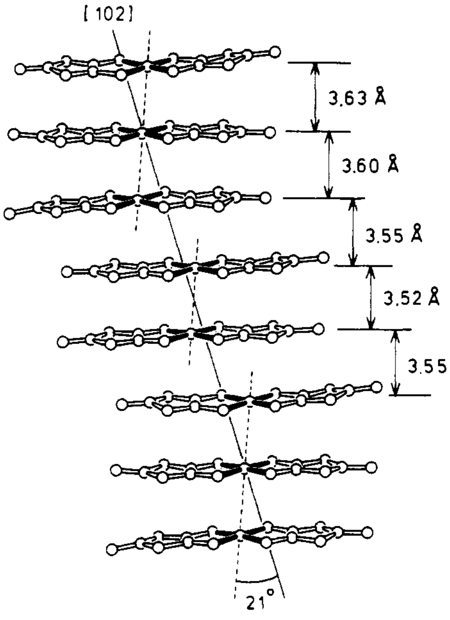

Figure 7. Stacking mode in **2**.

these two salts contain solvent molecules but, more importantly, the degree of oxidation of the anions is exactly the same as that found in **1** and **2**. Furthermore, the crystal structures of $[HNMe_3]_2[Ni(dmit)_2]_5 \cdot 2CH_3CN$ and $[H_3NMe]_2[Ni(dmit)_2]_5 \cdot 2CH_3CN$ show that some of the $Ni(dmit)_2$ molecules possess a similar distortion in their square-planar geometry.

Figure 5 shows the anionic lattice of compound **1**. It is almost identical to the packing mode found in **2**. Acceptor molecules form anionic stacks which lie side-by-side along the *b*-axis (**1**) or the *c*-axis (**2**). In this way, sheets of $Ni(dmit)_2$ units are created, with the dications and the solvent molecules positioned between two sheets. Tables VI and VII list all intermolecular S⋯S contacts shorter than 3.70 Å, the sum of the Van der Waals radii, found in **1** and **2**. It is obvious from Tables VI and VII and Figure 5 that most contacts can be found between neighboring stacks, rather than within the stacks themselves. Therefore, the conductivity will be most prominent in the interstacking direction.

Side views of one of the $Ni(dmit)_2$ columns in **1** and **2** (Figures 6 and 7, respectively) reveal that in compound **1** the stacks can be best described as being built up from monomers and dimers (diads) with the sequence monomer–dimer–dimer–monomer–dimer–dimer ... etc. The same sequence was found previously in

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Table IV. Final Coordinates and Equivalent Isotropic Thermal Parameters of the Non-Hydrogen Atoms for $[Me_3N(CH_2)_4NMe_3][Ni(dmit)_2]_5 \cdot 2CH_3CN$ (**2**)

atom	*x*	*y*	*z*	U_{eq},[a] Å^2
Ni(1)	0.2021 (3)	0.0197 (2)	−0.0847 (5)	0.0326 (4)
S(11)	0.1339 (5)	0.0960 (3)	0.1036 (7)	0.0398 (17)
S(12)	0.1426 (5)	0.2433 (3)	0.2160 (7)	0.0430 (19)
S(13)	0.2170 (6)	0.3682 (4)	0.2115 (9)	0.071 (2)
S(14)	0.2644 (5)	0.2413 (3)	−0.0214 (7)	0.0442 (19)
S(15)	0.2685 (5)	0.0936 (3)	−0.1521 (8)	0.0433 (19)
S(16)	0.1366 (5)	−0.0524 (3)	−0.0126 (7)	0.0384 (17)
S(17)	0.1401 (5)	−0.2032 (3)	−0.1421 (7)	0.0424 (17)
S(18)	0.1894 (7)	−0.3285 (4)	−0.3806 (8)	0.068 (2)
S(19)	0.2586 (5)	−0.2030 (3)	−0.3846 (8)	0.048 (2)
S(20)	0.2702 (5)	−0.0529 (3)	−0.2688 (7)	0.0362 (17)
C(11)	0.1750 (13)	0.1706 (8)	0.0871 (19)	0.034 (4)
C(12)	0.2027 (15)	0.2863 (10)	0.139 (2)	0.045 (4)
C(13)	0.2354 (15)	0.1667 (10)	−0.020 (2)	0.035 (4)
C(14)	0.1772 (14)	−0.1243 (9)	−0.139 (2)	0.027 (4)
C(15)	0.1917 (14)	−0.2512 (10)	−0.306 (2)	0.038 (4)
C(16)	0.2330 (13)	−0.1216 (8)	−0.2576 (17)	0.027 (4)
Ni(2)	0.39700 (10)	−0.04860 (10)	0.2582 (2)	0.0255 (5)
S(21)	0.3385 (2)	0.02550 (10)	0.4531 (3)	0.0355 (10)
S(22)	0.3482 (2)	0.17330 (10)	0.5664 (3)	0.0362 (10)
S(23)	0.4075 (3)	0.3012 (2)	0.5436 (4)	0.0619 (12)
S(24)	0.4613 (2)	0.17300 (10)	0.3175 (3)	0.0356 (10)
S(25)	0.4601 (4)	0.0262 (3)	0.1842 (7)	0.0371 (17)
S(26)	0.3323 (5)	−0.1204 (3)	0.3353 (7)	0.0355 (17)
S(27)	0.3437 (5)	−0.2721 (3)	0.2188 (8)	0.0491 (19)
S(28)	0.4225 (6)	−0.4067 (3)	0.0240 (9)	0.068 (2)
S(29)	0.4685 (5)	−0.2758 (3)	−0.0158 (7)	0.0502 (17)
S(30)	0.4678 (4)	−0.1246 (3)	0.0787 (7)	0.0359 (17)
C(21)	0.3718 (7)	0.0938 (5)	0.4406 (10)	0.024 (2)
C(22)	0.4017 (7)	0.2170 (5)	0.4878 (11)	0.032 (2)
C(23)	0.4297 (7)	0.0967 (5)	0.3209 (11)	0.028 (2)
C(24)	0.3706 (15)	−0.1932 (10)	0.214 (2)	0.031 (4)
C(25)	0.4089 (14)	−0.3222 (10)	0.074 (2)	0.040 (4)
C(26)	0.4349 (12)	−0.1930 (8)	0.0890 (18)	0.038 (4)
Ni(3)	0.6070 (2)	1.0520 (2)	0.7469 (4)	0.0295 (10)
S(31)	0.6712 (5)	0.9792 (3)	0.5618 (7)	0.0419 (17)
S(32)	0.6642 (5)	0.8299 (3)	0.4450 (7)	0.0460 (19)
S(33)	0.6049 (6)	0.7012 (3)	0.4591 (9)	0.062 (2)
S(34)	0.5455 (5)	0.8285 (3)	0.6848 (8)	0.0433 (19)
S(35)	0.5424 (2)	0.97840 (10)	0.8186 (3)	0.0314 (9)
S(36)	0.6737 (2)	1.1236 (2)	0.6733 (3)	0.0415 (10)
S(37)	0.6702 (2)	1.27340 (10)	0.7919 (3)	0.0391 (10)
S(38)	0.5992 (3)	1.4078 (2)	0.9952 (4)	0.0736 (14)
S(39)	0.5442 (2)	1.28010 (10)	1.0314 (3)	0.0453 (10)
S(40)	0.5373 (2)	1.12980 (10)	0.9308 (3)	0.0362 (10)
C(31)	0.6332 (15)	0.9055 (11)	0.575 (2)	0.034 (4)
C(32)	0.6014 (12)	0.7818 (8)	0.5372 (18)	0.034 (4)
C(33)	0.5797 (13)	0.9089 (9)	0.6921 (19)	0.023 (4)
C(34)	0.6356 (7)	1.1998 (5)	0.8124 (11)	0.028 (2)
C(35)	0.5993 (8)	1.3249 (6)	0.9532 (12)	0.044 (3)
C(36)	0.5812 (7)	1.2019 (5)	0.9112 (10)	0.029 (2)
Ni(4)	0.7975 (3)	0.9871 (2)	1.0848 (4)	0.0309 (10)
S(41)	0.8667 (2)	0.9111 (2)	0.9038 (3)	0.0356 (9)
S(42)	0.8589 (2)	0.7603 (2)	0.8045 (3)	0.0444 (10)
S(43)	0.8007 (3)	0.6331 (2)	0.8358 (4)	0.0642 (12)
S(44)	0.7364 (2)	0.7656 (2)	1.0410 (4)	0.0456 (11)
S(45)	0.7305 (2)	0.91650 (10)	1.1612 (3)	0.0326 (9)
S(46)	0.8631 (2)	1.0614 (2)	1.0184 (3)	0.0456 (11)
S(47)	0.8607 (5)	1.2092 (3)	1.1499 (7)	0.0434 (19)
S(48)	0.7954 (6)	1.3387 (4)	1.3678 (9)	0.068 (2)
S(49)	0.7366 (5)	1.2109 (3)	1.3866 (7)	0.0408 (17)
S(50)	0.7308 (4)	1.0625 (3)	1.2748 (7)	0.0343 (17)
C(41)	0.8304 (8)	0.8425 (5)	0.9176 (11)	0.033 (3)
C(42)	0.7943 (7)	0.7164 (5)	0.8993 (11)	0.030 (2)
C(43)	0.7669 (7)	0.8443 (5)	1.0461 (11)	0.029 (2)
C(44)	0.8301 (15)	1.1349 (10)	1.156 (2)	0.037 (4)
C(45)	0.7935 (13)	1.2561 (9)	1.3167 (19)	0.040 (4)
C(46)	0.7691 (15)	1.1325 (10)	1.266 (2)	0.035 (4)
Ni(5)	1.0078 (3)	0.08820 (2)	0.5747 (4)	0.0421 (5)
S(51)	0.9409 (5)	0.1640 (3)	0.7601 (7)	0.0442 (19)
S(52)	0.9339 (5)	0.3173 (3)	0.8502 (8)	0.0524 (19)
S(53)	0.9748 (6)	0.4463 (4)	0.8066 (9)	0.081 (2)
S(54)	1.0618 (5)	0.3119 (3)	0.6165 (7)	0.051 (2)
S(55)	1.0713 (5)	0.1602 (3)	0.4993 (7)	0.0475 (19)
S(56)	0.9476 (5)	0.0152 (3)	0.6490 (7)	0.0462 (17)
S(57)	0.9434 (2)	−0.1342 (2)	0.5190 (4)	0.0515 (11)
S(58)	0.9977 (3)	−0.2606 (2)	0.2895 (4)	0.0676 (12)
S(59)	1.0566 (2)	−0.1337 (2)	0.2692 (3)	0.0469 (10)
S(60)	1.0676 (2)	0.0142 (2)	0.3850 (3)	0.0443 (10)
C(51)	0.9778 (12)	0.2392 (8)	0.7312 (16)	0.029 (4)
C(52)	0.9844 (16)	0.3647 (11)	0.764 (2)	0.058 (5)
C(53)	1.0339 (17)	0.2358 (11)	0.625 (2)	0.044 (5)
C(54)	0.9776 (8)	−0.0566 (5)	0.5200 (12)	0.035 (3)
C(55)	0.9940 (8)	−0.1825 (5)	0.3633 (12)	0.040 (3)
C(56)	1.0291 (8)	−0.0622 (6)	0.4002 (12)	0.043 (3)
N(1)	0.4861 (14)	0.5003 (9)	0.486 (2)	0.055 (4)
N(2)	0.9230 (14)	0.5339 (9)	0.342 (2)	0.055 (4)
C(61)	0.5542 (12)	0.5184 (8)	0.3920 (17)	0.062 (4)
C(62)	0.6768 (14)	0.5156 (11)	0.485 (2)	0.054 (5)
C(63)	0.7404 (12)	0.5195 (8)	0.3633 (18)	0.036 (4)
C(64)	0.8352 (10)	0.5427 (7)	0.4407 (15)	0.042 (3)
C(65)	0.4007 (11)	0.4655 (8)	0.3917 (16)	0.083 (4)
C(66)	0.4395 (14)	0.5724 (9)	0.555 (2)	0.107 (5)
C(67)	0.5348 (11)	0.4618 (7)	0.6250 (16)	0.075 (4)
C(68)	0.8849 (13)	0.6034 (8)	0.294 (2)	0.102 (5)
C(69)	0.9307 (12)	0.4772 (8)	0.2089 (17)	0.080 (4)
C(70)	1.0344 (10)	0.5249 (7)	0.4449 (15)	0.070 (4)
N(3)	0.2573 (12)	0.4942 (8)	0.6940 (17)	0.077 (4)
C(71)	0.2619 (12)	0.4526 (8)	0.7566 (18)	0.047 (4)
C(72)	0.2764 (13)	0.4044 (9)	0.866 (2)	0.080 (5)
N(4)	0.1629 (13)	0.5564 (9)	0.179 (2)	0.100 (5)
C(73)	0.1287 (15)	0.5801 (10)	0.050 (2)	0.069 (5)
C(74)	0.1087 (11)	0.6205 (7)	−0.0625 (16)	0.054 (4)

[a] U_{eq} = $^1/_3$ of the trace of the orthogonalized *U*.

the structures of $[HNMe_3]_2[Ni(dmit)_2]_5 \cdot 2CH_3CN$ and $[H_3NMe]_2[Ni(dmit)_2]_5 \cdot 2CH_3CN$. In fact, the anionic part of the lattice of compound **1** is almost identical to that of $[HNMe_3]_2[Ni(dmit)_2]_5 \cdot 2CH_3CN$ and $[H_3NMe]_2[Ni(dmit)_2]_5 \cdot 2CH_3CN$. The stacks of Ni(dmit)$_2$ units in compound **2**, however, contain alternatively trimers (triads) and dimers (see Figure 7). Figures 8 and 9 show the various modes of overlap of the acceptor molecules along the stacks.

Apart from the solvent molecules, another difference between the lattice of **1** and **2** is the orientation of the dications with respect to the Ni(dmit)$_2$ molecules. In the structure of compound **1**, the carbon chain of the dication makes an angle of 65.8° with the plane through Ni(1)(dmit)$_2$, whereas this angle is only 28.4° in structure **2**.

Conductivity Measurements. Electrical conductivity was measured on single crystals in the temperature range 300–160 K. The four-probe contact method was used. Gold wires were glued to the crystal surface by gold paint. Over the whole temperature region, both compounds behave as *semi*conductors, exhibiting a room-temperature conductivity between 1 and 10^{-1} S cm^{-1}. The activation energies for **1** and **2** are 0.19 and 0.20 eV, respectively. This value for the room-temperature conductivity can be explained by taking into account the numerous molecular interactions among the dmit ligands, as shown in the crystal structure, which form an electrical conduction pathway. However, it is likely that both the large distortion in the acceptor molecules as well as the dimerization or trimerization within the stacks will result in charge localization. As a consequence, a thermally activated conductivity will be observed.

Conclusion and Discussion

$[Me_3N(CH_2)_4NMe_3][Ni(dmit)_2]_5 \cdot 2dmf$ and $[Me_3N(CH_2)_4NMe_3][Ni(dmit)_2]_5 \cdot 2CH_3CN$ are the first two Ni(dmit)$_2$ compounds containing a closed-shell, divalent cation. The problem of $[Me_3N(CH_2)_4NMe_3][Ni(dmit)_2]_2$ having a lower solubility than Ni(dmit)$_2$ salts which contain monovalent cations has been overcome by slightly modifying the electrocrystallization process, i.e. by using a mixture of dmf and acetonitrile instead of pure

Table V. Relevant Bond Distances (Å) and Angles (deg) for $[Me_3N(CH_2)_4NMe_3][Ni(dmit)_2]_5{\cdot}2CH_3CN$ (**2**)

Ni(1)–S(11)	2.186 (7)	S(24)–C(23)	1.721 (10)	C(31)–C(33)	1.35 (3)	S(53)–C(52)	1.60 (2)
Ni(1)–S(15)	2.162 (8)	S(25)–C(23)	1.688 (11)	C(34)–C(36)	1.225 (13)	S(54)–C(52)	1.81 (2)
Ni(1)–S(16)	2.145 (8)	S(26)–C(24)	1.66 (2)	Ni(4)–S(41)	2.144 (5)	S(54)–C(53)	1.71 (2)
Ni(1)–S(20)	2.127 (7)	S(27)–C(24)	1.75 (2)	Ni(4)–S(45)	2.152 (5)	S(55)–C(53)	1.72 (2)
S(11)–C(11)	1.785 (18)	S(27)–C(25)	1.689 (19)	Ni(4)–S(46)	2.158 (5)	S(56)–C(54)	1.666 (12)
S(12)–C(11)	1.683 (17)	S(28)–C(25)	1.66 (2)	Ni(4)–S(50)	2.182 (7)	S(57)–C(54)	1.753 (11)
S(12)–C(12)	1.64 (2)	S(29)–C(25)	1.76 (2)	S(41)–C(41)	1.627 (11)	S(57)–C(55)	1.664 (11)
S(13)–C(12)	1.70 (2)	S(29)–C(26)	1.737 (17)	S(42)–C(41)	1.750 (10)	S(58)–C(55)	1.580 (11)
S(14)–C(12)	1.745 (19)	S(30)–C(26)	1.590 (17)	S(42)–C(42)	1.799 (10)	S(59)–C(55)	1.851 (11)
S(14)–C(13)	1.67 (2)	C(21)–C(23)	1.444 (13)	S(43)–C(42)	1.658 (11)	S(59)–C(56)	1.667 (12)
S(15)–C(13)	1.71 (2)	C(24)–C(26)	1.52 (2)	S(44)–C(42)	1.617 (10)	S(60)–C(56)	1.798 (12)
S(16)–C(14)	1.680 (19)	Ni(3)–S(31)	2.116 (7)	S(44)–C(43)	1.744 (11)	C(51)–C(53)	1.29 (3)
S(17)–C(14)	1.794 (19)	Ni(3)–S(35)	2.162 (4)	S(45)–C(43)	1.621 (10)	C(54)–C(56)	1.341 (15)
S(17)–C(15)	1.725 (19)	Ni(3)–S(36)	2.153 (5)	S(46)–C(44)	1.738 (19)	N(1)–C(61)	1.50 (2)
S(18)–C(15)	1.58 (2)	Ni(3)–S(40)	2.181 (4)	S(47)–C(44)	1.68 (2)	N(1)–C(65)	1.48 (2)
S(19)–C(15)	1.79 (2)	S(31)–C(31)	1.74 (2)	S(47)–C(45)	1.834 (18)	N(1)–C(66)	1.48 (3)
S(19)–C(16)	1.790 (17)	S(32)–C(31)	1.73 (2)	S(48)–C(45)	1.655 (19)	N(1)–C(67)	1.51 (2)
S(20)–C(16)	1.628 (18)	S(32)–C(32)	1.831 (17)	S(49)–C(45)	1.608 (19)	N(2)–C(64)	1.53 (2)
C(11)–C(13)	1.33 (3)	S(33)–C(32)	1.635 (17)	S(49)–C(46)	1.73 (2)	N(2)–C(68)	1.48 (2)
C(14)–C(16)	1.42 (2)	S(34)–C(32)	1.628 (17)	S(50)–C(46)	1.66 (2)	N(2)–C(69)	1.46 (2)
Ni(2)–S(21)	2.163 (3)	S(34)–C(33)	1.796 (19)	C(41)–C(43)	1.532 (14)	N(2)–C(70)	1.50 (2)
Ni(2)–S(25)	2.181 (6)	S(35)–C(33)	1.640 (17)	C(44)–C(46)	1.40 (3)	C(61)–C(62)	1.60 (2)
Ni(2)–S(26)	2.157 (7)	S(36)–C(34)	1.793 (10)	Ni(5)–S(60)	2.135 (3)	C(62)–C(63)	1.52 (2)
Ni(2)–S(30)	2.143 (6)	S(37)–C(34)	1.733 (10)	Ni(5)–S(51)	2.158 (6)	C(63)–C(64)	1.41 (2)
S(21)–C(21)	1.597 (10)	S(37)–C(35)	1.844 (11)	Ni(5)–S(55)	2.142 (6)	N(3)–C(71)	1.09 (2)
S(22)–C(21)	1.754 (10)	S(38)–C(35)	1.652 (12)	Ni(5)–S(56)	2.127 (6)	C(71)–C(72)	1.46 (2)
S(22)–C(22)	1.602 (10)	S(39)–C(35)	1.631 (12)	S(51)–C(51)	1.806 (17)	N(4)–C(73)	1.27 (2)
S(23)–C(22)	1.701 (11)	S(39)–C(36)	1.731 (10)	S(52)–C(51)	1.741 (16)	C(73)–C(74)	1.35 (2)
S(24)–C(22)	1.798 (10)	S(40)–C(36)	1.767 (10)	S(52)–C(52)	1.68 (2)		
S(11)–Ni(1)–S(15)	92.1 (3)	C(22)–S(24)–C(23)	93.3 (5)	S(32)–C(31)–C(33)	120.8 (16)	S(46)–C(44)–C(46)	118.0 (15)
S(11)–Ni(1)–S(16)	86.8 (3)	Ni(2)–S(25)–C(23)	102.1 (4)	S(32)–C(32)–S(33)	117.3 (10)	S(47)–C(44)–C(46)	120.1 (15)
S(11)–Ni(1)–S(20)	178.7 (3)	Ni(2)–S(26)–C(24)	102.5 (7)	S(32)–C(32)–S(34)	113.2 (9)	S(47)–C(45)–S(48)	115.9 (10)
S(15)–Ni(1)–S(16)	178.7 (3)	C(24)–S(27)–C(25)	99.6 (10)	S(33)–C(32)–S(34)	129.5 (11)	S(47)–C(45)–S(49)	114.4 (10)
S(15)–Ni(1)–S(20)	86.6 (3)	C(25)–S(29)–C(26)	101.9 (9)	S(34)–C(33)–S(35)	123.5 (10)	S(47)–C(45)–S(49)	114.4 (10)
S(16)–Ni(1)–S(20)	94.5 (3)	Ni(2)–S(30)–C(26)	04.5 (6)	S(34)–C(33)–C(31)	111.3 (14)	S(48)–C(45)–S(49)	129.6 (11)
Ni(1)–S(11)–C(11)	101.9 (6)	S(21)–C(21)–S(22)	126.7 (6)	S(35)–C(33)–C(31)	125.1 (15)	S(49)–C(46)–S(50)	124.6 (12)
C(11)–S(12)–C(12)	93.2 (9)	S(21)–C(21)–C(23)	122.7 (7)	S(36)–C(34)–S(37)	116.9 (5)	S(49)–C(46)–C(44)	112.2 (15)
C(12)–S(14)–C(13)	95.3 (10)	S(22)–C(21)–C(23)	110.6 (7)	S(36)–C(34)–C(36)	122.3 (8)	S(50)–C(46)–C(44)	123.2 (15)
Ni(1)–S(15)–C(13)	104.0 (7)	S(22)–C(22)–S(23)	128.0 (6)	S(37)–C(34)–C(36)	120.6 (8)	S(51)–Ni(5)–S(55)	93.1 (2)
Ni(1)–S(16)–C(14)	101.1 (7)	S(22)–C(22)–S(24)	116.8 (6)	S(37)–C(35)–S(38)	116.7 (6)	S(51)–Ni(5)–S(56)	87.7 (2)
C(14)–S(17)–C(15)	98.9 (9)	S(23)–C(22)–S(24)	115.2 (6)	S(37)–C(35)–S(39)	113.4 (7)	S(51)–Ni(5)–S(60)	177.6 (2)
C(15)–S(19)–C(16)	101.0 (9)	S(24)–C(23)–S(25)	121.9 (6)	S(38)–C(35)–S(39)	129.9 (7)	S(55)–Ni(5)–S(56)	178.9 (3)
Ni(1)–S(20)–C(16)	101.7 (6)	S(24)–C(23)–C(21)	119.0 (7)	S(39)–C(36)–S(40)	119.8 (5)	S(55)–Ni(5)–S(60)	87.03 (19)
S(11)–C(11)–S(12)	118.6 (10)	S(25)–C(23)–C(21)	119.1 (8)	S(39)–C(36)–C(34)	117.4 (8)	S(56)–Ni(5)–S(60)	92.16 (19)
S(11)–C(11)–C(13)	119.8 (14)	S(26)–C(24)–S(27)	124.8 (12)	S(40)–C(36)–C(34)	122.7 (8)	Ni(5)–S(51)–C(51)	100.5 (5)
S(12)–C(11)–C(13)	121.4 (14)	S(26)–C(24)–C(26)	119.0 (14)	S(41)–Ni(4)–S(45)	93.97 (19)	C(51)–S(52)–C(52)	95.7 (9)
S(12)–C(12)–S(13)	125.2 (12)	S(27)–C(24)–C(26)	116.2 (13)	S(41)–Ni(4)–S(46)	88.75 (19)	C(52)–S(54)–C(53)	96.7 (10)
S(12)–C(12)–S(14)	116.4 (12)	S(27)–C(25)–S(28)	124.9 (12)	S(41)–Ni(4)–S(50)	178.1 (3)	Ni(5)–S(56)–C(53)	103.7 (8)
S(13)–C(12)–S(14)	118.3 (12)	S(27)–C(25)–S(29)	112.9 (11)	S(45)–Ni(4)–S(46)	177.2 (2)	Ni(5)–S(56)–C(54)	104.3 (5)
S(14)–C(13)–S(15)	124.2 (12)	S(28)–C(25)–S(29)	122.1 (11)	S(45)–Ni(4)–S(50)	85.3 (2)	C(54)–S(57)–C(55)	100.3 (5)
S(14)–C(13)–C(11)	113.5 (14)	S(29)–C(26)–S(30)	130.1 (10)	S(46)–Ni(4)–S(50)	92.0 (2)	C(55)–S(59)–C(56)	93.1 (5)
S(15)–C(13)–C(11)	122.1 (15)	S(29)–C(26)–C(24)	109.4 (12)	Ni(4)–S(41)–C(41)	103.0 (4)	Ni(5)–S(60)–C(56)	103.5 (4)
S(16)–C(14)–S(17)	121.9 (11)	S(30)–C(26)–C(24)	120.3 (13)	C(41)–S(42)–C(42)	99.1 (5)	S(51)–C(51)–S(52)	117.9 (9)
S(16)–C(14)–C(16)	119.7 (13)	S(31)–Ni(3)–S(35)	93.1 (2)	C(42)–S(44)–C(43)	102.6 (5)	S(51)–C(51)–C(53)	121.5 (14)
S(17)–C(14)–C(16)	118.0 (13)	S(31)–Ni(3)–S(36)	85.9 (2)	Ni(4)–S(45)–C(43)	103.6 (4)	S(52)–C(51)–C(53)	120.6 (15)
S(17)–C(15)–S(18)	127.7 (12)	S(31)–Ni(3)–S(40)	177.7 (3)	Ni(4)–S(46)–C(44)	103.5 (7)	S(52)–C(52)–S(53)	127.0 (13)
S(17)–C(15)–S(19)	111.0 (11)	S(35)–Ni(3)–S(36)	178.8 (2)	C(44)–S(47)–C(45)	93.1 (9)	S(52)–C(52)–S(54)	111.9 (12)
S(18)–C(15)–S(19)	121.2 (11)	S(35)–Ni(3)–S(40)	88.26 (15)	C(45)–S(49)–C(46)	100.1 (9)	S(53)–C(52)–S(54)	121.0 (13)
S(19)–C(16)–S(20)	126.2 (10)	S(36)–Ni(3)–S(40)	92.82 (18)	Ni(4)–S(50)–C(46)	103.2 (7)	S(54)–C(53)–S(55)	124.1 (12)
S(19)–C(16)–C(14)	110.9 (12)	Ni(3)–S(31)–C(31)	102.7 (7)	S(41)–C(41)–S(42)	128.1 (6)	S(54)–C(53)–C(51)	114.7 (15)
S(20)–C(16)–C(14)	122.8 (13)	C(31)–S(32)–C(32)	94.2 (9)	S(41)–C(41)–C(43)	120.3 (7)	S(55)–C(53)–C(51)	121.1 (17)
S(21)–Ni(2)–S(25)	92.26 (19)	C(32)–S(34)–C(33)	100.5 (9)	S(42)–C(41)–C(43)	111.6 (7)	S(56)–C(54)–S(57)	124.9 (7)
S(21)–Ni(2)–S(26)	86.29 (18)	Ni(3)–S(35)–C(33)	101.4 (6)	S(42)–C(42)–S(43)	118.5 (6)	S(56)–C(54)–C(56)	124.3 (9)
S(21)–Ni(2)–S(30)	175.1 (2)	Ni(3)–S(36)–C(34)	101.1 (3)	S(42)–C(42)–S(44)	113.6 (6)	S(57)–C(54)–C(56)	110.8 (8)
S(25)–Ni(2)–S(26)	178.5 (2)	C(34)–S(37)–C(35)	91.2 (5)	S(43)–C(42)–S(44)	128.0 (6)	S(57)–C(55)–S(58)	130.6 (7)
S(25)–Ni(2)–S(30)	87.8 (2)	C(35)–S(39)–C(36)	97.3 (5)	S(44)–C(43)–S(45)	127.8 (6)	S(57)–C(55)–S(59)	111.7 (6)
S(26)–Ni(2)–S(30)	93.6 (2)	Ni(3)–S(40)–C(36)	101.0 (3)	S(44)–C(43)–C(41)	113.1 (7)	S(58)–C(55)–S(59)	117.7 (6)
Ni(2)–S(21)–C(21)	103.8 (4)	S(31)–C(31)–S(32)	121.5 (11)	S(45)–C(43)–C(41)	119.1 (7)	S(59)–C(56)–S(60)	120.2 (6)
C(21)–S(22)–C(22)	100.3 (5)	S(31)–C(31)–C(33)	117.7 (15)	S(46)–C(44)–S(47)	121.8 (11)	S(59)–C(56)–C(54)	124.1 (9)
						S(60)–C(56)–C(54)	115.7 (8)

acetonitrile. No extra electrolyte could be added, however, due to the fact that an excess of 2,2,7,7-tetramethyl-2,7-diazoniaoctane bis(tetrafluoroborate) would force the $[Ni(dmit)_2]^-$ salt to precipitate from the solution. Apparently, the thickness of the electrodes, and therefore the current density, determines the formation of either salt **1** and **2**.

On comparison of the structures of **1** and **2** to that of $[Me_4N][Ni(dmit)_2]_2$, it is clear that the idea of substituting the Me_4N^+ cation for linear, divalent cations without changing the anionic part of the lattice has been unsuccessful: although the $Ni(dmit)_2$ units stack in a fashion not too different from the one found[3] in $[Me_4N][Ni(dmit)_2]_2$, the formal charge of the nickel

Table VI. Intermolecular S···S Contacts <3.70 Å in Compound **1**[a]

atom 1 ··· atom 2	symmetry operation	distance, Å
S(11)···S(26)	(x + 1, y + 1, z)	3.5942 (19)
S(11)···S(27)	(x + 1, y + 1, z)	3.676 (2)
S(11)···S(25)	(−x + 1, −y + 1, −z + 1)	3.537 (2)
S(11)···S(30)	(−x + 1, −y + 1, −z + 1)	3.636 (2)
S(12)···S(24)	(−x + 1, −y + 1, −z + 1)	3.662 (2)
S(12)···S(25)	(−x + 1, −y + 1, −z + 1)	3.566 (2)
S(12)···S(38)	(−x + 2, −y + 1, −z + 1)	3.587 (2)
S(13)···S(32)	(x, y, z)	3.548 (2)
S(14)···S(21)	(−x + 1, −y, −z + 1)	3.651 (2)
S(15)···S(30)	(x + 1, y, z)	3.604 (2)
S(15)···S(21)	(−x + 1, −y, −z + 1)	3.5658 (19)
S(15)···S(26)	(−x + 1, −y, −z + 1)	3.554 (2)
S(21)···S(35)	(−x + 1, −y, −z + 1)	3.640 (2)
S(21)···S(40)	(−x + 1, −y, −z + 1)	3.603 (2)
S(22)···S(28)	(−x, −y, −z + 1)	3.682 (2)
S(22)···S(34)	(−x + 1, −y, −z + 1)	3.660 (2)
S(22)···S(35)	(−x + 1, −y, −z + 1)	3.511 (2)
S(23)···S(38)	(x, y, z)	3.700 (2)
S(24)···S(31)	(−x + 1, −y + 1, −z + 1)	3.658 (2)
S(25)···S(31)	(−x + 1, −y + 1, −z + 1)	3.6402 (19)
S(25)···S(36)	(−x + 1, −y + 1, −z + 1)	3.529 (2)
S(26)···S(39)	(−x + 1, −y, −z + 1)	3.614 (2)
S(26)···S(40)	(−x + 1, −y, −z + 1)	3.647 (2)
S(27)···S(39)	(−x + 1, −y, −z + 1)	3.696 (2)
S(30)···S(31)	(x, y, z)	3.669 (2)
S(30)···S(36)	(−x + 1, −y + 1, −z + 1)	3.6626 (19)
S(30)···S(37)	(−x + 1, −y + 1, −z + 1)	3.571 (2)
S(31)···S(36)	(−x + 1, −y + 1, −z + 1)	3.582 (2)
S(31)···S(37)	(−x + 1, −y + 1, −z + 1)	3.498 (2)
S(35)···S(39)	(−x + 1, −y, −z + 1)	3.6356 (19)
S(35)···S(40)	(−x + 1, −y, −z + 1)	3.651 (2)
S(36)···S(36)	(−x + 1, −y + 1, −z + 1)	3.462 (2)
S(40)···S(40)	(−x + 1, −y, −z + 1)	3.4598 (19)

[a] Symmetry operation applied on second atom.

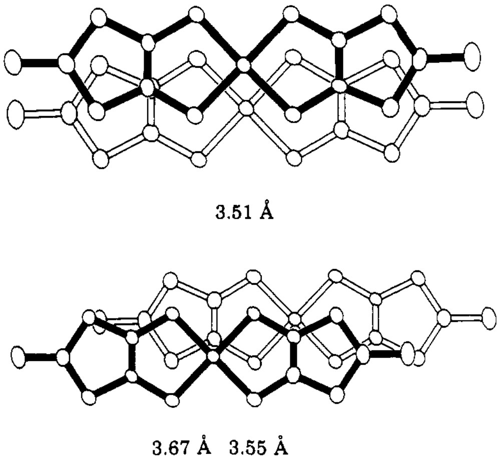

Figure 8. Modes of molecular overlap in **1**.

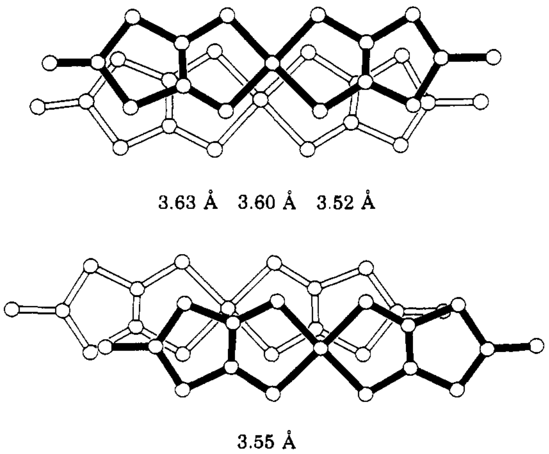

Figure 9. Modes of molecular overlap in **2**.

Table VII. Intermolecular S···S Contacts <3.70 Å in Compound **2**[a]

atom 1 ··· atom 2	symmetry operation	distance, Å
S(11)···S(46)	(x − 1, y − 1, z − 1)	3.644 (7)
S(11)···S(55)	(x − 1, y, z)	3.648 (9)
S(11)···S(60)	(x − 1, y, z)	3.625 (7)
S(12)···S(55)	(x − 1, y, z)	3.690 (9)
S(13)···S(23)	(x, y, z)	3.610 (9)
S(14)···S(24)	(x, y, z)	3.696 (7)
S(14)···S(40)	(x, y − 1, z − 1)	3.698 (7)
S(15)···S(21)	(x, y, z − 1)	3.683 (7)
S(15)···S(22)	(x, y, z − 1)	3.690 (7)
S(15)···S(25)	(x, y, z)	3.645 (9)
S(15)···S(40)	(x, y − 1, z − 1)	3.634 (8)
S(16)···S(41)	(x − 1, y − 1, z − 1)	3.650 (7)
S(16)···S(46)	(x − 1, y − 1, z − 1)	3.693 (7)
S(16)···S(56)	(x − 1, y, z − 1)	3.647 (9)
S(16)···S(60)	(x − 1, y, z)	3.697 (7)
S(18)···S(58)	(x − 1, y, z − 1)	3.608 (8)
S(19)···S(26)	(x, y, z − 1)	3.677 (9)
S(20)···S(21)	(x, y, z − 1)	3.568 (7)
S(20)···S(26)	(x, y, z − 1)	3.655 (9)
S(20)···S(35)	(x, y − 1, z − 1)	3.633 (7)
S(21)···S(60)	(x − 1, y, z)	3.482 (4)
S(22)···S(40)	(x, y − 1, z)	3.673 (4)
S(22)···S(55)	(x − 1, y, z)	3.571 (7)
S(23)···S(37)	(x, y − 1, z)	3.568 (5)
S(24)···S(40)	(x, y − 1, z − 1)	3.624 (4)
S(24)···S(50)	(x, y − 1, z − 1)	3.647 (6)
S(25)···S(35)	(x, y − 1, z − 1)	3.483 (7)
S(25)···S(45)	(x, y − 1, z − 1)	3.621 (6)
S(25)···S(50)	(x, y − 1, z − 1)	3.655 (8)
S(26)···S(59)	(x − 1, y, z)	3.558 (8)
S(27)···S(33)	(x, y − 1, z)	3.523 (10)
S(29)···S(44)	(x, y − 1, z − 1)	3.690 (8)
S(30)···S(34)	(x, y − 1, z − 1)	3.692 (9)
S(30)···S(44)	(x, y − 1, z − 1)	3.624 (7)
S(30)···S(45)	(x, y − 1, z − 1)	3.601 (6)
S(31)···S(45)	(x, y, z − 1)	3.671 (7)
S(31)···S(50)	(x, y, z − 1)	3.643 (9)
S(31)···S(57)	(x, y + 1, z)	3.695 (7)
S(35)···S(45)	(x, y, z)	3.630 (4)
S(36)···S(46)	(x, y, z)	3.655 (4)
S(36)···S(50)	(x, y, z − 1)	3.642 (7)
S(36)···S(51)	(x, y + 1, z)	3.649 (7)
S(36)···S(56)	x, y + 1, z)	3.651 (7)
S(37)···S(51)	(x, y + 1, z)	3.634 (7)
S(37)···S(52)	(x, y + 1, z)	3.660 (7)
S(41)···S(57)	(x, y + 1, z)	3.611 (4)
S(41)···S(59)	(x, y + 1, z + 1)	3.690 (4)
S(44)···S(58)	(x, y + 1, z + 1)	3.554 (5)
S(46)···S(56)	(x, y + 1, z)	3.527 (7)
S(47)···S(51)	(x, y + 1, z)	3.672 (9)
S(48)···S(54)	(x, y + 1, z + 1)	3.606 (10)

[a] Symmetry operation applied on second atom.

atoms in $[Me_4N][Ni(dmit)_2]_2$ is 3.5+, whereas the mean oxidation state of the metal centers in **1** and **2** is formally $Ni^{3.6+}$. More importantly, because of their considerable differences in geometry the acceptor molecules in the unit cells of **1** and **2** are not all structurally (and therefore electronically) equivalent, unlike the $Ni(dmit)_2$ units in $[Me_4N][Ni(dmit)_2]_2$. This would explain the *semi*conducting behavior of these salts.

The reason for the relatively higher degree of partial oxidation in **1** and **2** might be that, during the initial crystallization, there is simply no room for more positive charges, without the molecules having to adopt an energetically less favorable packing mode. The size and shape of the cations would therefore determine the final oxidation state of the anions. The degree of partial oxidation found in $[Bu_4N]_{0.29}Ni(dmit)_2$[28] and $[Ph_4As]_{0.25}Ni(dmit)_2$[29] supports the theory that bulky cations tend to induce a high oxidation state. Alternatively, from an electronic point of view, one could state

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(29) Valade, L.; Legros, J.-P.; Cassoux, P.; Kubel, F. *Mol. Cryst. Liq. Cryst.* **1986**, *140*, 335.

that in the case of **1** and **2** the absence of electrolyte in the $[Me_3N(CH_2)_4NMe_3][Ni(dmit)_2]_2$ solution results in a higher resistivity and thus increases the electric potential of the anode. This yields a higher oxidizing ability of the anode.

The latter theory is supported by the existence of the salts $[HNMe_3]_2[Ni(dmit)_2]_5{\cdot}2CH_3CN$ and $[H_3NMe]_2[Ni(dmit)_2]_5{\cdot}2CH_3CN$, which have recently been reported.[26,27] These two *semi*conductors were obtained *together* with the conducting 1:2 salts $[HNMe_3][Ni(dmit)_2]_2$[5] and $[H_3NMe][Ni(dmit)_2]_2$[27], which advocates the idea that it is the electrochemical oxidation conditions that determine the degree of oxidation, rather than the nature of the closed-shell cation. An important conclusion resulting from this analysis is that changing the electrooxidation conditions, e.g. by choosing a better a solvent for $[Me_3N(CH_2)_4NMe_3][Ni(dmit)_2]_2$, might indeed yield the desired oxidation state of $Ni^{3.5+}$. This means that although the goal of mimicking the crystal structure of $[Me_4N][Ni(dmit)_2]_2$ is not yet reached, a correct modification in the electrocrystallization process could result in a compound with the stoichiometry $[Me_3N(CH_2)_4NMe_3][Ni(dmit)_2]_4$. A salt with this formula would obviously have a greater possibility of having a packing mode similar to that of the superconducting $[Me_4N][Ni(dmit)_2]_2$.

Acknowledgment. We thank Ms. B. Pomarède and Ms. Dr. L. Valade for performing the conductivity measurements. We are indebted to Dr. J.-P. Legros for automatic X-ray diffractometer use, for providing information on and the coordinates of $[H_3NMe]_2[Ni(dmit)_2]_5{\cdot}2CH_3CN$ and $[HNMe_3]_2[Ni(dmit)_2]_5{\cdot}2CH_3CN$, and for his stimulating interest. Mr. S. Gorter collected the X-ray diffraction data for **1**. We are grateful to NWO (Nederlandse stichting voor Wetenschappelijk Onderzoek) and to the CNRS (Centre National de la Recherche Scientifique) in Paris for financial support. This research was in part sponsored by the Werkgroep Fundamenteel Materialen Onderzoek (WFMO).

Supplementary Material Available: Tables of crystal data and details of the structure determinations, atomic coordinates for the hydrogen atoms, thermal parameters of all non-hydrogen atoms, and all bond distances and angles for **1** and **2** (39 pages); listings of calculated and observed structure factors (78 pages). Ordering information is given on any current masthead page.

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Chemistry of Iron Oxophlorins. 1. ^1H NMR and Structural Studies of Five-Coordinate Iron(III) Complexes

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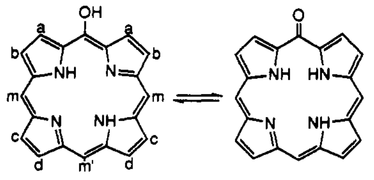
Received February 5, 1992

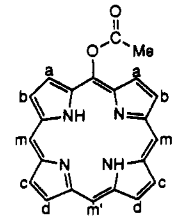
As part of a series of studies to understand the role of iron oxophlorin complexes in oxidative heme destruction, the spectroscopic, chemical, and structural features of a group of dioxygen-stable iron(III) complexes of octaethyloxophlorin are reported. Protonation or coordination of the meso oxygen of the oxophlorin ligand appears to stabilize these iron complexes and prevents their conversion to verdoheme through oxidation by molecular oxygen. The ^1H NMR spectrum of dimeric $[Fe^{III}(OEPO)]_2$ (where OEPO is the trianion of octaethyloxophlorin, **1**), is presented and analyzed. The presence of two paramagnetic centers produce marked variation in line widths and T_1's for the methylene protons. $[Fe^{III}(OEPO)]_2$ is cleaved by protic acids (HX) to form high-spin, five-coordinate $[XFe^{III}(OEPOH)]$, whose ^1H NMR and electron paramagnetic resonance spectra are analyzed. As a model for $[XFe^{III}(OEPOH)]$, the complex $[ClFe^{II}(OEPOAc)]$ (where the meso hydroxyl group has been acetylated) has been prepared and characterized by its ^1H NMR spectrum. The X-ray crystal structure of $[ClFe^{III}(OEPOAc){\cdot}CH_2Cl_2$ shows that the iron is five-coordinate with structural parameters consistent with high-spin ($S = {}^5/_2$) electronic structure. Crystals of $C_{39}H_{48}Cl_3FeN_4O_2$ form in the triclinic space group $P\bar{1}$ with $a = 10.238$ (2) Å, $b = 13.301$ (2) Å, $c = 15.088$ (3) Å, $\alpha = 77.610$ (2)°, $\beta = 71.820$ (2)°, and $\gamma = 75.430$ (2)°, at 130 K with $Z = 2$. Refinement of 4577 reflections with 456 parameters yielded $R = 0.051$ and $R_w = 0.053$. The environment about the acetoxy substituent is crowded, and restricted rotation at that site produces two isomers that are observed in solution.

Introduction

Oxophlorins (or oxyporphyrins), **1**, are porphyrin derivatives that have been oxygenated at one meso position.[1,2] Two tautomeric forms are possible: one, **1a**, with a hydroxyl group at the meso position, the other, **1b**, with a carbonyl group at that site. An iron oxophlorin complex is an intermediate in the conversion of heme to biliverdin in both the in vivo process that is catalyzed by heme oxygenase and the in vitro model system known as coupled oxidation (Scheme I; iron ligation and oxidation states unspecified, other structures have been proposed for verdoheme).[3,4] Coordinated iron is critically important in both processes. Por-

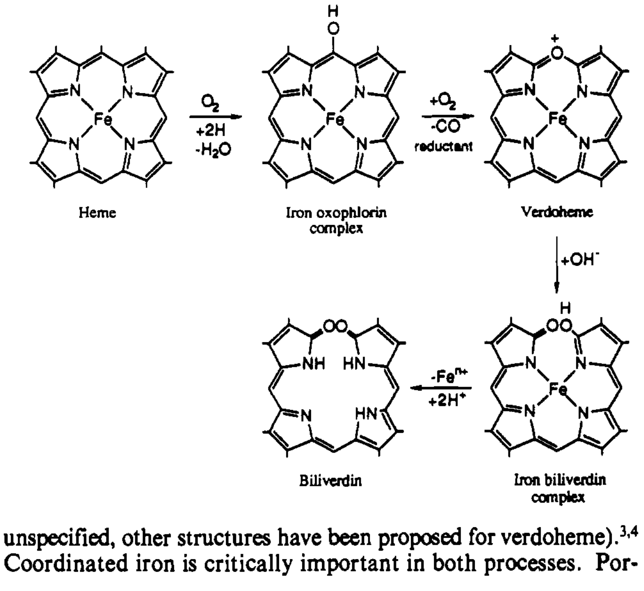


1a **1b**



2

Scheme I



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